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INELASTIC MOLECULAR SCATTERING

Roger William Fenstermaker

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CORRECTIONS TO TCI-392X

Page	Location	Correction
v i	line 12 up	"Kenematic" should be "Kinematic".
8	sketch	Sketch should include a mechanical chopper between beam source and velocity selector.
9	line 3 up	"f ₂ (0,0) = + $\frac{1}{6}$ (i.e., > 0)" should be "f ₂ (0,0) = - $\frac{1}{6}$ (i.e., < 0)."
13	line 12	"marrowed" should be "narrowed."
17	Eq. 13	Second = sign should be $\approx$ (due to anharmonicity).
20	line 4	(+ 2%)
20	line 9	"Scattering gas" should be "Crossed beam"
28	line 3	The sketch is actual size.
33	line 10	"broading" should be "broadening".
50	line 1	"X" should be "X _A ".
50	line 5 up	"cahrt" should be "chart".
53	line 4 up	"anomaly" should be "thought".
64	line 2	Add to legend "The peaks were arbitrarily normalized to the same 010> height."
111	line 4	"result-the" should be "result: the"
111	lines 6, 8	"Eq. B1" should be "Eq. C1" (two places).

INELASTIC MOLECULAR SCATTERING

by

Roger William Fenstermaker

A thesis submitted in partial fulfillment of the
requirements for the degree of

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INELASTIC MOLECULAR SCATTERING*

by

Roger William Fenstermaker

(Under the supervision of Professor Richard B. Bernstein)

ABSTRACT

A molecular beam study of the change in relative populations of the lower vibrational states of CsF upon collision with CO_2 is reported. Focused beams of CsF in specified vibrational-rotational states were prepared by means of a previously developed molecular beam electric resonance method employing microwave stimulated emission combined with quadrupole electric focusing fields. The ratio of populations of the two lowest vibrational states ($v = 1/v = 0$) was measured for one $(J,M) = (1,0)$ rotational state of CsF. This ratio was determined for the direct (unattenuated) CsF beam and then for the CsF beam attenuated by the scattering partner. The result was a small, but statistically

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*This research received financial support from: National Science Foundation Grant GB-16665, and from National Aeronautics and Space Administration Grant NGL 50-002-001.

significant increase (contrary to expectation) in the $v' = 1 / v' = 0$ population ratio due to scattering. This observation is considered to serve as evidence of inelastic scattering. It is interpreted assuming the possibility of both vibrational excitation and deexcitation of the CsF, but with kinematic factors enhancing detection of the excitation process.

Also included are two previously published papers on certain theoretical aspects of inelastic scattering, a part of the present thesis research. In the first, the sudden approximation has been used to produce numerical calculations of the angular distributions and energy dependence of rotational excitation cross sections for diatomic molecules in collision with atoms. The second demonstrates the equivalence of the Born approximation and the first-order time-dependent perturbation approximations for such systems, and presents analytical formulas for the rotational transition probabilities.

To my parents

whose lives have guided mine.

ACKNOWLEDGMENTS

Many people have helped to make this whole process possible, worthwhile, and (usually) enjoyable. I am especially grateful to Professor R. B. Bernstein, for the unselfish sharing of his insight and enthusiasm; to Ted Waech, who initiated this work, assisted me with the many discussions, and left me a working molecular beam machine; to the other members of the group, especially Bob Bickes, Mike Gersh, and Bob LaBudde whose assistance is gratefully acknowledged; to Professor E. W. Rothe of Wayne State University for his patience and encouragement in the thesis-writing stage of my work; to Don and Esther Macalady for their boundless supply of warm humanity during this same trying period; to Professor R. C. Woods, whose extensive assistance in overcoming problems of the microwave system was invaluable; to all of the members of the Chemistry Department machine shop for their skill and continual willingness to tackle new problems; to the Theoretical Chemistry Institute and its staff who have typed and reproduced this thesis and performed many other services for me in the past; Janice Boie for an outstanding and imaginative job of typing; and to my wife, Donna Kay, who makes it seem somehow worthwhile.

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I. INTRODUCTION

"The trouble with chemistry is that it is too difficult for chemists."

A. Einstein

The above quotation indicates why the molecular beam method¹ of studying molecular interactions is so attractive; it separates out single pairwise interactions between molecules, interactions which in principle are completely defined by the Schrödinger equation, but which in practice are greatly obscured by the gross averaging procedure of a bulk chemical reaction. This most evident attractive feature of molecular beams,¹ i.e., the production of spatially isolated molecules in closely defined velocity ranges, has been powerfully augmented in recent years by the concurrent ability to specify internal quantum states of the beam molecules.² In particular, inhomogeneous electric fields of various multipolar configurations have been utilized² to separate rotational states and spatially orient various simple polar molecules by means of the molecular electric Stark effect. Two examples are given below.³

1) The six-pole electric field selects ranges of rotational states of symmetric top molecules.⁴ The selected molecules can then be oriented with respect to a laboratory-fixed axis, and experiments which measure the reactive anisotropy of e.g., CH_3I or CF_3I with alkali atoms have been performed.⁵

2) The four-pole electric field focuses polar diatomic molecules in rotational states of negative induced dipole moment (i.e., molecules whose second-order Stark energy increases with electric field).²

This configuration has been used in experiments that measure the anisotropy of the intermolecular potential for TlF-rare gas and CsF-rare gas pairs⁶. It has been used in the determination of rotationally inelastic cross sections for state-selected TlF interacting with various collision partners.⁷ It is used for state enhancement in molecular beam electric resonance (MBER) spectroscopy.⁸ Recently, the MBER technique has been combined with microwave induced rotational stimulated emission to provide beams of "pure state" CsF useful for scattering studies.⁹ The beams consist of CsF in completely specified quantum states (rotational and vibrational). A significant portion of this thesis is concerned with the utilization of this technique. The goal was to observe a change in the relative population of vibrational states of CsF upon collision with other molecules.

The thesis is divided into six parts. Sections II-IV describe the experimental work, consisting of measurements of changes in the ratio of vibrational state populations in beams of state-selected CsF upon collision with other gas molecules, as noted above. The results are discussed in terms of vibrational excitation and de-excitation. Section V (with appendix) describes the theoretical work, mainly on rotational excitation, i.e., calculations utilizing the sudden approximation to compute the angular and energy dependence of the cross sections for rotational excitation of rotationally state-selected polar diatomic molecules in collision with atoms. The results are applied to the TlF experiments of Toennies.⁷ Section VI demonstrates the equivalence between the first-order perturbation limit of the time-dependent treat-

ment and the Born limit of the time-independent treatment for the case of rotationally inelastic collisions of diatomic molecules with atoms.

II. VIBRATIONAL STATE SELECTION OF CsF AND DESCRIPTION OF THE SCATTERING EXPERIMENT

A. General discussion of focusing

The focusing of polar molecules is made possible by the molecular electric Stark effect, which yields a net force on a neutral polar molecule placed in an inhomogeneous electric field $\vec{E}$. For a linear (e.g., diatomic) molecule in a $^1\Sigma$ state, the Stark energy is given by:

$$W = \sum_{i=0,2,4,\dots}^{\infty} W_i, \quad (1)$$

where W_0 is the molecular energy in the absence of an electric field. (For linear molecules with no component of angular momentum along the molecular axis, the odd orders in the perturbation expansion vanish.) The lowest-order field-dependent energy then is¹¹

$$W_2 = \frac{\mu_0^2 E^2}{\hbar^2/2I} f_2(J, M), \quad (2)$$

where μ_0 and I are the permanent molecular electric dipole moment and moment of inertia respectively, E is the magnitude of the electric field, and $f_2(J, M)$ is given by

$$\begin{aligned} f_2(J, M) &= \frac{J(J+1) - 3M^2}{2J(J+1)(2J-1)(2J+3)} && (\text{for } J, M \neq 0, 0) \\ &= -\frac{1}{6} && (\text{for } J, M = 0, 0). \end{aligned} \quad (3)$$

In an inhomogeneous field sufficiently weak that $W_4 \ll W_2$,

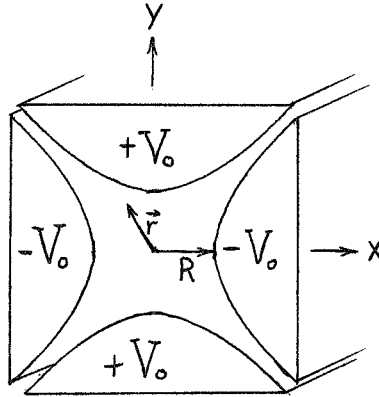
the molecules experience the following force:

$$\vec{F} = -\nabla W_2 = -\frac{\partial W_2}{\partial E} \nabla E \equiv \mu_{\text{eff}} \nabla E, \quad (4)$$

where

$$\mu_{\text{eff}} = -\frac{2\mu_o^2 E}{\hbar^2/2I} f_2(J, M). \quad (5)$$

Now consider the behavior of these molecules in a four-pole field with rods of hyperbolic cross section (usually approximated as circular), adjacent rods carrying alternate voltages of $+V_o$ or $-V_o$. See sketch:



The potential for this field is $V(x, y) = \frac{V_o}{R^2} (y^2 - x^2)$, and (6)

$$\vec{E} = -\nabla V = \frac{2V_o}{R^2} [x \hat{i} - y \hat{j}] \quad (7)$$

$$E = \frac{2V_0}{R^2} r \quad (8)$$

$$\nabla E = \frac{2V_0}{R^2} . \quad (9)$$

Then

$$F = -\frac{8\mu_0^2}{\hbar^2/2I} \frac{V_0^2}{R^4} f_2(J,M) r(t) = m \ddot{r}(t), \quad (10)$$

where m is the molecular mass and $r(t)$ is the time-dependent off-axis displacement. Note that Eq. (10) is of the form

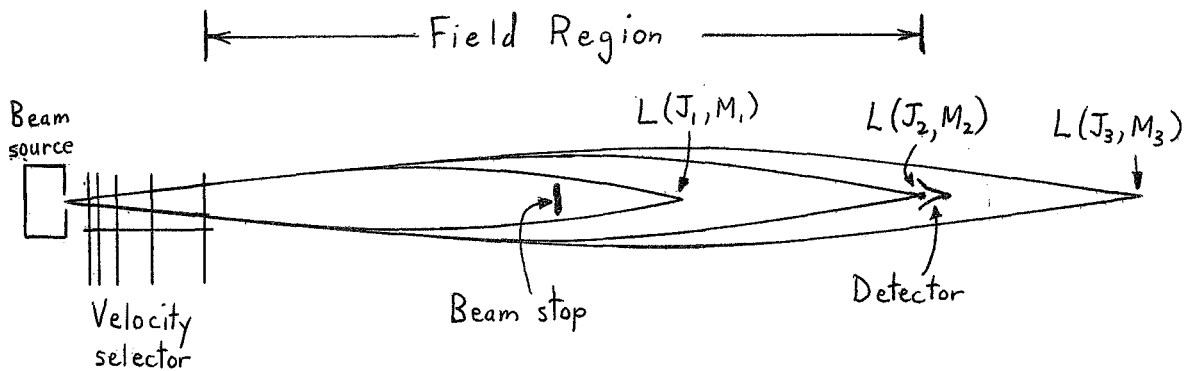
$$m \ddot{r} + \mathcal{H} r = 0 , \quad (11)$$

i.e., the solutions will be either exponential or sinusoidal in r , depending upon the sign of $\mathcal{H}$ (here, upon the sign of $f_2(J,M)$). In particular, molecules with $f_2(J,M) > 0$ which are injected, e.g., from a molecular beam source into the field with axial velocity $\gg$ radial velocity will execute simple harmonic motion with respect to the axis. If one assumes a single velocity v (for example, by the use of a mechanical velocity selector), then molecules effusing into the field from a small orifice on the axis will be brought back

into focus on the axis at a distance $L(=L(J,M))$, that is, a different distance for each J,M state) given by

$$L(J,M) = \frac{\pi R^2}{2\mu_0} \left(\frac{v}{V_0} \right) \left[\frac{m\hbar^2/2I}{2f_2(J,M)} \right]^{\frac{1}{2}}. \quad (12)$$

This is illustrated in the sketch below. Note that a beam stop much wider than either the source or detector is employed to eliminate the direct (unfocused) beam which contains all other (unwanted) rotational states.



(VERTICAL SCALE EXAGGERATED WITH
RESPECT TO THE HORIZONTAL SCALE)

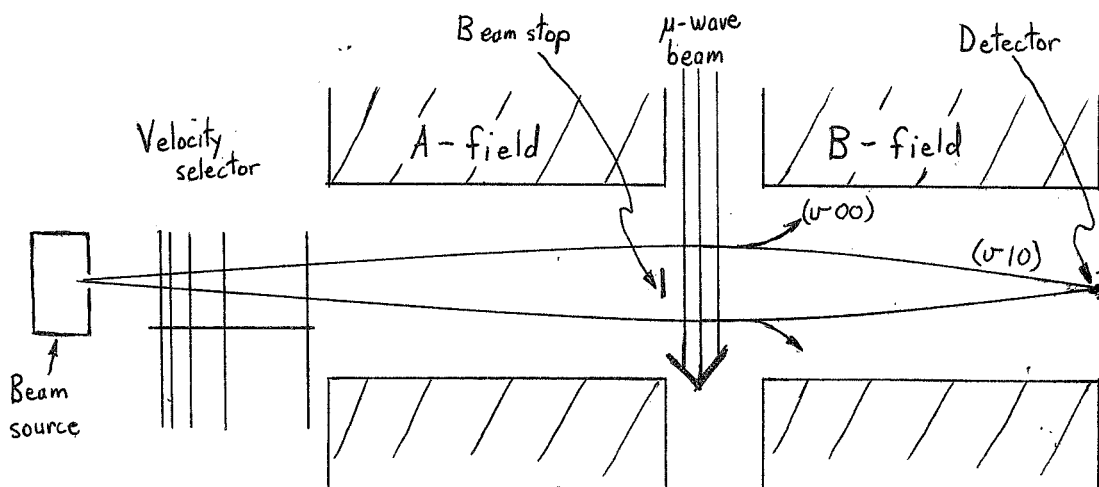
Note also, that if one hold L fixed and varies V_0 (or v), each individual rotational state i will be brought into focus at the detector when Eq. 12 is satisfied for $f_2(J_i, M_i)$.

B. Vibrational state selection

1. Method of selection of vibrational states

This section is largely a redescription of the vibrational state selection method (the "negative beam" or flop-out technique) from the Ph.D thesis of T. G. Waech.⁹ The experiments of the present author were in fact carried out on the same apparatus as that used by Waech. This apparatus had also been used previously in some of the reactive asymmetry experiments utilizing a hexapolar electric field, as noted earlier,¹⁰ after which it was refitted with the four-pole field and microwave facilities for the vibrational state selection, to be described below.

Utilizing the results of the previous section, one may consider a mechanically chopped (i.e., modulated off-and-on at 25 Hz) beam of velocity-selected polar diatomic molecules (e.g., CsF) for which the rod voltage V_0 on the A-and B-fields cause the states $(J,M) = (1,0)$ to be focused at the detector, a hot tungsten wire, which produces by surface ionization Cs^+ ions that are multiplied and detected by a phase sensitive detector (PSD): See sketch:



This apparatus is similar to a typical MBER design,^{8a} except that there is only a single obstacle, and the A- and B-fields each deflect the particles through a quarter-wavelength, rather than the usual half wavelength. The signal I' recorded by the detector will consist of the desired component $(J,M)=(1,0)$ (which includes all vibrational quantum numbers, ν) as well as an unwanted component due to scattering of the CsF around the beam stop by residual background molecules in the vacuum chamber, and perhaps surface scattering of the CsF by the field rods, etc. The unwanted component can obviously have any value of (νJM) . In principle, one can reduce this unwanted component with better vacuum and by suitable collimation, trapping, etc., to avoid surface scattering.

If one now introduces a crossed beam of microwave radiation of frequency ν^* into the C-field region to stimulate the transition

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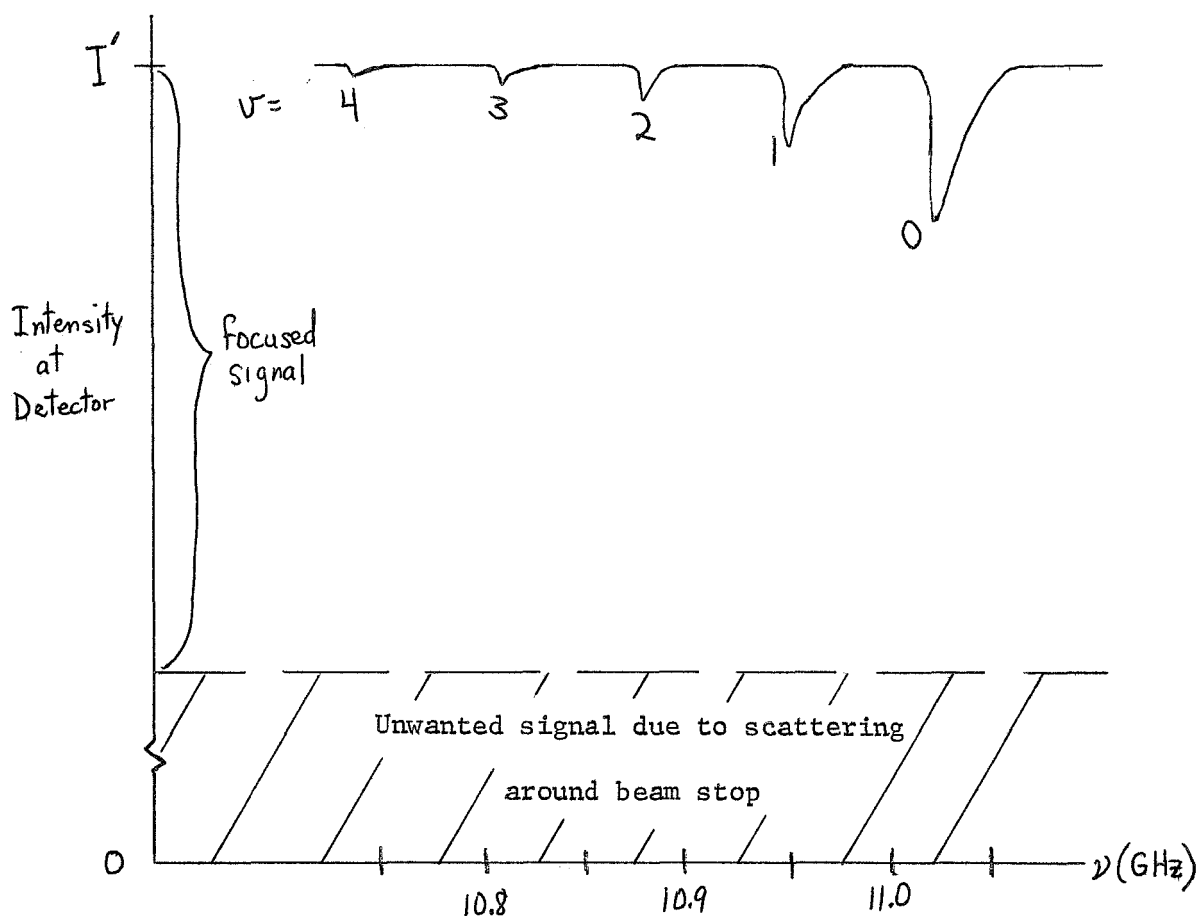
* At this point, the definition of four different symbols is re-emphasized:

V = velocity of particles (cm sec^{-1})
 V_0 = voltage on quadrupole field rods (volts or KV)
 ν = vibrational quantum number
 ν = frequency of microwave radiation (Hz).

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$(\nu 10) \longleftrightarrow (\nu 00)$, one observes a net decrease ("flop out") in signal at the detector due to the fact that the newly formed $(\nu 00)$ molecules have $f_2(0,0) = +\frac{1}{6}$ (i.e., > 0), and are lost from the beam as they take diverging exponential trajectories (see previous sketch). Since this rotational transition frequency ν depends on the vibrational

state (to a good approximation¹¹ $\nu = 2c[B_e - \alpha(\nu + \frac{1}{2})]$, where c is the speed of light, B_e and α are 5.527265 GHz and 35.247 MHz respectively, for CsF^{12} .), then a scan of the microwave spectrum in this region will result in "knocking out" successively up to 50% of the molecules in states with $(J,M) = (1,0)$ and $\nu = 0,1,2,\dots$ (see sketch following):



If one now square-wave-modulates the microwaves off-and-on at a low frequency, e.g., 25 Hz and again detects the beam with a phase sensitive detector (PSD), the constant I' will not be seen; only the "loss" signal, i.e., the $(\nu 10)$ which is transformed to $(\nu 00)$ and

is deflected from the beam will produce an AC signal out of phase with the reference. If the phase of the signal is inverted, it appears as a positive trace with a zero baseline. (See Figs. 1 and 2 for a tracing of some typical data from the recorder chart; these are similar to Fig. 2 of Ref. 9a and Fig. III D. 1 of Ref. 9b.) This modulated microwave molecular beam signal will hereafter be referred to as the MMB signal.

The zero baseline (i.e., the fact that the minimum between resolved peaks corresponds to the electronic "beam off" zero of the PSD) implies that there is no overlap between adjacent ($v'10$) states in the MMB frequency spectrum $I(v)$. It then becomes valid to identify the signal ($v'10$) as $|v'10\rangle$, i.e., a beam of "pure-state" quantum-mechanical kets. More importantly, the $|v'10\rangle$ intensity is proportional to the flux of CsF in the designated state, and provides a direct measure of the relative numbers of molecules in vibrational state v' .

As a final note to this section, it turns out that the velocity selector was not needed for the MMB frequency scans. Originally, it served the dual purpose of cutting down on the gross amount of unwanted signal due to scattering around the beam stop and unwanted signal from other rotational states whose $f_2(J,M)$ and velocity allowed them (for a given V_0 on the rods) to reach the detector along with ($v'10$); both of these sources no longer contribute when the microwaves are modulated.⁹

2. Factors affecting peak shapes

At least three factors influence the shape of the peaks in the "spectrum" (i.e., the plot of $I(\nu)$, the various $|v=10\rangle$ intensities as a function of the frequency ν of the microwave radiation).

These factors are: a) the amount of reflections of the microwaves within the transmission system, b) the microwave power level, and c) the electric field in the C-field transition region.

Factors a) and b) above are closely related. It is observed experimentally that only $\approx 1\text{ mW}$ of microwave power is needed to saturate the transitions, but this results in lines that are badly broadened, often so much so that they overlap. In other words, although the natural linewidth should be considerably less than 0.5 MHz,¹³ high power and/or reflections can produce lines of width $\gtrsim 70$ MHz. (See Fig. 3 for a representative curve tracing illustrating this effect.)

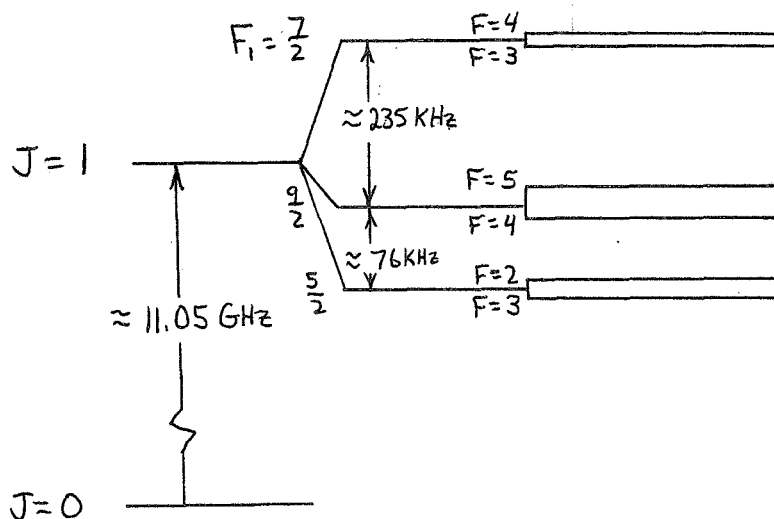
It was noted in the present work that a significant amount of attenuation (≈ 30 dB) had to be introduced into the waveguide in order to reduce the linewidth to ≈ 1 MHz. The broadening at lower attenuation apparently was due to reflections back into the klystron and frequency shifts in the klystron. It was thus necessary to have a microwave source of sufficient power capability such that it could be attenuated by 30 dB and still deliver enough power ($\approx 150\text{--}300\text{ }\mu\text{W}$) into the region of the molecular beam (C-field).

With respect to the electric field in the transition region, Waech showed¹⁴ that a variation from 0 to ≈ 100 V/cm will yield a line-

width of order 12 MHz. To reduce this width to ≈ 0.5 MHz means that the field must vary only from 0 to about 20 V/cm. To obtain this homogeneity, it is necessary either to move the transition region several cm. away from the ends of the A-field rods (not possible with the present experimental apparatus) or to provide electrical isolation (e.g., a grounded conducting shield) between the field rods and the transition region. This latter method was the one actually used (see section III A).

3. Hyperfine structure

One other factor that affects the peak shapes is the hyperfine structure of the rotational transition. The last series of experiments, with lines narrowed to ≈ 1 MHz showed a small, regularly occurring feature on the low-frequency side of each $|v=10\rangle$ peak. This can be seen in Figs. 1 and 2, where the arrows point to the partially resolved structure. The separation of the two peak positions is ≈ 300 KHz, corresponding fairly closely to the splittings observed by English and Zorn.¹⁵ for the zero-field hyperfine levels of $^{133}\text{Cs}^{19}\text{F}$. See the following sketch, which is a reproduction of Fig. 1 of Ref. 15:



Complete resolution of all these states is not possible (nor necessarily desirable) with the apparatus in its present condition. To achieve complete separation, better frequency stability and lower DC electric fields in the transition region are required. English and Zorn¹⁵ used an applied DC field of 1.5 V/cm in order to observe transitions among the F-states of the J=1 level; this compares with a range of $\approx 0-50$ V/cm estimated for the present experimental arrangement. In spite of this limitation on resolution of the hyperfine levels, the partial discrimination (i.e., between the $F_1 = 7/2$ and the unresolved $F_1 = 9/2, 5/2$ levels) is a good measure of the capability of the apparatus in its present form, and suggests that a complete resolution could be achieved (with only modest experimental refinements) if desired.

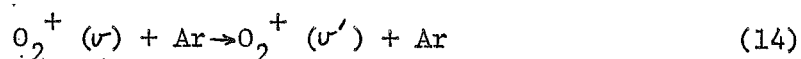
C. Description of scattering experiment

1. Background

Once a method exists that gives an accurate ratio of populations of certain quantum mechanical states (such as that described in Section IIB), it is natural to consider an experiment that might change those populations. Allowing the given ensemble of states to interact with other molecules is such an experiment, one which gives information about the inelastic processes of chemical and physical interest occurring during collisions. The present work involves beams of molecules which differ only by being in different vibrational states, and the collision experiment chosen is one which involves inelastic vibrational scattering.

Inelastic vibrational collisions have been observed previously in beam experiments by several workers in the ion-molecule field. Dittner and Datz¹⁶ have measured the energy loss (due to vibrational inelasticity) of Na^+ ions and of neutral Na atoms scattered from H_2 (and D_2) in the relative kinetic energy range 3-29 ev, and similar energy losses for K^+ ions and neutral K atoms scattered from D_2 in the relative kinetic energy range 10-32 ev. Toennies and co-workers have performed similar experiments for $\text{Li}^+ + \text{H}_2$ (and D_2),¹⁷ with sufficient resolution to "separate" the Li^+ ions corresponding to various final vibrational states of H_2 (or D_2).^{17a} Mahan and co-workers¹⁸ have observed vibrationally inelastic collisions in the large-angle scattering of N_2^+ by He, although their resolution was not sufficient to separate individual states. Moore and Doering¹⁹ studied the collision

of 100-600 ev. protons with H_2 (and D_2) and with N_2 , and have resolved processes corresponding to the excitation of the first four excited vibrational levels in H_2 (D_2) and the first excited vibrational level in N_2 . Recently, Cosby and Moran²⁰ have published angular distributions of the vibrationally inelastic transition probabilities for the process



with $\nu=0$ and $\nu' = 0, 1, 2, \dots, 13$, and energy distributions for the $\nu=0 \rightarrow \nu' = 1, 2, 3$ process in $O^+ + O_2 (X^3\Sigma_g)$. The results are interpreted in terms of a semiclassical model.

Non-beam methods of determining vibrational transition rates often involve the excitation of a specific vibrational level in a gas sample by means of monochromatic radiation. The decay of the population of this excited state is then monitored by the intensity of its fluorescence spectrum or by the rate at which the molecules cease to absorb the exciting radiation, both methods giving information about collision processes which depopulate the excited state.²¹ Recently, this type of experiment has been given impetus by the development of lasers which serve as the required intense source of monochromatic radiation.²²

The scattering experiment in the present work attempts to measure changes in the relative state population ratios of the rotational-vibrational state-selected beams of CsF upon attenuation by scattering due to a second (crossed) beam of molecules or a scattering gas. Because of the difficulty in separating elastic from inelastic events (i.e., molecules reaching the detector don't carry tags

identifying the process by which they got there), one cannot easily determine how much of the attenuation is due to elastic scattering and how much (if any) is due to inelastic scattering processes. Nevertheless, a change in the ratios of the populations of the $|\nu 10\rangle$ states (in particular the ratio $|110\rangle/|010\rangle$ is necessarily caused by some scattering process that is different for the different states under consideration. This ratio change is the measured experimental quantity, to be described below.

2. The present experiment

The present scattering experiment consists of repetitive measurements of the "peak heights" in the frequency scans $I(\nu)$ (see Section IIB and Figs. 1 and 2) for two selected quantum states $|\nu JM\rangle$ ($= |010\rangle$ and $|110\rangle$) for a MMB of CsF. This establishes the population ratio $|110\rangle/|010\rangle$ for the vibrational states in the beam. This ratio should, in principle, be defined by the temperature of the beam oven if one assumes that the CsF was in thermal equilibrium with the oven as it was emitted. Then

$$\frac{|110\rangle}{|010\rangle} = \exp\left[-\frac{E_{|110\rangle} - E_{|010\rangle}}{k T_{\text{oven}}}\right] = \exp\left[-\frac{\hbar \omega_e}{k T_{\text{oven}}}\right]. \quad (13)$$

(Hereafter, this ratio of populations will be abbreviated I_1/I_0 .)

Moran and Trischka²³ have verified that the ratio of populations of vibrational states given by Eq. 13 is, in fact, satisfied for beams of LiF and LiCl.

The value of this ratio I_1/I_0 for the direct CsF beam is to be compared with its value after the CsF beam has been attenuated by a

a secondary crossed beam (or a scattering gas), typically CO_2 . As in Ref. 23, the peak heights were chosen as the monitor of the vibrational populations in order to facilitate a rapid replication of the microwave frequency scans (both with and without scattering gas), in an attempt to minimize the effects of long term drifts.*

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* As an alternative, the area under the curve $I(\nu)$ for a given transition might be a more correct quantity to measure, but two factors make this impractical with the present apparatus. First, the noise level in the portion of the curve which is Stark-shifted to higher frequencies than that of the zero-field transition introduces a large uncertainty into what is only a small portion of the total integrated $|v10\rangle$ intensity. Second, long-term drift would be much more troublesome, since the complete frequency scan takes 3-10 times as long.

- - - - -

Even if some systematic error exists which would produce a ratio I_1/I_0 for the unattenuated beam that does not satisfy Eq. 13 (and this is evidently the case; see Section IV B), the experiment is designed so as to compensate for such an error. The measurement of the I_1/I_0 ratio is done identically in all cases on a given day, the only difference being the presence or absence of the secondary beam (or gas). Any systematic errors should be present in both cases; any change in the ratio I_1/I_0 can be due only to a scattering process which is different for the $v=1$ state than for the $v=0$ state.

One such process is vibrationally inelastic scattering, which the present experiment is intended to observe.

The experimental procedure is as follows: the CsF MMB is tuned up, usually on the state $|010\rangle$, to obtain a maximum intensity (for a given oven temperature) on the PSD. Then, following the method to be described in Section IIIC. 3, the heights of the $|010\rangle$ and $|110\rangle$ peaks are recorded by sweeping the microwave frequency slowly through each transition maximum, and rapidly between maxima. As quickly as possible, one then obtains intensities corresponding to $\nu=0, \nu=1, \nu=0, \nu=1, \dots, \nu=0$. The data from such a set of measurements, typically 4 peaks of $\nu=0$ and 3 peaks of $\nu=1$, are defined as a "cluster". After one "cluster," the system is again tuned up on the $\nu=0$ peak maximum and scattering gas is admitted to the crossed beam apparatus until the $\nu=0$ peak is attenuated by 20-35%. (For attenuation magnitudes, see Table 1.) The procedure of scanning the $\nu=0$ and $\nu=1$ peaks is then begun again, and data are taken with the attenuated CsF beam, to determine another "cluster". The scattering gas is pumped out and another cluster is measured. Scattering gas is then readmitted for determination of a fourth cluster. This process is continued until enough data has been taken, or until something breaks down.

One important experimental requirement that must always be fulfilled in order that the final data accurately reflect the beam intensity received at the detector (see Section IIIA for a description of the detector) is that the electron multiplier be operated in a

TABLE 1

Summary of percentage attenuations

Date	Method of Attenuation	Attenuating Gas	Cluster #	% Attenuation ($\pm \approx 2\%$)
Jan. 24	Scattering Gas	CO ₂	1	24
Jan. 24	Scattering Gas	CO ₂	2	28
Feb. 16	Scattering Gas	CO ₂	3	28
Feb. 16	Scattering Gas	CO ₂	4	35
Mar. 20	Scattering Gas	CO ₂	5	30
Mar. 20	Crossed Beam	CO ₂	6	27
Mar. 20	Crossed Beam	CO ₂	7	24
Mar. 20	Crossed Beam	CO ₂	8	29
Mar. 20	Crossed Beam	CO ₂	9	23
Mar. 1	Crossed Beam	Trichlor*	**	34
Mar. 1	Crossed Beam	Argon	**	32

* 1,1,1-trichloroethane

** Not numbered

linear mode (constant gain). To a lesser extent, this problem of maintaining linearity exists for all the elements in the detector circuitry: the PSD and the chart recorder must operate in a linear fashion, and the elements of the ion lenses in the detector assembly must be maintained at constant voltages (see Section IIIA). The multiplier, however, is different in that it exhibits a systematic nonlinearity that grows worse as the signal magnitude increases. This nonlinearity is relatively easy to avoid in practice; one need only not "overload" it by extracting too large a current from its output. For a discussion of this point, see Section IIIE. Also, for a related piece of data which indicates that this nonlinear effect was absent in the present experiments, see Section IID.2.

D. Experimental problems

Several troublesome experimental problems are discussed below. Each of these was annoying, but not particularly serious. Unfortunately, they are much easier to describe than to explain and/or overcome.

1. Loss of detector activation

The 0.25 mm tungsten wire which served as a surface ionization detector (see Section IIIA) was normally almost 100% efficient in forming Cs^+ ions from the CsF that struck it. It was operated at a moderate red glow, by means of a filament current of 3.5-3.6 amp. This current (temperature) offered the best compromise between excessive noise at the high extreme (i.e., current $\gtrsim 3.8$ amp) due to emission of large amounts of alkali ions that are normally embedded in the tungsten crystalline matrix, and at the other extreme, loss of AC signal due to the too-long pre-ionization residence times ($\gtrsim 10$ msec) of the Cs atoms on the wire at current levels $\lesssim 3.0$ amp.

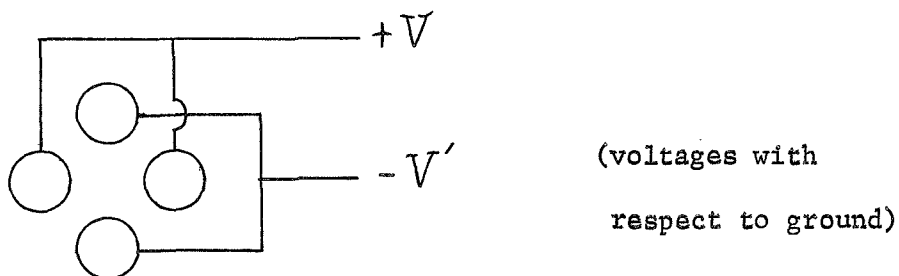
It was found that after about one hour of operation at 3.5 amp, the signal began to decline rather rapidly; this was due to loss of detector efficiency, rather than to actual decrease in beam intensity. The detector efficiency could be restored by passing a current of ≈ 4.1 amp. through the wire and simultaneously adding liquid nitrogen to the cap surrounding the detector (see Fig. 4) assembly for a few minutes. Upon reducing the detector current to its base value of ≈ 3.5 amp, it would then detect at 100% efficiency again.

The reason for this signal decline is not understood; the most likely explanation is that the work function of the wire has been

decreased by the "poisoning" effect noted by Touw and Trischka²⁴. The substance most likely to be responsible for this is the hydrocarbon diffusion pump oil, but this is somewhat unexpected, as the liquid nitrogen baffles between the diffusion pumps and the molecular beam chamber should have minimized backstreaming of this type (see Section IIIA for characterization of the vacuum system).

2. Asymmetric voltages on focusing field rods

The focusing of rotational states of polar diatomic molecules in an ideal four-pole field assembly depends only on the difference voltage ΔV on adjacent field rods. In Section IIA, ΔV was given by $\Delta V = V_0 - (-V_0) = 2V_0$, i.e., the magnitude of the voltage was the same on all rods, and the system was symmetric with respect to ground. This need not be the case, and in fact the largest MMB $|v10\rangle$ signal (i.e., peak intensity) is obtained with an asymmetric voltage on the rods:



Unfortunately, this asymmetric rod voltage produces stronger "end effects," i.e., larger stray electric fields in the C-field

transition region, and leads to much greater Stark broadening of the lines. This was the reason for the introduction of the isolation shields, described in Section IIIA.2, to surround the C-field region (i.e., to narrow the range of transition frequencies by isolating the region from the stray electric fields). With this arrangement, the linewidth observed (see Fig. 3) has a FWHM of ≈ 1 MHz, although there is still a small amount of signal up to ≈ 5 MHz higher in frequency than that of the zero-field transition. To get an integrated intensity for a given ν , then, one must span this whole 5 MHz range.

3. Slow decline of signal with time

The oven temperature stabilized easily; it remained constant to ca. ± 0.04 mv (± 1 $^{\circ}$ K) out of ≈ 28 mv (≈ 950 $^{\circ}$ K). These voltages represent the temperature of the oven as sensed by two chromel-alumel thermocouples ($1 \text{ mv} \approx 25$ $^{\circ}$ K) attached to the oven (see Section IIIB). In spite of this apparent constant temperature, the $|\nu 10\rangle$ MMB signal typically showed a slow decline of up to $\approx 50\%$ of its original value (i.e., that obtained just after the oven reached 28 mv) over the several hours during which a typical MMB experiment was carried out. This effect was troublesome, as the steady decrease in AC signal (with the noise level remaining approximately constant) was what usually limited the useful lifetime of the experiment. Trivial explanations of this decrease, i.e., plugging of the slit, corrosion of the slit by impurities, etc., do not seem to be the actual cause. Another possible explanation of this effect could be the increased formation

of dimers.²⁵ The oven slit was kept $\gtrsim 25$ °K hotter than the main body of the oven during the initial warm-up, and more power was put through the heaters near the slit than through those at the other end of the oven where the CsF charge was located. Nevertheless, the oven temperature probably became slightly more uniform as the operating temperature was reached and maintained, thus increasing the percentage of dimers emitted.²⁶

This signal decline is interesting from another standpoint however, as it sheds light on the possible nonlinearity of the Bendix electron multiplier, a problem mentioned in Section IIC and discussed in Section IIIE. In the discussion, it is noted that overloading the multiplier will result in a measured I_1/I_0 ratio that is smaller than its true value. In the present experiment, if the multiplier were significantly overloaded, then the decline in signal with time would result in an increasing I_1/I_0 ratio for CsF (measured in the absence of scattering gas). That this is not the case can be seen (to some extent) in Figs. 11 - 14, which are plots of I_1/I_0 as a function of time during a given experiment, and more clearly, from the data analysis of Section IVC. The graphs and the analysis show that in spite of a large scatter for the individual measurements, the long-term variation of the unattenuated I_1/I_0 ratio is essentially zero. This provides confirmatory evidence that multiplier nonlinearity is not a problem here.

III. EXPERIMENTAL APPARATUS

Section III describes the physical apparatus in which the experiment was carried out. Except for changes in the microwave system and the beam production systems, the basic apparatus is almost unchanged from the thesis work of T. G. Waech.^{9b} In Section IIIA, a brief description of the basic apparatus is presented, with frequent referral to Ref. 9b, in which a more complete description (including photographs and drawings) is given. Section IIIB of the present work is a description of the beam system and scattering center. Section IIIC details the microwave system. Section IIID suggests possible improvements for future experiments, and Section IIIE is a precautionary note about the problem of "saturation" due to high current levels in the Bendix electron multiplier in the detector assembly.

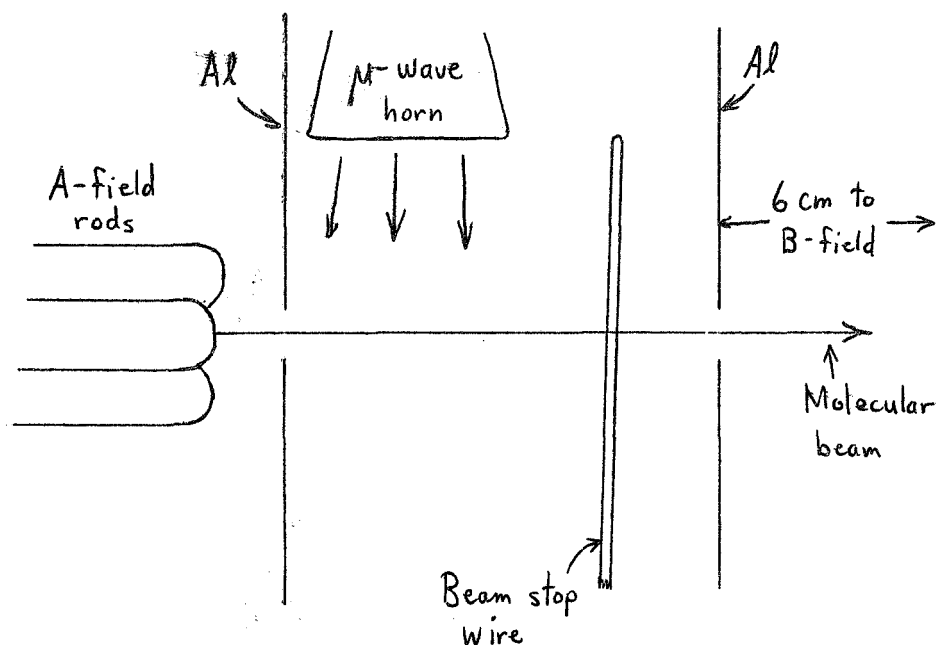
A. Basic apparatus and operating conditions.

The apparatus consists of two differentially pumped chambers (see Ref. 9b, Figs. VA.1, VA.2, and VA.3). The smaller oven chamber is made of brass, and the larger main chamber (containing the velocity selector, focusing fields and detector assembly) is of stainless steel. The pumping system is also the same as in Ref. 9b, except that Consolidated Vacuum Corp. "Convoil-20" hydrocarbon diffusion pump oil is used in all three pumps. In addition to the diffusion pumps, there are large liquid nitrogen cooled surfaces in both chambers. This cryogenic pumping is especially important in the oven chamber, where the 2-inch diffusion pump is inadequate without it. Typical operating pressures (nominal ion gauge readings) in the oven chamber are: $1-2 \times 10^{-6}$ torr with the CsF at its equilibrium temperature, but without scattering gas, and $1-5 \times 10^{-5}$ torr with scattering gas (the highest pressure obtained with noncondensable argon). The main chamber pressure was typically $1-2 \times 10^{-7}$ torr.

The CsF beam (either direct or attenuated) passes through the aperture from oven to main chamber, through the velocity selector, the four-pole field which selects the (1,0) rotational state, the microwave (C-field) transition region, then is refocused by the second four-pole field onto the detector.

The velocity selector and the four-pole field have been described previously.^{9b} The C-field transition region differs from that of Ref. 9 in that two grounded sheet metal aluminum plates were inserted perpendicular to the beam to isolate this region from the stray DC electric

fields caused by the end effects of the 4-pole rods (mentioned in Section IID.2). The plates each had a 0.635 cm dia. hole for passage of the beam. The following sketch (to scale, and looking down on the system) illustrates the placement of the shields:



Note the closeness of the A-field rods to the transition region. It is probable, in fact, that the residual "end effect" electric field penetrating into the hole in the first Al sheet is responsible for the line broadening beyond the natural (calculated) value of ≈ 0.5 MHz.

The detector has also been described previously.^{9b, 10} The photographs (Fig. 4) in the present work are included to show the surface ionization assembly (the construction of which was a part of the thesis work¹⁰ of R. J. Beuhler) in its present state of refinement. In the present work, only the 0.25 mm W wire (refer to Fig. 4B) was used for surface ionization. It was operated at a moderate red glow by passage

of a current of 3.5 - 3.6 amps. The ions formed on the wire were focused by the einzel lens and injected into the quadrupole mass-filter, whose resolution was adjusted experimentally to give as noise-free a transmission of Cs^+ as possible. (The main use of the mass-filter in the present work is to discriminate against K^+ ions emitted from the W wire.)

The mass-selected Cs^+ ions are refocused by a second einzel lens and strike the input dynode of a Bendix M306 electron multiplier operated at a gain of ≈ 1000 (1 Cs^+ yields ≈ 1000 electrons). (See Section III E for a cautionary note about the signal levels in the multiplier.) The output from the multiplier goes to a cathode follower (input resistance $10^7 \Omega$), then to the PSD, which detects the 25 Hz component of the signal and whose rectified output is displayed on a strip chart recorder, from which the tracings in Figs. 1 and 2 were taken. A block diagram of the entire detection system is given in Fig. III-4 of Ref. 10 and Fig. VC.1 of Ref. 9b.

B. The scattering system.

The beam system consists of an oven (see Figs. 5, 6, and 7) from which the CsF effuses, and a secondary source, an array of parallel capillary tubes which are directed perpendicular to the direction of the CsF beam. The capillary array was used only in the last two experiments, however; in all preceding experiments, the scattering gas was admitted non-directionally via an opening in the wall of the oven chamber.

The CsF oven was a typical stainless steel effusive source with a single slit 0.25 mm by 5.0 mm, with the long dimension horizontal (to be compatible with the beam stop and detector wire, also horizontal). It had coiled tungsten heaters at both ends, and the slit end was normally kept $\approx 25^\circ\text{K}$ hotter than the "stock". Two chromel-alumel thermocouples are used to measure the oven temperature: one is bolted onto the back of the oven, and the other is located deep inside a hole in the oven, close to the slit. The oven is shown, in photographs and in a drawing, in Figs. 5A, 6, and 7.

The capillary array is described in Figs. 5B, 6, and 7. It is a Brunswick Collimated Hole Structure, sample #2. The area of the array is 5.8 mm x 1.7 mm; the capillary tubes are 3.0 mm long and 0.025 mm (nominal) radius. The array is nominally 41% open, giving a total of ≈ 2200 tubes. An estimated flow rate for the noncondensable argon (i.e., product of pressure rise in the chamber when scattering gas is added and the estimated speed of the diffusion pump) is $\approx 1.8 \times 10^{16}$ molecules/sec. The flow rate per tube is 8×10^{12} molecules/sec, resulting

in a calculated²⁹ angle, $\chi_{1/2}$, at which the intensity of the secondary beam is $\frac{1}{2}$ that in the forward direction, of $\approx 5^\circ$.

C. Microwave system

1. General description

The microwave system is similar to that of Ref. 9b, with several important changes as designated. The assembly consists of a microwave source (a Varian X-13 klystron, described in Section IIIC.2) coupled into a transmission system which carries the microwave radiation into the vacuum chamber to the vicinity of the molecular beam. After leaving the klystron, the microwaves pass through a ferrite isolator and a variable attenuator, then are emitted into a 1 cm air gap. In the air gap, they are modulated (chopped) mechanically at 25 Hz by a rotating wheel (see Section IIIC.4). The microwaves that get through the chopper are recollected by a horn antenna and pass into a 10dB directional coupler, then through a window into the vacuum chamber, where they are "broadcast" from another horn antenna into the C-field transition region. The sidearm of the directional coupler contains a wavemeter and crystal detector for monitoring the frequency and power level of the microwaves. (For photographs, a block diagram of the microwave system, and a complete listing of the component parts, see Figs. 8-10).

The microwave transmission system was made up of (mismatched) components intended for several frequency bands. It was therefore advantageous to have enough microwave power available to operate with appreciable attenuation in order to minimize the problem of reflected waves and "frequency pulling" of the klystron (see following section).

2. Klystron and power supply.

The early experiments employed a Polarad 1107H microwave source (3.8-8.2 GHz) and Polarad Model 1509 frequency doubler (10.0-15.5 GHz). Also, one run was made with a Hewlett-Packard (HP) Model 8690A sweep oscillator (generously loaned by Prof. R. C. Woods). The HP source demonstrated the advantage of having a greater power capability. The Polarad source was necessarily operated at peak power, and its output power spectrum $P(\nu)$ varied widely with frequency ν . Another annoying feature was the necessity of operating at low attenuation with concomitant broadening of the CsF peaks.

For these reasons, a new microwave source was obtained: a Varian X-13 klystron (forced-air cooled), powered by a HP 716B klystron power supply. Typical operating conditions were:

Beam voltage: - 365 v (with respect to chassis ground)
 Reflector voltage: - 340 v (with respect to beam supply)
 Beam current: ≈ 32 ma

These settings resulted in a power output of >100 mw, at 11 GHz. Under typical experimental conditions, this was reduced ≈ 30 dB by the attenuator and ≈ 2 dB due to the air gap, resulting in approximately 150 - 300 μ w delivered into the region of the molecular beam. (The X-13 can deliver somewhat more power than 100 mw if one desires to work with a higher attenuator setting (to minimize the reflections discussed in Section IIB.2) while maintaining the same power delivered to the molecular beam.)

3. Details of frequency sweep.

The electric tuning range of the X-13 klystron (i.e., the region over which the frequency may be varied by holding the resonant cavity size fixed and varying the reflector voltage) is only barely wide enough to cover both the $|010\rangle$ and $|110\rangle$ peaks, which are separated by $2\alpha = 70.494 \text{ MHz}^{12}$. Therefore, in order to permit slow scans through the peaks ($\Delta\nu \cong 1 - 2 \text{ MHz}$) and rapid change between the peaks, the following mechanical method was used to vary the frequency by changing the cavity size:

A Hurst Model 112RC synchronous motor which turned at 1.0 revolution/hr was geared down by a 50:1 worm. The driven output of this assembly was coupled to the micrometer screw which adjusts the cavity size of the klystron (see Fig. 8B). Power for the motor came from an RCA Model WA-44C audio oscillator, amplified by a Knight Model KN3220A power amplifier. A 60 Hz setting on the RCA oscillator then yielded the desired frequency sweep rate of $\approx 0.8 \text{ MHz/min}$. (The sweep rate could be changed from about 0.5 to 3.0 MHz/min by altering the frequency of the oscillator. See Fig. 10 for a block diagram of the microwave apparatus.)

Since the final experimental data consisted of measurements of peak heights only for the two rotational transitions, it was possible to use the following techniques to go rapidly from peak to peak while scanning slowly (0.8 MHz/min) through the regions of peak maxima:

a) The motor was left running all the time, being connected/disconnected to the klystron by tightening/loosening a set screw on the output shaft of the motor.

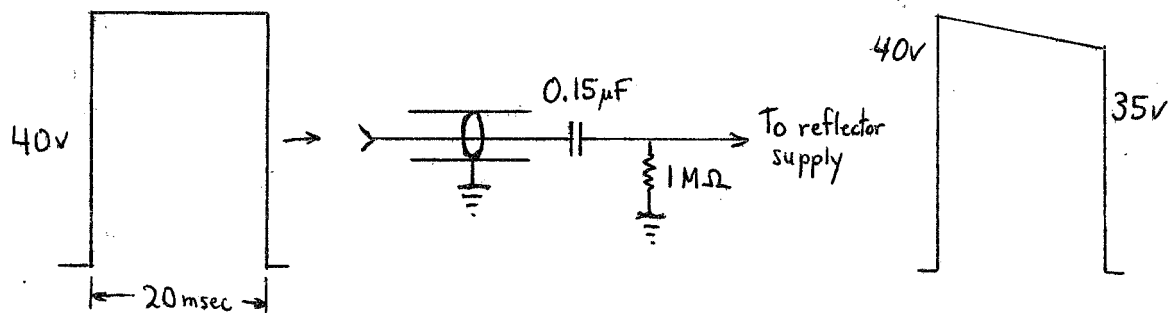
b) The approximate frequency was set rapidly by a hand turn ($\approx 1 \frac{1}{2}$ revolution) of the dial which connects to the motor (see Fig. 8B).

c) The set screw was tightened and the oscillator set at about 240 Hz (≈ 3.2 MHz/min). As the transition frequency was neared, the oscillator was cut back to 60 Hz to sweep through the peak maximum.

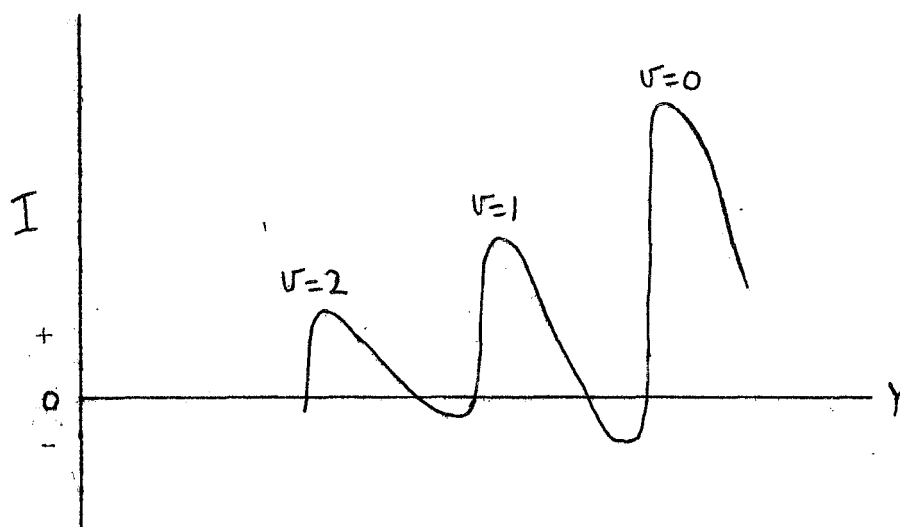
d) The set screw was loosened and the process repeated for another transition frequency.

4. Method of modulation.

The method of modulation of Ref. 9 was used initially. A 40 volt square wave at 25 Hz was applied to the "Mod in" input of the 716B klystron power supply, which was set on "external modulation". A portion of this signal served as a reference for the PSD. It was soon discovered however, that the input circuitry of the 716B for this mode caused severe droop distortion (5.3 volt) of the waveform. See sketch:



The result was a combination of a "square wave plus ramp" signal going to the klystron reflector, resulting in a frequency modulation of several MHz in 20 msec. This frequency variation produced a molecular beam resonance signal which varied with time during each 20 msec "on-period" of the μ -waves. The time variation yielded a greatly distorted "spectrum" $I(\nu)$, including a negative signal in places (due to the out-of-phase components caused by the unwanted frequency modulation) as the klystron was swept through the transition (see sketch).



Here, $\nu = \nu + \delta\nu$, i.e., the sum of the "nominal" frequency setting ν which is swept by varying the cavity size, and $\delta\nu$ which is due to the unwanted electrical frequency modulation. The zero of the vertical axis is Z , the electronic ("beam off") zero of the apparatus. Note that this is an early experiment with greatly (≈ 50 MHz) broadened lines.

A purely mechanical method of modulation was finally adopted, as shown in Fig. 9. The slotted wheel, rotating at 25 Hz, chops (at constant frequency and phase) both the microwave beam and the reference

signal from the lamp which is sensed by the small photocell. The power loss in the waveguide is small (≈ 2 dB) if the air gap is less than 1 cm. The power for the chopper motor was furnished as follows: a 25 Hz Connor-Winfield Model P125B solid state oscillator is powered by an Eico Model 1020 DC supply. The oscillator output is amplified by a Knight Model KN3220A power amplifier, and one end of the amplified signal is phase shifted by a 2 μ F capacitor in order to derive a 3-phase signal. This 3-phase signal powers a Globe Industries, Inc. Model 53A117-2 synchronous motor, which drives the chopper (see Figs. 9 and 10).

D. Suggestions for future improvements

Several possible improvements suggest themselves. Aside from improving inadequacies of the basic apparatus, i.e., better pumping, better design of crossed molecular beam system etc., the main area for improvement is in the microwave system-transition region.

1. The transition region

Reduction of the inhomogeneous electric fields in the transition region will result in less Stark broadening and greatly narrowed lines. Aside from the improvement of S/N due to the concentration of more of the MMB signal into a narrower frequency range, it might make it practical to scan the transition $|v_{10}\rangle$ electronically (see Section IIID.3).

The Stark broadening of the $|v_{10}\rangle$ lines is due mainly to the penetration of the electric field from the ends of the quadrupole rods into the "C-field" transition region. This was the reason for the success of the aluminum sheets that partially isolated the transition region from these end effects.

A better solution for the problem of isolating the transition region might be to carry out the transitions in a microwave "cavity" inside the vacuum chamber. This would serve the dual purpose of requiring less power (i.e., the microwaves would be confined to the region of the beam rather than being "broadcast" out into the vacuum chamber) and of isolating the molecules from stray DC fields. The cavity would presumably have suitable holes cut in its sides to let the molecular beam go through. One problem with this arrangement would be that of tuning

the cavity inside the vacuum, however.

2. Electronic amplitude modulation of klystron

There are at least two methods of electronic amplitude (off/on) modulation of the microwaves that should be somewhat better than the method currently used. The first of these, is a commercial PIN modulator. It is a semiconductor device (PIN = Positive, Intrinsic, Negative) composed of a number of PIN diodes which are mounted as shunt elements across a transmission line. These elements can act as variable resistors to the passage of microwave energy. The device would be mounted in the waveguide; it is controlled by a 25 Hz square wave of a few volts amplitude, and provides $> 35\text{dB}$ of differential attenuation during the OFF part of the cycle. It is easier to operate than the present method and more reliable (but much costlier).

A second, less costly method, makes use of the 25 Hz, 40 volt square wave generator of Ref. 9 for external modulation of the klystron (see also Section IIIC.4). In order to reduce the droop distortion of the 40 v square wave to an acceptable level, one must increase the capacitance in the input circuitry of the 716B power supply from its present value of $0.15\ \mu\text{F}$ to $\approx 5 - 10\ \mu\text{F}$. The object, of course, is to make the magnitude of the unwanted frequency modulation (in MHz) due to the droop distortion of the modulating signal much smaller than the width of the CsF line. Even the increase in capacitance mentioned above may not be sufficient if the lines are made very narrow by the techniques mentioned in Section IIID.1. In that case however, it might be possible to exploit this factor (see the section immediately following).

3. Electronic frequency modulation of klystron

The droop distortion that was so troublesome when the transitions were broadened $\gtrsim 50$ MHz and the unwanted frequency modulation was ≈ 3 MHz can be turned to positive advantage if the opposite situation holds. For a transition with width ≈ 500 KHz, the whole range of transition frequencies is spanned during the 20 msec "on time" of the microwaves, and the signal recorded by the lock in amplifier will be a measure of the integrated intensity of the peak.

Electronic frequency modulation yields several advantages:

a) The integrated intensity is probably the proper quantity to measure; it is proportional to the total population of a $|v=10\rangle$ vibrational state.

b) The intensity is considerably easier to measure because one can tune up the peak value of the integrated area and then remain at this maximum value and average out the short-term noise. This is not possible when the frequency is scanned (as in the present work). There, one must try to extract the peak height from a significant amount of short-term ($\approx 1-5$ sec) noise on a curve that is sharply peaked.

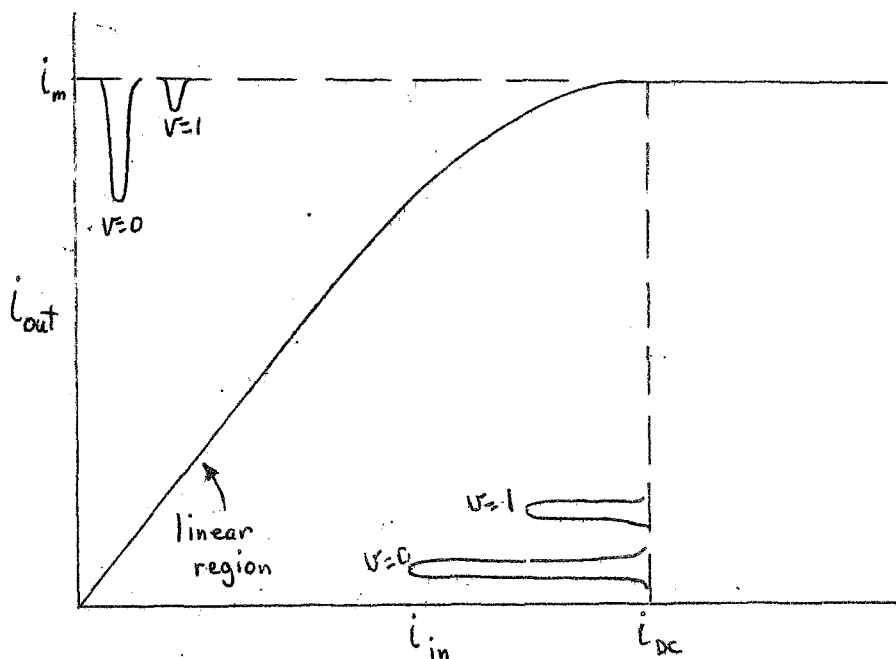
c) Concurrently, electronic modulation lends itself to signal-averaging instruments, since transients can be averaged out electronically.

d) If a PIN modulator is used for amplitude modulation, it might be advantageous to do the electronic frequency modulation at a considerably higher frequency (≈ 10 KHz) than the chopping frequency. This will eliminate entirely the effects of the RC coupling to the klystron power supply.

E. Current levels in the electron multiplier

Many molecular beam experiments develop an AC signal by means of mechanical chopping of the beam by some sort of chopping wheel. This was done in the present experiment, in fact, as is noted in the first part of Section IIB.1. Under these conditions, essentially all of the ions that reach the multiplier will represent signal which has been modulated at the reference frequency (here, 25 Hz).

This is no longer the case when the microwave source (or some other parameter, such as the voltage on the rods) is modulated. Then, as before, the AC component will still be the only thing detected by the PSD, but now there is a large DC background of unmodulated CsF that strikes the wire, is ionized, mass selected, and impinges on the multiplier. This DC background, perhaps ten times the size of the AC signal, can drive the multiplier into a nonlinear region and result in spurious readings. The following sketch, a representation of the "transfer function" of the multiplier operating at a preset voltage (i.e., a preset nominal gain) illustrates this effect.



The sketch is an extreme case in which the large input puts the multiplier far into its nonlinear region (i_m is the maximum current that can be extracted from the multiplier, on the order of 10^{-5} amp). The I_0 and I_1 intensities are indicated as negative ("flop-out") peaks subtracted from i_{DC} , the DC background. The nonlinearity results in $(I_1/I_0)_{out} / (I_1/I_0)_{in} < 1$, i.e., an apparent decrease in the intensity ratio of the beam. Addition of scattering gas to attenuate the CsF signal (including the DC background) will bring the multiplier into a more nearly linear region, resulting in a larger apparent value of $(I_1/I_0)_{out}$. If the multiplier had been badly overloaded, this effect could have explained the measured increase of I_1/I_0 for the attenuated CsF beam.

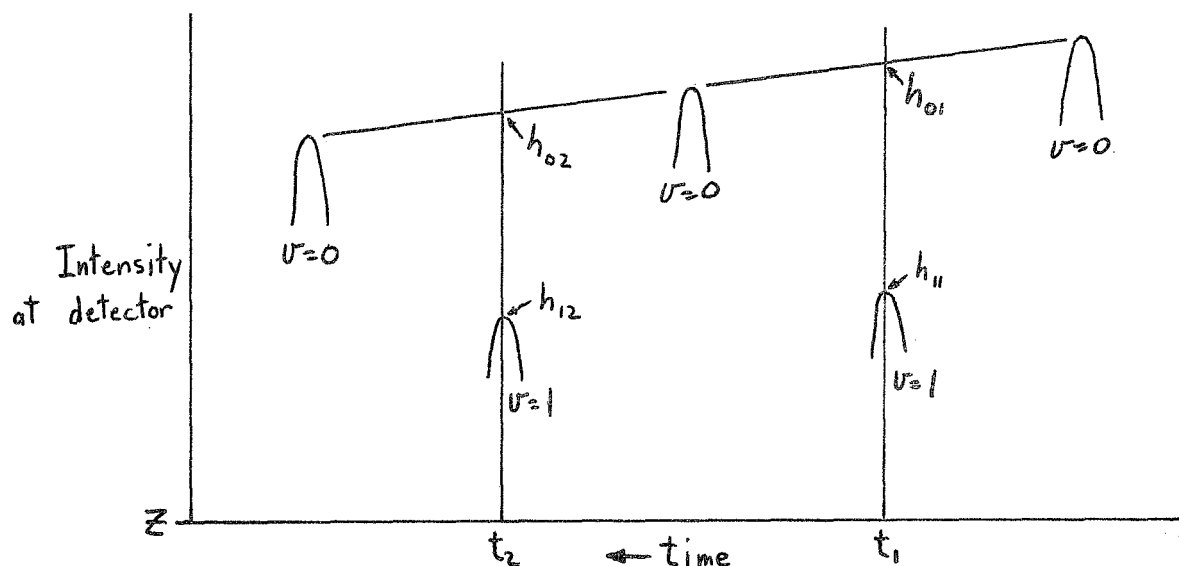
In the present experiment however, care was always taken to keep the multiplier output well below its rated maximum output current of 10^{-7} amp. This section is included as a warning that when a small AC signal is superimposed on a large DC background, some independent measurement of the total signal should be made, e.g., by an electrometer, to determine that the multiplier is not overloaded.

IV. DATA ANALYSIS AND DISCUSSION

A. Treatment of raw data

Typical raw data are shown in the chart tracings of Figs. 1 and 2. The data consist of recordings of the strong peaks $|010\rangle$ and $|110\rangle$ (I_0 and I_1 respectively) taken from the scans of $I(z)$ as described in Section IIC, upon which is superimposed a significant amount of presumably random short-term noise and long-term drift. It is desired to extract accurate values for the ratio I_1/I_0 from data such as these, both for the direct beam and for the beam attenuated by scattering. However, the data reduction is complicated by two sources of inconstancy: first, one must "filter" the peak height out of the short-term noise as accurately as possible, and second, one must correct the overall signal for long-term drift due to such causes as loss of detector activation (see Section IID.1), slow changes in the intensities of the beams, etc.

The peak heights are determined "by eye", with the attempt made to locate as carefully as possible the maximum of the peak in the "center of gravity" of the accompanying noise. (In other words, one tries to locate the peak height where it would be in the absence of the short-term noise.) Compensation for drift is then accomplished by means of a rather conventional linear time interpolation procedure as shown in the following sketch. The sketch is an idealization of the chart tracing, with the short-term random noise removed and only the transition maxima shown:



The time dependence (i.e., drift) is assumed to be linear between $|010\rangle$ peaks (for lack of a better method), and the attempt is made to determine what the $|010\rangle$ intensity would be if it were measured at the same time as the $|110\rangle$ intensity. Since the $| \rangle$ symbol denotes the actual heights measured and not the desired interpolated values, the symbols h_{0i} and h_{1i} are introduced to define the peak heights (or maximum intensities) of the $|010\rangle$ and $|110\rangle$ measured at the "same" time t_i . Now, define $R_i = h_{1i} / h_{0i}$, the ratio of peak intensities $I(v=1)/I(v=0)$ (cf. I_1/I_0). A single value of R_i is defined as one "measurement". Typically, one obtains several of the R_i under identical conditions (i.e., close together in time and either all without scattering gas or all with the same addition of scattering gas); these several R_i are defined as a "cluster" of measurements. Thus, the sketch above illustrates two measurements R_1 and R_2 which form a cluster of two points. These definitions are used in the statistical analysis of the ratio data, described in Section IVC.

B. Results of ratio graphs

Plots of the R_i for experiments on four separate days are shown in Figs. 11-14. The abscissa is the elapsed time, starting from an arbitrary zero. The choice of time as a coordinate is somewhat arbitrary and serves mainly to display the data. Figs. 11-13 show experiments in which CO_2 was the scattering gas, and Fig. 14, an experiment employing 1,1,1-trichloroethane and argon. Figs. 11 and 12 summarize experiments in which the scattering gas was introduced into the oven chamber nondirectionally, i.e., through an opening in the chamber wall. The capillary array (which was more like an actual crossed beam) was installed for the runs summarized in Figs. 13 and 14.

The two values of R_i (i.e., the pairs of connected points on Figs. 11-14) at each time t_i are not separate data, but rather are two independent readings of the same charts. This serves a purpose which can be expressed in two similar ways. On the one hand, it gives some idea of the precision of an individual chart reading by checking its reproducibility. Secondly, it provides replicative data that is used to evaluate the statistical variance in the act of reading the chart. This variance adds to the total uncertainty in the magnitude of the change in R upon scattering, and must be taken into account in any statistical analysis that attempts to define the standard deviation or confidence interval for this magnitude.

Several observations are apparent upon examination of the R_i plots (Figs. 11-14):

The basic ratio for the unattenuated CsF beam (hereafter denoted by R^0), while constant as nearly as can be determined during the

(via Eq. 10 or 12) through the replacement of I (or E_e) and μ_0 by their proper values B_{ν}^{12} and μ_{ν}^{28} which depend on vibrational state. The proper rod voltage for maximum transmission will then depend slightly on vibrational state. When these quantities are put into Eq. 12, one calculates (for a fixed value of L) that the voltage that gives maximum focused intensity for $\nu=1$ is 1% less than that needed to maximize the $\nu=0$. Experimentally, a 1% change in rod voltages (when they are tuned up for maximum intensity) produces a negligible change in the focused signal.

This calculation is not the whole answer, however. It is possible that some combinations of oven, four-pole fields and detector positions could cause different focusing for different states. While it would be rather difficult to calculate whether this effect is the cause of the anomalous ratio, one can demonstrate experimentally that it probably is not. If it were the cause, then presumably the reason for the large changes in the ratio from experiment to experiment would be the difference in relative alignment of the oven, detector, beam stop, and microwave horn with respect to the fixed four-pole fields for each experiment. This implies that it should be possible to change the ratio during a run by moving the above components, either singly or in combination. This was found not to be the case experimentally -- the ratio did not change significantly when these components were intentionally moved during a run. Furthermore, one would expect that if the ratio were lower than theoretical when the apparatus was tuned up for the maximum intensity of the $|010\rangle$ state, then tuning up on $|110\rangle$

should result in a ratio that is higher than theoretical. This was tried and had no effect. Thus, the reason for the anomalous ratio remains obscure.

In spite of this unpredictable discrepancy between the theoretical and measured values of the ratio for CsF in the absence of scattering gas, it is observed that the addition of a scattering gas to produce overall attenuation of the main beam yields a ratio which is greater in all cases than it was in the absence of scattering gas. It is a small increment with a large uncertainty in its magnitude, but its existence is established at a confidence level better than 95% (see next section).

C. Analysis of data

The data from the scattering experiments have been summarized in Figs. 11-14. The individual "clusters" of data are indicated by the brackets in these graphs. In general, each cluster of ratios measured in the presence of scattering gas (these ratios hereafter denoted as R^S) has a cluster of R^O measurements taken between them (i.e., no two clusters R^S are adjacent). This is not the case in Fig. 13, where clusters 6-7 and 8-9 were made with no R^O measurements intervening. These clusters of CO_2 ratios R^S are independent, though, in that they were observed by measuring one cluster of data for scattering gas, evacuating the oven chamber and then readmitting the gas for another cluster measurement. This was done to produce a larger number of clusters in order to improve the statistical significance of the effect.

In analyzing the data, attention is confined to experiments utilizing CO_2 as a scattering gas. Close examination of these results (Figs. 11-13) reveals a significant fact. If one compares the average value of the ratio R^S within a scattering cluster with the average of the ratio R^O for adjacent clusters without scattering, then one observes in all cases that the cluster average of R^S is greater than these average values of R^O . For the nine clusters utilizing CO_2 , the ratios of the cluster averages R^S for scattering to the adjacent cluster averages R^O ranges from 1.003 to 1.051. These nine ratios (hereafter defined as $X \equiv R^S/R^O$) have an average value of 1.021 and a standard deviation of 0.004. The "student's t-value" for a two-ended 95% confidence interval with eight degrees of freedom is 2.31, resulting in

an effect $X = 1.021 \pm 0.011$ at a confidence level of 95%. This primitive method of analysis is designated Method A.

If a more detailed analysis is desired, then a decision must be made as to what is considered to be the basic measurement being taken: is it the individual determinations of the h_i , or are whole clusters the fundamental quantity being observed? The two different assumptions will yield different magnitudes and estimated uncertainties for the value of X .

The details of these analyses are sketched below. They were carried out by R. A. LaBudde, whose kind assistance is gratefully acknowledged. The first of these methods considers the clusters to be the basic experimental quantity measured and the second assumes the same for the individual h_i .

The method of equivalent clusters (denoted as Method B) assumes that all clusters are measured with equal precision and that there is a single distribution of cluster variances. Analysis in this manner results in a value of X_B of 1.019 with a standard deviation of 0.005 and eleven degrees of freedom, yielding $X_B = 1.019 \pm 0.012$ (95% confidence level).

The final method, that of equivalent measurements (Method C), assumes that there is a uniform error associated with measurement of the data and of reading the cahrt; further, that there is a cluster error only when significant. This analysis yields $X_C = 1.016$ with a standard deviation of 0.005 and 40 degrees of freedom. This give a final result $X_C = 1.016 \pm 0.009$ (95% confidence level). These results are summarized in Table 2.

TABLE 2

Summary of data analyses

Method	X	Standard deviation	Degrees of freedom	Error*
A	1.021	0.004 ₇	8	± 0.011
B	1.019	0.005 ₄	11	± 0.012
C	1.016	0.004 ₇	40	± 0.009

* at 95% confidence level

Although the three methods of data analysis give results of different magnitude, they are in accord in that the uncertainty associated with the 95% confidence interval for each calculation is $< 2/3$ of the size of the effect, and that the magnitude of the effect agrees (among the three methods) to within the stated errors of the analyses. Thus, the existence of the effect ($X > 1.00$) is confirmed at better than a 95% confidence level, but with a large uncertainty in its magnitude. Note that $X > 1$ implies preferential vibrational excitation ($\Delta v = +1$) of CsF colliding with CO_2 (in terms of the laboratory signal detected in line with the CsF beam).

D. Discussion of results

1. An apparent anomaly: preferential excitation

The observation of $X > 1$ upon attenuation of the CsF beam by a crossed beam of CO_2 has been demonstrated in the previous section. This effect is not peculiar to CO_2 as a scattering gas; Fig. 13 suggests that a similar increase occurs for argon and 1,1,1-trichloroethane, although there are insufficient data for these cases to yield statistical significance to the effect. Also, some early data taken by T. G. Waech³⁰ indicated a similar effect for H_2O used as a scattering gas. The nonintuitive direction of the effect is illustrated by a simple temperature argument: "cold" (room temperature) CO_2 collides with vibrationally "hot" CsF and makes the CsF "hotter" (i.e., raises I_1/I_0). This result was quite unexpected; in fact it was the opposite of what was expected initially.

Results contrary to preconceived notions are good in that they demand extra evidence before their existence is believed. They also tend to reduce bias, conscious or otherwise, in interpretation of the data. In the present case, the early results (starting with the preliminary observations of T. G. Waech) were viewed with skepticism and were accepted only when the CO_2 measurements were repeated under different conditions and the effect confirmed on several occasions.

A further anomaly is that the elastic scattering, if it is dependent on the vibrational state of the CsF molecule, would tend to make $X < 1$. Because of the increase in the dipole moment and polarizability with vibrational state, it is reasonable to expect an increase of 2-3%

in the long-range C_6 constant. Since the scattering intensity as a function of angle is proportional to $(C_6)^{1/3}$, one might expect the low-angle residual CsF to be enriched in the state $V = 0$ by $\approx 1\%$. This of course is the opposite of the measured effect. The next section attempts to resolve this apparent anomaly.

2. Kinematic considerations

A plausible explanation for the "contraintuitive" effect ($X > 1$) is as follows: * vibrational excitation and deexcitation of the CO_2

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*The author appreciates a preliminary, tentative suggestion of this explanation by M. E. Gersh.

- - - - -

are both occurring, but the detector "sees" a much larger fraction of the scattering due to the former process than that of the latter.

As an example, consider the velocity vector triangle for collision of CsF with CO_2 (shown in Fig. 14). In this figure, the velocity of CO_2 is the most probable velocity α , where

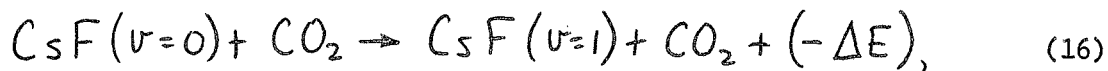
$$\alpha = \left(\frac{2kT}{m} \right)^{1/2} = 336 \text{ m/sec at } 300^\circ\text{K.} \quad (14)$$

For the focusing fields used in the experiment, the CsF velocity is given by^{9b}

$$V(\text{m/sec}) = 502 V_0(kv), \quad (15)$$

where, as before, V_0 is the rod voltage. Thus, with a typical value of V_0 of 1.0 Kv, $v_{\text{CsF}} = 502$ m/sec. For right angle collisions, the above velocities yield $v_{\text{rel}} = 604$ m/sec, and thus, a center of mass relative kinetic energy E_{rel} of 1.035×10^{-13} erg ($=521 \text{ cm}^{-1}$). This is greater than the energy ($=349.32 \text{ cm}^{-1}$ for CsF^{12}) needed to excite the $0 \rightarrow 1$ vibrational mode.

Referring back to Fig. 12, the circle (sphere) labelled "excitation" and " $\Delta v = +1$ " designates the locus in velocity space of all CsF molecules scattered inelastically by the process:



where the initial and final relative kinetic energies are related through ΔE (349.32 cm^{-1}) by energy conservation:

$$\frac{1}{2} M v_{\text{rel}}^2 = \frac{1}{2} M v_{\text{rel}}'^2 + \Delta E, \quad (17)$$

where M is the reduced mass of the system $\text{CsF} - \text{CO}_2$.

Similarly, the sphere marked "deexcitation" ($\Delta v = -1$) refers to the exothermic reverse process.

Now consider the scattered signal that is seen by the detector in the present experiment. The collimator in front of the four-pole field transmits beam molecules with an angular divergence of 0.97° in the laboratory (LAB) (as illustrated in Fig. 7), and allows them to be

focused onto the fixed detector. This implies that the only scattered molecules detected are those whose velocity vector (after scattering) terminates within the region of the 0.97° angular acceptance of the quadrupolar field. A drawing illustrating this is shown in Fig. 15. One notes that the excitation process, whose circle terminates nearly on the CsF LAB velocity vector ($\theta_d = 0^\circ$, since the detector is directly in the path of the CsF beam) allows a wide range of center-of-mass (C. M.) angles to appear in the 0.97° laboratory angular range. This phenomenon, known as "Jacobian cusping", (i.e., that a "large" range of C. M. angles are crowded into a narrow range of LAB angles) yields great enhancement of the scattered signal observed at the cusp angle (here at a LAB scattering angle $\theta_d = 0$). This enhancement does not occur for the deexcitation process. (See Fig. 16 for an illustration of the Jacobian cusping.)

A second process (also shown in Fig. 16) that adds to the enhanced detection of the excitation product is that it is confined to a smaller region in velocity space than is the deexcitation product; thus, a fixed laboratory detector angle will see "more" of the excitation process than the deexcitation. These two effects are strictly kinematic in origin and may be evaluated quantitatively (see Warnock and Bernstein³¹). One obtains the following relation for the ratio of the average differential solid angle LAB cross section $(d^2I/d^2\Omega)_{ex}$ for excitation to that for deexcitation at a LAB scattering angle $\theta_d = 0$ from Eq. 39 of Ref. 31:

$$\frac{\left(\frac{d^2 I}{d^2 \Omega}\right)_{ex}}{\left(\frac{d^2 I}{d^2 \Omega}\right)_{dx}} = \frac{\frac{\sigma_{ex} g_{ex}(\theta_{ex})}{W_{ex}'^2 |\cos \beta_{ex}|}}{\frac{\sigma_{dx} g_{dx}(\theta_{dx})}{W_{dx}'^2 |\cos \beta_{dx}|}} = \frac{[\sigma_{ex} g_{ex}(\theta_{ex})]}{[\sigma_{dx} g_{dx}(\theta_{dx})]} \times \frac{W_{dx}'^2 |\cos \beta_{dx}|}{W_{ex}'^2 |\cos \beta_{ex}|}, \quad (18)$$

where

σ_{ex}, σ_{dx} = integral cross sections for excitation and deexcitation,
respectively

$g_{ex}(\theta_{ex}), g_{dx}(\theta_{dx})$ = C. M. angular distributions of these cross sections,

W_{ex}', W_{dx}' = C. M. recoil velocities,

β_{ex}, β_{dx} = angle between $\hat{Q}_d$ and W_{ex}' and W_{dx}' , respectively.

(Many of these symbols are defined in Fig. 16.)

Little is known a priori about the σ and the $g(\theta)$ for this system. Presumably, for a kinetic energy only ca. 1.5 times threshold,

σ_{ex} is considerably smaller than σ_{dx} (which has no threshold). Regarding the angular distributions $g(\theta)$, the only reliable existing calculations are those for He - H₂ by Micha and Rotenberg³², which have indicated preferential forward C. M. scattering for vibrational energy transfer, in contrast to the backscattering results inferred from more primitive arguments by earlier workers. This is important, as the vibrationally inelastic scattering (if it occurs) at $\hat{Q}_d = 0$ will correspond to C. M. angles of 9° and 56° for excitation and deexcitation respectively (i.e., scattering into the forward hemisphere). The results of Ref. 32, therefore, suggest that the present explanation of the unexpected experimental results is not immediately ruled out on a theoretical basis.

The other factors in Eq. (18) are known more definitely. Given any pair of values of V_{CO_2} and V_{CsF} , the ratio $(W'_{dx}/W'_{ex})^2$ is readily computed, and the range of $|\cos \theta_{dx}|/|\cos \theta_{ex}|$ can be exactly evaluated from a diagram such as Figs. 15 or 16. For example, in Fig. 15, $(W'_{dx}/W'_{ex})^2 = 5.2$, and $|\cos \theta_{dx}|$ has a range of 0.93 to 0.94, while the range of $|\cos \theta_{ex}|$ is 0.0 to 0.36. Both the W' and $\int$ factors enhance detection of the excited product then, especially the $|\cos \theta_{ex}| \rightarrow 0$ (although this singularity is not observed in practice due to lack of resolution). Nevertheless, they constitute a considerable enhancement (by a factor in excess of 15) for detection of the excitation process relative to the deexcitation process.

For the velocity of CsF in the above example (502 m/sec), the part of the enhancement just noted due to $|\cos \theta_{ex}| \rightarrow 0$ is almost independent of the velocity of the CO_2 crossed beam. It will occur whenever the C. M. recoil velocity of CsF, W'_{CsF} is equal in magnitude to the perpendicular distance ($\equiv D$) from the C. M. point to the line connecting the scattering center with the detector at angle θ_d (i.e., whenever $\theta_{ex} = 90^\circ$). To achieve this, one requires $\frac{W'_{\text{CsF}}}{D} = 1$. The kinematic algebra for two beams intersecting at an angle β yields

$$\frac{W'_{\text{CsF}}}{D} = \frac{[V_{\text{CO}_2}^2 + V_{\text{CsF}}^2 - 2 V_{\text{CO}_2} V_{\text{CsF}} \cos \beta - \frac{2}{M} \Delta E]^{\frac{1}{2}}}{V_2 \sin \beta} \quad (19)$$

For the present work $\beta = 90^\circ$, and

$$\frac{W'_{\text{CsF}}}{D} = \frac{[V_{\text{CO}_2}^2 + V_{\text{CsF}}^2 - \frac{2}{M} \Delta E]^{\frac{1}{2}}}{V_{\text{CO}_2}} \quad (20)$$

For $V_{\text{CsF}} = 502$ m/sec, there is a fortuitous near-cancellation of the second and third terms in the square root. Then $W'_{\text{CsF}}/D \cong 1$ for all V_{CO_2} , and the pronounced $\mathcal{J}$ enhancement (Jacobian cusping) will be present (to a greater or lesser degree) for a wide range of speeds of the CO_2 molecules in the crossed beam. For the case of the scattering gas (rather than crossed beam), Eq. 19 indicates that the Jacobian cusping will be present for a small range of angles around $\beta = 90^\circ$; at any rate, the W' enhancement will always be present.

A question arises as to the velocity selecting properties of the four-pole field (as derived by Waech^{9b}). He calculated a velocity band-pass of $\frac{\Delta V_{\text{max}}}{V} = 0.21$; if this was the case in the present work, the excitation process would not be seen at $\Theta_d = 0$. The author feels, however, that Waech's calculation refers to a perfect alignment of oven slit, beam stop, and detector. In the present work, the beam stop was occasionally moved by enough to change the ratio over a range $\frac{\Delta V_{\text{max}}}{V} = 1$. This problem is one that needs to be investigated more thoroughly in the future; one way would be to scan the velocity range transmitted with the velocity selector; it should separate signal from excitation and deexcitation processes.

In summary, an increase in the ratio I_1/I_0 for CsF has been observed when the CsF beam is attenuated by scattering gas. The effect is small and has a large uncertainty in its magnitude. An attempt has been made to show that this effect could arise from preferential detection of vibrational excitation over the (more probable) deexcitation process. In order to say anything more definite, considerably more (and better) data is needed, information from systematic variation of both Θ_d and V_{CsF} .

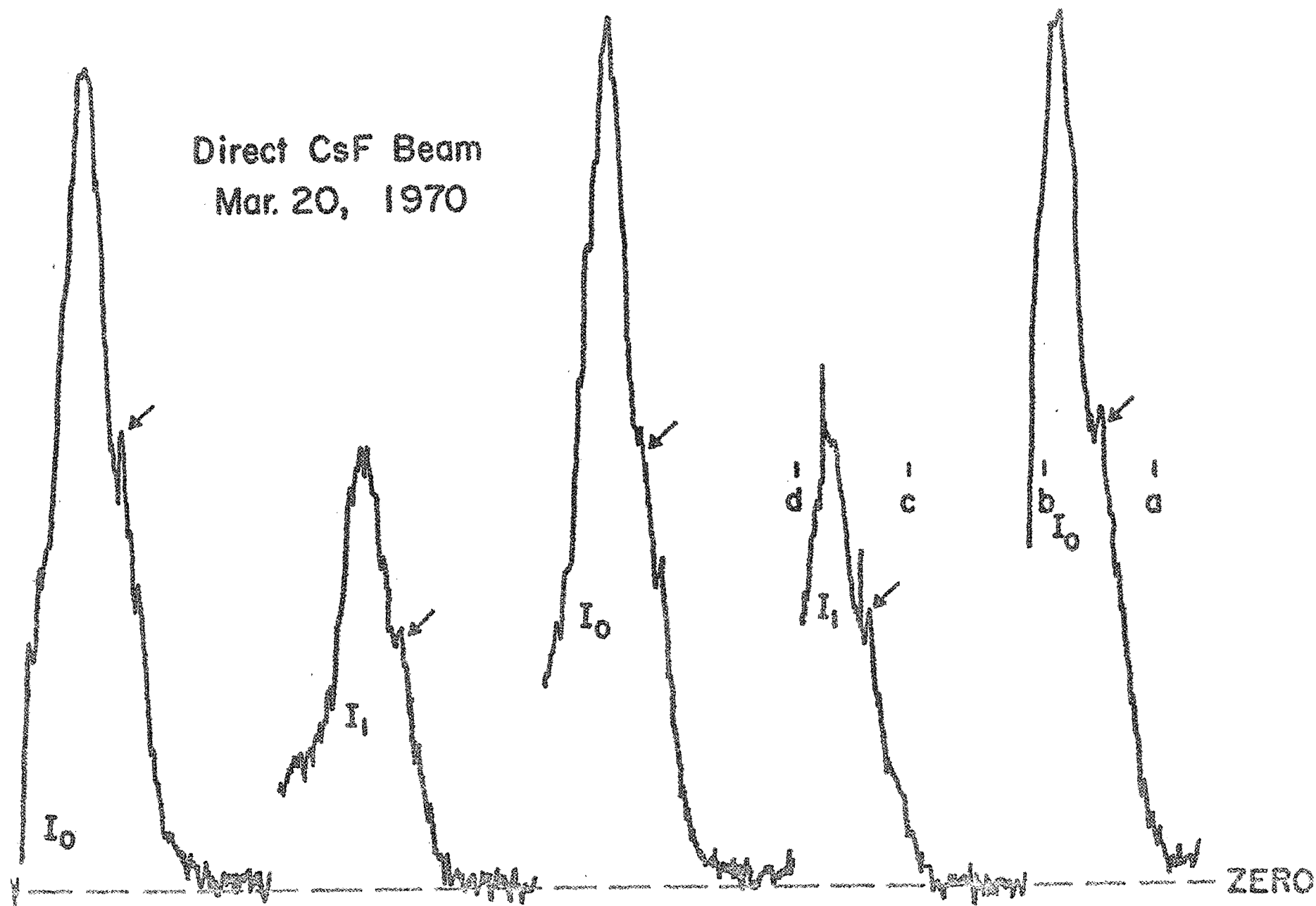
E. Figures

Figure 1. Chart tracing of the direct CsF beam.

This figure shows recorder chart tracing of frequency scans of the $|010\rangle$ and $|110\rangle$ intensities. Frequency markers, to locate the scale for the peaks, are as follows: $a = 11.018$, $b = 11.020$, $c = 10.948$, $d = 10.950$ (all in GHz). The scans are made with the klystron sweeping upward in frequency, starting just below the low-frequency edge of the transition. The low-frequency sides of the peak scans may sometimes be distorted from their true shapes (i.e., too steep) because the frequency sweep was begun at a rapid rate ($\approx 3\text{ MHz/min}$), then reduced to 0.8 MHz/min as the maximum was approached. The peak was scanned through, and then the klystron was tuned up on another peak.

Two features are to be noted. First, the "ZERO" is the electronic "no beam" zero of the BSD (lock-in amplifier). It is from this line that the peak heights are measured. Second, the arrowheads point to side peaks due to two unresolved hyperfine levels, i.e., $F_1 = 9/2$ and $7/2$ ¹⁵ of the $^{133}\text{Cs}^{19}\text{F}$, which (together) are partially resolved from the $F_1 = 7/2$ level (the main peak).

Direct CsF Beam
Mar. 20, 1970



← TIME ← FREQUENCY

Figure 1

Figure 2. Chart tracing of attenuated CsF beam.

This cluster of data for a CsF beam attenuated by ca. 27% by CO₂ is traced from the chart of the experiment of the same day as Fig. 1. The direct (unattenuated) $|010\rangle$ CsF beam appears noisier than it actually is due to the narrowness of the peak and the difficulty of setting the klystron to an exact frequency mechanically. Much of this noise disappears when the klystron frequency is swept mechanically. This cluster of data is that marked CO₂ (6) on Fig. 13. Note that, as in Fig. 1, the arrowheads denote the partially resolved hyperfine structure.

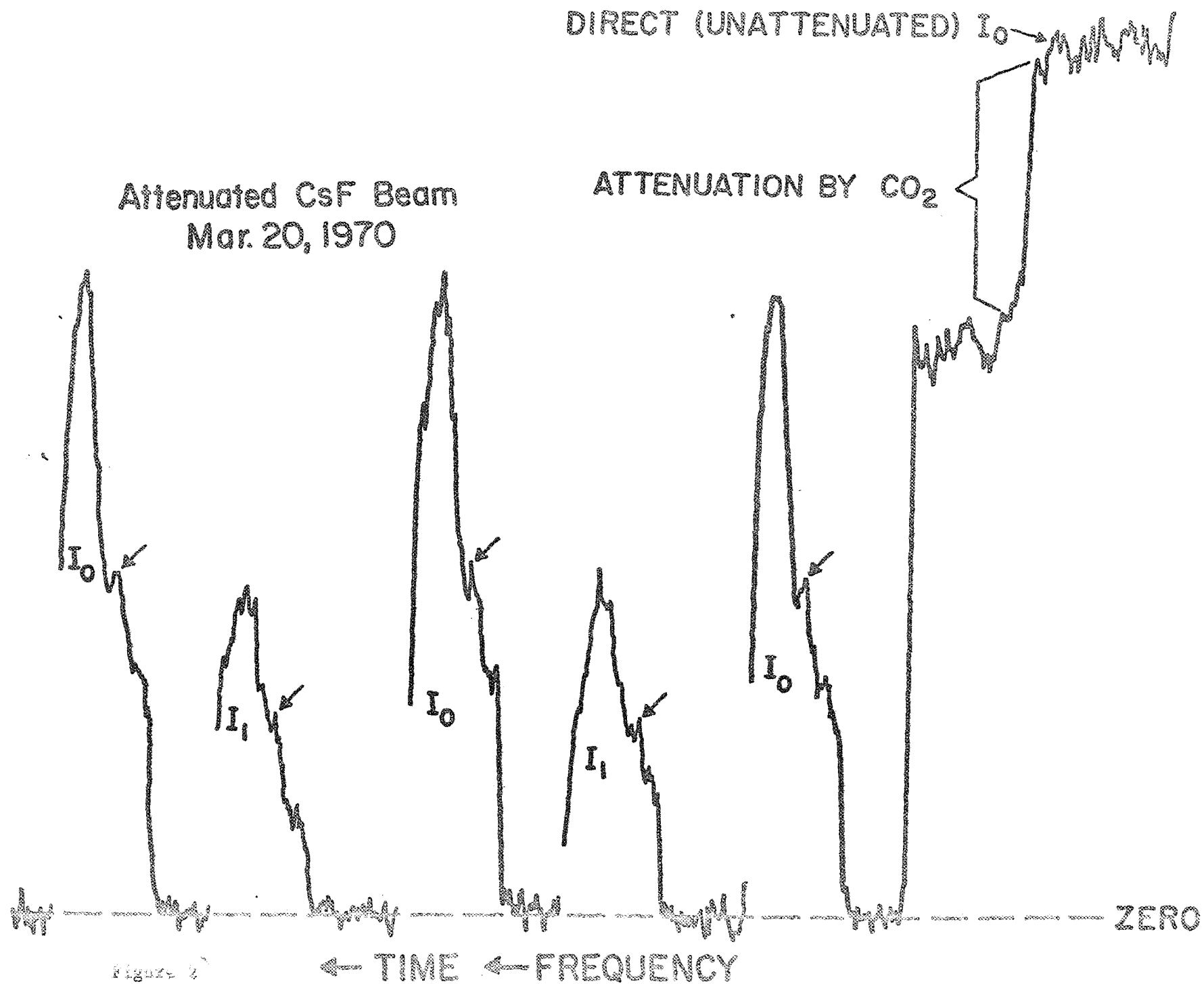


Figure 2

Figure 3. Peak shapes as a function of microwave power level.

This figure is a plot of the apparent intensity of $|010\rangle$ and $|110\rangle$ as a function of the microwave frequency for three different microwave power levels (delivered to the region of the molecular beam):

Curve A: 2.8 mw

Curve B: 1.4 mw

Curve C: ~ 0.3 mw

These apparent widths at higher power levels probably depend greatly on the reflections in the waveguide, as well as the power level itself. The A and B curves are thus not to be considered as accurate power-broadened peak shapes, but instead, examples of the influence of increased power and reflections on the linewidth.

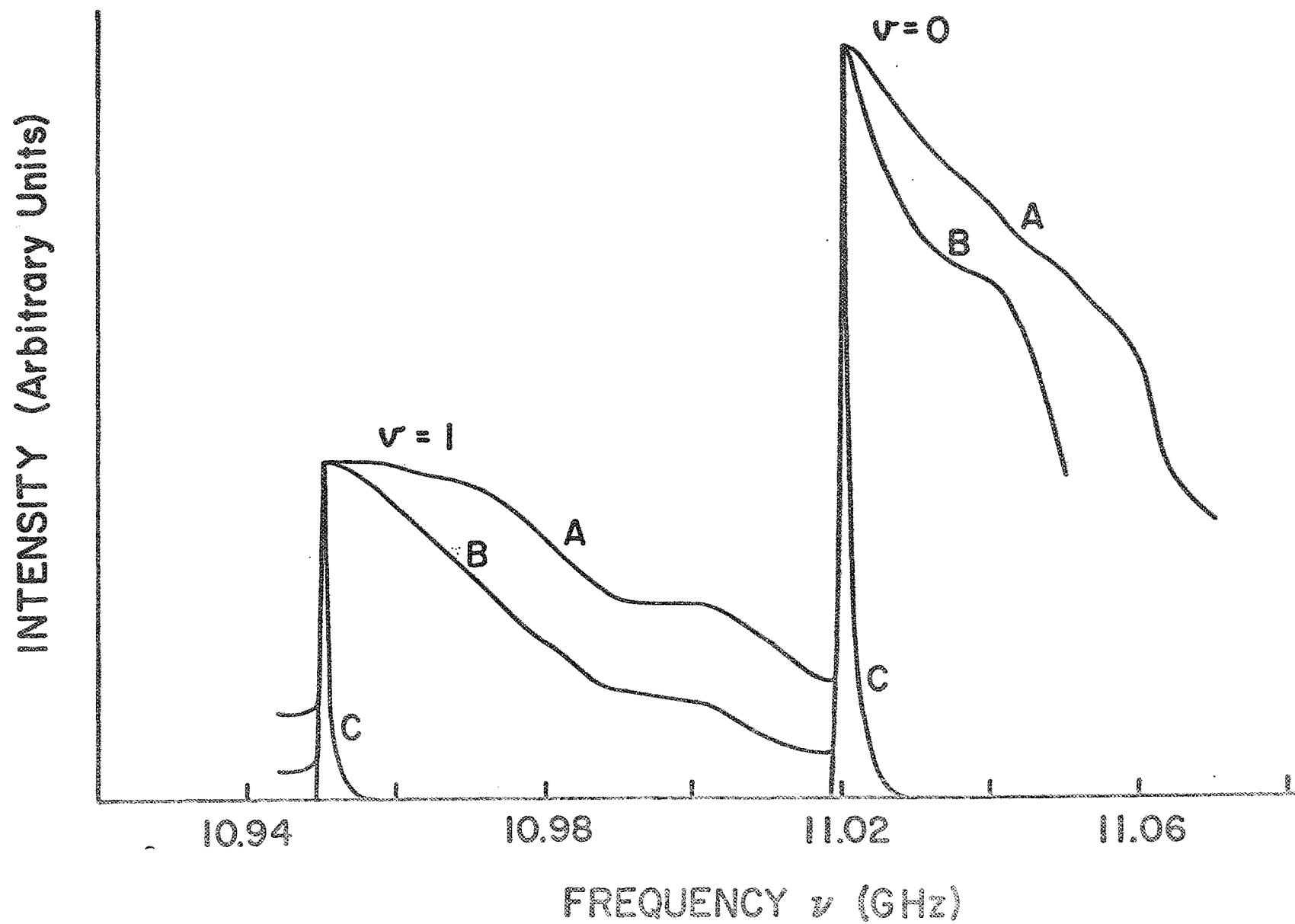


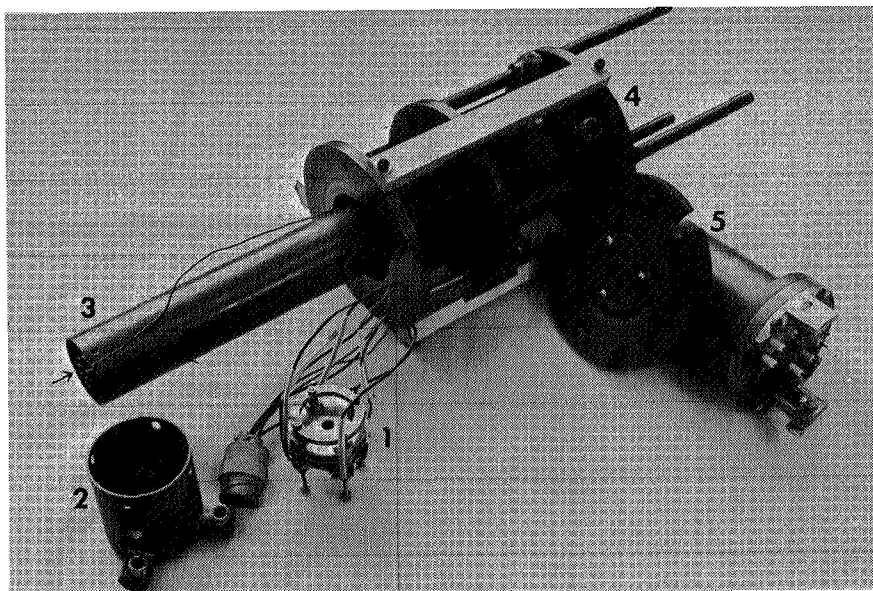
Figure 4. Detector assembly.

A. Exploded view of detector system. The numbered parts are as follows: 1, ionizer and electrostatic (einzell) lens assembly (described below). 2, liquid nitrogen cold trap into which the ionizer fits. (The cold trap has an entrance hole for the beam and an exit hole for the un-ionized CsF that misses the wire.) 3, tube covering the quadrupole mass spectrometer. The arrow points to the entrance of the mass spectrometer. 4, exit end of mass spectrometer. 5, section which bolts onto location 4 and which contains a second einzel lens (seen in the photograph) which refocuses the mass-selected ions onto the Bendix M306 electron multiplier located inside housing 5.

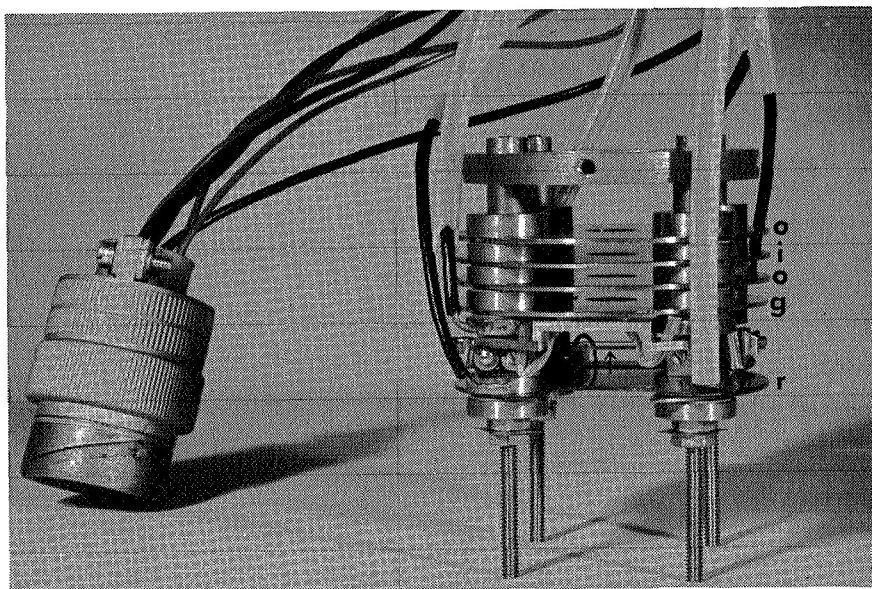
B. Close-up view of ionizer. The construction of this assembly was a part of the Ph.D. thesis work of R. J. Beuhler.¹⁰ This photograph supersedes Photographs 8 and 9 of Ref. 10 and Figs. VC.3 and VC.6 of Ref. 9b. The arrow points to the two surface ionization "hot wire" ionizers. One is a 0.25 mm dia. W wire used in the present work; the other is a 0.025 mm thick x 1.1 mm wide ribbon composed of 92% Pt - 8% W. From top to bottom, the lens elements and approximate operating voltages with respect to ground are:

o - grounded plate	0 v
i - outer einzel lens element	+ 45 v
o - inner einzel lens element	- 270 v
g - outer einzel lens element	+ 45 v
r - repeller	+ 50 v

In addition, the detector wire itself is operated at a typical voltage of + 35 v.



A



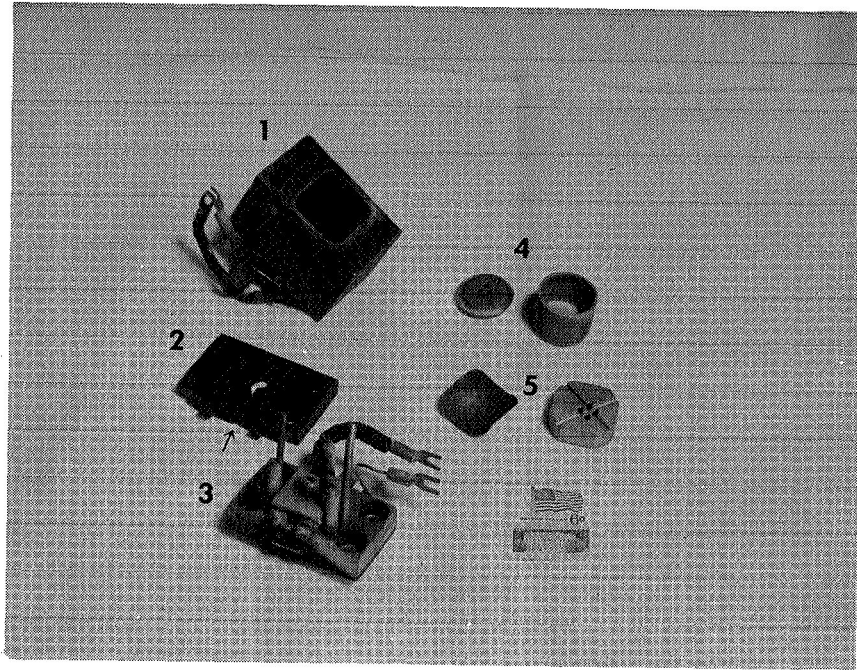
B

Figure 4

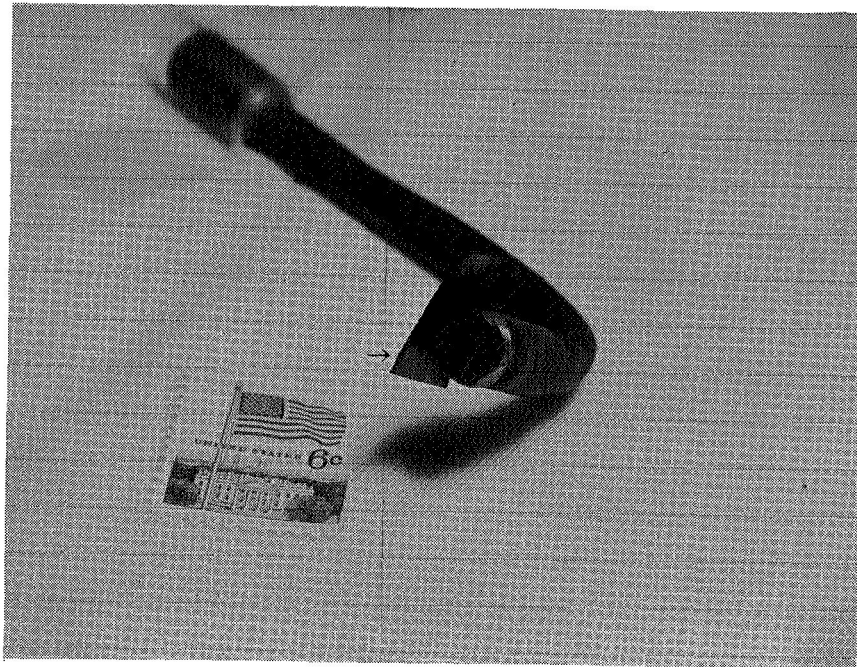
Figure 5. Beam sources.

A. The CsF oven disassembled. Pieces 1, 2, and 3 bolt together to form the main body of the oven with the position of the slit shown by the arrow. Pieces 4 comprise a monel "pill box" which holds the CsF sample. Its purpose is to prevent the CsF from clogging the slit if too-rapid heating causes bubbling within the sample. Pieces 5 are two different "splash plates" (a further protection against a clogged slit) placed between pill box and slit. Except for 4, the entire oven is stainless steel. For slit dimensions, see Fig. 7.

B. Secondary beam source. The scattering gas for the crossed beam enters the far end of the tube which is press fitted into a vacuum-tight line coming through the chamber wall. The output end of the source is an array of capillary tubes, described more fully in the legend for Fig. 7. The arrow points to a plate that shields the ends of the capillary holes from being clogged by CsF effusing obliquely from its oven slit. (For a better illustration of this, see Figs. 6B and 7).



A



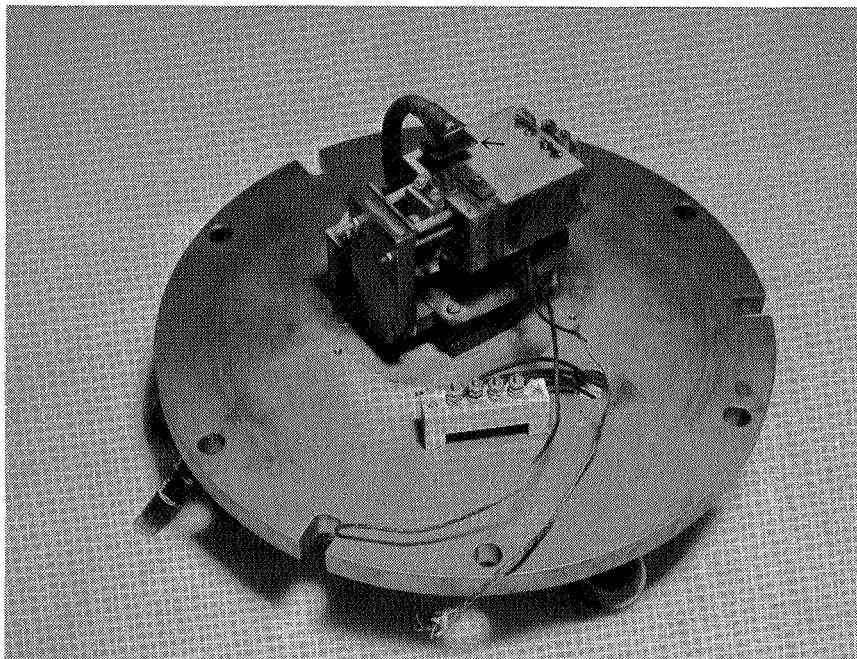
B

Figure 5

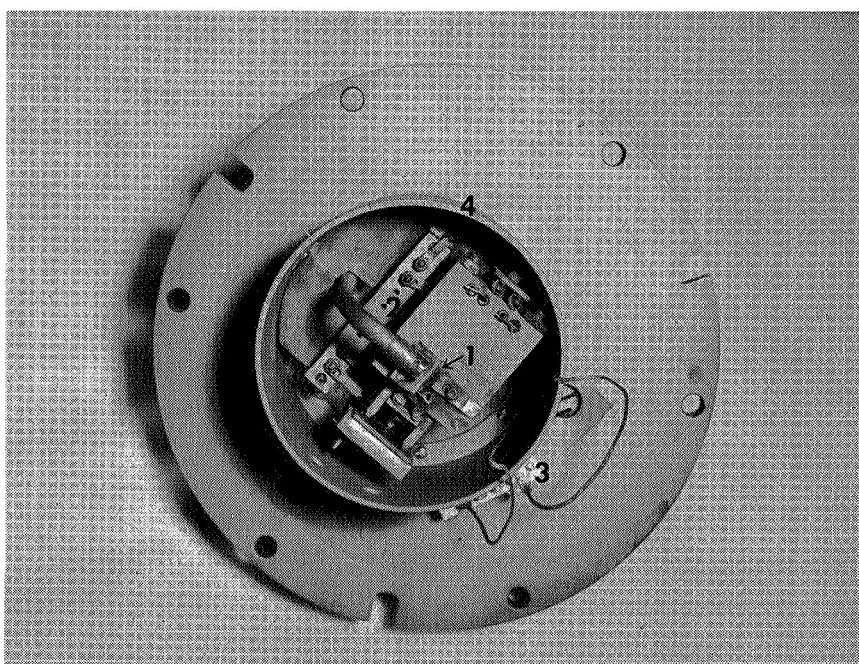
Figure 6. The scattering system assembled.

A. CsF oven and crossed beam source assembled in their normal position on the flange. The oven is held in position by a combination of screws and standoff pins. The secondary beam source, as noted before, is held in place by a "press" fit into the flange. The plate denoted by the arrow shields the capillary array from the CsF beam.

B. Another view of the scattering assembly. Numbered features are: 1, the oven slit. Here one can see again the plate that shields the capillary array. 2, boron nitride terminal block for attaching oven heaters to external connections. 3, a similar boron nitride block for connecting thermocouple leads. 4, a bronze cylinder serving as a thermal shield for the hot oven.



A



B

Figure 6

Figure 7. Drawing of the scattering system.

Shown is a 2X scale drawing of a side view of the beam systems and scattering center. The CsF (Alfa Inorganics, Inc.) effuses from the 0.25 mm x 5 mm horizontal slit from a fairly standard stainless steel oven. The CsF crystals are loaded initially into the monel reservoir ("pill box") pictured in Fig. 5A; this helps to prevent clogging of the slit. The CsF beam is defined by the collimator opening to the 4-pole A-field which subtends a 0.97° aperture at the slit. The light dashed line illustrates the function of the shield (see Figs. 5A and 6), i.e., protecting the capillary array. The CsF faces a large liquid nitrogen cooled surface (not shown in the drawing), 2.85 cm from the slit.

The capillary array is a Brunswick Collimated Hole Structure, sample #2, having 41% transparency with tubes 3.0 mm long and nominal radius 0.025 mm. The cross sectional open area of the array is 5.8 mm x 1.7 mm, with the long dimension perpendicular to the direction of the CsF beam. This orientation provides uniform attenuation over the entire width of the CsF beam (see Fig. 6A).

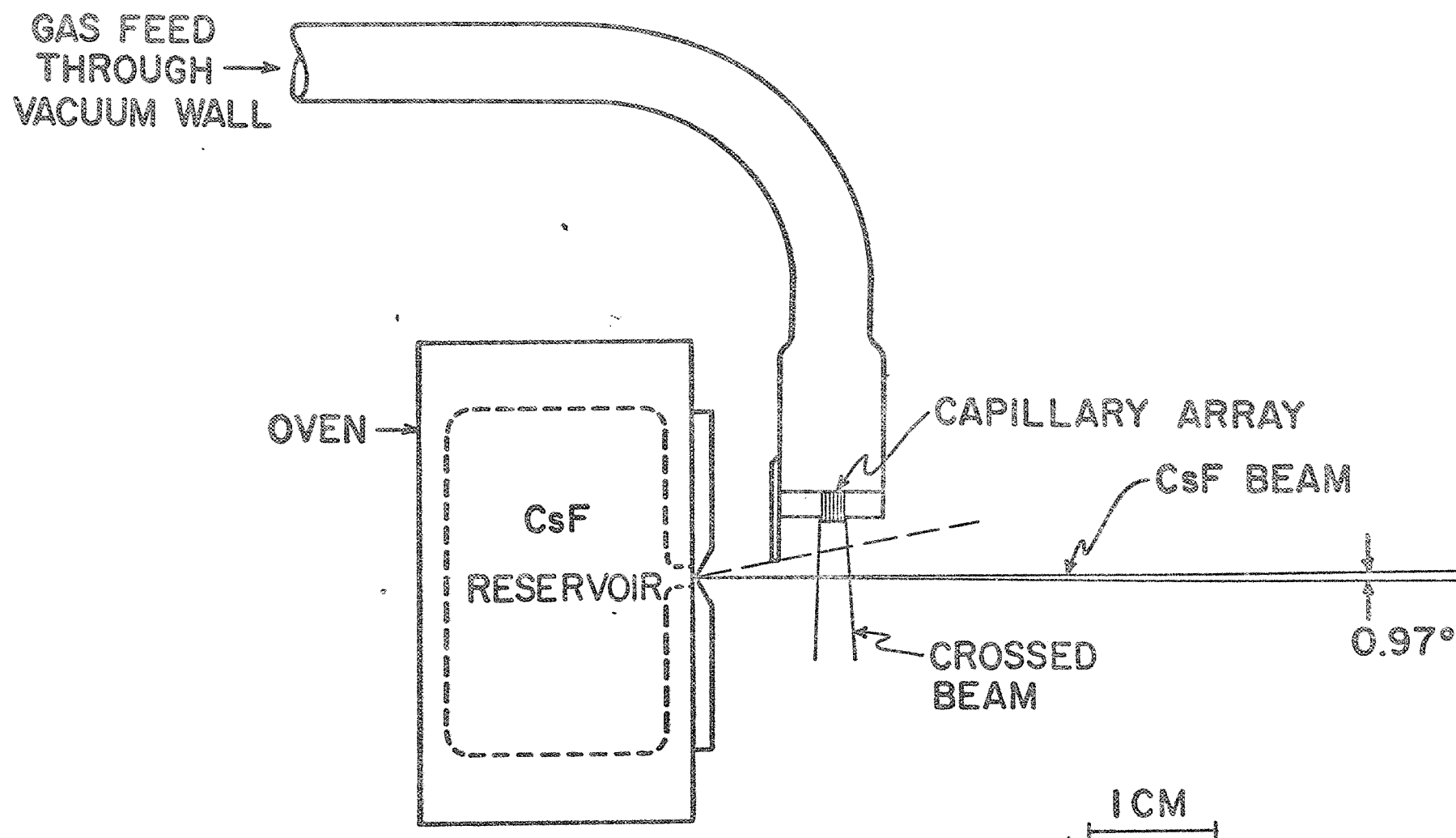
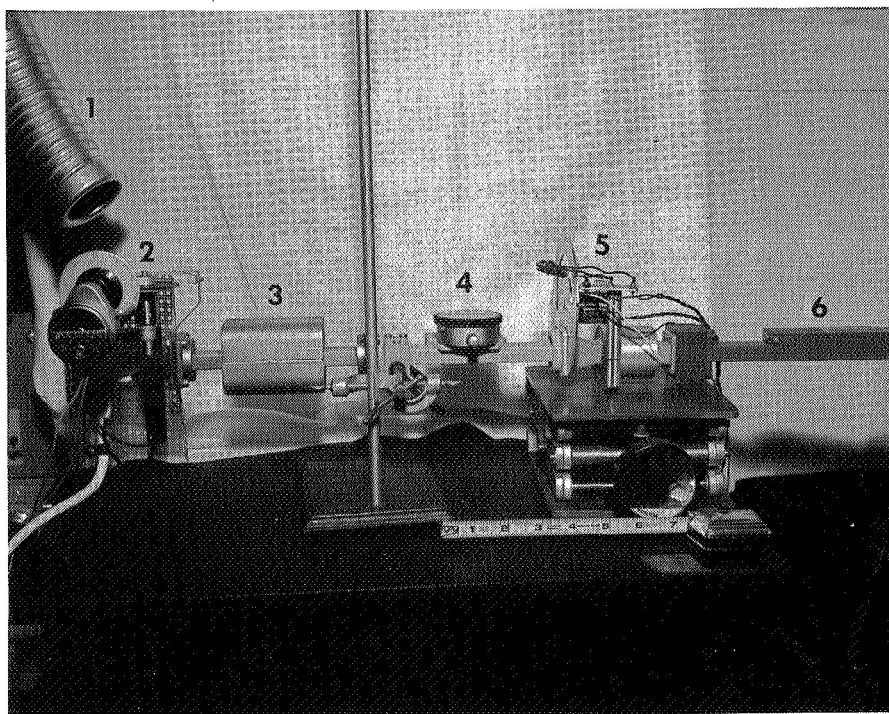


Figure 7

Figure 8. Components of the microwave system.

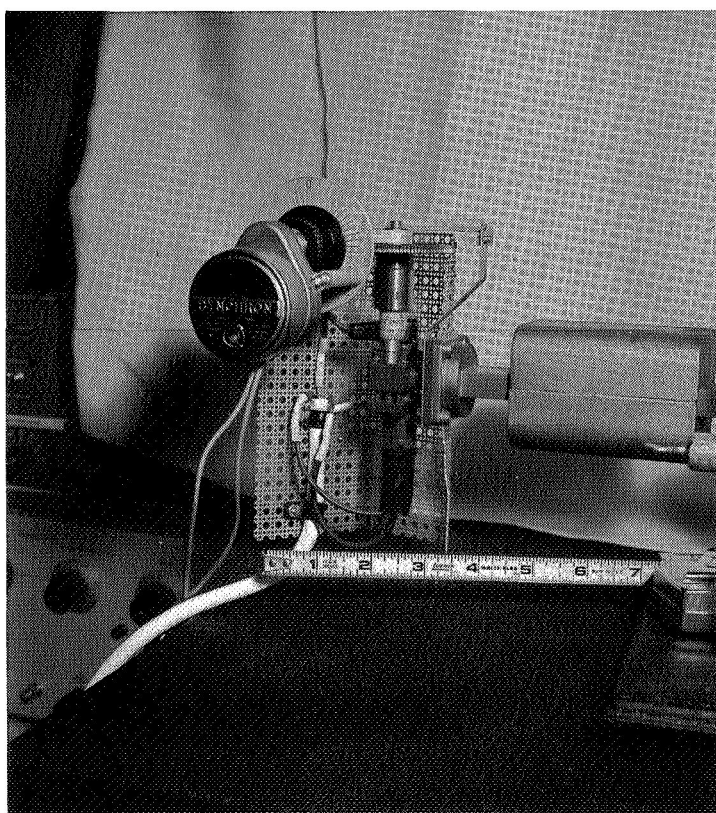
A. Various components of the microwave system. Numbered features are: 1, flexible hose from fan for air-cooling the klystron. 2, Varian X-13 klystron and worm gear drive, partially obscured by a Hurst Synchron 112RC motor (one revolution/hr.). 3, Microlab/FXR Model X157A Ferrite isolator. 4, PRD Model 195B variable attenuator. 5, Homemade microwave chopper (25 Hz) in an air gap in the waveguide. The Globe Industries Inc. motor #53A117-2 which powers the chopper is mounted on top of a Polarad Ca-Ks horn antenna which recollects the modulated microwaves. 6, Hewlett-Packard X752C directional coupler. The main channel ends (off the right of the picture) in an Andrew 55000-75 pressure window which is joined to a waveguide entering the vacuum chamber and terminates in another Polarad Ca-Ks horn ≈ 2.3 cm from the molecular beam. The 10dB sidearm of the directional coupler terminates in a Hewlett-Packard Model M532A wavemeter and Hewlett-Packard M424A crystal detector. (See Fig. 10 for a block diagram of the microwave system).

B. Klystron and frequency sweep assembly. The output of the 1 rev/hr motor goes to a 50:1 worm gear assembly, whose large driven gear can be seen attached to the cavity adjustment micrometer screw. This arrangement results in a scan rate of ≈ 0.8 MHz/min.



75

A



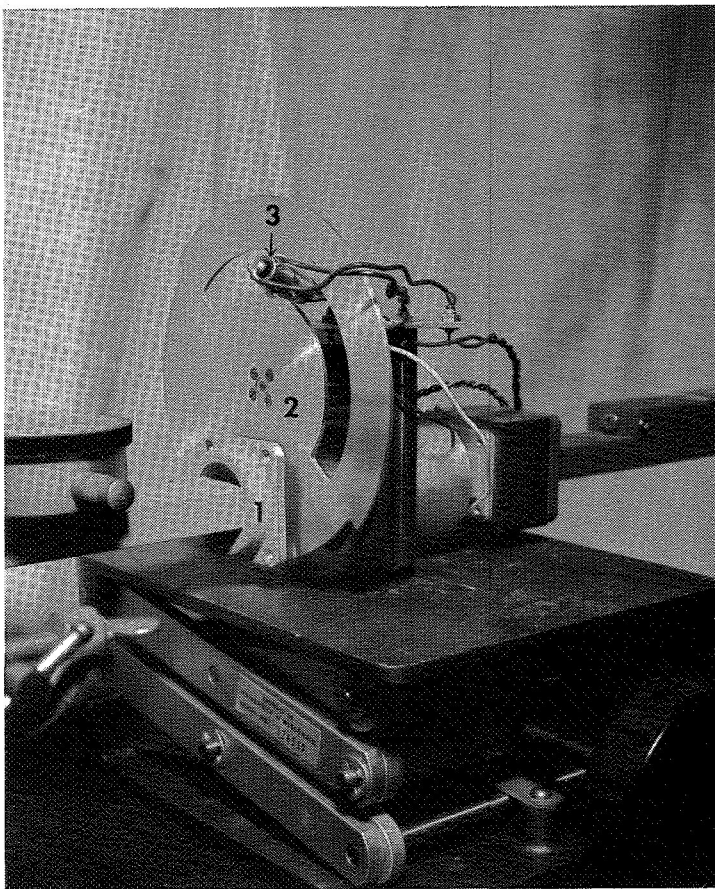
B

Figure 8

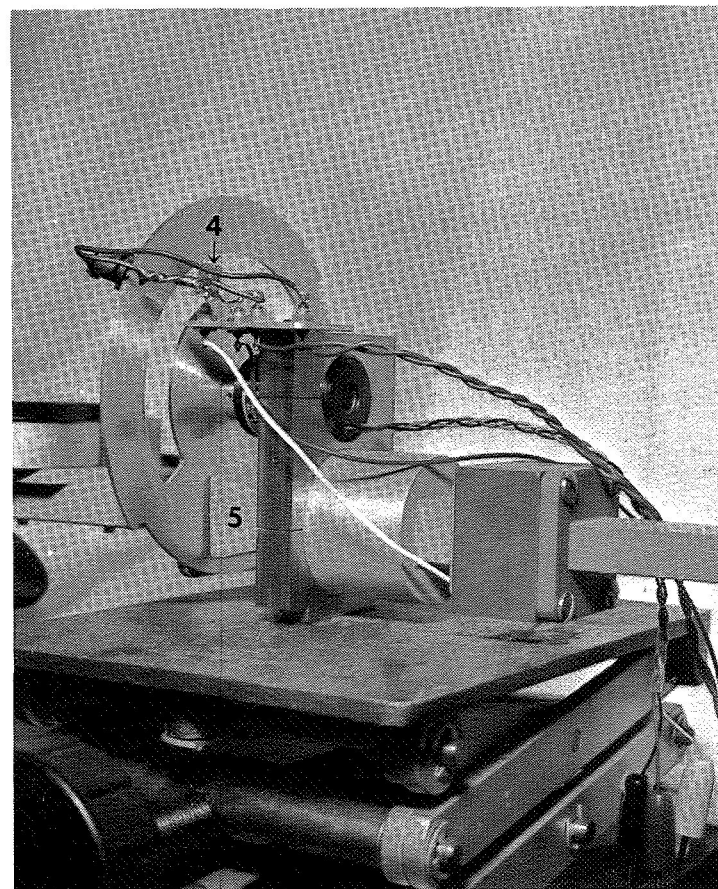
Figure 9. Two views of microwave mechanical modulation system.

A. View of the microwave chopping wheel from the klystron side. Numbered features are: 1, the end of the PRD variable attenuator and the beginning of the air gap in the klystron. 2, the chopper wheel. 3, light bulb whose chopped output provides a reference signal for the PSD.

B. View from the other side of the chopper. Numbered features are: 4, photocell which senses the chopped light from the bulb and whose output serves as a reference signal for the PSD. 5, Polarad Ca-Ks horn antenna which recollects the chopped microwaves for transmission into the vacuum system.



A



B

Figure 9

Figure 10. Block diagram of microwave system.

This drawing shows the arrangement of the various components of the microwave system. Most of the system is described in the legend of Fig. 8. The oscillator, amplifier and motor drive for frequency sweeping the klystron are described in Section IIIC.3; the mechanical chopping assembly for the microwave beam is described in Section IIIC.4.

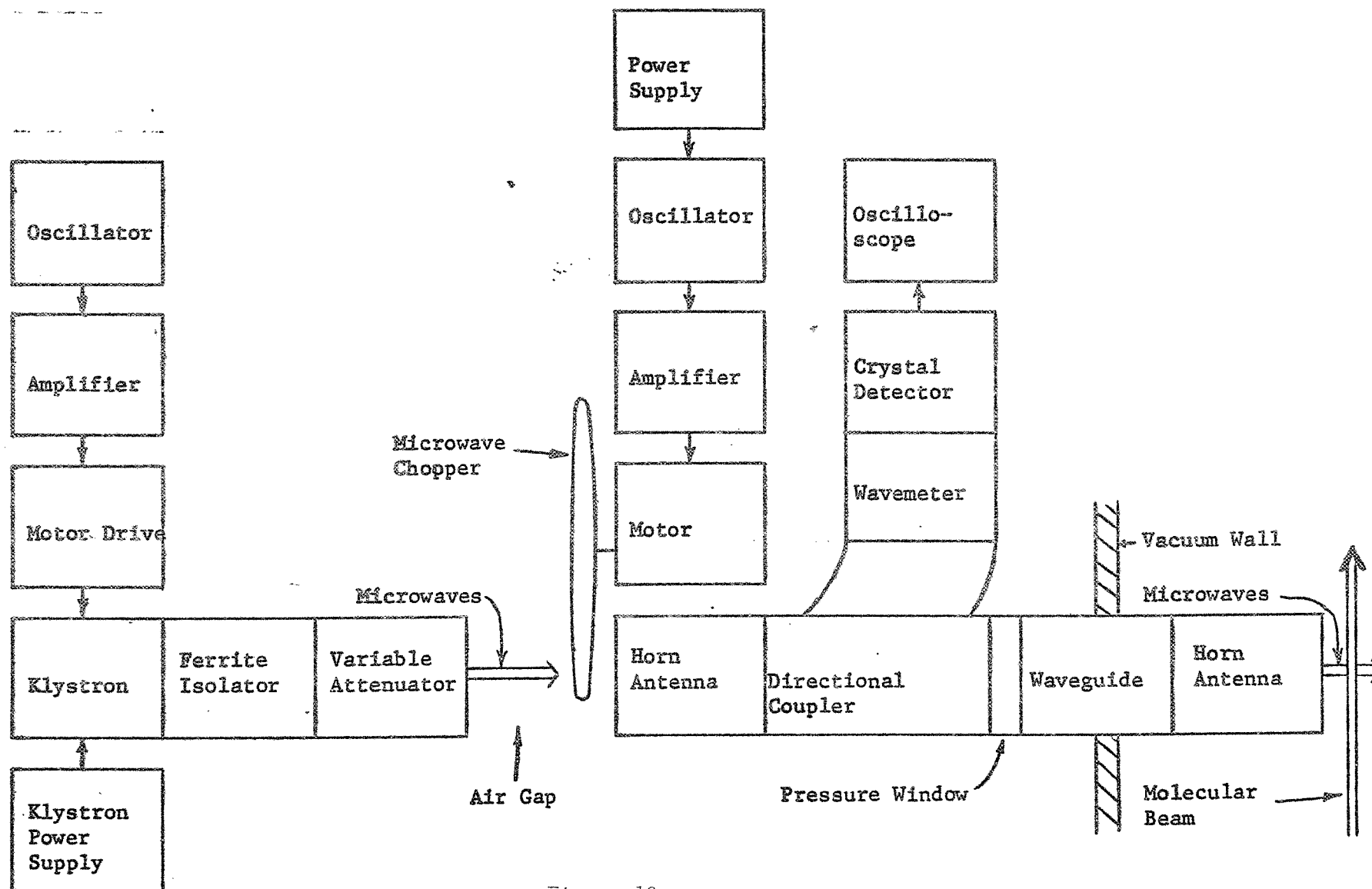


Figure 10

Figure 11. R_1 versus time (Jan. 24, 1970).

Results of the experiment of Jan. 24 without the crossed beam, i.e., CO_2 added to the scattering chamber diffusely (through a hole in the chamber wall). The circles denote the I_1/I_0 ratio for the direct CsF beam; the triangles indicate ratios measured with the CsF beam attenuated by scattering gas. As noted in the text, the two points at each time t_1 are a result of independent chart readings.

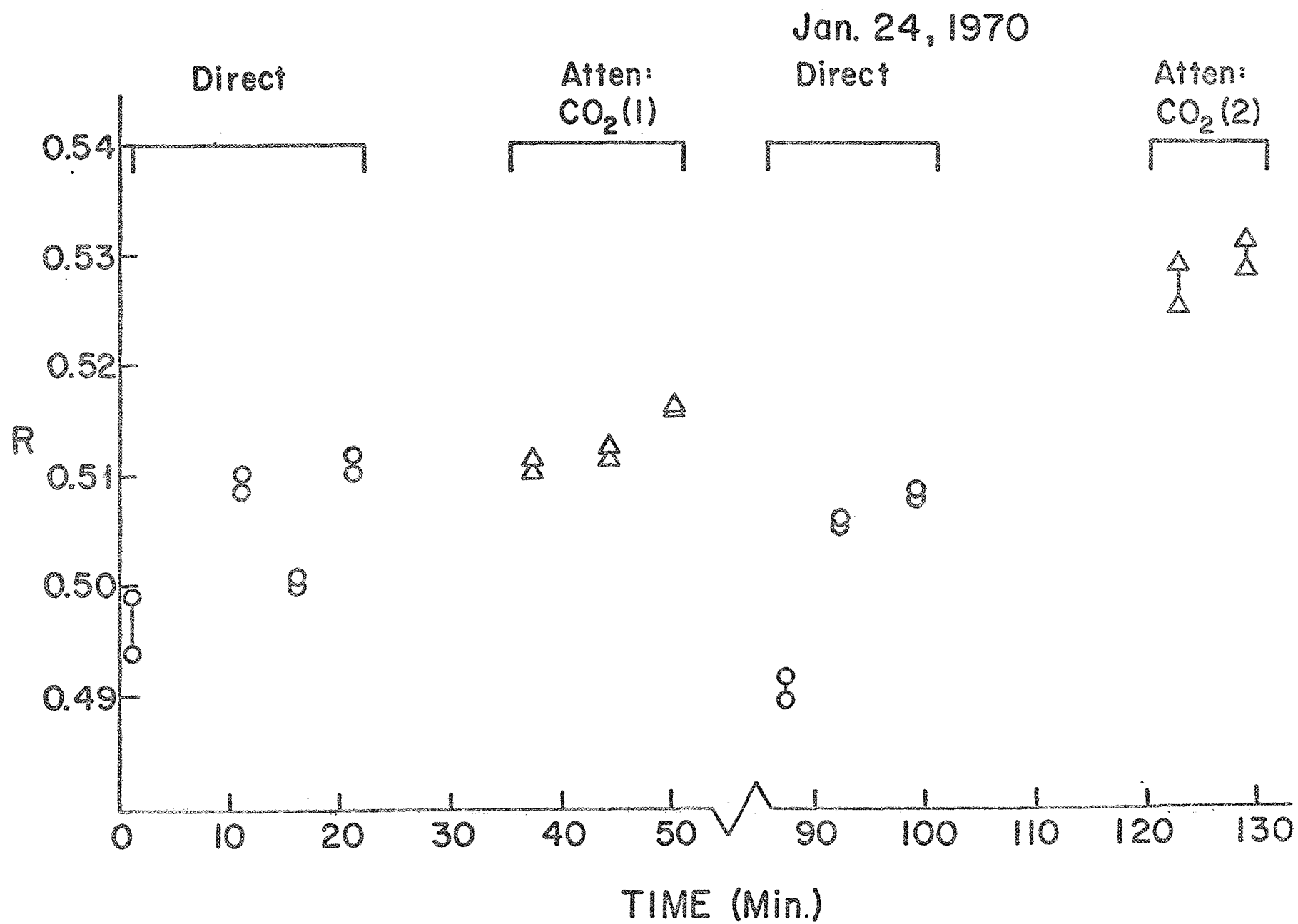


Figure 11

Figure 12. R_i versus time (Feb. 16, 1970).

Results of a second experiment. Otherwise, as in Fig. 11.

Feb. 16, 1970

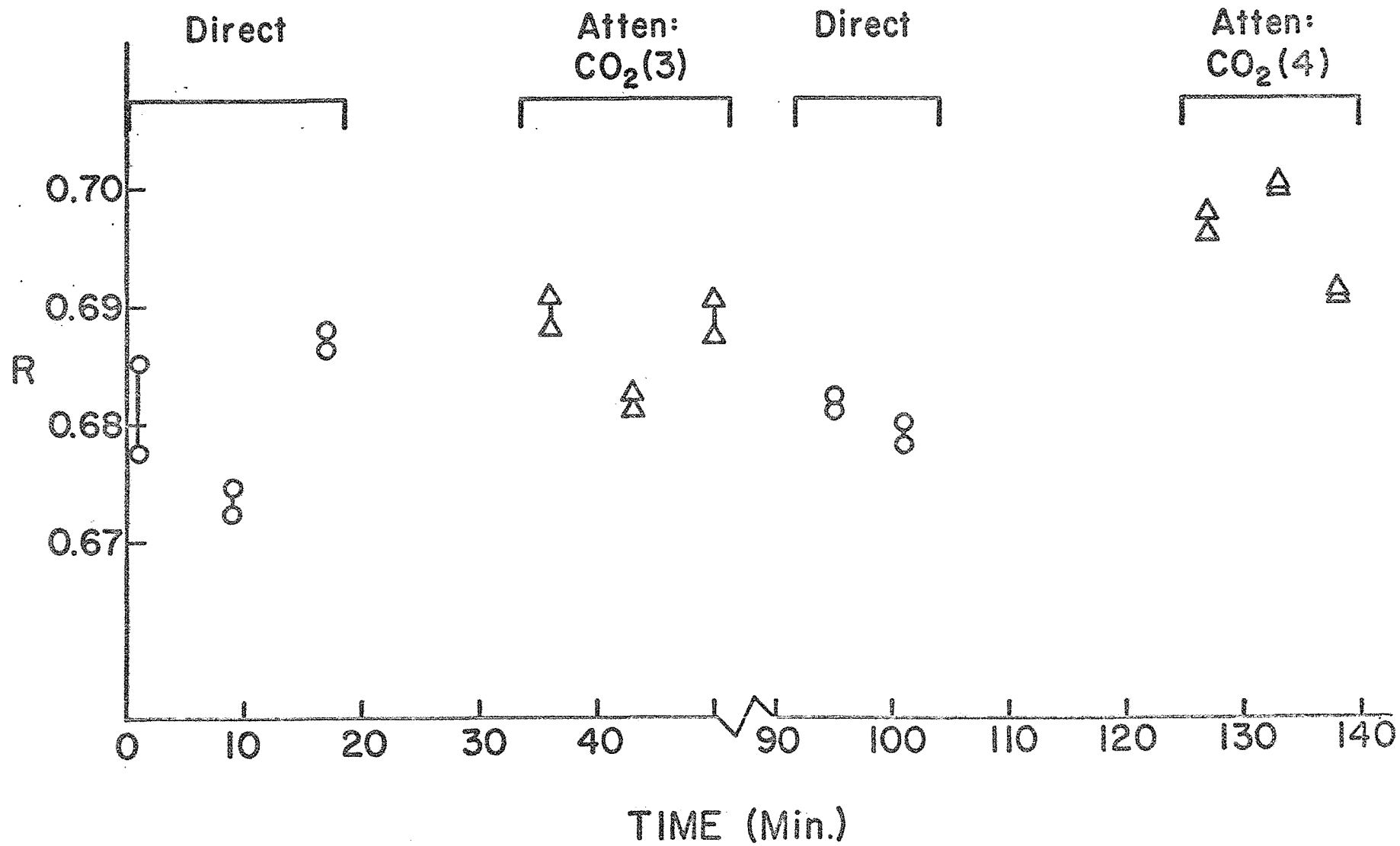


Figure 12

Figure 13. R_i versus time (Mar. 20, 1970).

Results of another experiment. In contrast to the first two (scattering gas) experiments of Figs. 11 and 12, the crossed beam arrangement of Figs. 6 and 7 was used here. Otherwise, as in Fig. 11.

Mar. 20, 1970

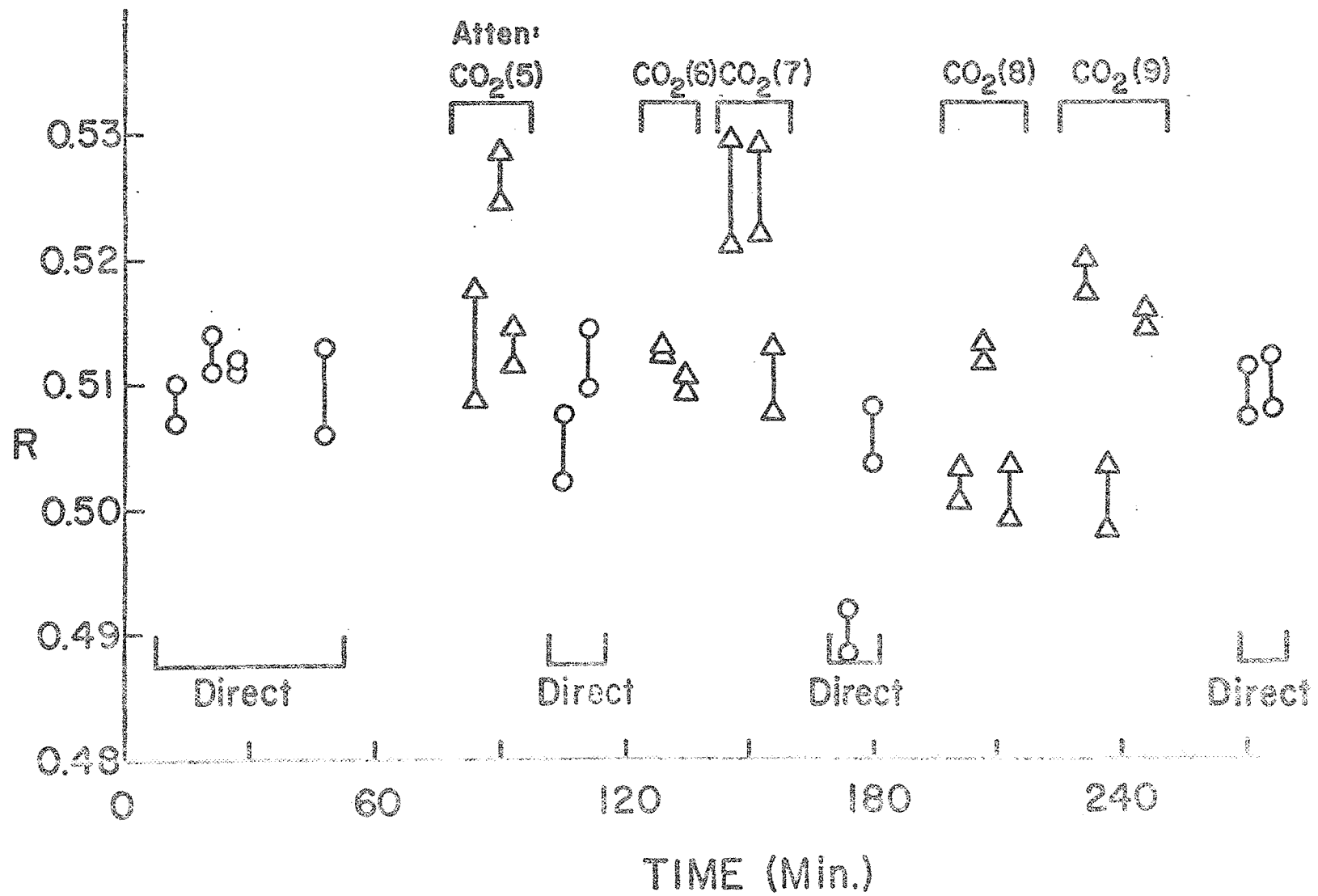


Figure 13

Figure 14. R_1 versus time (Mar. 1, 1970).

Results of another experiment, utilizing 1,1,1-trichloroethane and argon in the crossed beam configuration of Figs. 6 and 7. Otherwise, as in Fig. 13.

Mar. 1, 1970

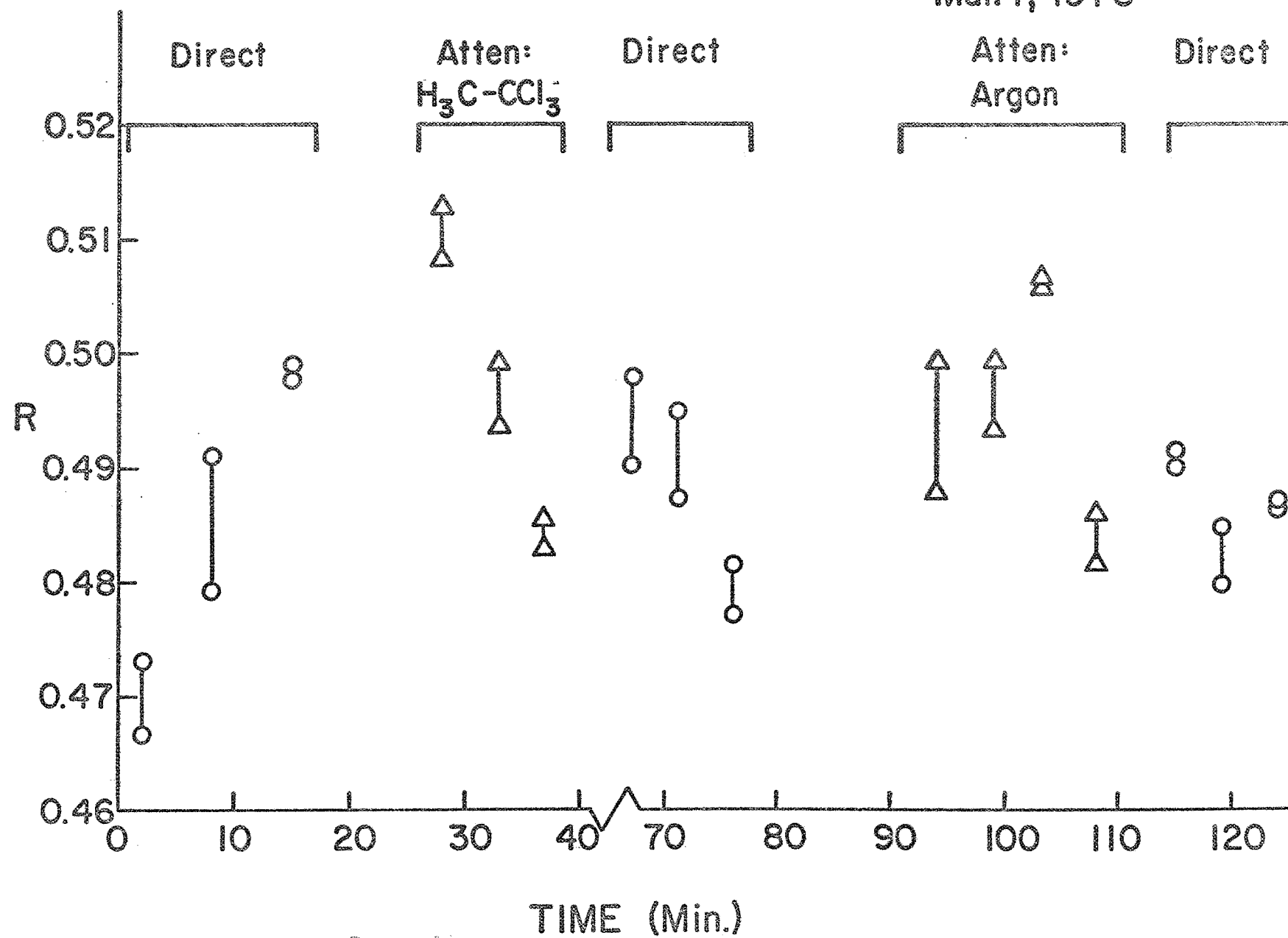


Figure 14

Figure 15. Velocity vector diagram for CsF-CO₂ scattering.

This Newton diagram illustrates the circles (spheres) that define the locus of the CsF center of mass velocities after collision with CO₂. The initial laboratory velocity of the CsF (502 m/sec) corresponds to the nominal velocity transmitted by the four-pole fields under typical operating conditions (see Section IVD.2). Here, $\propto$ denotes the most probable velocity (336 m/sec) of CO₂ at room temperature. The circles marked "excitation" and "deexcitation" define post-collision CsF which has acquired or lost, respectively, a vibrational quantum of energy from the available relative kinetic energy. Note that the "excitation" circle is essentially tangent to the direct (laboratory) CsF velocity vector. For a detector angle $\theta_d = 0$, this enhances the inelastic signal due to excitation by a phenomenon known as "Jacobian cusping" (see text, Section IVD.2 and Fig. 16).

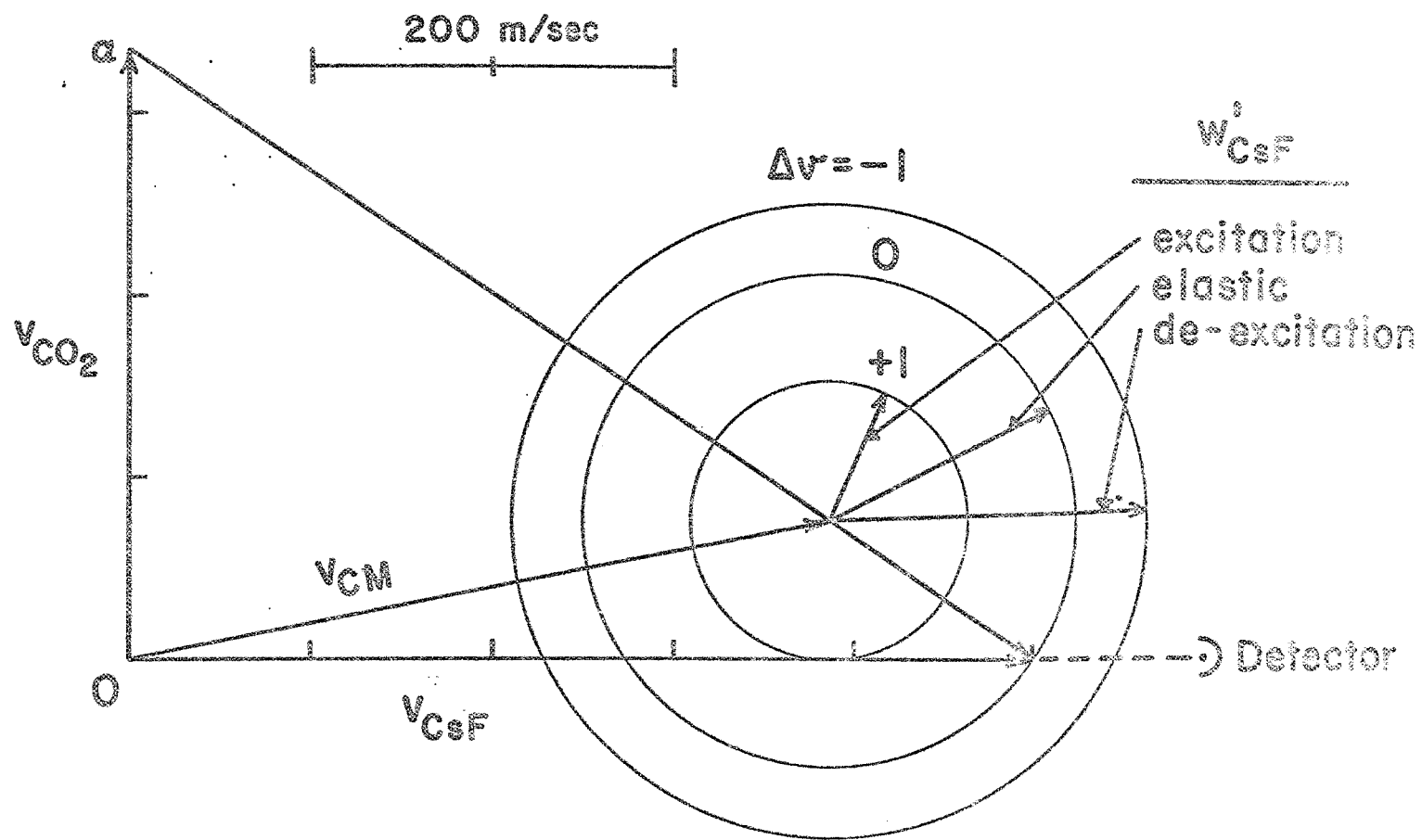


Figure 12

Figure 16. Factors influencing enhanced detection of excitation process.

Section IVD.2 of this work (or Eq. 38 of Ref. 30) indicates that the ratio for detection of excitation to that of deexcitation processes is proportional to $(W'_{dx} / W'_{ex})^2 |\cos \zeta_{dx}| / |\cos \zeta_{ex}|$. Here, W'_i is the center of mass recoil velocity for inelastic process i , and ζ_i is the angle between W'_i and Θ_d . This figure attempts to distinguish the velocity (W') effect from the angular (ζ) effect.

The angle Θ_d is the angle the detector makes with the scattering center, zero angle coinciding with the CsF beam (in the present work, $\Theta_d = 0$). Now consider the detector set at angle Θ_1 in the figure and subtending the angle indicated by the short, heavy arc. A larger fraction of the excitation process (indicated by angular range $d\Theta_b$) is received by the detector than that of deexcitation ($d\Theta_a$). This effect is due largely to the W' factor - the excitation sphere is smaller and a given laboratory "slice" out of velocity space (i.e., a given small arc subtended by the detector) corresponds to a larger solid angle for this process.

At Θ_d , the W' factor is still present. Now, however, the $\cos \zeta$ factor becomes important. Obviously, there is a different range of ζ values for both inelastic processes, but only the median value is illustrated here (ζ_c and ζ_d). Note that ζ_c is small and $|\cos \zeta_c| \approx 1$. On the other hand, $\zeta_d = 90^\circ$ and $|\cos \zeta_d| = 0$. This illustrates the further enhancement of detection of the excitation process due to "Jacobian cusping".

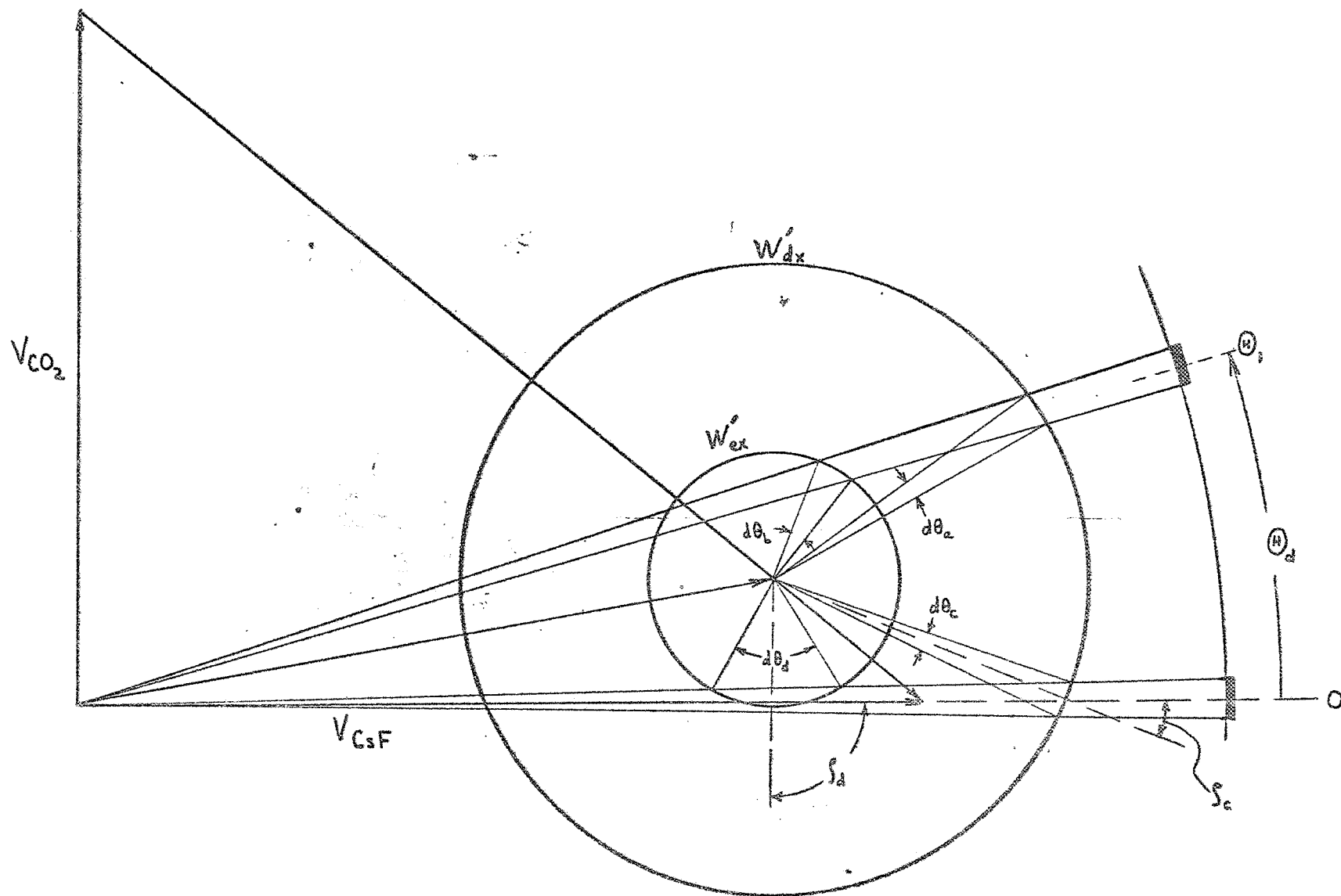


Figure 16

Figure 17. Effect of CO_2 velocity distribution on inelastic scattering kinematics.

The "Jacobian cusping", i.e., the tangency of the "excitation" circle noted in Fig. 16, is almost independent of the secondary beam velocity. Shown here are the loci of intersections of the various "excitation" and "deexcitation" circles near $\theta_d = 0$. Over the whole range of the CO_2 velocity distribution, there is essentially complete coalescence of the tangents for the $\Delta v = +1$ circles, leading to a significant overall "Jacobian cusp" enhancement of the observable $(\theta_d = 0)$ signal. (For an analysis of this coalescence effect, see Section IVD.2.) Values of V_{CO_2} of 0.48α and 1.64α correspond to the half-intensity velocities for thermal CO_2 .

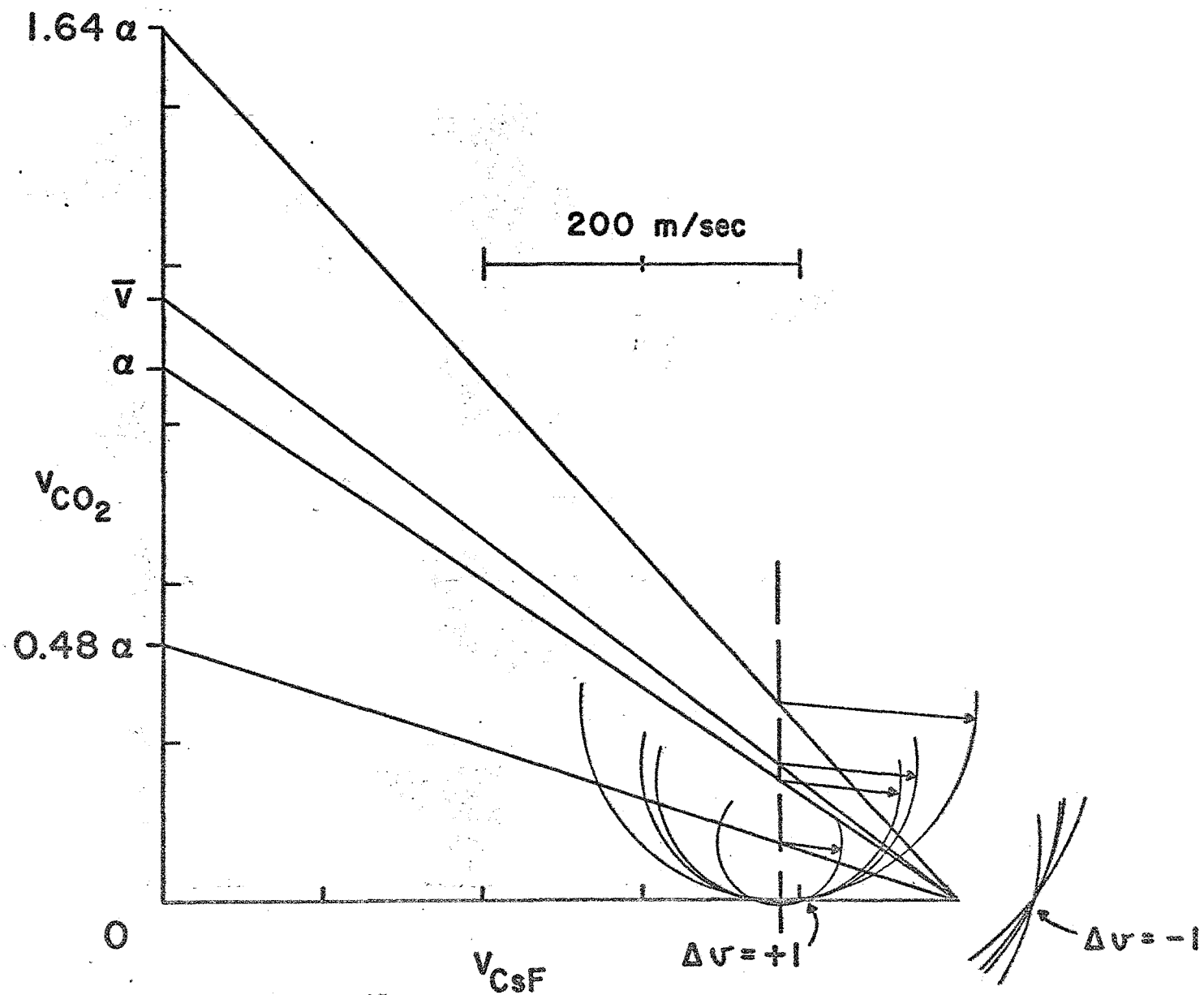


Figure 17

F. References

(References for Chapters V and VI are contained within Chapters V and VI)

1. The following are several important review articles:
 - a. N. F. Ramsey, "Molecular Beams", (London: Oxford University Press, 1956);
 - b. D. R. Bates and I. Estermann, eds., "Advances in Atomic and Molecular Physics", Vol. 1, (New York: Academic Press, Inc., 1965), Chapter 5 by H. Pauly and J. P. Toennies, pp. 195-389;
 - c. J. Ross, ed., "Advances in Chemical Physics", Vol. 10, (New York: Interscience Publishers, 1966);
 - d. B. Bederson and W. L. Fite, eds., "Methods of Experimental Physics", Vol. 7A, (New York: Academic Press, Inc., 1968), Chapter 3.1 by H. Pauly and J. P. Toennies, pp. 227-341;
 - e. H. Hartmann, ed. "Chemische Elementarprozesse", (New York: Springer-Verlag, 1968). Chapter by J. P. Toennies, pp. 157-218.
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3. For a listing of the various field configurations and the states they select, the reader is referred to Table II of Ref. 1d, p. 260.
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 - b. P. Brooks, E. M. Jones, and K. Smith, J. Chem. Phys. 51, 3073 (1969).

5. a. P. R. Brooks and E. M. Jones, J. Chem. Phys. 45, 3449 (1966);
 b. R. J. Beuhler, R. B. Bernstein, and K. H. Kramer, J. Am. Chem. Soc. 88, 5331 (1966);
 c. R. J. Beuhler and R. B. Bernstein, Chem. Phys. Letters 2, 166 (1968); Erratum 3, 118 (1969);
 d. P. R. Brooks, J. Chem. Phys. 50, 5031 (1969);
 e. R. J. Beuhler and R. B. Bernstein, J. Chem. Phys. 51, 5305 (1969).
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 b. H. G. Bennewitz, R. Haerten, and G. Müller, Z. Physik 226, 139 (1969);
 c. H. G. Bennewitz, R. Gengenbach, R. Haerten, and G. Müller, Z. Physik 226, 279 (1969);
 d. H. G. Bennewitz and R. Haerten, Z. Physik 227, 399 (1969);
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 - a. L. Wharton, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallagher, and V. E. Derr, J. Chem. Phys. 38 1203 (1963);
 - b. F. H. deLeeuw, R. van Wachem, and A. Dymanus, J. Chem. Phys. 50, 1393 (1969);

- c. A. J. Hebert, F. J. Lovas, C. A. Melendres, C. D. Hollowell, T. L. Storey, Jr., and K. Street, Jr., J. Chem. Phys. 48, 2824 (1968);
 - d. G. Graff, R. Schonwasser, and M. Tonutiti, Z. Physik 199, 157 (1967);
 - e. T. C. English and J. C. Zorn, J. Chem. Phys. 47, 3896 (1967).
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 - b. For a more complete account, see T. G. Waech, Ph.D. thesis, Chemistry Department, University of Wisconsin, 1968, available as Univ. of Wisconsin Theoretical Chemistry Institute Report WIS-TCI-325X; also available from University Microfilms, Ann Arbor, Mich.
10. See references 5b, c, e. For a more complete account of the apparatus used in this work, see R. J. Beuhler, Ph.D. thesis, Chemistry Department, University of Wisconsin, 1968, available as Univ. of Wisconsin Theoretical Chemistry Institute Report WIS-TCI-326X; also available from University Microfilms, Ann Arbor, Mich.
 11. C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy", (New York: McGraw-Hill Book Co., Inc., 1955) p. 251.
 12. S. E. Veazey and W. Gordy, Phys. Rev. 138, A1303 (1965).
 13. See Ref. 8a, for example, for linewidth calculations and measurements in an MBER experiment very similar to the present one, but involving LiF.

14. See Ref. 9b, pp. IIID.1-IIID.2.
15. See Ref. 8e. In this experiment, great care had to be taken to eliminate stray fields.
16. a. P. F. Dittner and S. Datz, "Proc. VI Internat. Conf. on the Physics of Elec. and At. Coll.", (Cambridge: MIT Press, 1969) p. 469;
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See also:
b. T. F. Moran and P. C. Cosby, J. Chem. Phys. 51, 5724 (1969).
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26. It is known that the fraction of dimers decreases as the region of the oven slit is heated hotter than the body of the oven. An illustration of this fact for beams of NaF is given in Table I of the article by M. Eisenstadt, G. M. Rothberg, and P. Kusch, J. Chem. Phys. 29 797 (1958). This same article gives data for CsF, which suggests that using their oven and conditions, the fraction of dimers would be about 10% at $\approx 950^{\circ}\text{K}$, the operating temperature of the present work.
27. A direct (beam) experiment yielding a vibrational lifetime $\tau_{1 \rightarrow 0}$ of $\cong 7 \times 10^{-3}$ sec for TlF has been published. See G. Graff, "Z. Physik 155, 433 (1959). In the present apparatus, the transit time for going from oven to C-field is 1×10^{-3} sec.
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32. D. A. Micha and M. Rotenberg, Chem. Phys. Letters 6, 79 (1970).

V. SUDDEN APPROXIMATION IN ATOM-DIATOMIC SCATTERING

A. Introduction

The experimental section of this thesis was mainly concerned with vibrational inelasticity in low energy scattering. The next two chapters deal with rotationally inelastic collisions. Chapter V (with appendix) is a reprint of published work utilizing the sudden approximation to calculate the angular and energy dependence of inelastic cross sections for diatomic molecules colliding with atoms. The numbering of pages, equations, and references within the reprint is self-contained.

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Sudden Approximation Applied to Rotational Excitation of Molecules by Atoms. III. Angular Distribution and Energy Dependence of the Inelastic Scattering*

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(Received 27 July 1967)

The sudden approximation for rotational excitation of diatomic polar molecules by atomic impact is applied, yielding semiclassical angular distributions of rotational transition cross sections and their energy dependence. The results for a model system (intended to approximate TlF-Ar) are not inconsistent with the experimental findings of Toennies. The dominant excitations are those allowed by first-order time-dependent perturbation theory, but the strong coupling (due principally to the large long-range anisotropy in the potential) produces extensive excitation to remote open channels, i.e., those forbidden by low-order perturbation theory. The main prediction of the present work is the presence of a single major peak in each of the various differential polar inelastic cross sections; with increasing collision energy, these maxima trend to smaller angles and increase in peak intensity.

I. INTRODUCTION

In Paper II¹ the sudden approximation was applied to the computation of rotational transition probabilities and inelastic integral cross sections for the scattering of polar diatomic molecules by atoms. The calculations were based upon a modified L-J (12,6) potential which included both short- and long-range anisotropies. The results showed that at thermal energies the long-range anisotropies (principally the $R^{-7} \cos^2\theta$ dipole-quadrupole term) were of principal importance in determining the inelasticity. In the present work, these computations have been extended to yield the angular distributions of the various rotational excitation cross sections and their energy dependence. The results have relevance to the molecular-beam measurements by Toennies² of (partial) inelastic cross sections for the TlF-rare-gas systems.

* This research received financial support from the National Aeronautics and Space Administration Grant NsG-275-62. Report WIS-TCI-240, July 1967, gives a more detailed account of the present work.

¹ R. B. Bernstein and K. H. Kramer, *J. Chem. Phys.* **44**, 4473 (1966), hereafter referred to as Paper II. For Paper I, see *J. Chem. Phys.* **40**, 200 (1964). For comments on the validity of the sudden approximation applied to the rotational excitation problem, see P. Pechukas and J. C. Light, *J. Chem. Phys.* **44**, 3897 (1966).

² (a) J. P. Toennies, *Z. Physik* **182**, 257 (1965). (b) For his original (preliminary) report, see *Discussions Faraday Soc.* **33**, 96 (1962); (c) *Atomic Collision Processes*, M. R. C. McDowell, Ed. (North-Holland Publ. Co., Amsterdam, 1963), p. 1113.

The present status of the various theoretical approaches to the rotational excitation problem have been reviewed by Takayanagi³; more recent and relevant papers include those of Toennies,⁴ of Gordon and collaborators,⁵ and Dalgarno and coworkers.⁶

II. COMPUTATION OF THE TRANSITION PROBABILITIES

The method of II was used throughout. To allow smoother interpolation, additional values of the action integrals $S(n, p, q)$ and deflection angles $\chi(b^*, E^*)$ were computed at finer intervals in the important regions of the reduced impact parameter b^* (for reduced energies E^* of 1, 3, 10, 30, and 100). The transition probabilities $P_{j\alpha}(b^*, E^*)$ for the excitation from state $j, m \equiv \alpha$ to $j', m' \equiv \beta$ were computed as before from these action integrals via Eq. (14) of Paper II for assigned values of a_2, b_1, b_2 , and c , the anisotropy parameters. For all of the present calculations, the de Boer quantum parameter Λ^* was fixed at 0.1.

³ K. Takayanagi, *Advances in Atomic and Molecular Physics*, D. R. Bates and I. Estermann, Eds. (Academic Press Inc., New York, 1965), Vol. 1, p. 149.

⁴ J. P. Toennies, *Z. Physik* **193**, 76 (1966).

⁵ R. G. Gordon, *J. Chem. Phys.* **45**, 1635, 1643, 1649 (1966); **46**, 448 (1967); R. J. Cross and R. G. Gordon, *ibid.* **45**, 3571 (1966); R. J. Cross, *ibid.* **46**, 609 (1967).

⁶ A. Dalgarno, R. J. W. Henry, and C. S. Roberts, *Proc. Phys. Soc. (London)* **88**, 611 (1966); A. C. Allison and A. Dalgarno, *ibid.* **90**, 609 (1967).

TABLE I. Reduced inelastic cross sections for transitions from the 00 state and the 10 state. Parameters: full set.

σ^*	E^*				
	1	3	10	30	100
A. 00 state (entries are either $\sigma_{j'm',00}^*$ or $\sigma_{j',00}^{*a}$)					
$j'm'=10$	0.005 ₈	0.002 ₂	0.000 ₃	0.000 ₃	0.000 ₂
11	0.371	0.322	0.268	0.225	0.184
$j'=1$	0.748	0.646	0.537	0.450	0.368
$j'm'=20$	0.097	0.089	0.079	0.071	0.063
21	0.017	0.009 ₃	0.004 ₀	0.003 ₄	0.001 ₅
22	0.236	0.232	0.211	0.180	0.152
$j'=2$	0.603	0.571	0.510	0.438	0.371
$j'm'=30$	0.010	0.004 ₂	0.004 ₁	0.003 ₁	0.003 ₆
31	0.036		0.035		0.029
32	0.013		0.002 ₂		0.000 ₃
33	0.073		0.060		0.040
$j'=3$	0.253		0.197		0.144
$j'm'=40$	0.018	0.019	0.017	0.017	0.015
41	0.014		0.003 ₉		0.002 ₄
42	0.023		0.023		0.022
43	0.012		0.003 ₀		0.000 ₈
$j'=4^b$	0.116		0.077		0.065
$\Sigma\sigma_{j'm',00}^*$	1.720		1.323		0.948
$\sigma_{inel,00}^*$	5.04	4.13	3.31	2.73	2.19
$\Sigma\sigma_{j'm',00}^*/\sigma_{inel,00}^*$	0.341		0.400		0.433
B. 10 state (entries are either $\sigma_{j'm',10}$ or $\sigma_{j',10}$)					
$j'm'=11$	0.010	0.005 ₆	0.002 ₉	0.002 ₁	0.000 ₉
$j'm'=20$	0.017	0.007 ₂	0.005 ₅	0.003 ₃	0.002 ₈
21	0.285	0.257	0.220	0.188	0.157
22	0.005 ₆	0.002 ₄	0.000 ₉	0.000 ₄	0.000 ₂
$j'=2$	0.597	0.526	0.447	0.379	0.317
$j'm'=30$	0.089	0.087	0.083	0.078	0.074
$\sigma_{inel,10}^*$	4.57	3.68	2.92	2.35	1.88

^a All entries have been corrected for the contribution of the "tail" of $P(b^*)$ above $b^*=3$.

^b The summed value for $\sigma_{4,00}^*$ is low because of the omission of $\sigma_{44,00}^*$.

The extent of the computations was as follows:

Type (a): "Full parametrization," designated "full set," i.e., both long-range anisotropies ($a_2=0.3$, $c=2.0$) and short-range ($b_1=b_2=0.5$). For $\alpha=00$ and $\beta=00, 10, 11, 20, 21, 22, 30, 40$, and for $\alpha=10$ and $\beta=10, 11, 20, 21, 22, 30$, the calculations were performed at $E^*=1, 3, 10, 30, 100$. For $\alpha=00$ and $\beta=31, 32, 33, 41, 42, 43$; at $E^*=1, 10, 100$.

Type (b): Long-range anisotropies only, i.e., $a_2=0.3$, $c=2.0$, $b_1=b_2=0.0$. For $\alpha=00$ and $\beta=00, 10, 11, 20, 21, 22, 30, 40$, and for $\alpha=10$ and $\beta=10, 11, 20, 21, 22, 30$, the calculations were performed at $E^*=1, 100$.

Type (c): Short-range anisotropies only, i.e., $a_2=c=0.0$, $b_1=b_2=0.5$. Computations as for Type (b).

III. ANGULAR DISTRIBUTIONS

The differential inelastic cross sections may be obtained⁷ (within the semiclassical framework) from the

⁷ See Paper I; also J. L. J. Rosenfeld and J. Ross, J. Chem. Phys. **44**, 188 (1966).

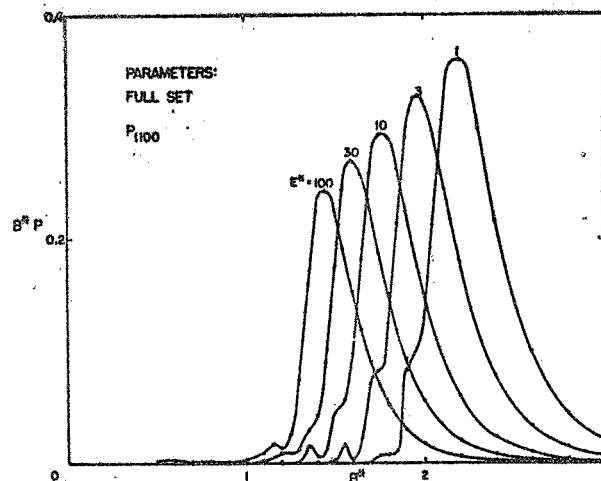


FIG. 1. Plots of b^*P_{1100} vs b^* for the full set of anisotropy parameters and for reduced energy $E^*=1, 3, 10, 30, 100$.

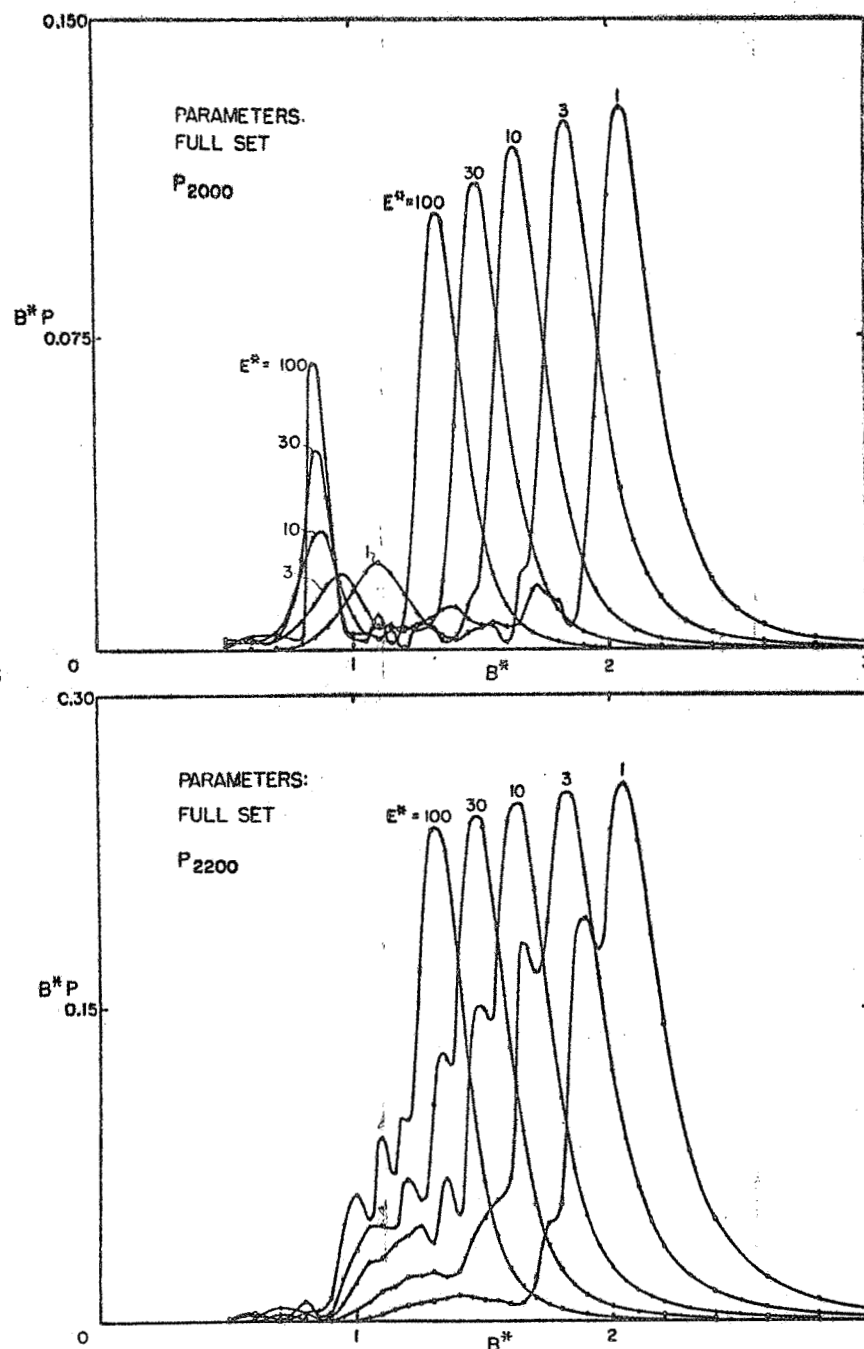


FIG. 2. Plots of b^*P_{2000} and b^*P_{2200} vs b^* ; otherwise as in Fig. 1.

transition probabilities by means of an inventory over the 1, 3, 5, ... branches of the classical deflection function $\chi(b^*, E^*)$. At reduced energies $E^* > 1$, no more than three branches are obtained, so that the differential inelastic polar angle cross section $d\sigma_{\beta\alpha}(\chi)/d\chi$ is given by

$$2\pi \sin\chi d\chi [d\sigma_{\beta\alpha}(\chi)/d\Omega] = [d\sigma_{\beta\alpha}(\chi)/d\chi] d\chi \\ = \sum_{i=1}^3 2\pi b_i P_{\beta\alpha}(b_i) db_i \quad (1)$$

and

$$\frac{d\sigma_{\beta\alpha}^*(\chi)}{d\chi} = 2 \sum_{i=1}^3 \frac{b_i^* P_{\beta\alpha}(b_i^*)}{|d\chi/db_i^*|}, \quad (2)$$

where $\sigma_{\beta\alpha}^*$ is the usual reduced cross section, i.e., in units of $\pi\sigma_{LJ}^2$. (For TIF-Ar, this quantity is estimated to be $\sim 25 \text{ \AA}^2$.) The values of $d\chi/db_i^*$ were obtained by numerical (quadratic) differentiation of the $\chi(b^*)$ table available from II (plus additional calculated values), except at suitably low angles where the more

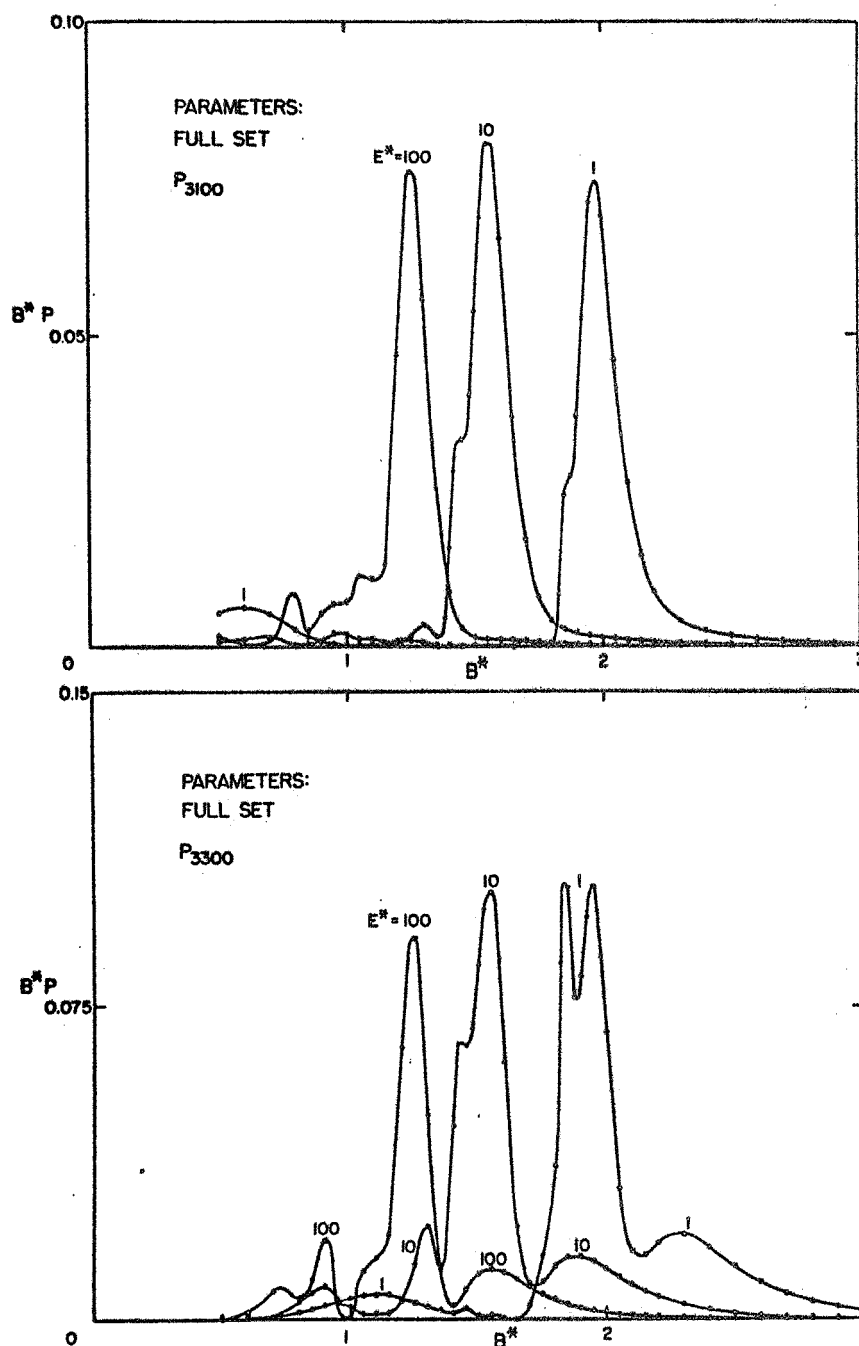


FIG. 3. Plots of b_{3100}^* and b_{3300}^* vs b^* for $E^* = 1, 10, 100$; otherwise as in Fig. 1.

accurate analytical form⁸

$$|d\chi/db^*| \cong \frac{1}{2}45\pi(b^*)^{-7}(E^*)^{-1} \quad (3)$$

was used directly.

Thus, for each desired value of the center-of-mass deflection angle χ , the appropriate values of b_i^* , $|d\chi/db_i^*|$, and $b_i^*P_{\beta\alpha}(b_i^*)$ were obtained by inter-

⁸ (a) From the Kennard low-angle approximation, expressed in the present notation. (b) R. B. Bernstein, *Molecular Beams*, J. Ross, Ed. (John Wiley & Sons, Inc., New York, 1966), Chap. 3, p. 81.

polarization⁹ and employed in Eq. (2) to yield $d\sigma_{\beta\alpha}^*(\chi)/d\chi$ at the specified energy E^* .

At the same time, it was convenient for comparison to calculate the differential elastic cross sections which would have been obtained on the assumption of no

⁹ For large b^* , E^* (e.g., ≥ 3 , ≥ 10 , respectively), first-order perturbation-approximated values of $P_{\beta\alpha}(b^*)$ were adequate. These approximate calculations of $P_{\beta\alpha}^{(1)}(b^*)$ were more convenient to use than those obtained by interpolation from tables of calculated $\{\sqrt{1/\pi}\}$ the full sudden approximation P^s .

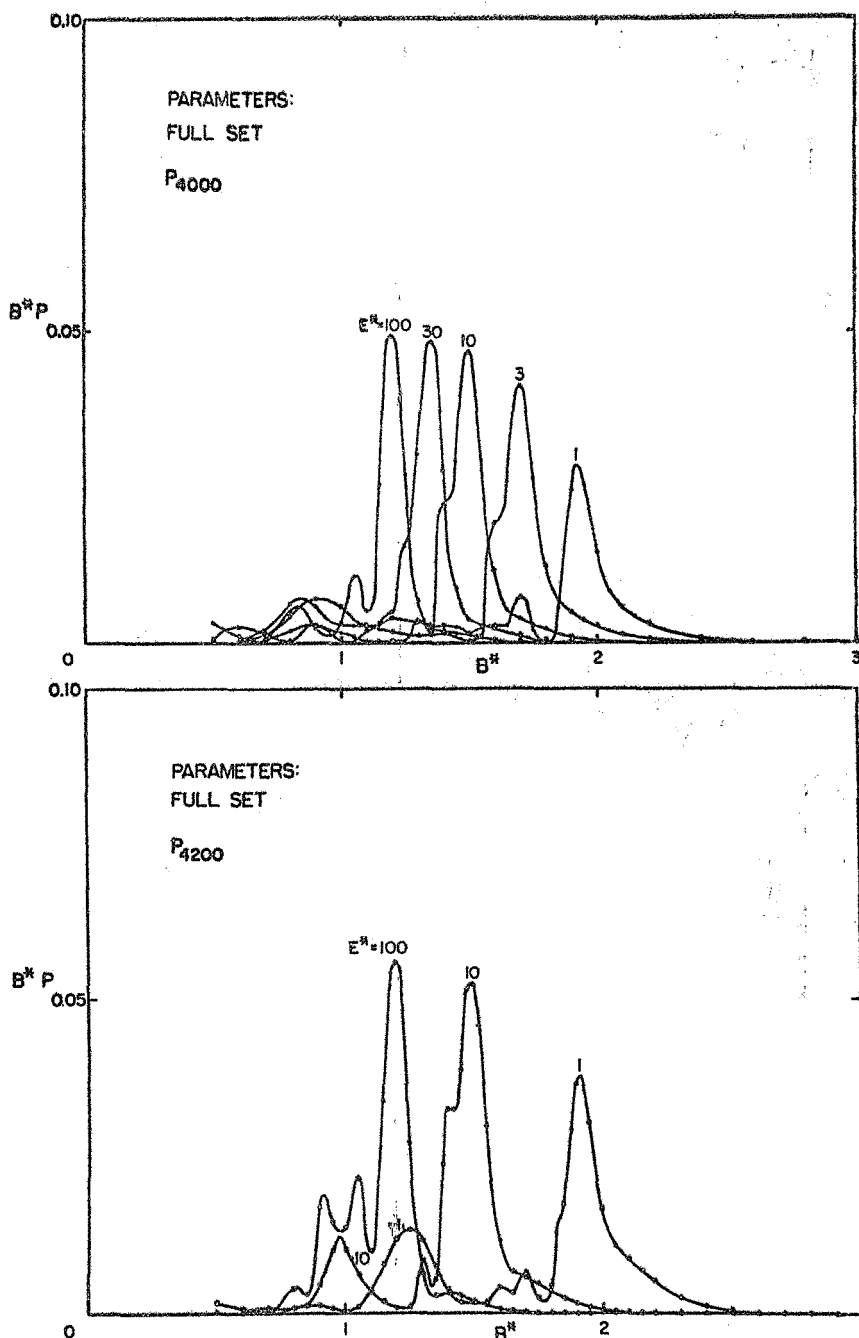


FIG. 4. Plots of b^*P_{4000} and b^*P_{4200} vs b^* . The values of b^*P_{4200} are plotted for $E^*=1, 10, 100$; otherwise as in Fig. 1.

inelastic scattering, i.e.,

$$\left(\frac{d\sigma^*}{d\chi}\right)_{\text{null}} = 2 \sum_{i=1}^3 b_i^* \left| \frac{d\chi}{db_i^*} \right|^{-1}. \quad (4)$$

This calculation [Eq. (4), using the present values of $d\chi/db_i^*$] gave results in agreement with those obtained from Desai's¹⁰ values of the Mason¹¹ scattering function $\rho(\chi, E^*)$:

$$\left(\frac{d\sigma^*}{d\chi}\right)_{\text{null}} = 7.0 \times 10^2 (E^*)^{-1/3} \chi_{\text{deg}}^{-4/3} \rho(\chi, E^*). \quad (5)$$

¹⁰ R. C. Desai, J. Chem. Phys. 44, 77 (1966).

¹¹ E. A. Mason, J. Chem. Phys. 26, 667 (1957).

A slight problem arises with respect to the very low angles, i.e., the "quantum region" $\chi < \theta_{\text{orit}}$, where θ_{orit} is some critical angle below which the classical treatment is invalid.^{8b} In the present case, for an L-J (12,6) potential,

$$\theta_{\text{orit}} \cong \frac{1.96}{k(Q/\pi)^{1/2}} = 0.118 (\Lambda^*)^{6/5} (E^*)^{-2/5}, \quad (6)$$

where the total cross section Q has been approximated by the Schiff-Landau-Lifshitz (SLL) equation

$$Q \cong Q_{\text{SLL}} = 8.083 (C_6/\hbar v)^{2/5}. \quad (7)$$

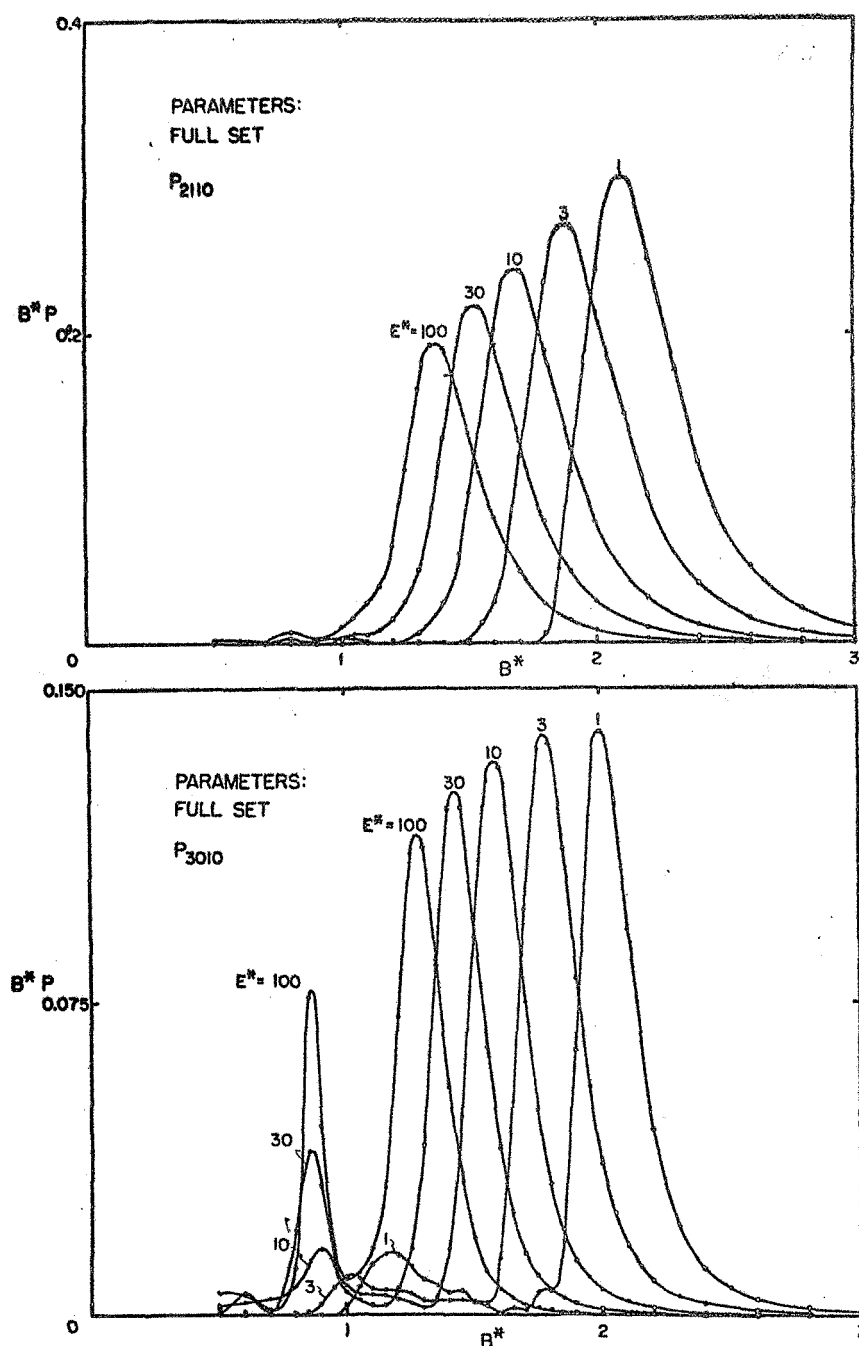


Fig. 5. Plots of b^*P_{2110} and b^*P_{3010} vs b^* ; otherwise as in Fig. 1.

For $\Lambda^*=0.1$ and $E^*\geq 1$, $\theta_{crit}\leq 0.43$ deg. Thus the present computations were not carried below $\frac{1}{2}$ deg. (However, it might be possible to extend them to smaller angles using a recently developed low-angle quantum treatment.¹²) It should be noted that within the framework of the present treatment [from Eqs.

(2), (3), the Appendix of this paper, and Eq. (9) of Paper I], $d\sigma_{\beta\alpha^*}/d\chi\rightarrow 0$ as $\chi\rightarrow 0$, regardless of energy.

In transforming the results of $b^*P_{\beta\alpha}(b^*)$ to $d\sigma_{\beta\alpha^*}(\chi)/d\chi$, the additional weighting of the long-range contribution [via the denominator of Eq. (2)] is expected to emphasize the outermost peak in $b^*P(b^*)$, thus resulting in a very simple angular distribution function peaking at fairly low angles (see Results).

IV. INELASTIC CROSS SECTIONS

The inelastic integral cross sections were obtained by numerical (Simpson's rule) and/or graphical inte-

¹² K. H. Kramer, "Rotational Excitation and Small Angle Molecular Scattering in the Sudden Approximation," Rept. WIS-TCL-212, January 1967. Here it is also pointed out that the conclusion of I regarding the zero-angle limiting behavior of the differential inelastic cross sections is in error; finite values at $\chi=0$ are indeed possible.

gration of the $b^*P_{\beta\alpha}(b^*)$ curves:

$$\sigma_{\beta\alpha}^*(E^*) = 2 \int_0^\infty b^*P_{\beta\alpha}(b^*, E^*) db^*. \quad (8)$$

(In practice, the region of integration was limited to $0.5 \leq b^* \leq 4.0$, encompassing $\geq 99\%$ of the cross sections.) As a check, these cross sections may also be obtained from the inelastic angular distributions via the identity

$$\sigma_{\beta\alpha}^* = \int_0^\pi \frac{d\sigma_{\beta\alpha}^*}{d\chi} d\chi. \quad (9)$$

(Once again, the actual range of integration used was limited, here from $0^\circ \leq \chi \leq 40^\circ$, also encompassing $\geq 99\%$ of $\sigma_{\beta\alpha}^*$.) The results were found to agree within 3%. The more precise results are believed to be those obtained from the Simpson's rule integration of $b^*P_{\beta\alpha}(b^*)$; they are presented in the Results section.

V. RESULTS

A. Energy Dependence of Cross Sections

Table I.A gives the results of computation of the partial integral cross sections $\sigma_{\beta\alpha}^*$ for $\alpha=00$, $\beta=10$, 1 ± 1 , 20 , 2 ± 1 , 2 ± 2 , 30 , 40 for $E^*=1, 3, 10, 30, 100$;

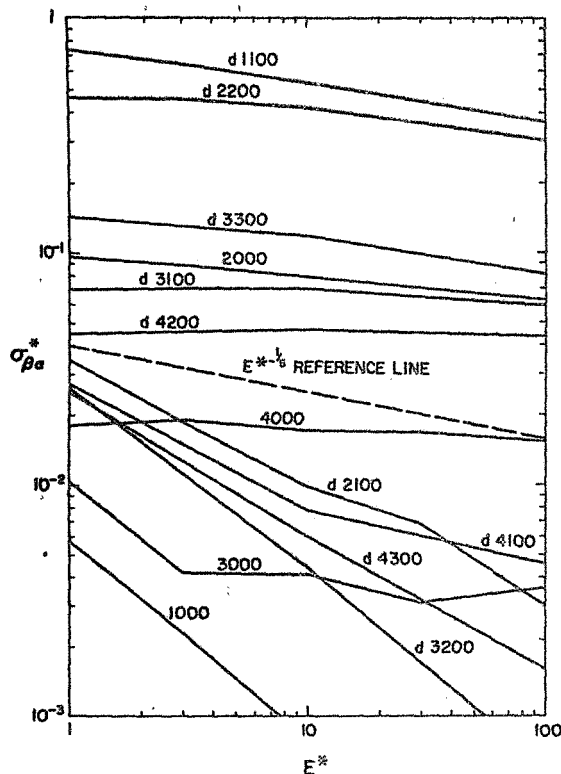


FIG. 6. Log-log plot of the energy dependence of the various $\sigma_{\beta\alpha}^*$ for $\alpha=00$ and full set of parameters. Entries denoted by $dj'm'00$ are $2\sigma_{\beta\alpha}^*, j'm'00$. The calculated points are connected by straight lines. The calculated points are connected by straight lines. The $(E^*)^{-1/2}$ reference line (arbitrarily placed) represents the energy dependence of the total inelasticity.

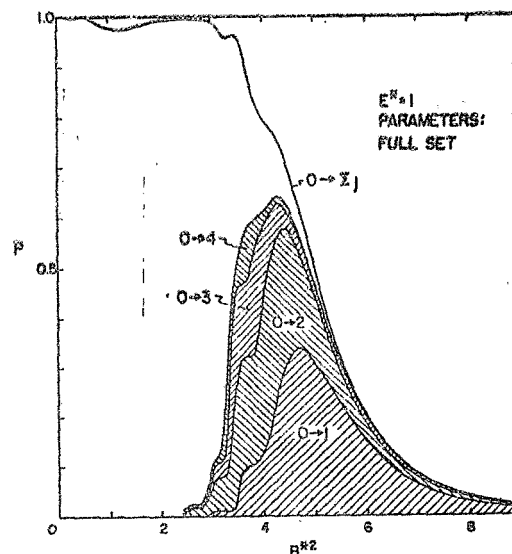


FIG. 7. Incremental contributions to $P_{\text{inel},00}[(b^*)^2]$ from $j'=1, 2, 3, 4$, for full set of parameters; $E^*=1$.

and $\beta=3\pm1, 3\pm2, 3\pm3, 4\pm1, 4\pm2, 4\pm3$ for $E^*=1, 10, 100$. Table I.B lists the $\sigma_{\beta\alpha}^*$ for $\alpha=10$ and $\beta=1\pm1, 20, 2\pm1, 2\pm2, 30$ for the same values of E^* .

Figures 1-4 show the energy dependence of the transition probabilities for the important transitions from the $\alpha=00$ state, i.e., plots of $b^*P_{\beta\alpha}(b^*)$ for fixed values of the anisotropy parameters and for various states β . Figure 5 illustrates the same effect for two transitions from the $\alpha=10$ state.

Figure 6 shows the energy dependence of the inelastic cross sections for $\alpha=00$. Figure 7 illustrates the incremental contribution of each individual Δj transition probability to the total inelastic transition probability from $\alpha=00$. (Note that in Fig. 7 and Table I.A, the entries for $\Delta j=4$ are incomplete due to neglect of the transitions $00 \rightarrow 4\pm4$.)

Figure 8 shows the dependence of the 2200 transition probability on the anisotropy parameters. In both cases, the plots compare (f) full parametrization: $a_2=0.3, c=2.0, b_1=b_2=0.5$; (l) long-range anisotropy only: $a_2=0.3, c=2.0, b_1=b_2=0.0$; and (s) short-range anisotropy only: $a_2=c=0.0, b_1=b_2=0.5$. The upper and lower plots compare behavior for $E^*=1$ and 100 , respectively.

B. Angular Distributions

Figure 9 shows the angular distributions for $E^*=1$ ($\alpha=00$ and 10 , respectively) plotted as $d\sigma_{\beta\alpha}^*(\chi)/d\chi$, the reduced differential polar inelastic scattering cross section. These functions are closely related to the physical quantities that would be measured in a crossed molecular beam experiment. For nonzero m' , the cross sections have been doubled (since the $\pm m'$ states are not distinguishable); these doubled values are denoted by $dj'm'jm$.

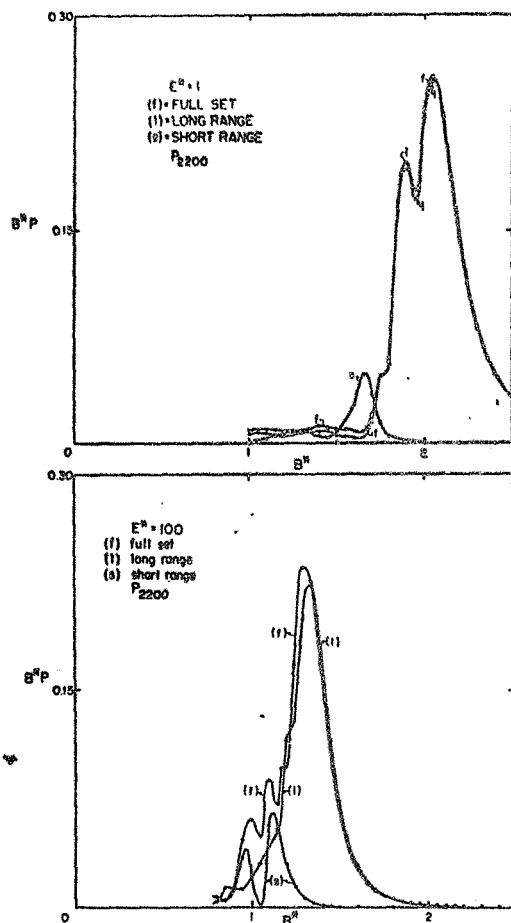


FIG. 8. Plots of b^*P_{2200} vs b^* contrasting three sets of anisotropy parameters: (f) full set; (l) long range only; and (s) short range only. The upper and lower plots are for $E^*=1$ and 100, respectively.

Figure 10 illustrates the energy dependence of several of the differential cross sections in the region of their main maxima. Figure 11 shows the angular distributions and magnitudes of several of the $\sigma_{\beta\alpha}^*$ compared with the null or "elastic" cross section (which would obtain if $a_2=b_1=b_2=c=0$), calculated via Eq. (5).

VI. DISCUSSION

A. Energy Dependence of the Cross Sections

Inspection of Table I reveals a number of interesting features. First, it is noted that for low Δj (1 or 2) the selection rules of II give a reliable indication of the relative importance of the various transitions: first-order perturbation "allowed" transitions show cross sections at least fivefold greater than "forbidden" ones, over the whole energy range. For higher transitions ($\Delta j=3$ or 4), however, this distinction is less pronounced; for these, it appears that the selection rules are better indicators at the higher energies. Second,

the cross sections for those transitions listed are seen to account for only about 40% of the total inelasticity. Thus there must be a great many higher-order transitions, each contributing small increments to the transition probabilities at successively smaller impact parameters (cf. Fig. 7), which, in aggregate, account for the inventory of the total inelastic cross section.

This is further elucidated by consideration of the energy dependence of the various cross sections. In Fig. 6, the $(I^*)^{-1/2}$ "reference line" (arbitrarily placed) represents the energy dependence of the total inelasticity (see II); however, the "allowed" transition cross sections show a smaller fractional decrease with increasing energy for increasing Δj , while the "forbidden" ones maintain a strong energy dependence. This suggests that many more forbidden outgoing channels are opening up at higher energies, where their combined influence probably gains importance relative to the allowed transitions.

It is interesting to note that for small Λ^* (i.e., $\Lambda^* \lesssim 0.5$), the total inelastic integral cross section may

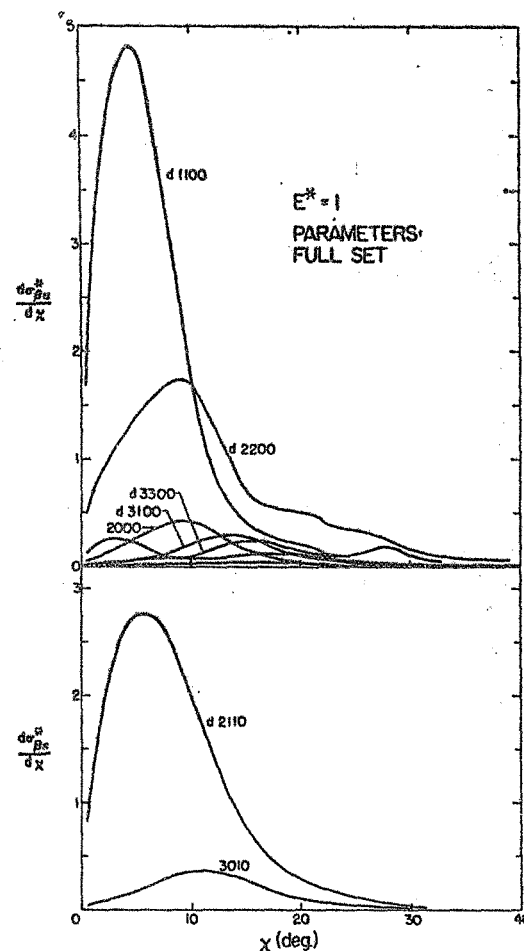


FIG. 9. Plots of $d\sigma_{\beta\alpha}^*/d\chi$ vs χ for full set of anisotropy parameters; $E^*=1$. The upper and lower plots are for $\alpha=00$ and 10, respectively. In the upper plot, the two unmarked curves refer to the transitions 4000 (lower of the two) and d4200.

be estimated without considering in detail the forbidden transitions. In II it was pointed out that a good approximation for $\sigma_{inel,\alpha}^*$ was $S_{inel,\alpha}^* \equiv [b^* (P_{inel,\alpha} = \frac{1}{2})]^2$. Evaluation of S^* , however, required computations of $P_{inel,\alpha}(b^*) = 1 - P_{\alpha\alpha}(b^*)$ by the sudden-approximation program. A simpler estimate of $\sigma_{inel,\alpha}^*$ may be obtained from first-order perturbation calculations of the allowed transitions, as follows.

As seen in Fig. 7, in the vicinity of $P = \frac{1}{2}$, the sum of the 0→1, 2, and 3 transitions totals to nearly $\frac{1}{2}$; most of this total arises from the first-order perturbation-allowed transitions. This suggests the following simple procedure for estimation of S^* . Using the analytical first-order perturbation-theory expressions for the transition probability $P_{\beta\alpha}^{(1)}(b^*, E^*)$ (in the straight-line approximation of I), as given in the Appendix,

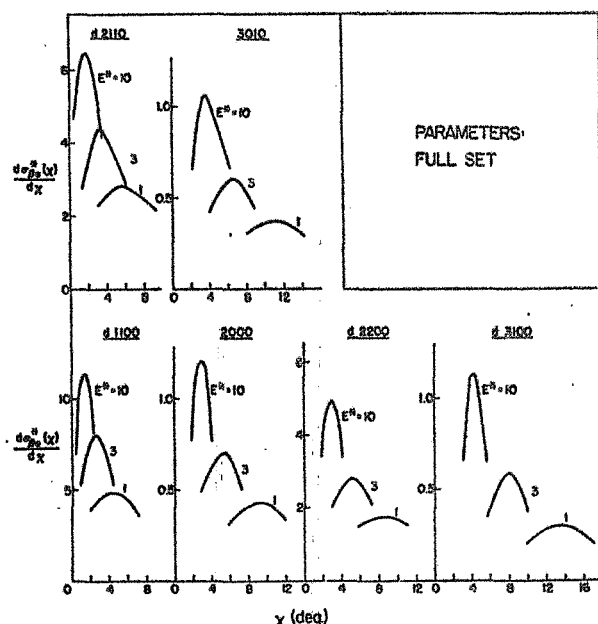


FIG. 10. Energy dependence of the principal maxima of various $d\sigma_{\beta\alpha}^*(\chi)/d\chi$ for full set of anisotropy parameters.

solve for the value of b^{*2} at which

$$\sum_{\beta \neq \alpha} P_{\beta\alpha}^{(1)}(b^*) = \frac{1}{2}.$$

The resulting total cross section, designated

$$S_{inel,\alpha}^{*(1)} \equiv [b^* (P_{inel,\alpha}^{(1)} = \frac{1}{2})]^2,$$

is found to agree well with $S_{inel,\alpha}^*$ and $\sigma_{inel,\alpha}^*$, as shown in Table II. (However, see Appendix for the limits of validity of this procedure.)

B. Dependence on Anisotropy Parameters

The dependence of the transition probabilities on anisotropy parameters is quite reasonable. Two features are noted in Fig. 8 for a representative transition which was selected because it shows the following effects most clearly. The first is that of an approximate

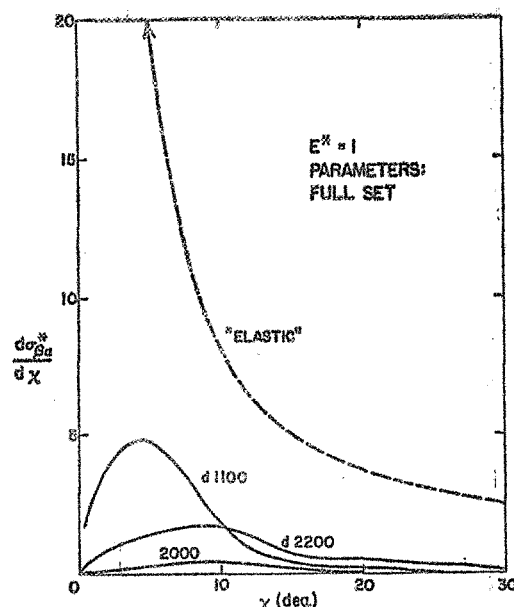


FIG. 11. Plot of several of the $d\sigma_{\beta\alpha}^*(\chi)/d\chi$ (for the full set of anisotropy parameters) compared with $(d\sigma^*(\chi)/d\chi)_{null}$, i.e., the "null elastic" differential cross section for the case where all anisotropy parameters have been set equal to zero; $E^* = 1$.

"additivity" of the transition probabilities due to different anisotropies. The peaks in the (l) curves and the (s) curves "combine" to give (approximately) the peaks in the (f) curves. The second is that the main peak (i.e., that at largest b^*) obtained for the full set of anisotropies is well approximated in all cases by the values obtained with the long-range anisotropies only. Thus for practical purposes, the main peak in the angular distribution can be calculated neglecting the short-range anisotropies (about which less is known in any case).

C. Angular Distributions

The appearance and relative magnitudes of the angular distributions for $E^* = 1$ are seen in Fig. 9. All show a single, prominent peak (with the exception of $d3300$) at fairly low angles. The forbidden transitions (not shown) are smaller and give broad peaks at higher angles.

Several interesting effects are noted in Fig. 10. First, for a fixed value of E^* , the angle of the peak increases as the magnitude of Δj is increased. Clas-

TABLE II. Comparison of exactly computed values with approximate values of the total inelastic integral cross sections. Parameters: Full set.

E^*	$\sigma_{inel,00}^*$	$S_{inel,00}^*$	$S_{inel,00}^{*(1)}$
1	5.04	4.98	5.13
3	4.13	4.06	4.25
10	3.31	3.27	3.46
30	2.73	2.68	2.87
100	2.19	2.15	2.33

sically, this implies greater importance of "head-on" collisions (with smaller b^*) for the excitation of higher rotational states. Thus for $E^*=1$ and $j=0$, the peak positions for $j'=1, 2, 3$, and 4 are $\sim 5^\circ, 10^\circ, 14^\circ$, and 17° , respectively. An analogous trend is found for the forbidden transitions. Second, concerning the energy dependence of the individual cross sections, in all cases, a strong trend of the peak position toward lower values of χ is noted as the energy increases. Also seen is a narrowing and heightening of the main peak with increasing energy.

In an attempt to make a connection with the experiments of Toennies,²⁰ it is interesting to consider the result of a hypothetical experiment consisting of a monochromatic beam of TlF ($v \cong 3.0 \times 10^4$ cm sec⁻¹) crossed (at 90°) with a beam of Ar ($\bar{v} \cong 4.3 \times 10^4$ cm sec⁻¹). For a laboratory acceptance angle $\chi_{lab} = 0.5$ deg, the center-of-mass angle¹³ $\chi_{c.m.} = 3.5$ deg, and one would expect to see $> 25\%$ of the inelastic cross section for the $\Delta j=1$ transition, but only $\sim 8\%$ of that for the $\Delta j=2$ transition (cf. Fig. 9). Thus for a set of conditions not too dissimilar from those of Ref. 2(c), the $\Delta j=1$ cross section would be "favored" relative to $\Delta j=2$ by a factor of about 3. For the angular distributions in Fig. 9, this yields the ratio $\sigma_{\Delta j=2}/\sigma_{\Delta j=1} = 0.27$. This effect tends to bias the results of observation in favor of low Δj transitions and helps to explain the small observed²⁰ ratio $\sigma_{inel,app}^{(10-30)}/\sigma_{inel,app}^{(20-30)} < 0.17$. Presumably, in the future it will be possible to measure the important low-angle portion of the angular distributions for the separate transitions and, by comparison with computations, to deduce the long-range anisotropy of the intermolecular potential.

APPENDIX: FIRST-ORDER-PERTURBATION-THEORY (STRAIGHT-LINE APPROXIMATION) TRANSITION PROBABILITIES

Upon expanding the exponential in Eq. (1) of Paper II, or dropping the cosine term in Eq. (15) of II (and replacing the sine with the angle), and following the procedure in I for the straight-line approximation, one obtains analytical expressions which lead

¹⁹ R. B. Bernstein, Science 144, 141 (1964).

to the "allowed" transition probabilities as a function of b^* , E^* , Λ^* , and the anisotropy parameters. The results are

$$\begin{aligned}\Lambda^*(E^*)^{1/2} \langle 11 | G | 00 \rangle &\cong 3.022c(b^*)^{-6} - 3.790b_1(b^*)^{-11}, \\ \Lambda^*(E^*)^{1/2} \langle 20 | G | 00 \rangle &\cong 1.655a_2(b^*)^{-8} - 1.629b_2(b^*)^{-11}, \\ \Lambda^*(E^*)^{1/2} \langle 22 | G | 00 \rangle &\cong -3.379a_2(b^*)^{-8} \\ &\quad + 2.439b_2(b^*)^{-11}, \\ \Lambda^*(E^*)^{1/2} \langle 31 | G | 00 \rangle &\cong -0.303c(b^*)^{-6}, \\ \Lambda^*(E^*)^{1/2} \langle 33 | G | 00 \rangle &\cong 0.912c(b^*)^{-6},\end{aligned}\quad (A1)$$

where $G = (1/\hbar) \int V dt$ with $P_{\beta\alpha}^{(1)} = [\langle \beta | G | \alpha \rangle]^2$. For sufficiently high b^* and E^* , these expressions for $P_{\beta\alpha}^{(1)}$ are found to reproduce the numerical values of $P_{\beta\alpha}$ obtained by the full sudden computational program. However, they have been applied to the estimation of $P_{inel,00}$ in a region (at lower b^*) where each of the individual $P_{\beta\alpha}^{(1)}$ is known to be too high. The results of Table II, however, indicate that the perturbation results are still useful in this region. The specific equation employed is

$$\begin{aligned}P_{inel,00}^{(1)} &= 2[\langle 11 | G | 00 \rangle]^2 + [\langle 20 | G | 00 \rangle]^2 \\ &\quad + 2[\langle 22 | G | 00 \rangle]^2 + 2[\langle 31 | G | 00 \rangle]^2 \\ &\quad + 2[\langle 33 | G | 00 \rangle]^2.\end{aligned}\quad (A2)$$

Upon substituting Eq. (A1) into (A2) and setting $P_{inel,00}^{(1)} = \frac{1}{2}$, the following implicit equation in $S^*_{inel,00}^{(1)}$ (the first-order perturbation approximation to the total inelastic integral cross section) is obtained:

$$\begin{aligned}(\Lambda^*)^2 E^* &= 51.140a_2^2 x^{-8} + 40.225c^2 x^{-6} - 76.710a_2 b_2 x^{-8} \\ &\quad - 91.632b_1 c x^{-8.5} + (57.465b_1^2 + 29.103b_2^2) x^{-11},\end{aligned}\quad (A3)$$

where x denotes $S^*_{inel,00}^{(1)}$. Equation (A3) was used to obtain the first-order approximate values of $S^*_{inel,00}^{(1)}$ in Table II. The validity of this approximation has been tested for several other parameter sets with good results. For Λ^* in the range 0.1 to 0.5, $S^*_{inel,00}^{(1)}$ reproduces $S^*_{inel,00}$ to within 7%; for higher Λ^* , $S^*_{inel,00}^{(1)}$ is found to be significantly smaller than $S^*_{inel,00}$, so the approximation becomes of little value.

C. Appendix. Perturbation expansion for the $P_{\alpha\alpha}$.

In connection with the problem considered in the appendix to J. Chem. Phys. 47, 4417 (1967), namely, the computation of approximations to $P_{inel,\alpha}$ ($= 1 - P_{\alpha\alpha}$) where $\alpha = 00$ and 10 , it is worthwhile to consider a perturbation expansion for $P_{\alpha\alpha}$. For $G = \frac{1}{\hbar} \int V dt$,

$$P_{\beta\alpha} = \left| \langle \beta | \exp \left[-\frac{i}{\hbar} \int V(t) dt \right] | \alpha \rangle \right|^2 = \left| \langle \beta | \sum_{l=0}^{\infty} \frac{(-iG)^l}{l!} | \alpha \rangle \right|^2$$

$$[\langle \beta | \text{Re} | \alpha \rangle]^2 + [\langle \beta | \text{Im} | \alpha \rangle]^2, \quad (\text{C1})$$

where Re and Im are the real and imaginary parts of the integral.

For $\beta = \alpha$, consider the first-order limit:

$$P_{\alpha\alpha}^{(1)} = \left| \langle \alpha | (1 - iG) | \alpha \rangle \right|^2 = [\langle \alpha | \alpha \rangle]^2 + [\langle \alpha | G | \alpha \rangle]^2$$

$$= 1 + [\langle \alpha | G | \alpha \rangle]^2 \geq 1 ! \quad (\text{C2})$$

Thus, the first-order limit yields a transition probability ≥ 1 for all impact parameters, a rather unexpected (and unacceptable) result.

Now consider the second-order result:

$$\begin{aligned}
 P_{\alpha\alpha}^{(2)} &= \left| \langle \alpha | \left(1 - iG - \frac{G^2}{2} \right) | \alpha \rangle \right|^2 \\
 &= \left[\langle \alpha | \left(1 - \frac{G^2}{2} \right) | \alpha \rangle \right]^2 + \left[\langle \alpha | G | \alpha \rangle \right]^2. \quad (C3)
 \end{aligned}$$

Another surprising result--the second-order term does nothing to "tone down" the ill-behavior of the first-order term. The expansion of Eq. B1 separates into real and imaginary parts, with alternate powers of G contributing to one or the other of the terms in the mod square of Eq. B1.

In particular, since the expansion should be accurate in the region $P_{\alpha\alpha} = 1/2$, one needs good values for both the real and imaginary parts (it is found in the exact numerical integrations, for instance, that both parts contribute the same general magnitude to the transition probability). To get acceptable accuracy from the imaginary part of the perturbation expansion however, the third order term (at least) must be included, and this is very messy for even a simple potential with few anisotropy terms. It is concluded therefore, that the direct perturbation expansion is of little use for this problem.

VI. COMPARISON OF APPROXIMATIONS IN INELASTIC SCATTERING

A. Introduction

Chapter VI is a comparison of the time-dependent and time-independent hierarchies for rotational excitation in atom-diatom molecule collisions. Equivalence between the Born and first order perturbation limits is demonstrated. Again, numbering of pages, equations and references is self-contained within the reprint.

The authors are grateful to Dr. Merle Pattengill for pointing out that the specialization to the high- j limit (which was not noted in the text) need not have been invoked in Eqs. 21 and 28.

Molecular Collisions. X. Restricted-Distorted-Wave-Born and First-Order Sudden Approximations for Rotational Excitation of Diatomic Molecules*

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Although a number of approximation methods have been widely used in the field of molecular rotational excitation and scattering, their interrelationships and ranges of applicability have not always been clearly established. The present work is a comparison of several of these approximations. Considered are the time-independent treatments such as the distorted wave approximation (DWA), the restricted distorted wave (RDW) and the RDW-Born approximations, and the time-dependent ones such as the sudden approximation (SA), full trajectory and straight-line limit, and the first-order perturbation approximations. Equivalence is demonstrated between the RDW-Born and first-order SA, and convenient analytical forms are presented for the resulting transition probabilities.

I. INTRODUCTION

The theory of rotational excitation and scattering of diatomic (rigid-rotor) molecules by structureless atoms has been well formulated,^{1,2} but exact computations remain a formidable task.^{2,3} Thus a large number of approximation methods have been introduced and many approximate calculations carried out for model systems.² The few available direct experimental measurements⁴ of specific rotational transitions (obtained via the molecular-beam technique) are of insufficient accuracy to check even such approximate calculations. In view of the uncertainty in the intermolecular potentials, such a check would hardly be definitive in any case. On the other hand a proper test of the various approximations (i.e., by comparison with complete and numerically accurate close-coupled computations of the differential or integral inelastic cross section for a given assumed potential) is extremely time consuming even with present-day computers, except for low energies⁵ or for hydrogenic systems.⁶

Thus, it is of interest to compare the various approximation methods from a theoretical viewpoint and

to determine, by computation when necessary, the range of validity of the more useful ones in the hope that reliable working approximation schemes can be identified and equations expressed in practical form.

One may consider a hierarchy of approximate treatments for the transition probabilities employing either time-dependent (TD) or time-independent (TI) perturbation methods. The TD hierarchy can be listed (in order of decreasing rigor) as follows: first, the infinite-order (time-ordered) exact formal expression^{7a} is reduced to the Magnus approximation^{7b}; next to the sudden, i.e., "first Magnus" approximation⁸ (retaining the term

$$\exp\left(-\frac{i}{\hbar} \int V dt\right)$$

but neglecting the $\exp(i\omega_{mn}t)$ factor); then to the in-plane trajectory SA⁹ (neglecting angular momentum conservation); then to the straight-line trajectory SA (the high-energy approximation)^{9a}; finally to the first-order perturbation result¹⁰ (keeping only the first-order term

$$\left(-\frac{i}{\hbar} \int V dt\right)$$

in the expansion of the SA exponential). Similarly, the TI hierarchy begins with the infinite set of coupled equations¹¹; is reduced to the truncated close-coupled

* Work supported by National Aeronautics and Space Administration Grant NGL-50-002-001 and National Science Foundation Grant GP-7409.

¹ For a review, see K. Takayanagi, *Advan. At. Mol. Phys.* **1**, 149 (1965).

² (a) Much of the recent literature is referenced in C. F. Curtiss and R. B. Bernstein, *J. Chem. Phys.* **50**, 1168 (1969); a misprint occurred in Eq. (15); a factor of $2M/\hbar^2$ on the right was omitted. Other recent related articles include: (b) R. J. Cross, Jr., *ibid.* **49**, 1753 (1968); (c) W. H. Miller, *ibid.* **49**, 2373, (1968); (d) R. J. Cross, Jr., *ibid.* **50**, 1036 (1969); (e) J. Reuss and S. Stolte, *Physica* **42**, 111 (1969).

³ R. G. Gordon has recently developed an efficient computational method for solving the many-channel coupled equations, *J. Chem. Phys.* **51**, 14 (1969).

⁴ (a) J. P. Toennies, *Discussions Faraday Soc.* **33**, 96 (1962); *Z. Physik* **182**, 257 (1965); *Recent Advan. Aerothermochem. (AGARD)* **12**, 237 (1967). (b) A. R. Blythe, A. E. Grosser, and R. B. Bernstein, *J. Chem. Phys.* **41**, 1917 (1964).

⁵ W. Erlwein, M. von Seggern, and J. P. Toennies, *Z. Physik* **211**, 35 (1968).

⁶ (a) A. C. Allison and A. Dalgarno, *Proc. Phys. Soc. (London)* **90**, 609 (1967). (b) B. R. Johnson and D. Secrest, *J. Chem. Phys.* **48**, 4682 (1968).

⁷ (a) See, for example, F. J. Dyson, *Phys. Rev.* **75**, 486 (1949). (b) P. Pechukas and J. C. Light, *J. Chem. Phys.* **44**, 3897 (1966). Also a recent extension by R. D. Levine, *Chem. Phys. Letters*, **2**, 76 (1968).

⁸ (a) K. Alder and A. Winther, *Kgl. Danske Videnskab., Mat. Fys. Medd. Selskab.* **32**, 8 (1960); (b) D. W. Robinson, *Helv. Phys. Acta* **36**, 140 (1963).

⁹ (a) K. H. Kramer and R. B. Bernstein, *J. Chem. Phys.* **40**, 200 (1964); (b) R. B. Bernstein and K. H. Kramer, *ibid.* **44**, 4473 (1966); (c) R. W. Fenstermaker and R. B. Bernstein, *ibid.* **47**, 4417 (1967).

¹⁰ See Ref. 9(c) for limiting expressions.

¹¹ See, for example, (a) G. Gioumiosis and C. F. Curtiss, *J. Chem. Phys.* **29**, 996 (1958); (b) A. M. Arthurs and A. Dalgarno, *Proc. Roy. Soc. (London)* **A256**, 540 (1960); (c) W. D. Davison, *Discussions Faraday Soc.* **33**, 71 (1962); (d) Ref. 6(b).

approximation with both open and closed channels¹²; then open channels only¹³ (the usual S -matrix method); then to higher-order distorted wave approximations¹⁴ including the renormalized DWA¹⁵; the "infinite-order" DWA¹⁶; and the statistical (dominant-coupling plus DW) approximation.¹⁵ Next is the ordinary DWA¹⁷; the RDWA^{2a}; the DW-Born approximation¹⁸; the modified wavenumber (MWN) approximation¹⁹ (which neglects angular momentum conservation); and finally, the simple Born approximation (BA),²⁰ which can also be further reduced in certain limits, to be considered.

The present paper restricts consideration to the relations among the lower levels of these hierarchies, below the level of the DWA and the SA.

In the following section the restricted distorted-wave approximation^{2a} is reduced to the Born limit, and in the subsequent section the sudden approximation⁹ is correspondingly reduced to the first-order limit for explicit comparison. For the examples chosen (atom-diatom scattering), the two treatments yield equivalent results under certain conditions; it is important to establish these limits in order to deal with practical applications. Although this equivalence has been shown previously^{20d} in certain special cases,²¹ the present treatment is somewhat more general in scope and is carried through to yield identical "working formulas" from both treatments.

II. THE DISTORTED-WAVE APPROXIMATION

For the present problem of atom-diatom molecule scattering, the anisotropic interaction potential is taken to be a sum of a short-range repulsion and a long-range attraction, each of the factorizable form

$$V(R, \Theta) = V_0(R)[1 + a_L P_L(\cos\Theta)], \quad (1)$$

where $L=1$ or 2 , with the asymmetry coefficient a_L independent of R . Two commonly employed forms of

the spherical term, $V_0(R)$ are investigated:

$$V_0(R) = C_n R^{-n}, \quad (2a)$$

$$V_0(R) = C_\rho e^{-R/\rho}, \quad (2b)$$

where n is the index of the inverse power potential of "strength" C_n (positive for repulsive or negative for attractive potentials) and ρ is the range parameter of the exponential potential of strength C_ρ (which may also be positive or negative). The expressions for the RDWA transition probabilities, $P(j'j)$ for this problem are essentially given in Appendix B of Ref. 2(a). (It is noted that in the present approximation, contributions to the over-all transition probabilities are additive from the various anisotropic terms in the potential.) However, it is instructive to present here a brief derivation, designed for the specific potentials [Eqs. (1), (2)] of interest, and which defers the "large l " restriction until the final reduction [identical to Eqs. (A12)–(A18) of Ref. 2(a)].

The starting point is the equation for the J th partial cross section, $\sigma^J(j', j)$ for the excitation of the molecule from j to j' (irrespective of m_j and $m_{j'}$; the problem of the m transitions is discussed in Sec. III):

$$\sigma^J(j', j) = \frac{\pi}{k_{jj}^2} \left(\frac{2J+1}{2j+1} \right) \sum_{l=|j-j'|}^{J+j} \sum_{l'=|j-j'|}^{J+j'} |S^J(jl; j'l')|^2, \quad (3)$$

where the symbols are those of Refs. 11(b) and 15. Considering first a pure $P_2(\cos\Theta)$ anisotropy, one obtains

$$\sigma^J(j', j) = \frac{4\pi}{k_{jj}^2} \left(\frac{2J+1}{2j+1} \right) \frac{k_{j'j}}{k_{jj}} \times \sum_w a_2^2 [f_2(j'l'; jl; J)]^2 [q(j'l'; jl; J)]^2, \quad (4)$$

where the f_2 coefficients are those of Percival and Seaton²² and the radial quadrature q is similar to that of Eq. (47) of Ref. 2(a):

$$q(j'l'; jl; J) = \frac{2\mu}{\hbar^2 k_{j'j}} \int_0^\infty w_{j'l'} j^{jl}(R) V_0(R) w_{jl} j^{jl}(R) dR. \quad (5)$$

The total cross section for $j \rightarrow j'$ scattering is thus

$$\sigma(j', j) = \sum_{J=0}^\infty \sigma^J(j', j) = \frac{4\pi k' a_2^2}{(2j+1) k^3} \sum_{J=0}^\infty (2J+1) \times \sum_w [f_2(j'l'; jl; J)]^2 [q(j'l'; jl; J)]^2, \quad (6)$$

where $k = k_{jj}$ and $k' = k_{j'j}$.

If the distortion potential^{11b,15} $\langle j'l'; J | V | jl; J \rangle$ differs only slightly from V_0 , the w 's and the resulting q 's

¹² Reference 6(b). Also: R. D. Levine, B. R. Johnson, J. T. Muckerman, and R. B. Bernstein, Chem. Phys. Letters 1, 517 (1968); J. Chem. Phys. 49, 56 (1968).

¹³ References 6, 11(b)–11(d). Also: W. A. Lester, Jr., and R. B. Bernstein, Chem. Phys. Letters 1, 207, 347 (1967); J. Chem. Phys. 48, 4896 (1968). See also R. G. Gordon, Ref. 3.

¹⁴ References 11(b)–11(d). Also: (a) W. D. Davison, Proc. Roy. Soc. (London) A280, 227 (1964); (b) R. Kolodziejski, Acta. Phys. Polon. 10, 223 (1951); 31, 783 (1967).

¹⁵ R. B. Bernstein, A. Dalgarno, H. S. W. Massey, and I. C. Percival, Proc. Roy. Soc. (London) A274, 427 (1963).

¹⁶ R. J. Cross, Jr., J. Chem. Phys. 48, 4838 (1968).

¹⁷ See Refs. 11(b), (c). Also: C. S. Roberts, Phys. Rev. 131, 209 (1963).

¹⁸ See, for example, (a) W. F. Ford, Phys. Rev. 157, 1226 (1967); (b) Ref. 2(c).

¹⁹ K. Takayanagi; see Ref. 1 for complete literature on the MWNA.

²⁰ See, for example, (a) Ref. 15; (b) R. J. Cross, Jr., and R. G. Gordon, J. Chem. Phys. 45, 3571 (1966); (c) R. J. Cross, Jr., Ph.D. thesis, Harvard University, Boston, Mass., 1965; (d) R. J. Cross, Jr., J. Chem. Phys. 47, 3724 (1967).

²¹ See Refs. 9(a), 20(b), and J. M. Peek, Phys. Rev. 160, 124 (1967).

²² I. C. Percival and M. J. Seaton, Proc. Cambridge Phil. Soc. 53, 654 (1957).

depend negligibly on total J , and the order of summation in Eq. (6) may be inverted, giving

$$\sigma(j', j) = \frac{4\pi k' a_2^2}{(2j+1)k^3} \sum_{l=0}^{\infty} \sum_{l'=|l-2|}^{l+2} [q(j'l'; j'l)]^2 \times \sum_{J=J_1}^{J_2} (2J+1) [f_2(j'l'; j'l; J)]^2, \quad (7)$$

where J_1 is the larger of $|l-j|$ and $|l'-j'|$, and J_2 is the smaller of $l+j$ and $l'+j'$. If one takes advantage of the orthonormality of the f_2 coefficients, then Eq. (7) reduces to

$$\sigma(j', j) = \frac{4\pi k' a_2^2}{5k^3} (2j'+1) \begin{pmatrix} j' & j & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 \sum_{l=0}^{\infty} (2l+1) \times \sum_{l'=|l-2|}^{l+2} (2l'+1) \begin{pmatrix} l' & l & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 [q(j'l'; j'l)]^2. \quad (8)$$

This may be written in terms of a transition probability $P_l(j', j)$,

$$\sigma(j', j) = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) P_l(j', j), \quad (9)$$

where

$$P_l(j', j) = \frac{4a_2^2 k'}{5} (2j'+1) \begin{pmatrix} j' & j & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 \times \sum_{l'} (2l'+1) \begin{pmatrix} l' & l & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 [q(j'l'; j'l)]^2. \quad (10)$$

The only nonzero values of $P_l(j', j)$ occur for $j'=j$, $j \pm 2$ and

$$P_l(j \pm 2, j) = \frac{3}{10} a_2^2 \frac{k'}{k} g_{\Delta j}(j) \times \left[\frac{3}{8} \frac{l(l-1)}{(l-\frac{1}{2})(l+\frac{1}{2})} q_{l,-2}^2 + \frac{1}{4} \frac{l(l+1)}{(l-\frac{1}{2})(l+\frac{3}{2})} q_{l,0}^2 + \frac{3}{8} \frac{(l+1)(l+2)}{(l+\frac{1}{2})(l+\frac{3}{2})} q_{l,2}^2 \right], \quad (11)$$

where

$$g_2(j) = (j+1)(j+2)/(j+\frac{1}{2})(j+\frac{3}{2}),$$

$$g_{-2}(j) = j(j-1)/(j-\frac{1}{2})(j+\frac{1}{2}),$$

and notation for the q 's has been simplified: $q(j', l+\Delta l; j, l) \rightarrow q_{l, \Delta l} \equiv q_{l, \nu}$. For large l , this reduces to Eqs. (A16)–(A18) of Ref. 2:

$$P_l(j \pm 2, j) = \frac{3}{10} a_2^2 (k'/k) g_{\pm 2} \left[\frac{3}{8} q_{l,-2}^2 + \frac{1}{4} q_{l,0}^2 + \frac{3}{8} q_{l,2}^2 \right]. \quad (12)$$

Similarly, for the case of a $P_1(\cos\Theta)$ anisotropy, one

obtains

$$P_l(j \pm 1, j) = \frac{2}{3} a_1^2 (k'/k) g_{\Delta j}(j) \times \left[\frac{1}{2} \frac{l}{(l+\frac{1}{2})} q_{l,-1}^2 + \frac{1}{2} \frac{(l+1)}{(l+\frac{3}{2})} q_{l,1}^2 \right], \quad (13)$$

where

$$g_1(j) = (j+1)/(j+\frac{1}{2}),$$

$$g_{-1}(j) = j/(j+\frac{1}{2}),$$

which for large l reduces to Eqs. (A12)–(A14) of Ref. 2(a):

$$P_l(j \pm 1, j) = \frac{2}{3} a_1^2 (k'/k) g_{\pm 1} \left[\frac{1}{2} q_{l,-1}^2 + \frac{1}{2} q_{l,1}^2 \right]. \quad (14)$$

The essential remaining problem is the evaluation of the $q_{l, \nu}$. In the Born limit, the total interaction term is ignored in the distorted wave equation [Eq. (12) of Ref. 15]. In this limit, the radial wavefunction is simply related to the Bessel function, i.e., $w_{l, \nu}^{JH}$ is approximated by

$$w_{l, \nu}^{JH} \sim (\frac{1}{2} \pi k' R)^{1/2} J_{l+1/2}(k' R), \quad (15)$$

and $q_{l, \nu}$ is given approximately by

$$q_{l, \nu} = \pi \left(\frac{k}{k'} \right)^{1/2} \frac{\mu}{\hbar^2} \int_0^{\infty} J_{l+1/2}(k' R) V_0(R) J_{l+1/2}(k R) R dR. \quad (16)$$

Note that

$$q_{l,0} = -\eta_l^{\text{Born}}, \quad (17)$$

where η_l^{Born} is the Born-approximated elastic-scattering phase shift. Integrals of this form have been considered elsewhere.^{20,23,24}

The Born approximation is strictly valid only when l , k , and k' are large. It is found that in the limit, when $k'=k$, and $(l+\frac{1}{2})/k \cong (l'+\frac{1}{2})/k' \cong b$, one obtains the following asymptotic (a) result:

$$q_{l,0}^{(a)} = \frac{\mu}{\hbar^2 k} \int_b^{\infty} \frac{V_0(R) R dR}{(R^2 - b^2)^{1/2}}, \quad (18a)$$

$$q_{l,1}^{(a)} = q_{l,-1}^{(a)} = \frac{\mu b}{\hbar^2 k} \int_b^{\infty} \frac{V_0(R) dR}{(R^2 - b^2)^{1/2}}, \quad (18b)$$

$$q_{l,2}^{(a)} = q_{l,-2}^{(a)} = \frac{\mu}{\hbar^2 k} \int_b^{\infty} \frac{V_0(R) (2b^2 - R^2) dR}{R(R^2 - b^2)^{1/2}}. \quad (18c)$$

A. Inverse Power Potential

For an inverse power potential of the form of Eq. (2a), these integrals may be readily evaluated, and one finds that

$$q_{l, \nu}^{(a)} = [b V_0(b) / \hbar v] D_{n, \nu} = (C_n / \hbar v b^{n-1}) D_{n, \nu}, \quad (19)$$

²³ (a) C. F. Curtiss, *J. Math. Phys.* 5, 561 (1964); (b) See also Ref. 20(c).

²⁴ (a) R. B. Bernstein, *Molecular Beams*, J. Ross, Ed. (Interscience Publishers, Inc., New York, 1966), Chap. 3, p. 75. See also (b) R. B. Bernstein, *J. Chem. Phys.* 38, 515 (1963).

TABLE I. Numerical values of quantities in Eqs. (20) and (22) for the inverse n th power potential: D_{nv} , F_{n1} and F_{n2} for $v = \Delta l = 0, \pm 1, \pm 2$ and $\Delta f = \pm 1, \pm 2$.

n	v	D_{nv} [Eqs. (20)]	F_{n1} [Eq. (22a)]	F_{n2} [Eq. (22b)]
6	0	0.58905		
	± 1	0.53333	0.18963	0.06072
	± 2	0.39270		
7	0	0.53333		
	± 1	0.49087	0.16064	0.05399
	± 2	0.38095		
8	0	0.49087		
	± 1	0.45714	0.13932	0.04857
	± 2	0.36816		
9	0	0.45714		
	± 1	0.42951	0.12299	0.04412
	± 2	0.35556		
10	0	0.42951		
	± 1	0.40635	0.11008	0.04040
	± 2	0.34361		
11	0	0.40635		
	± 1	0.38656	0.09962	0.03725
	± 2	0.33247		
12	0	0.38656		
	± 1	0.36941	0.09098	0.03456
	± 2	0.32214		

where $v = \hbar k / \mu$ is the initial relative velocity and the D_{nv} are numerical constants:

$$D_{n0} = \pi^{1/2} \Gamma(\frac{1}{2}(n-1)) / 2\Gamma(\frac{1}{2}n), \quad (20a)$$

$$D_{n1} = \pi^{1/2} \Gamma(\frac{1}{2}n) / 2\Gamma(\frac{1}{2}(n+1)), \quad (20b)$$

$$D_{n2} = [(n-2)/n] D_{n0}. \quad (20c)$$

[Note that Eqs. (19) and (20a) yield, via Eq. (17), the conventional expression²⁴ for the Jeffreys-Born (JB) elastic-scattering phase shift for the inverse power potential.] With this result one finds that the transition probabilities $P(j \pm L, j | n)$ given by Eqs. (12) and (14) are of the form

$$\begin{aligned} P(j \pm L, j | n) &= [a_L b V_0(b) / \hbar v]^2 F_{nL} \\ &= [C_{nL} a_L / \hbar v b^{n-1}]^2 F_{nL}, \end{aligned} \quad (21)$$

where for $P_1(\cos\theta)$ anisotropy the selection rule re-

quires that $j' = j \pm 1$ and

$$F_{n1} = \frac{1}{8} \pi \{ \Gamma(\frac{1}{2}n) / \Gamma(\frac{1}{2}(n+1)) \}^2, \quad (22a)$$

and for $P_2(\cos\theta)$ anisotropy $j' = j \pm 2$ and

$$F_{n2} = \frac{3\pi}{40} \frac{(n^2 - 3n + 3)}{n^2} \{ \Gamma(\frac{1}{2}(n-1)) / \Gamma(\frac{1}{2}n) \}^2. \quad (22b)$$

Numerical values of the D_{nv} and F_{nv} are given in Table I.

Several computations were performed for the inverse sixth power potential and $P_2(\cos\theta)$ anisotropy in order to determine the range of l for which the quadratures q_{lv} [Eq. (16)] are well approximated by Eqs. (18). Parametrization is given in terms of reduced energy $E^* (= \mu v^2 / 2\epsilon)$, reduced wavenumber $A (= k\sigma)$, and reduced impact parameter $b^* (= (b/\sigma) \cong (l + \frac{1}{2})/A)$, where σ and ϵ are the "range" and "strength" parameters of the potential.^{9b,24a} Note that for an inverse sixth power potential ($V_0 = 4\epsilon\sigma^6/R^6$) and $k' = k$, Eq. (16) reduces to

$$q_{lv} = \frac{2\pi A^6}{E^*} \int_0^\infty J_{l+\frac{1}{2}}(x) J_{l+\frac{1}{2}}(x) x^{-5} dx. \quad (23)$$

Thus the quadrature depends only on l and v ; A and E^* are merely scaling factors.

The integrations in Eq. (16) were performed numerically (by Gaussian quadrature, exact to four significant figures) and also, by Cross' method,²⁶ which is analytical within the semiclassical approximation. (The two agree within the four-figure accuracy of the numerical quadrature.) These results are compared with the asymptotic [large l ; Eqs. (18)] Born approximation in Table II; they are discussed in Sec. IV. A related comparison of computations by the full DWA, the RDWA, and the Born approximation has recently been published.²⁶

B. Exponential Potential

For the exponential potential [Eq. (2b)], Eq. (16) reduces to

$$q_{lv}^{(a)} = [b V_0(b) / \hbar v] D_{lv} = (b C_v / \hbar v) e^{-b/l} D_{lv}, \quad (24)$$

where

$$D_{lv} = \frac{e^{b/l}}{b} \int_b^\infty \frac{R e^{-R/l} dR}{(R^2 - b^2)^{1/2}}, \quad (25a)$$

$$D_{v1} = e^{b/l} \int_b^\infty \frac{e^{-R/l} dR}{(R^2 - b^2)^{1/2}}, \quad (25b)$$

$$D_{v2} = \frac{e^{b/l}}{b} \int_b^\infty \frac{(2b^2 - R^2) e^{-R/l} dR}{R(R^2 - b^2)^{1/2}}. \quad (25c)$$

²⁶ Cf. Refs. 20(b), 20(c). The authors are grateful to Professor Cross for a private communication which was of considerable help in this matter.

²⁶ R. E. Olson and R. B. Bernstein, J. Chem. Phys. 50, 246 (1969).

TABLE II. Comparison, for the inverse sixth power potential, of values of q_l , calculated by the exact Born formula and the asymptotic (large l) Born approximation. $E^* = 10.0$, $A = 28.17$ (symbols defined in the text).

l	b^*	Exact Born results [Eq. (16)]			Asymptotic Born approx. [Eq. (18)]	
		$q_{l,0}$	$q_{l,-2}$	$q_{l,+2}$	$q_{l,0}^{(a)}$	$q_{l,\pm 2}^{(a)}$
12	0.444	199.4	202.9	90.0	193.0	128.7
24	0.870	6.729	5.529	3.671	6.673	4.449
48	1.722	0.2199	0.1628	0.1325	0.2195	0.1463
96	3.425	0.007043	0.004946	0.004459	0.007039	0.004693

The first two integrals may be written in terms of the modified Bessel functions,

$$D_{\rho 0} = \exp(b_{\rho}^*) K_1(b_{\rho}^*), \quad (26a)$$

$$D_{\rho 1} = \exp(b_{\rho}^*) K_0(b_{\rho}^*), \quad (26b)$$

where $b_{\rho}^* = b/\rho$. The third integral may be written in the form

$$D_{\rho 2} = \exp(b_{\rho}^*) \left[2 \int_{b_{\rho}^*}^{\infty} K_0(x) dx - K_1(b_{\rho}^*) \right]. \quad (26c)$$

Using asymptotic expansions for the Bessel functions one may obtain a (semiconvergent) series expansion for these $D_{\rho j}$, for large values of b_{ρ}^* :

$$D_{\rho j} = \left(\frac{\pi}{2b_{\rho}^*} \right)^{1/2} \left[1 + \sum_{k=1}^K C_{jk} (b_{\rho}^*)^{-k} \right]. \quad (27)$$

Here K is the value of the index k beyond which the terms in the series become larger. The first few coefficients C_{jk} are listed in Table III. The coefficients of $D_{\rho 0}$ yield [when combined with Eq. (17)] a previously obtained^{24b} expression for the high-energy approximation to the elastic-scattering (l th partial wave) phase shift for the exponential repulsive potential.

Using these results for the $D_{\rho j}$ yields the transition probabilities $P(j \pm L, j | \rho)$:

$$\begin{aligned} P(j \pm L, j | \rho) &= [a_L b V_0(b) / \hbar v]^2 G_{\rho L} \\ &= [a_L b C_{\rho} e^{-b_{\rho}^*} / \hbar v]^2 G_{\rho L}. \end{aligned} \quad (28)$$

Again, for large values of b_{ρ}^* , $G_{\rho 1}$ and $G_{\rho 2}$ may be

expressed in the form of power series as follows:

$$G_{\rho 1} = \frac{\pi}{3b_{\rho}^*} \left[1 + \sum_{k=1}^K H_{1k} (b_{\rho}^*)^{-k} \right], \quad (29a)$$

$$G_{\rho 2} = \frac{3\pi}{20b_{\rho}^*} \left[1 + \sum_{k=1}^K H_{2k} (b_{\rho}^*)^{-k} \right], \quad (29b)$$

where the first few H_{Lk} are listed in Table III.

Computations were performed for the exponential potential and $P_2(\cos \Theta)$ anisotropy in order to compare Eqs. (16) and (18). Parametrization was as follows:

$$E_{\rho}^* = \mu v^2 / 2C_{\rho}, \quad \frac{A}{\rho} = k_{\rho}, \quad A_{\rho} = k_{\rho}$$

and

$$b_{\rho}^* = (l + \frac{1}{2}) / A_{\rho}.$$

For the purpose of computation, Eq. (16) is rewritten:

$$q_{l\rho} = \frac{\pi}{2E_{\rho}^*} \int_0^{\infty} J_{l+\frac{1}{2}}(x) J_{l-\frac{1}{2}}(x) \exp\left[-\frac{x}{A_{\rho}}\right] x dx. \quad (30)$$

In this case, it is noted that these quadratures do depend on the range of the potential and the kinetic energy [in contrast to the "scaling" situation for the inverse power potential, Eq. (23)].

The integrations of Eq. (16) were performed numerically as before. These results are compared with those obtained by the asymptotic approximation of Eqs. (18) in Table IV; they are discussed in Sec. IV.

TABLE III. Expansion coefficients C_{jk} [Eq. (27)] and H_{Lk} [Eqs. (29)] for the exponential potential.

k	C_{0k}	C_{1k}	C_{2k}	H_{1k}	H_{2k}
1	3/8	-1/8	-13/8	-1/4	-9/4
2	-15/128	9/128	273/128	5/32	165/32
3	105/1024	-75/1024	-5415/1024	-21/128	-1677/128
4	-4725/32 768	3675/32 768	606 795/32 768	253/1024	90 171/2048
5	72 763/262 144	-39 535/262 144	-21 866 355/262 144	-4035/8192	-1 532 475/8192

TABLE IV. Comparison, for the exponential potential, of values of q_b calculated by the exact Born formula and the asymptotic (large l) Born approximation. Parametrization as defined in text.

l	b_p^*	A_p	E_p^*	Exact Born results [Eq. (16)]			Asymptotic Born approx. [Eq. (18)] ^a	
				$q_{1,0}$	$q_{1,-2}$	$q_{1,2}$	$q_{1,0}^{(a)}$	$q_{1,\pm 2}^{(a)}$
6	1.384	4.695	0.3	3.54	0.717	0.895	3.55±0.06	...
12	2.662			1.26	0.700	0.546	1.26	0.664±0.205
24	5.218			0.130	0.108	0.0754	0.130	0.0904±0.0013
48	10.33			0.00107	0.00109	0.00073	0.00107	0.00088
6	0.4378	14.848	3.0	2.12	-0.764	-0.444	...	...
12	0.8419			1.66	-0.0445	0.0756	1.671±0.101	...
24	1.650			0.916	0.283	0.284	0.916±0.007	...
48	3.266			0.236	0.140	0.127	0.236	0.134±0.016
6	0.1384	46.95	30.0	0.762	-0.548	-0.481	...	...
12	0.2662			0.727	-0.369	-0.321	...	...
24	0.5218			0.639	-0.142	-0.117	0.632±0.090	...
48	1.033			0.459	0.044	0.056	0.461±0.016	...

^a The $\pm$ entries indicate the uncertainty due to truncation of the semi-convergent series at the proper term. Blanks indicate cases in which the

asymptotic series does not converge at all.

III. THE SUDDEN APPROXIMATION

In this section, the transition probabilities are computed from the first-order straight-line limit of the sudden approximation. The interaction potentials considered here are the same as those in Sec. II. The notation is essentially that of Ref. 9(b).

The first-order transition probability for transition from state jm to $j'm'$ is given by

$$P(j'm'jm) = |\langle j'm' | G | jm \rangle|^2, \quad (31)$$

where

$$G(\theta, \phi) = \hbar^{-1} \int_{-\infty}^{\infty} V(t) dt. \quad (32)$$

The coordinates involved are illustrated in Fig. 1 of Ref. 9(a), where the orientation angles of the molecule, θ and ϕ , are taken to be constant. $V(t)$ is the potential of interaction between the atom and the diatomic molecule as a function of time as the atom moves along a classical trajectory relative to the stationary molecule. This trajectory is approximated⁹ by a planar one governed by the central potential (V_0) alone.

Again consider a potential of the form of Eq. (1). Using this form in the last pair of equations, one finds

that for inelastic collisions

$$P(j'm'jm) = \frac{aL^2}{\hbar^2} \left| \iiint Y_{j,m'}(\theta, \phi) * V_0(R) P_L(\cos\Theta) \times Y_{j,m}(\theta, \phi) \sin\theta d\theta d\phi dt \right|^2, \quad (33)$$

where Θ is a function of θ , ϕ , and t determined by the classical trajectory. Since Θ is the angle between the axis of the diatomic molecule and the line from the molecule to the atom with direction angles θ' , ϕ'

$$P_L(\cos\Theta) = [4\pi/(2L+1)] \sum_{\nu} Y_{L,\nu}(\theta', \phi') * Y_{L,\nu}(\theta, \phi). \quad (34)$$

If this expression is used in the previous equation, then integration over the angles gives

$$P(j'm'jm) = \frac{4\pi(2j+1)(2j'+1)}{(2L+1)} aL^2 \times \left(\begin{matrix} j & j' & L \\ 0 & 0 & 0 \end{matrix} \right) \left(\begin{matrix} j & j' & L \\ m & -m' & m'-m \end{matrix} \right)^2 |V_{L,m'-m}|^2, \quad (35)$$

where

$$V_{L,\nu} = \hbar^{-1} \int_{-\infty}^{\infty} V_0[R(t)] Y_{L,\nu}[\theta'(t), \phi'(t)] dt. \quad (36)$$

The dependence of R , θ' , and ϕ' on the time t depends parametrically on θ_0 and ϕ_0 , the angles describing the initial direction of approach, the impact parameter b , and an azimuthal angle, ϵ , measured in a plane normal to the initial direction. The three angles ϕ_0 , θ_0 , ϵ form a set of Eulerian angles and may be used to describe a rotation of the coordinate system. In the new coordinate system the initial direction of approach is along the z axis, and the azimuthal angle is zero. Then

$$Y_{L'}(\theta', \phi') = \sum_{\mu} D^L(\phi_0, \theta_0, \epsilon)_{\mu\nu} Y_{L'}(\theta', 0), \quad (37)$$

where θ' is the polar angle of a point along the trajectory in the new coordinate system. Thus

$$V_{L\nu} = \sum_{\mu} D^L(\phi_0, \theta_0, \epsilon)_{\mu\nu} \bar{V}_{L\mu}, \quad (38)$$

where

$$\bar{V}_{L\mu} = \hbar^{-1} \int_{-\infty}^{\infty} V_0[R(t)] Y_{L\mu}[\theta'(t), 0] dt. \quad (39)$$

$\bar{V}_{L\mu}$ is the integral of the potential evaluated in a coordinate system in which the atom approaches in the z direction [cf. Ref. 9(a)].

Combining Eqs. (35) and (38), one obtains

$$P(j'm'jm | Eb\phi_0\theta_0\epsilon) = \begin{pmatrix} j & j' & L \\ m & -m' & m'-m \end{pmatrix}^2 \sum_{\mu\mu'} D^L(\phi_0, \theta_0, \epsilon)_{\mu, m'-m} \times P(j'j | Eb)_{\mu\mu'} D^L(\phi_0, \theta_0, \epsilon)_{\mu', m'-m}^*, \quad (40)$$

where

$$P(j'j | Eb)_{\mu\mu'} = \frac{4\pi(2j+1)(2j'+1)}{(2L+1)} a_L^2 \begin{pmatrix} j & j' & L \\ 0 & 0 & 0 \end{pmatrix}^2 \bar{V}_{L\mu} \bar{V}_{L\mu'}^*. \quad (41)$$

The transition probability given by Eq. (40) depends on both the impact parameter b and the azimuthal angle ϵ . Averaging over ϵ eliminates the dependence on ϕ_0 and yields

$$P(j'm'jm | Eb\theta_0) = \begin{pmatrix} j & j' & L \\ m & -m' & m'-m \end{pmatrix}^2 \times \sum_{\mu} |D^L(0, \theta_0, 0)_{\mu, m'-m}|^2 P(j'j | Eb)_{\mu\mu}. \quad (42)$$

The degeneracy averaged cross section is the sum over m' and the average over m of the detailed cross section. The corresponding transition probabilities are

$$P(j'j | Eb) = (2j+1)^{-1} \sum_{mm'} P(j'm'jm | Eb\theta_0). \quad (43)$$

From the last result it follows that

$$P(j'j | Eb) = [(2L+1)(2j+1)]^{-1} \sum_{\mu} P(j'j | Eb)_{\mu\mu}. \quad (44)$$

This result is clearly independent of the direction of the incoming atom.

For the case $L=1$ [$P_1(\cos\theta)$ anisotropy], the following detailed transition probabilities are obtained from Eqs. (41) and (42):

$$P(j+1, m, jm) = \frac{\pi a_1^2 [(j+1)^2 - m^2]}{3 (j+\frac{3}{2})(j+\frac{1}{2})} [\cos^2\theta_0 |\bar{V}_{10}|^2 + \sin^2\theta_0 |\bar{V}_{11}|^2], \quad (45a)$$

$$P(j-1, m, jm) = \frac{\pi a_1^2 [j^2 - m^2]}{3 (j+\frac{1}{2})(j-\frac{1}{2})} [\cos^2\theta_0 |\bar{V}_{10}|^2 + \sin^2\theta_0 |\bar{V}_{11}|^2], \quad (45b)$$

$$P(j+1, m\pm 1, jm) = \frac{\pi a_1^2 (j\pm m+1)(j\pm m+2)}{12 (j+\frac{3}{2})(j+\frac{1}{2})} [\sin^2\theta_0 |\bar{V}_{10}|^2 + (1+\cos^2\theta_0) |\bar{V}_{11}|^2], \quad (45c)$$

$$P(j-1, m\pm 1, jm) = \frac{\pi a_1^2 (j\mp m-1)(j\mp m)}{12 (j+\frac{1}{2})(j-\frac{1}{2})} [\sin^2\theta_0 |\bar{V}_{10}|^2 + (1+\cos^2\theta_0) |\bar{V}_{11}|^2], \quad (45d)$$

and for $L=2$ [$P_2(\cos\theta)$ anisotropy]:

$$P(j+2, m, jm) = \frac{9\pi a_2^2 [(j+2)^2 - m^2][(j+1)^2 - m^2]}{320 (j+\frac{5}{2})(j+\frac{3}{2})(j+\frac{1}{2})} [(3\cos^2\theta_0 - 1)^2 |\bar{V}_{20}|^2 + 12\sin^2\theta_0 \cos^2\theta_0 |\bar{V}_{21}|^2 + 3\sin^4\theta_0 |\bar{V}_{22}|^2], \quad (46a)$$

$$P(j-2, m, jm) = \frac{9\pi a_2^2 [j^2 - m^2][(j-1)^2 - m^2]}{320 (j+\frac{3}{2})(j-\frac{1}{2})(j-\frac{3}{2})} [(3\cos^2\theta_0 - 1)^2 |\bar{V}_{20}|^2 + 12\sin^2\theta_0 \cos^2\theta_0 |\bar{V}_{21}|^2 + 3\sin^4\theta_0 |\bar{V}_{22}|^2], \quad (46b)$$

$$P(j+2, m\pm 1, jm) = \frac{3\pi a_2^2}{80} \frac{[(j+1)^2 - m^2][j\pm m+3][j\pm m+2]}{(j+\frac{5}{2})(j+\frac{3}{2})^2(j+\frac{1}{2})} [3 \sin^2\theta_0 \cos^2\theta_0 |\bar{V}_{20}|^2 + (4 \cos^4\theta_0 - 3 \cos^2\theta_0 + 1) |\bar{V}_{21}|^2 + \sin^2\theta_0(1 + \cos^2\theta_0) |\bar{V}_{22}|^2], \quad (46c)$$

$$P(j-2, m\pm 1, jm) = \frac{3\pi a_2^2}{80} \frac{[j^2 - m^2][j\mp m-1][j\mp m-2]}{(j+\frac{1}{2})(j-\frac{1}{2})^2(j-\frac{3}{2})} [3 \sin^2\theta_0 \cos^2\theta_0 |\bar{V}_{20}|^2 + (4 \cos^4\theta_0 - 3 \cos^2\theta_0 + 1) |\bar{V}_{21}|^2 + \sin^2\theta_0(1 + \cos^2\theta_0) |\bar{V}_{22}|^2], \quad (46d)$$

$$P(j+2, m\pm 2, jm) = \frac{3\pi a_2^2}{1280} \frac{[j\pm m+1][j\pm m+2][j\pm m+3][j\pm m+4]}{(j+\frac{5}{2})(j+\frac{3}{2})^2(j+\frac{1}{2})} [3 \sin^4\theta_0 |\bar{V}_{20}|^2 + 4 \sin^2\theta_0(1 + \cos^2\theta_0) |\bar{V}_{21}|^2 + (1 + 6 \cos^2\theta_0 + \cos^4\theta_0) |\bar{V}_{22}|^2], \quad (46e)$$

$$P(j-2, m\pm 2, jm) = \frac{3\pi a_2^2}{1280} \frac{[j\mp m-3][j\mp m-2][j\mp m-1][j\mp m]}{(j+\frac{1}{2})(j-\frac{1}{2})^2(j-\frac{3}{2})} [3 \sin^4\theta_0 |\bar{V}_{20}|^2 + 4 \sin^2\theta_0(1 + \cos^2\theta_0) |\bar{V}_{21}|^2 + (1 + 6 \cos^2\theta_0 + \cos^4\theta_0) |\bar{V}_{22}|^2]. \quad (46f)$$

The problem is thus reduced to the evaluation of the integrals of the potential, $\bar{V}_{L\mu}$, defined by Eq. (39). These integrals may be readily evaluated only in the straight-line approximation, i.e., assuming a linear trajectory with a constant relative velocity v . In this approximation⁹ [which corresponds to the asymptotic (a) approximation of Sec. II],

$$R = (b^2 + v^2 t^2)^{1/2}, \quad (47)$$

$$\cos\bar{\theta}' = vt/R. \quad (48)$$

Using these relations one obtains

$$\bar{V}_{10}^{(a)} = 0, \quad (49a)$$

$$\bar{V}_{11}^{(a)} = \left(\frac{3}{2\pi}\right)^{1/2} \frac{b}{\hbar v} \int_b^\infty \frac{V_0(R) dR}{(R^2 - b^2)^{1/2}}, \quad (49b)$$

$$\bar{V}_{20}^{(a)} = \left(\frac{5}{\pi}\right)^{1/2} (\hbar v)^{-1} \int_b^\infty \frac{[1 - (3b^2/2R^2)] RV_0(R) dR}{(R^2 - b^2)^{3/2}}, \quad (49c)$$

$$\bar{V}_{21}^{(a)} = 0, \quad (49d)$$

$$\bar{V}_{22}^{(a)} = \frac{1}{2} \left(\frac{15}{2\pi}\right)^{1/2} \frac{b^2}{\hbar v} \int_b^\infty \frac{V_0(R) dR}{R(R^2 - b^2)^{1/2}}. \quad (49e)$$

On comparing these expressions with the TI Born approximation expressions given by Eq. (18), one finds the equivalences

$$\bar{V}_{11}^{(a)} = \left[\frac{3}{2}(\pi^{-1})\right]^{1/2} q_{11}^{(a)}, \quad (50a)$$

$$\bar{V}_{20}^{(a)} = \frac{1}{2} \left[5(\pi^{-1})\right]^{1/2} (q_{10}^{(a)} - 3q_{12}^{(a)}), \quad (50b)$$

$$\bar{V}_{22}^{(a)} = \frac{1}{2} \left[\frac{15}{2}(\pi^{-1})\right]^{1/2} (q_{10}^{(a)} + q_{12}^{(a)}), \quad (50c)$$

and thus

$$\sum_\mu |\bar{V}_{1\mu}^{(a)}|^2 = 3(\pi^{-1}) (q_{11}^{(a)})^2, \quad (51a)$$

$$\sum_\mu |\bar{V}_{2\mu}^{(a)}|^2 = 5(\pi^{-1}) \left[\frac{1}{2}(q_{10}^{(a)})^2 + \frac{3}{2}(q_{12}^{(a)})^2\right]. \quad (51b)$$

When these expressions along with Eq. (41) are used in the expression for the degeneracy-averaged transition probabilities [Eq. (44)] obtained by the TD methods, one obtains expressions which are identical with those given by Eqs. (12) and (14), obtained from the RDW approximation to the TI expressions in the large l limit. The above TD formulation has also been obtained by a different method of summation, giving identical results (see Appendix).

Eqs. (46a) and (46e) [in connection with Eqs. (49)] agree with the results of Ref. 9(a) for the special cases treated there. Eqs. (45) and (46) also reproduce the m and j selection rules of Ref. 9(b) for the "parallel" configuration. However, the present results disagree in the "perpendicular" case; "Rule 2" of Ref. 9(b) appears to be incorrect. For the "perpendicular" configuration there are no m selection rules.

IV. CONCLUDING REMARKS

In general, these first-order methods can be expected to give accurate transition probabilities only when the probabilities are small. Since the S matrix in the DWA is not unitary, its Born limit cannot be better. Similarly, for the TD case, although the sum of the transition probabilities from a given state cannot exceed unity in the SA, this restriction is lost in the first-order straight-line approximation.

For the Born treatment, the accuracy of the asymptotic approximation compared to the exact Born results depends on the form of the radial potential $V_0(R)$. For the inverse power potential (results shown in Table

II) the quadratures [Eq. (23)] are independent of the energy. Thus, the goodness of the asymptotic approximation depends only on l , ν , and the power of the potential. For the example chosen, provided $l \gtrsim 24$, $q_{10}^{(a)}$ agrees with q_{10} within 1%. However, similar agreement for q_{12} and $q_{1,-2}$ would require $l \gtrsim 100$.

The situation is quite different however, for the exponential potential (Table IV). Here, the exact Born quadrature [Eq. (30)] does depend on the energy, and it appears that b_p^* rather than l is the best index of the accuracy of the asymptotic approximation. For $b_p^* \lesssim 1.0$, the approximation is within 1% for q_{10} ; however $q_{1,\pm 2}^{(a)}$ still has not converged for $b_p^* > 10$.

It is also noted that the accuracy of the asymptotic results improves as the incident energy decreases. Thus the best agreement between exact Born and asymptotic results is expected in a region where the high-energy approximation itself is inappropriate. This appears to be a serious qualification of the usefulness of the asymptotic formulas for the case of the exponential potential.

The equivalence of the Born approximation and the first-order limit of the sudden approximation for the collision of a diatomic molecule and an atom has been

demonstrated explicitly. Formulas have been derived for the detailed inelastic transition probabilities for rotational transitions $j m \rightarrow j' m'$ [Eqs. (45) and (46)]. The degeneracy-averaged transitions probabilities ($j \rightarrow j'$) for an inverse power potential $V_0(R) = C_n R^{-n}$ are given by

$$P(j \pm L, j | n) = F_{nL} (C_n a_L / \hbar v b^{n-1})^2, \quad (52)$$

where the factor F_{nL} is a known, slowly varying function of n (Table I), a_L is the coefficient of the L th-order Legendre anisotropy, $v = \hbar k / \mu$ is the magnitude of the relative velocity, and b is the impact parameter. For an exponential potential $V_0(R) = C_p e^{-R/\rho}$, the transition probabilities are

$$P(j \pm L, j | \rho) = G_{pL} (C_p a_L b e^{-b/\rho} / \hbar v)^2, \quad (53)$$

where G_{pL} is a known factor which, for large b/ρ is proportional to $1/b$. Note that Eqs. (52) and (53) show the same quadratic dependence on a_L , $1/v$, and the strength parameter of the potential (C_p or C_n); also, they both exhibit a strong inverse dependence upon the impact parameter.

APPENDIX

This appendix presents an alternate method of reducing the TD-SA formulation to the Born results for the $j \rightarrow j'$ transition probability. The formulation and notation follow Ref. 9(b), and the case illustrated is for the inverse power potential, Eqs. (1) and (2a), with $n=6$ and $L=2$.

In a situation similar to Ref. 9(b), the molecule is at rest in a weak electric field $\mathbf{E}$ and has eigenfunctions $Y_j^m(\theta, \phi)$. The atom (whose coordinates are $(\theta'(t), \phi'(t))$) approaches from an arbitrary direction, v . Then, analogous to Eq. (32), one can define G in terms of a new set of angles (θ'', ϕ'') with respect to v :

$$\begin{aligned} G(\theta'', \phi'') &= \hbar^{-1} \int V dt = \frac{C_6}{\hbar v \sigma^5} \{ S_{00}^{(6)} + a_2 (S_{00}^{(6)} - 6^{1/2} S_{22}^{(6)}) C_0^{(2)}(\theta'', \phi'') + a_2 S_{22}^{(6)} [C_{-2}^{(2)}(\theta'', \phi'') + C_2^{(2)}(\theta'', \phi'')] \} \\ &= 2D \{ S_{00}^{(6)} + E C_0^{(2)}(\theta'', \phi'') + F [C_{-2}^{(2)}(\theta'', \phi'') + C_2^{(2)}(\theta'', \phi'')] \}, \end{aligned} \quad (A1)$$

where D , E , and F are obvious abbreviations, and

$$C_m^{(2)}(\theta'', \phi'') = [4\pi/(2l+1)]^{1/2} Y_l^m(\theta'', \phi''). \quad (A2)$$

In the first-order limit, the S integrals are given by

$$S_{00}^{(6)} \cong \frac{3}{8} (\pi \sigma^5) b^{-5}, \quad (A3a)$$

$$S_{22}^{(6)} \cong \frac{5}{8} \pi \left(\frac{3}{2}\right)^{1/2} \sigma^5 b^{-5}. \quad (A3b)$$

[For a more complete account, see Ref. 9(b), which treats the "parallel" case $\mathbf{v} \parallel \mathbf{E}$.]

Next $Y_j^m(\theta, \phi)$ is redefined in terms of the (θ'', ϕ'') :

$$Y_j^m(\theta, \phi) = \sum_{\mu} Y_j^{\mu}(\theta'', \phi'') D^j(\phi_0, \theta_0, \epsilon)_{\mu m}, \quad (A4)$$

where $(\phi_0, \theta_0, \epsilon)$ are the Euler angles that relate the (θ, ϕ) reference frame to that of (θ'', ϕ'') .²⁷ This yields an

²⁷ (a) A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, N.J., 1960), p. 61. See also (b) D. M. Brink and G. R. Satchler, *Angular Momentum* (Clarendon Press, Oxford, England, 1962).

equation for the inelastic transition probability which is equivalent to Eq. (43):

$$P(j'j | Eb\phi_0\theta_0\epsilon) = [4D^2/(2j+1)] \sum_{mm'} | \langle \sum_{\mu'} D^{(j')*}(\phi_0\theta_0\epsilon)_{\mu'm'} Y_{j,\mu'}(\theta'', \phi'') | \{ EC_0^{(2)}(\theta'', \phi'') + F[C_{-2}^{(2)}(\theta'', \phi'') + C_2^{(2)}(\theta'', \phi'')] \} | \sum_{\mu} Y_{j\mu}(\theta'', \phi'') D^j(\phi_0\theta_0\epsilon)_{\mu m} \rangle |^2. \quad (A5)$$

For $j'=j\pm 2$, the following result is obtained:

$$P(j\pm 2, j | Eb\phi_0\theta_0\epsilon) = [4D^2/(2j+1)] \sum_{mm'} | \sum_{\mu} E\langle j\pm 2, \mu | C_0^{(2)} | j\mu \rangle D_{\mu m, (j\pm 2)*} D_{\mu m}^j + \sum_{\mu} F\langle j\pm 2, \mu-2 | C_{-2}^{(2)} | j\mu \rangle D_{\mu-2, m, (j\pm 2)*} D_{\mu m}^j + \sum_{\mu} F\langle j\pm 2, \mu+2 | C_2^{(2)} | j\mu \rangle D_{\mu+2, m, (j\pm 2)*} D_{\mu m}^j |^2. \quad (A6)$$

Integration over $\phi_0, \theta_0, \epsilon$ is required to remove the dependence on the direction of approach:

$$P(j\pm 2, j | Eb) = \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} P(j\pm 2, j | Eb\phi_0\theta_0\epsilon) \sin\theta_0 d\phi_0 d\theta_0 d\epsilon. \quad (A7)$$

Consider the reduction of a typical term in the mod square of Eq. (A6). Define T_{fh} , a part of Eq. (A7), as follows:

$$T_{fh} = (2j+1)^{-1} \sum_{mm'} \sum_{\mu\nu} \langle j\pm 2, \mu+f | C_f^{(2)} | j\mu \rangle \langle j\pm 2, \nu+h | C_h^{(2)} | j\nu \rangle \times \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} D^{(j\pm 2)*}(\phi_0\theta_0\epsilon)_{\mu+f, m'} D^{(j)*}(\phi_0\theta_0\epsilon)_{\nu m} D^j(\phi_0\theta_0\epsilon)_{\mu\nu} D^{j\pm 2}(\phi_0\theta_0\epsilon)_{\nu+h, m'} \sin\theta_0 d\phi_0 d\theta_0 d\epsilon, \quad (A8)$$

where f and h may be 0, +2, or -2.

The integral over $(\phi_0, \theta_0, \epsilon)$ of the product of the four rotation matrices can be evaluated utilizing Eqs. 4.3.2 and 4.6.1 of Ref. 27(a)

$$\begin{aligned} & \iiint D_{\mu+f, m'}^{(j\pm 2)*} D_{\nu m}^{(j)*} D_{\mu\nu}^j D_{\nu+h, m'}^{j\pm 2} \sin\theta_0 d\phi_0 d\theta_0 d\epsilon \\ &= 8\pi^2 \sum_{Kxz'} (2K+1) \begin{pmatrix} j\pm 2 & j & K \\ \nu+h & \mu & x' \end{pmatrix} \begin{pmatrix} j\pm 2 & j & K \\ m' & m & x \end{pmatrix} \begin{pmatrix} j\pm 2 & j & K \\ \mu+f & \nu & x' \end{pmatrix} \begin{pmatrix} j\pm 2 & j & K \\ m' & m & x \end{pmatrix}. \end{aligned} \quad (A9)$$

Substituting this result and Eq. 4.6.3 of Ref. 27(a) into Eq. (A8) gives

$$\begin{aligned} T_{fh} &= (8\pi^2) (2j+1\pm 4) \begin{pmatrix} j\pm 2 & j & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 \sum_{\mu\nu Kxz'} (-1)^{\mu+f+\nu+h} (2K+1) \begin{pmatrix} j\pm 2 & j & 2 \\ -(\mu+f) & \mu & f \end{pmatrix} \begin{pmatrix} j\pm 2 & j & 2 \\ -(\nu+h) & \nu & h \end{pmatrix} \\ & \times \begin{pmatrix} j\pm 2 & j & K \\ \nu+h & \mu & x' \end{pmatrix} \begin{pmatrix} j\pm 2 & j & K \\ \mu+f & \nu & x' \end{pmatrix} \sum_{mm'} \begin{pmatrix} j\pm 2 & j & K \\ m' & m & x \end{pmatrix} \begin{pmatrix} j\pm 2 & j & K \\ m' & m & x \end{pmatrix}. \end{aligned} \quad (A10)$$

The result of these summations is

$$T_{fh} = \frac{8}{3}\pi^2 (2j+1\pm 4) \begin{pmatrix} j\pm 2 & j & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 \delta_{\mu+f, \nu+h} \delta_{\mu\nu}. \quad (A11)$$

[Note that the off-diagonal terms in Eq. (A6) vanish.] When Eq. (A11) for the various T_{fh} terms is substituted into Eq. (A7), the result is found to be identical with that previously derived in Secs. II and III,