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SEMI-ANNUAL STATUS REPORT

Infrared Laboratory Studies of Synthetic Planetary Atmospheres

Grant NGR 17-001-026

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KANSAS STATE UNIVERSITY · MANHATTAN, KANSAS

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Infrared Laboratory Studies of Synthetic Planetary Atmospheres

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This report covers work for the period
1 December 1969 to 31 May 1970

It was prepared by

Prof. Dudley Williams, Department of Physics
Kansas State University, Manhattan, Kansas

Date: 1 June 1970

I. ABSTRACT OF RESEARCH TO DATE

The general program represents an extension and generalization of an earlier program dealing chiefly with telluric gases. The basic instrumentation includes three Perkin-Elmer Model 112 spectrometers equipped with prisms to cover the range between the visible and 40 microns, one Perkin-Elmer Model 421 grating instrument for the 2- to 18 micron region, and a Perkin-Elmer Model far-infrared spectrograph for the region 12 to 330 microns; this basic instrumentation was supplied by Kansas State University.

The initial stages of the research were involved with a test of Burch's law of multiplicative transmittance for mixed absorbing gases when their lines are broadened by H_2 and He, which are constituents of the atmospheres of the major planets. The results, which have resulted in journal publication, indicate that the multiplicative law as originally formulated can be applied with confidence.

The broadening of individual lines in the CO fundamental by various gases has been investigated. The results indicate that the ratio of the "self-broadening ability" of CO to the "line-broadening ability" of foreign gases is greater for lines in the band wings than for lines near the band center when the molecular mass of the broadener is less than that of CO. The results have been interpreted in terms of a phenomenological theory. Studies of the relative line broadening abilities of foreign gases have provided information that can be used to provide optical collision cross sections for individual lines in the CO fundamental; this work is still in progress.

Other work has been done on the determination of line strength S and half-width for individual CO lines as a function of temperature.

The results at reduced temperatures indicate (1) that line strengths S can be satisfactorily predicted by the Herman-Wallis expression but (2) that at very low temperatures the line half-widths differ markedly from values calculated by applying the "hard-sphere" approximations of kinetic theory to values of γ^0 measured at NPT. This work is being continued.

Measurements of total band absorptance $\int A(\nu)d\nu$ as a function of absorber thickness w and total effective pressure P_e have been made at various temperatures T for bands of CO and N_2O. This work is being extended to various other planetary gases.

Attempts have been made to develop a phenomenological theory of line broadening that will adequately account for the phenomena we have observed for the CO fundamental and those reported for more highly polar gases. This theory has been successful in accounting for the variation of line half-wdith with line number observed in our work on CO and in the studies of HCl-line broadening conducted in other laboratories. A preliminary draft of a paper on the subject has been completed.

Laboratory measurements of nitric-acid vapor absorptance have been compared with balloon measurements at the University of Denver in arriving at an estimate of the quantity of nitric acid vapor present in the earth's atmosphere in the region of the ozone layer.

Funds from university sources have been used to purchase a partially completed high resolution spectrograph for use in the region between 2 microns and 5 microns. The instrument has now been completed at Kansas State University. Preliminary tests show that resolution has been reached nearing 50 percent of the Rayleigh limit at amplifier gains and spectrograph slitwidths that can be employed in routine operation.

Cumulative List of Publications*

1. "Further Studies of Overlapping Absorption Bands," Tubbs, Hathaway and Williams, J. Opt. Soc. Amer. 57, 570 (1967) P.
2. "Foreign-Gas Groadening of Absorption Lines in the CO Fundamental," Draegert, Chai, and Williams, J. Opt. Soc. Amer. 57, 570 (1967) P.
3. "Broadening of Absorption Lines in the CO Fundamental," Chai, Draegert, Williams, Bull. Am. Phys. Soc. 12, 542 (1967) P.
4. "Further Studies of Overlapping Abosrption Bands," Tubbs, Hathaway, and Williams, App. Opt. 6, 1422 (1967).
5. "Strengths and Half Widths of CO Lines at Reduced Temperatures," Hoover, Hathaway, and Williams, J. Opt. Soc. Amer. 58, 739 (1968) P.
7. "Line Widths in Vibration-Rotation Bands," Williams, Bull. Am. Phys. Soc. II 13, 569 (1968) P.
8. "Comparison for Collision Cross Sections for Line Broadening in the CO fundamental," Chai and Williams, J. Opt. Soc. Amer. 58, 1395 (1968).
9. "Collisional Broadening of CO Absorption Lines by Foreign Gases," Draegert and Williams, J. Opt. Soc. Amer. 58, 1399 (1968).
10. "Absorption in the Wings of Rotational Lines in the CO Fundamental", Chai and Williams, Bull. Am. Phys. Soc. II 13, 906 (1968).
11. "Foreign-Gas Broadening of Lines in the CO Fundamental," Williams, Proceedings 23rd Symposium on Molecular Structure, Ohio State University, p. 89 (1968), P.
12. "Infrared Absorptance of Carbon Monoxide at Low Temperatures," Hoover and Williams, J. Opt. Soc. Amer. 59, 28 (1969).

13. "Nitric-Acid Vapor in the Earth's Atmosphere," Rhine, Tubbs, and Williams, J. Opt. Soc. Amer. 59, 483 (1969) P.

14. "Nitric-Acid Vapor above 19 km in the Earth's Atmosphere," Rhine, Tubbs, and Williams. Applied Optics 8, 1500 (1969).

15. "Half Widths of Collision-Broadened Lines of CO and HCl", Williams, Wenstrand, and Brockman, J. Opt. Soc. Amer. 59, 1526 (1969). P

16. "A Czerny-Turner Spectrograph for the Infrared", Tubbs and Williams (Spring Meeting of the Optical Society of America).

II. PROGRESS DURING THIS REPORT PERIOD

A. Absorption-Line Broadening

A copy of the paper summarizing the results of our phenomenonological theory of line broadening is appended to this report. This simple theory has been applied in detail with surprising success to CO and HCl line broadening in the infrared. It also happens to be applicable to CO_2 and HBr line broadening but fails in certain significant respects when applied to HF. The paper is now being reviewed by several people who have worked in the field.

Some twenty years ago Anderson's theory of line broadening was published and seemed to give "final answers" to the general problem. Although the Anderson theory is one of great elegance and seeming generality, its complexities are such that it has never been applied in detail to an entire infrared band. Whether our readily applicable phenomenological approach will merit journal publication remains to be seen. It will, however, serve as a guide to pertinent problems in our atmospheric program.

B. Absorption of Gases at Reduced Temperatures

We have received, after some delay, the sapphire-to-metal seals to be used on the low temperature absorption cell. All other parts of the cells have been fabricated in our departmental shop. The separate portions of the cell have now been vacuum tested and the cell is apparently ready for use.

C. High-Resolution Instrumentation

The high-resolution spectrograph has now been completed and tested in various ways. A short report on certain novel features of this instrument was presented at the spring meeting of the Optical Society of America. A copy of the abstract is appended to the present report.

Also included in the present report are figures giving (1) the optical lay-out of the instrument, (2) certain design details, (3) results obtained with CO at low pressure, (4) results obtained with CO_2 at low pressure, and (5) results obtained with methane at low pressure. On the basis of the spectral tracings known, it would appear that a resolving power of 50,000 should be attainable in routine operation.

Work has been done on the line strengths of lines in the ν_3 fundamental of CO_2 at 300° C. Considerable attention has been devoted to the development of computer programs for use in reduction of the data obtained with the high-resolution instrument.

D. Development of a Program for the New Spectrograph

Discussions of important, relevant problems for our planetary atmospheric program have been held with Dr. B. Farmer at the Jet Propulsion Laboratory and with Dr. W. S. Benedict. Among the problems selected have been: (1) CO_2 absorption and line-broadening at reduced temperatures, a subject which is applicable to Martian studies; (2) broadening of CO lines by CO_2, which is important in the determination of CO abundances on Mars and Venus, and (3) studies of CH_4 absorption at low temperatures, which is a subject that needs survey experimental work prior to analysis but which must be done for interpretation of the observed spectra of Jupiter and the outer planets.

III. PERSONNEL

Dr. Dudley Williams, Regents' Professor of Physics:

Chief Investigator (WOC)

Dr. Basil Curnutte, Professor of Physics:
Senior Associate (WOC)
Lloyd Tubbs, B.S.: Graduate Research Fellow
John Carson, B.S.: Graduate Research Assistant

Graduate Degrees Granted under the Grant
An-Ti Chai - Ph.D.
Gary M. Hoover - Ph.D.
David Schmieder - M.S.

Note: Negotiations have been made with Dr. Charles Robertson to work part-time under the grant as a Research Associate. Dr. Robertson received his B.S. degree with Jack Taylor at Southwestern in Memphis and his Ph.D. with E. K. Plyler at Florida State University, where he is spending the current year as a postdoctoral fellow. Dr. Robertson comes with excellent recommendations.

IV. PLANS FOR THE NEXT REPORT PERIOD

A. The calculated and measured line strengths in the CO fundamental and ν_3 fundamental of CO_2 will be compared at various temperatures.

B. Measurements leading to a determination of line broadening of CO lines by CO_2 will be initiated. This work should be useful in determining CO abundance in the atmospheres of Mars and Venus.

C. Preliminary work will be done on mapping the methane absorption spectrum at reduced temperatures.

D. Further work will be done in developing computer programs for use in data reduction.

Submitted 1 June 1970

Signed: Dudley Williams
Dudley Williams

Appendices: 1. "Collisional Broadening of Infrared Absorption Lines"
2. "A Czerny-Turner Spectrograph for the Infrared"

irst Choice Instrumentation Second Choice Infrared Other Molecular Spectroscopy

☐ Czerny-Turner Spectrograph for the Infrared*
(Title of paper, in upper and lower case)

Lloyd M. Tubbs and Dudley Williams
(Author)

Physics Kansas State University
(Department) *(Institution)*

Cardwell Hall Manhattan Kansas 66502
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A 2.2-meter Czerney-Turner spectrophotometer has been constructed and is currently being operated in the 3 to 5 micro-meter wavelength range of the infrared. The instrument, which employs a 20-cm echelette grating with 300 lines/mm, is operated in the double-pass mode and is equipped with an intermediate slit. A Nernst-glower source and an indium-antimonide detector are used with 1080-Hz beam modulation and tuned narrow-band signal amplification to record absorption spectra of gaseous samples. The complete optical path is evacuated to facilitate operation in regions of atmospheric absorption. A separate small evacuated sample chamber, which is separated from the main vacuum system, has been provided. Certain novel features of the grating drive, slit controls, and techniques used in detector mounting and cooling will be discussed. Resolution of approximately 0.05 cm^{-1} at 2130 cm^{-1} is routinely obtained with good signal-to-noise ratio. With somewhat lower signal-to-noise ratios, the resolving power approaches sixty percent of the Rayleigh diffraction limit. Typical results obtained in different spectral regions within the range of the instrument will be shown.

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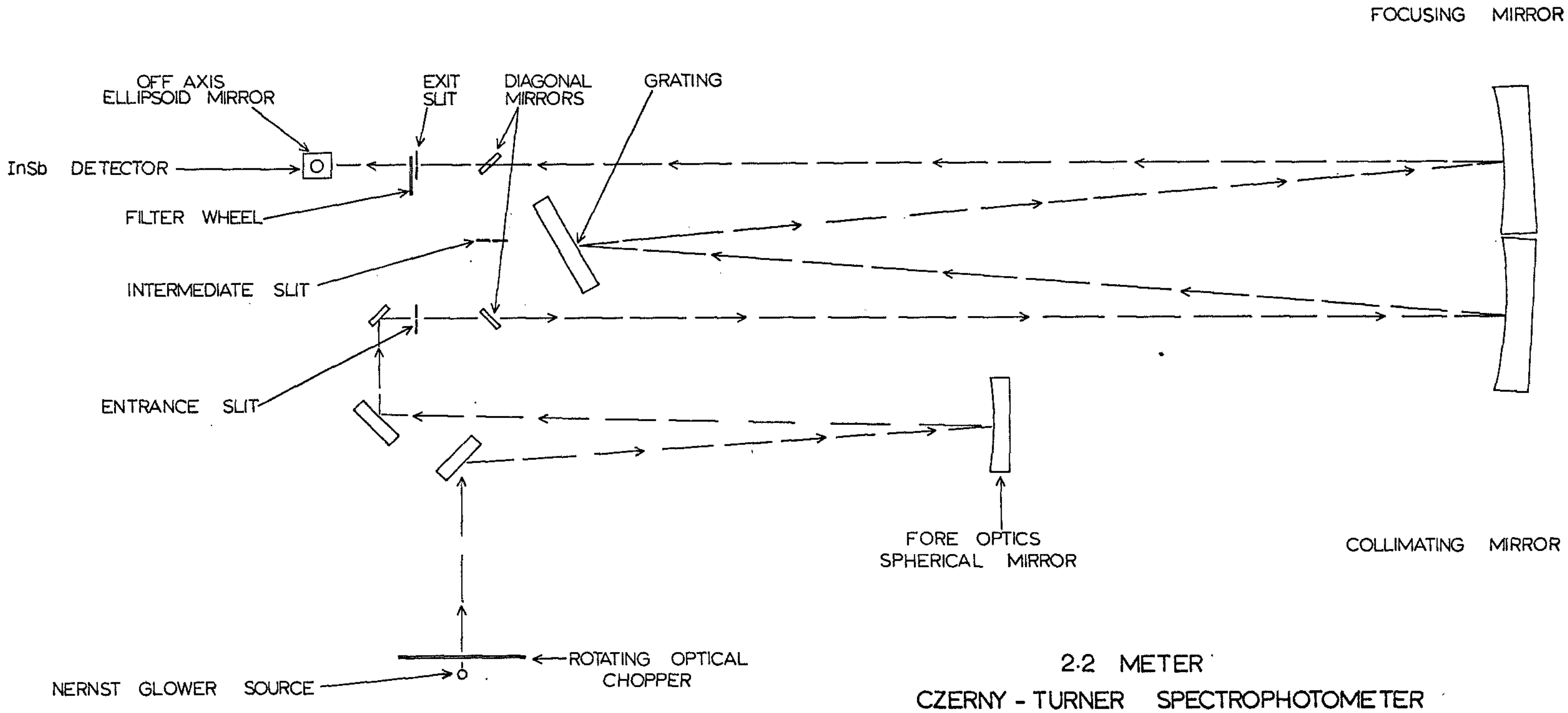
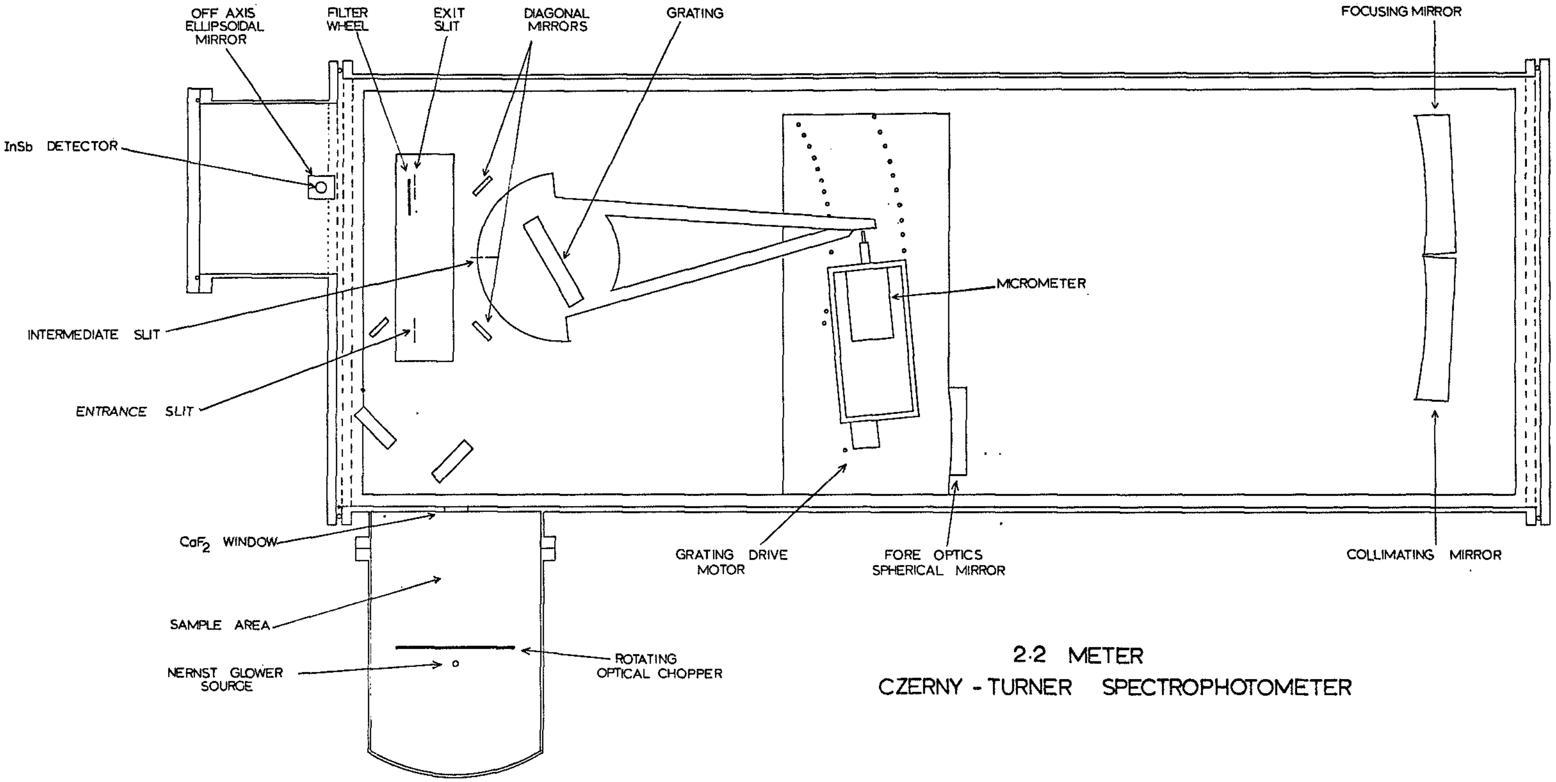
The first author should be an OSA member or, if he is not a member, his name should be followed by the words: "introduced by" followed by the OSA-member-sponsor's name.

(12 minutes)
Estimated time for presentation



2.2 METER
CZERNY - TURNER SPECTROPHOTOMETER



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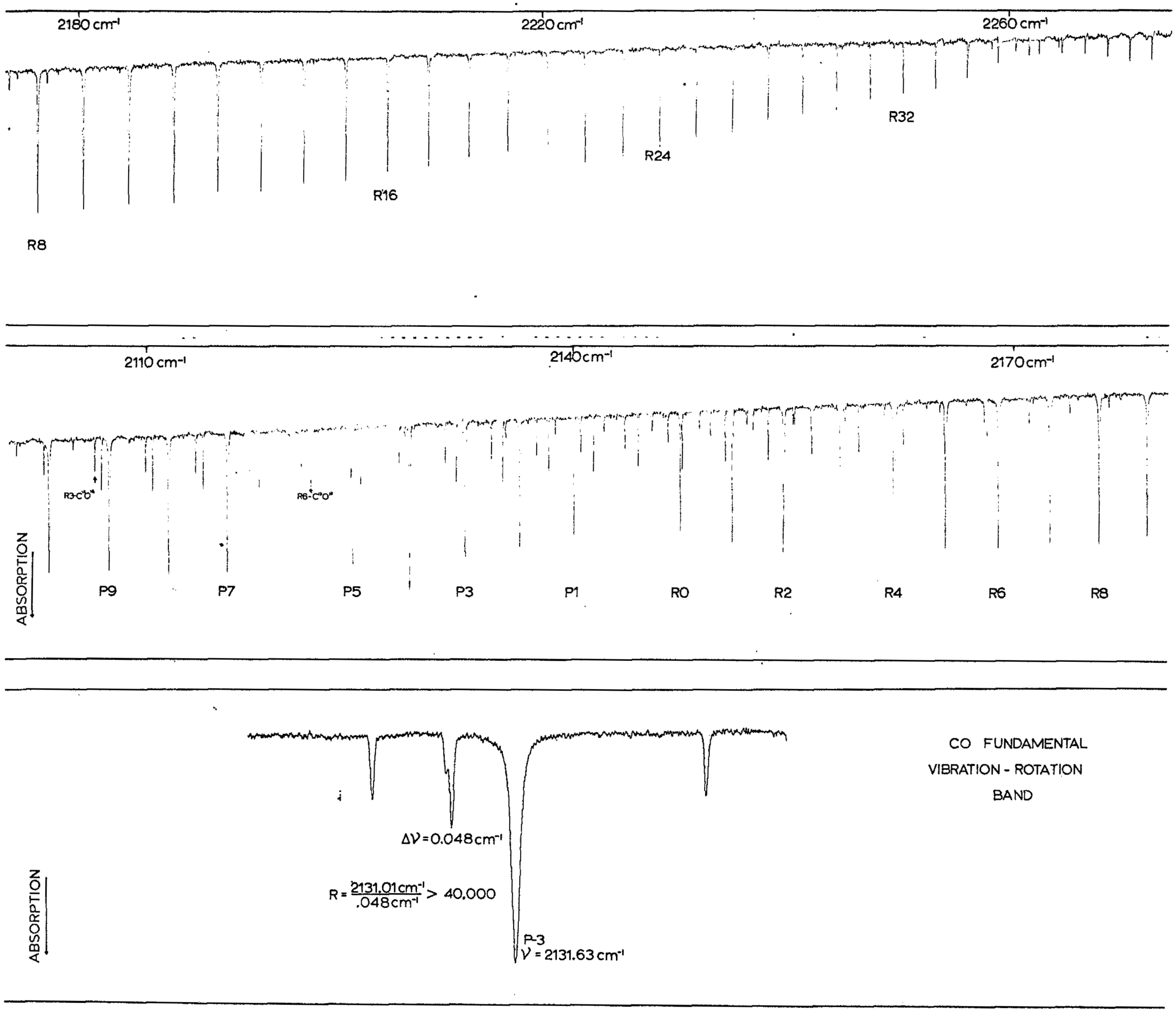
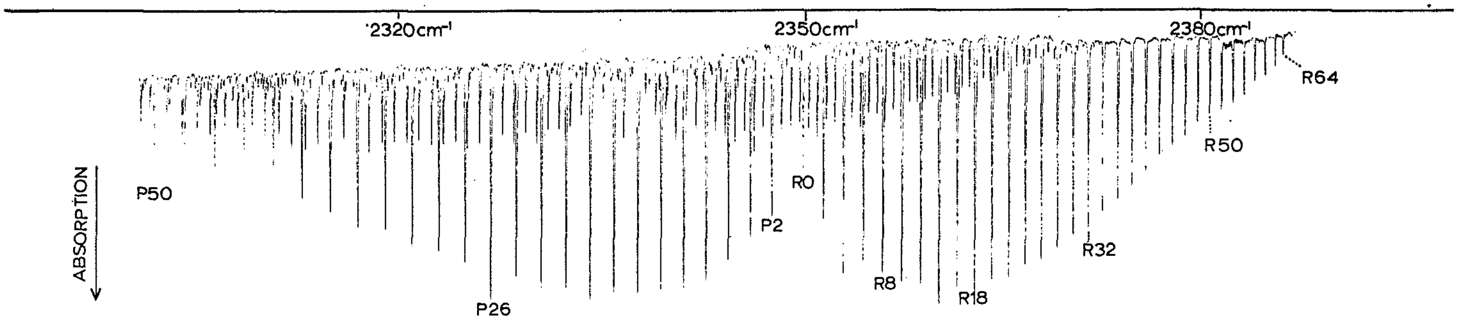
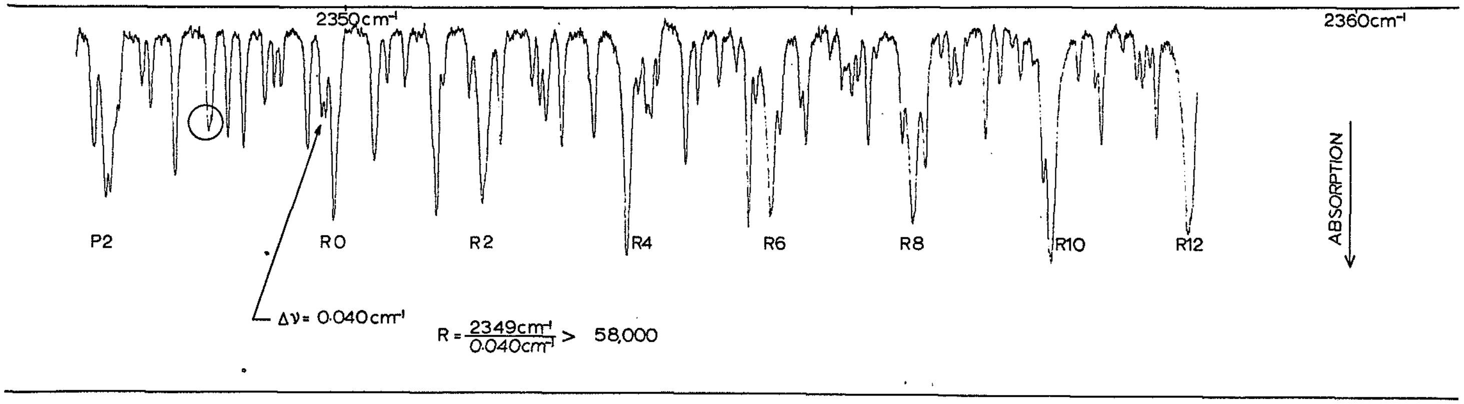
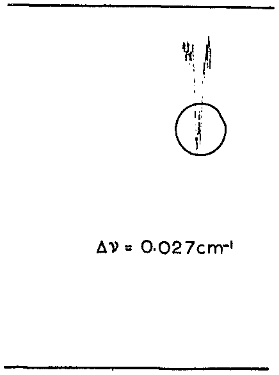


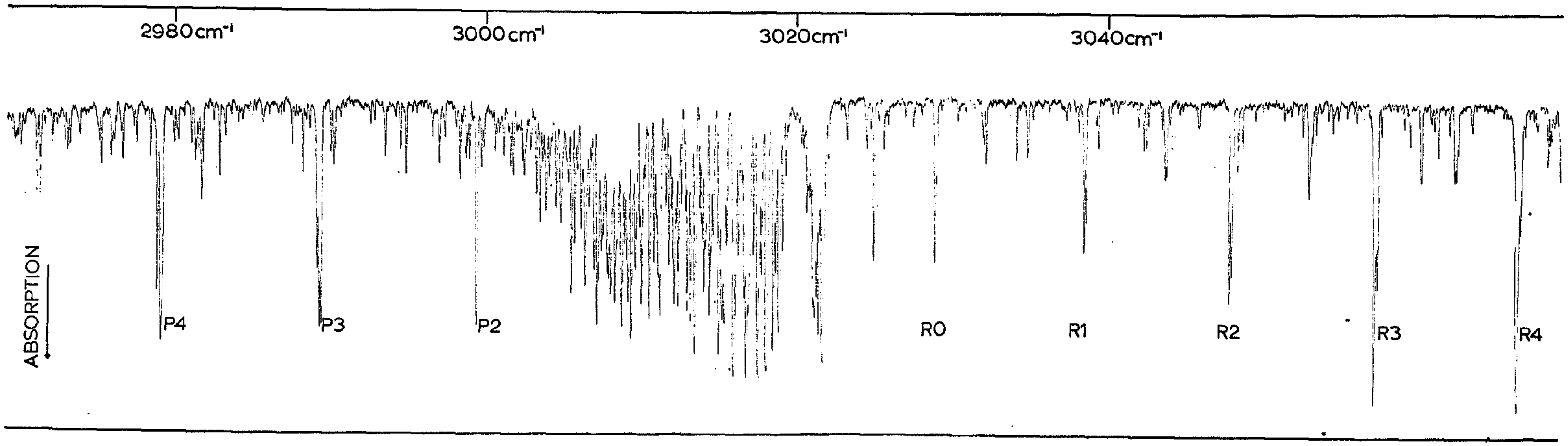
CO FUNDAMENTAL
VIBRATION - ROTATION
BAND

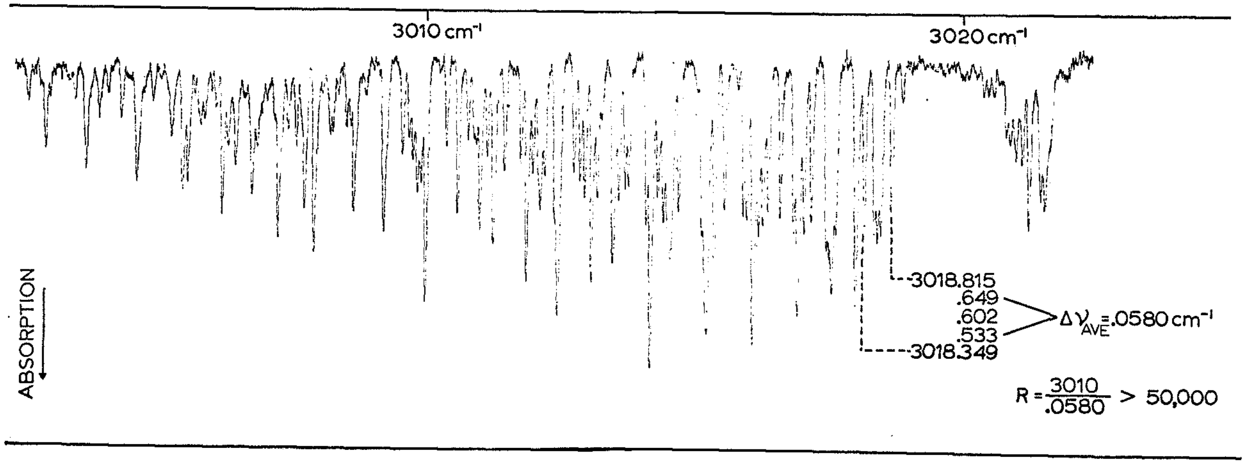






Carbon Dioxide Band at 2349 cm^{-1}
Frequency Measurements from
R. Oberly & K. Rao
Journal of Molecular Spectroscopy
25, 138 - 165 (1968)





CH$_4$ ν_3 BAND

FREQUENCY MEASUREMENTS

EARLE K. PLYLER
EUGENE D. TIDWELL
LANDIN R. BLAINE

J. RESEARCH N.B.S. 64A 201 (1960)

Collisional Broadening of Infrared Absorption Lines[*]

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[*] Work supported in part by the National Aeronautics and Space Administration of the U.S.A.

(Summary)

The Lorentz half widths of collisionally broadened lines in the rotation-vibration bands of diatomic molecules vary with line number $|m|$ in the P and R branches. The observed variation of half-width for lines in the $0 \rightarrow 1$ and $0 \rightarrow 2$ bands of CO and HCl are interpreted in terms of a simple semi-classical theory. One dominant process is assumed to consist of diabatic hard collisions involving transitions from each rotational level to all higher rotational levels together with inverse processes; the effectiveness of this process, which varies from line to line, is described in terms of an empirically adjusted collision cross section, a maximum collision parameter related to independently measured molecular properties, and upon the availability of the required energy and angular momentum in molecular collisions. The second source of line broadening, assumed to be the same for all lines, includes adiabatic collisions and also diabatic soft collisions and can be represented by a single empirically adjusted cross section. The simple theory is applied successfully ~~to~~ self-broadening of CO lines and to foreign-gas broadening of CO and HCl; for HCl self-broadening an additional cross section for resonant-dipole processes must be included. Possible applications of the simple theory to HBr, HF, and CO_2 are discussed. The simple theory presented represents a semi-empirical approximation that may prove useful pending the development of complete theories based on first principles.

After appropriate corrections have been made for instrumental effects, the finite widths of absorption lines in gas samples at extremely low pressure can be attributed to the limited radiative lifetimes of molecules in initial and final states and to Doppler broadening. At higher sample pressures, the greater observed widths of infrared absorption lines can be attributed to the effects of molecular collisions. In the present paper we present a simple phenomenological model that seems to account satisfactorily for certain aspects of the observed collisional broadening of lines in the fundamental and first overtone vibration-rotation bands of CO and HCl.

The spectral transmittance $T(\nu)$ of a gas sample is given by the relation: $T(\nu) = \exp[-k(\nu)w]$, where $k(\nu)$ is the Lambert spectral absorption coefficient and w is the absorber thickness or optical density of the sample. At pressures of one atmosphere or less, the shape of a collisionally broadened absorption line is described in good approximation by the Lorentz expression:

$$k(\nu) = \frac{S}{\pi} \cdot \frac{\gamma}{(\nu_0-\nu)^2+\gamma^2} \tag{1}$$

where the line strength $S = \int k(\nu)d\nu$ depends on the quantum mechanical probabilities for radiative transitions between the initial and final states and on the populations of these states; γ represents the half-width of the line between frequencies at which $k(\nu) = k(\nu_0)/2$.

In terms of simple theory $\gamma = 1/2\pi\tau_c = f_c/2\pi$, where τ_c is the mean time between collisions and f_c is the corresponding mean collision frequency.

The mean collision frequency is given by the relation

$$f_c = N \overline{V} \sigma \qquad (2)$$

where N is the number of molecules per unit volume and is thus proportional to the sample pressure, σ is the collision cross section, and $\overline{V}$ is an appropriate average relative speed of the colliding molecules; for a gas sample at temperature T, it is convenient to use the most probable relative speed $\overline{V} = \sqrt{2kT/\mu}$, where k is Boltzmann's constant and μ is the reduced mass of the collision pair.

Extensive experimental studies of the half-widths of lines in the rotation-vibration bands of CO have been made in several laboratories (1-8). Although there are some relatively minor disagreements between the absolute values of the half-widths as measured in different laboratories, nearly all investigators report a gradual decrease of γ for self-broadening with increasing line number $|m|$ in both P and R branches; $m = J + 1$ in the R-branch and $m = -J$ in the P-branch, where J is the rotational quantum number of the initial level involved in the radiative transition. The values of γ for foreign-gas broadening show a somewhat similar variation with line number $|m|$ for most foreign gases studied, but γ values for H_2, D_2, and He show little variation with $|m|$.

Extensive experimental work has also been done on the determination of the half-widths of lines in the spectrum of HCl (9-13). The results obtained indicate that the value of γ for self-broadening first increases with increasing $|m|$ to a maximum at $|m| = 3$ for samples at room temperature and thereafter decreases with increasing $|m|$; the value of $|m|$ at which γ is a maximum is a function of temperature. The values of γ for foreign gas broadening of HCl lines vary with line number $|m|$ in a manner roughly similar to the corresponding variations noted above for foreign gas broadening of CO.

Impact theories (14,15, 16, 19, 20) of spectral line broadening treat the observed half-width γ as the sum of two parts. One part γ_A is associated with adiabatic or elastic collisions in which the absorber remains in its original energy level following collision; such collisions lead to a broadening of the level by an amount $\Delta E_A = h/2\pi\tau_A$ where τ_A is the mean time between adiabatic collisions and is therefore the time in which the energy levels of the isolated molecule can be specified. The other part γ_D is associated with diabatic or inelastic collisions which remove the absorbing molecule from its original level; the level broadening in this case is given by the relation $\Delta E_D = h/2\pi\tau_D$ where τ_D is the average lifetime of the absorbing molecule in its original energy level.

One of the most detailed impact theories of line broadening was developed by Anderson (19) and its application to the broadening of molecular absorption lines has been discussed in considerable detail by Tsao and Curnutte (20). This theory implies definite selection rules for diabatic collisions in which the distances between the centers of colliding molecules are sufficiently great to permit valid description of the collision in terms of specific electric multipole interactions; however, several types of interactions may, of course, be involved simultaneously.

For closer collisions involving exchange or "overlap" forces there are no definite selection rules. One of the difficulties in applying the Anderson theory results from the fact that many of the numerous specific interaction parameters are not precisely known and must be simultaneously adjusted when experimental results are compared with the theoretical treatment.

Similar difficulties are encountered in employing the statistical theories (17, 18, 21, 22) which attempt to account for line broadening in terms of the perturbations of the energy levels of the isolated absorbing molecule by the average values of the fields of neighboring molecules. After valiant but largely unsuccessful attempts to account for their experimental results on broadening of CO lines in terms of statistical theories involving dispersion forces, dipole-dipole forces, and dipole-induced dipole forces, Crane-Robinson and Thompson (4) suggested that the observed variation with line number $|m|$ may be interpreted on more general considerations of the dominant broadening processes involved rather than on the detailed nature of the forces during collision. Some progress in this direction has been made by Benedict _et al._ (9) in their moderately successful attempt to account for the observed self-broadening of the lines of the HCl fundamental in terms of the so-called resonant-dipole-billiard-ball (RDBB) approximation. In this approximation, $\gamma = \gamma_{BB} + \gamma_{RD}$ where the billiard-ball half width γ_{BB} is the same for all lines and results from adiabatic collisions and all types of diabatic collisions except for those involving resonant-dipole interactions, in which lifetimes of molecules in a given rotational level are limited by the direct exchange of quanta between molecules in adjacent rotational levels. Because of resonant-dipole interactions, the lifetimes of molecules in the most highly populated rotational states are shorter than those of molecules in other states. Benedict was able to account for the maximum value of γ in the vicinity of $|m| = 3$. The agreement between observed halfwidths and those calculated on the RDBB approximation is poorer in other parts of the HCl band.

PRESENT MODEL

The model proposed in the present paper was adopted after detailed examination of the experimental results for self-broadening of CO and foreign-gas broadening of both CO and HCl. We noted that the general variation of γ with $|m|$ is strongly influenced by the mass of the molecule responsible for the broadening process. Thus, the ratio of the self-broadening γ for CO to γ for N_2-broadening of CO is the same for all values of $|m|$; the molecular masses of CO and N_2 are equal. Although the number of electrons in CO and N_2 are equal, the two molecules differ in that CO has a small dipole moment and N_2 a large quadrupole moment. Thus, although the specific interactions in terms of electric multipoles are quite different, the relative variations of γ with $|m|$ are nearly identical. Similarly, in the CO spectrum the ratio of γ for CO_2 (M = 44) broadening to γ for Ar (M = 40) is approximately the same for all values of $|m|$, even though the molecular structures of CO_2 and Ar are greatly different. A similar relationship exists for γ due to He and D_2 in spite of their quite different structures. Crane-Robinson and Thompson investigated broadening of CO lines by a series of polyatomic hydrocarbon gases; although they differ in magnitude from gas to gas, the values of γ for all these polyatomic gases vary with $|m|$ in strikingly similar fashion.

In view of these observations, we have, for purposes of calculation, adopted a model involving an adiabatic broadening half-width γ_A which is tentatively assumed to be constant for all lines in the absorption band and is thus somewhat similar to the constant γ_{BB} broadening halfwidth proposed by Benedict (9). The variation of total γ with $|m|$ must therefore be attributed to variations in the diabatic half-width $\gamma_{D,|m|}$. We have assumed that the dominant $|m|$-dependent process consists of diabatic collisions in which translational kinetic energy is transformed into increased rotational energy of the absorbing molecule and that the net effect of all other diabatic collisions is to maintain the equilibrium population of each rotational energy level in a manner consistent with our assumptions. In view of the similarities of the γ-vs-$|m|$ dependence for such different broadeners as CO_2 and Ar, we have tentatively assumed that all collisions are close encounters in which no selection rules are involved; <u>i.e.</u>, that collision-induced transitions from an initial energy level to all higher levels are equally probable provided sufficient energy and angular momentum are available.

The kinetic energy in a binary collision available for conversion to rotational energy of the absorber is $(1/2)\mu V^2$, where μ is the reduced mass of the collision pair and V is the relative velocity. In view of the high vibrational energies of CO and HCl, few collisions in samples at $300^{\circ}K$ involve sufficient energy to produce vibrational energy transitions; however, nearly every collision involves sufficient translational kinetic energy to cause transitions between the more closely spaced lower rotational levels in both ground and excited vibrational states. The minimum relative velocity V_E required to produce a rotational transition from level rotational E(J) to a higher level E(J') is given by the expression

$$V_E = \sqrt{2[E(J')-E(J)]/\mu} = \sqrt{2hcB/\mu}\ \sqrt{J'(J'+1)-J(J+1)} \qquad (3)$$

where B is the otational constant of the absorbing diatomic molecule and centrifugal distortion effects are neglected.

If the transformation of translational kinetic energy to rotational energy were the only consideration, the variation of $\gamma_{D,|m|}$ with $|m|$ at a given sample temperature would be the same for all broadening gases, since the Maxwellian translational kinetic energy distribution is independent of molecular mass. However, the conservation of angular momentum must also be considered. When the absorbing molecule is in the rotational state J prior to collision and higher state J' after collision, its angular momentum has increased by $(J'-J)h/2\pi$. The total angular momentum involved in a collision is μVb, where μ is again the reduced mass of the collision pair, V the relative velocity of the colliding molecules, and b is the impact parameter. By considering the absorbing molecule in rotational state J and spatial quantum number M = J in a weak field parallel to the Z-axis, we note that molecules with components of relative velocity components parallel to the XY plane can produce transitions J → J' with M → M' provided sufficient angular momentum is available. Thus, the minimum velocity V_P required to provide the angular momentum required for a transition J → J' is

$$V_P = (J'-J)h/2\pi\mu b. \tag{4}$$

By comparison of (3) and (4), we note that $V_P > V_E$ for small values of the impact parameter b but that $V_E > V_P$ for larger values of this parameter.

Thus, for small values of b, dynamical limitations involving conservation of angular momentum are of dominant importance; these dynamical limitations are greatest for the small values of μ involved in collisions of the absorbing molecule with light molecules such as H_2, D_2, and He. For larger values of b, mass-independent energy limitations become dominant. We note, however, that the dominance of energy limitation occurs at a smaller value of b for large values of μ; thus, energy limitations become dominant at small values of b in collisions between an absorbing molecule and heavy molecules such as Xe, Kr, or the large polyatomic hydrocarbons studied by Crane-Robinson and Thompson (4). These differences between the effects of heavy broadeners and light broadeners are qualitatively in accord with the experimental results discussed above.

In order to make a quantitative comparison with experiment, we have assumed that the diabatic half-width $\gamma_{D,|m|}$ for lines involving transitions from initial level J can be written $\gamma_{D,|m|} = \phi(|m|)\gamma_D$, where γ_D is a constant for a given absorber and broadener and $\phi(|m|)$ is a factor that depends on the availability of the energy and angular momentum for collision-induced transitions from level J to higher levels J'. Since we have assumed that all collisions are close collisions involving exchange forces, no selection rules are involved, and all collisions J → J' are equally probable providing sufficient energy and angular momentum are available. Another assumption is that there is a maximum value b_o for a given collision pair; since only close collisions are involved, b_o is related to the size for the electron clouds of the colliding molecules.

Under these assumptions, we make use of the normalized Maxwellian distribution of relative velocities

$$dP = 4\pi \left[\frac{\mu}{2\pi kT}\right]^{3/2} V^2 \exp\left(-\mu V^2/2kT\right) dV$$

$$dP = 4\pi \left[\frac{1}{\pi \bar{V}^2}\right]^{3/2} V^2 \exp-(V/\bar{V})^2 \, dV \qquad (5)$$

where dP is the probability that the relative velocity of the colliding molecules is between V and V+dV. The probability P that the relative velocity $V \geq V_{Min}$ is given by the expression

$$P = 4\pi \left[\frac{1}{\pi \bar{V}^2}\right]^{3/2} \int_{V_{Min}}^{\infty} V^2 \exp-(V/\bar{V})^2 \, dV. \qquad (6)$$

Thus, for a given value of b, we may determine the probability $P_{J \to J'}(b)$, of a collision in the range b to b + db involving sufficient relative velocity to produce transition J → J' by using as the lower limit V_{Min} the larger of the velocities V_E or V_P given in (3) and (4), respectively. The sum $P_J(b)$ of the probabilities

$$P_J(b) = \sum_{J'=J+1}^{\infty} P_{J \to J'}(b), \tag{7}$$

where the sum involves all values of $J' > J$, can be taken as a measure of the effectiveness of collisions in the conversion of translational energy to the rotational energy of the absorbing molecule. A plot of $P_J(b)$-vs-b for collisions of CO with D_2 and He is given in Fig. 1(A); the initial J-value is indicated at the end of each curve. As expected, all curves start from zero at b = 0, since for this value $V_{Min} = \infty$. With increasing b, the curve for an initial value J increases as long as the value of $P_J(b)$ is influenced by values of V_{Min} imposed by the angular-momentum limitation (4). For sufficiently large values of b, the values of V_{Min} are determined completely by the energy limitation (3); at these large values of b, each curve in Fig. 1 becomes horizontal at a value of $P_J(b)$ characteristic of J. As indicated in Fig. 1(B) the energy limitation becomes dominant at a smaller value of b for Xe broadening.

The effectiveness P_J of a given broadener in causing collision-induced transitions from a given rotational level J to upper levels is proportional to the integral

$$P_J = \int_0^{b_0} P_J(b)\,db \qquad (8)$$

where the upper integration limit is related to the actual molecular dimensions but is to be determined ultimately by comparison with experimental data. The influence of the choice of b_0 on the value of P_J is illustrated in Fig. 2, where the curves have been normalized to unity for P_0. Plots of P_J for CO collisions with H_2 are shown in Fig. 2(A) and with D_2 and He in the Fig. 2(B) panel for three different choices of b_0; for these collisions, in which angular-momentum limitations are largely dominant, the choice of b_0 strongly influences the shape of the P_J-vs-J plot. Figure 2(C) gives a similar plot for CO-Xe collisions, in which energy limitations are largely dominant; in this case, the P_J-vs-J plots are indistinguishable for b_0 values of 2.0, 2.5, and 3.0 A. Thus, for heavy broadeners the choice of b_0 is relatively unimportant.

With the proper choice of b_0, curves of the type shown in Fig. 2 give the diabatic collision broadening of the initial levels of the radiative transitions involved in the vibration-rotation absorption bands. However, the observed absorption lines will also be broadened as a result of the broadening of the upper energy levels involved in the radiative transitions. Since vibrational relaxation times τ_V of diatomic molecules are typically much larger than rotational relaxation times, we have ignored the influence of collision-induced vibrational transitions and have assumed that the collision processes involved in broadening the rotational levels in the upper vibrational states are the same as those involved in broadening the rotational levels of molecules in the ground vibrational state. In arriving at the value of $\phi(|m|)$ to be used in the relation $\gamma_{D,|m|} = \phi(|m|)\gamma_D$, we have assumed that $\phi(|m|) = [P_J + P_{J''}]/2$; where J" is the quantum number J+1 or J-1 of the final rotational state in the upper vibrational state. We thus assume the same collision processes for molecules in the ground and excited vibrational states and recall that the values of rotational numbers are the same in the +m lines (J→J+1) and -m lines (J+1→J) in the absorption band.

COMPARISON WITH CARBON-MONOXIDE MEASUREMENTS

On the basis of the model described above we have applied the relation

$$\gamma_{|m|} = \gamma_A + \phi(|m|)\ \gamma_D \tag{9}$$

to the experimental results obtained by Hunt, Toth, and Plyler (6) for the self-broadening of CO lines in the first overtone and by Draegert and Williams (7) for foreign-gas broadening of CO lines in the fundamental by monatomic and diatomic gases. In fitting the data we regard γ_A and γ_D as directly adjustable parameters but note that the function $\phi(|m|)$ is based on an adjustable impact parameter b_O directly related to molecular sizes. We found that satisfactory fits to experimental data for noble-gas broadening could be obtained by setting b_0 approximately equal to one-half the CO internuclear distance plus the covalent radius of the monatomic broadeners; for broadening by diatomic broadeners, satisfactory fits to experimental results can be obtained with b_0 approximately equal to one-half the CO internuclear distance plus one-half the internuclear distance of the diatomic broadener. Thus, although the value of b_0 is essentially an adjustable parameter, b_0 can be related to molecular data obtained from other sources.

A comparison of the results calculated on the basis of the present model with the results of Plyler is given in Fig. 3. The ordinate in the figure gives a parameter γ^0 numerically equal to γ for a sample pressure of 1 atm; in view of the relation between γ and collision frequency f_c, we note that in samples at other pressures can be obtained by multiplying γ^0 by the sample pressure in atmospheres. The agreement between calculated and observed values can be regarded as reasonably satisfactory for all thirty lines covered in the experimental study. However, we note that a somewhat improved fit to lines near $|m| = 0$, where calculated values are low, and near $|m| = 30$, where calculated values are high, could have been achieved at the expense of a somewhat poorer fit in the range $|m| = 6$ to 20, where experimental measurements are somewhat more reliable.

A comparison of observed and calculated values of γ^0 for foreign gas broadening of carbon monoxide is given in Table I along with the parameters γ_A^0, γ_B^0, and b_o employed in each calculation. We note that with the adjustment of only these three parameters we are able to fit the observed data of Draegert and Williams (7) to within approximately ±10 percent for most of the 19 rotational lines for which experimental data are available. This agreement is remarkable in view of the fact that estimates of the uncertainties in the experimental values for foreign-gas broadening are at least ±5 percent and may be somewhat larger for weak lines nearest the band center and in the far wings of the band. The corresponding experimental results of Crane-Robinson and Thompson (4) could easily have been employed in Table I; with slightly different values of γ_A, γ_D, and b_o, the agreement between observed and calculated values would have been satisfactory. In order to give a graphical comparison between the observed and calculated values for foreign-gas broadening of CO lines, we have plotted in Fig. 4 the optical collision cross-sections σ given by the relation $\sigma = f_c/N\overline{V} = 2\pi\gamma^o/N_o\overline{V}$, where N_o is the number of molecules per unit volume at a pressure of 1 atm. The values of σ for monatomic broadeners are plotted in Fig. 4(A) panel; we note that the observed and calculated values agree to within less than ±10 percent for nearly all monatomic broadeners. An equally satisfactory or even better agreement for diatomic broadeners can be noted in Fig. 4(B). Thus, we conclude that our suggested model gives a fairly satisfactory account of the Draegert-Williams study of CO line broadening.

In Table II we also present our analysis of Crane-Robinson and Thompson's results for molecules not covered in the Draegert-Williams study. The agreement between calculated and observed values of γ^o for the diatomic broadeners can be regarded as satisfactory. Satisfactory analyses have also been achieved for the broadening of CO lines by polyatomic molecules, for which the impact parameter is large and the limiting value V_P is small; under these circumstances the energy limitations become dominant and the γ-vs-$|m|$ variations are similar for all hydrocarbons studied. The poorest agreement between calculated results and those obtained by Crane-Robinson and Thompson involve the polar broadeners HCl, NH_3, and SO_2, for which dipole-dipole or dipole-induced dipole interactions with CO are probably important.

COMPARISON WITH HYDROGEN CHLORIDE MEASUREMENTS

In applying the proposed scheme to the self-broadening of HCl lines, it is necessary to include an additional parameter to take account of the resonant-dipole interactions that lead to a maximum in the γ^{O}-vs-$|m|$ plots based on experiment. We have therefore assumed that

$$\gamma = \gamma_A + \phi(|m|)\ \gamma_D + f\gamma_{RD} \tag{10}$$

where f is the fraction of the molecules in the adjacent rotational states involved in rotational resonance (9); thus, we make use of four adjustable parameters: γ_A, γ_D, b_o, and γ_{RD}. A comparison of our calculated values of the half-widths of self-broadened HCl lines with observed values for the fundamental (9) and first-overtone (11) bands are given in

Fig. 5. The agreement between calculated and observed values is excellent in all parts of the band and is better than that obtained with Benedict's RDBB approximation in which only two fitted parameters are employed; a comparison of the two sets of values with the observed values is given in Table III.

In the case of foreign-gas broadening of HCl lines, we have been able to fit the experimental results of Babrov, Ameer and Benesch (11) for lines by means of relation (9) involving three adjustable parameters. Comparison of calculated and observed values of γ^o is given in Fig. 6, in which the adopted values of b_o, γ_A^o, and γ^o are listed for each broadener. We note that agreement is excellent for Ne and CO_2, satisfactory for He, Ar, CO, O_2, N_2, and H_2, and poorest for D_2. In view of the satisfactory agreement obtained for H_2 and He, the poor agreement for D_2 is difficult to understand; in the case of broadening of HCl lines by HBr there is no agreement at all between the observed values of γ^o and values of γ^o calculated from our model; however, since HCl and HBr both have large dipole moments, the lack of agreement with our simple theory, which involves only exchange forces, is not at all surprising.

In view of the large dipole moment of HCl, it is possibly surprising that our simple model has been applicable at all. However, the results shown in Fig. 6 indicate that we have met with fair success for foreign-gas broadening; the results shown in Fig. 5 and Table III indicate that we also meet with surprising success for self broadening of HCl, provided we include an additional resonant-dipole parameter γ_{RD}. Thus, it would appear that the sharp cut-off we have employed at impact parameter b_0 in our plots of $P_J(b)$ in Fig. 1 can be somewhat relaxed. Translated into conventional cross-section terminology, such a relaxation would involve a hard sphere of radius r_0 associated with exchange forces surrounded by a softer sphere associated with multipole interactions; the potential V(r) could be regarded as very large in the range $r = 0$ to r_0, where it would be joined smoothly to a potential $V(r) \sim 1/r^n$ in a manner similar to that suggested by Tsao and Curnutte (20) for the phase-shift parameter of Anderson's theory. Selection rules would apply for interactions involving impact parameters $b > r_0$. Collision cross sections for such a potential are temperature dependent. In the final section of the present paper we indicate that soft collisions are actually necessary for the success of our model.

FURTHER APPLICATIONS

In view of the influence of temperature on the Maxwellian distribution of relative velocities, our model predicts that the halfwidths of lines of small number $|m|$ relative to those of large $|m|$ should be enhanced as the sample temperature is reduced; this prediction has been verified by the work of Hoover and Williams (23). At high temperatures the γ-vs-$|m|$ plot becomes flatter in accord with expectations. However, it is possibly disappointing, though not surprising, that different values of the adjustable parameters, γ_A and γ_D, must be employed at different temperatures; this result implies that the collision cross sections σ_A and σ_D are temperature dependent and therefore velocity dependent. In their studies of HCl at various temperatures, Goldring and Benesch (13) note that the successful use of the RDBB approximation also requires a variation of σ_{BB} with temperature; this result is in accord with our results for CO.

Although we have applied our model in detail only to existing data for CO and HCl, we have also considered Madden's quantitative study of CO_2 absorption in the vicinity of the ν_2 fundamental (24). He has reported values of γ^o ranging from 0.126 cm^{-1} at $|m| = 4$ to 0.06 cm^{-1} at $|m| = 56$. The observed gradual decrease of γ^o with increasing $|m|$ can readily be described in terms of the present model. Similarly, for HBr and DCl the observed variations of γ^o with $|m|$ for various foreign gas broadeners show a gradual decrease that could be fitted by the present model; for lines of these absorbing gases broadened by H_2 the decrease in γ^o with increasing $|m|$ is much larger than that for CO and HCl.

In view of the extremely wide spacing of its rotational levels, HF presents a case of special interest. Our present model, with the addition of a resonant-dipole parameter can provide agreement with observed γ values; the agreement is comparable with that obtained by Mason and Nielsen (25) in their application of the RDBB model. The studies of Smith (26) and Wiggins (27) have covered the line-broadening effects of twenty-four foreign gases. For twenty of these gases the results are in accord with expectations based on our simple model; however, the exceptions are rather interesting. Hydrogen-broadening values (26) of

γ^o show an unexpectedly large decrease with increasing $|m|$; this result is similar to that for HBr and DCl and, with proper choices of γ_A and γ_D, can be described in terms of our model. However, for HF broadening by the polyatomic gases UF_6 and MoF_6, Smith (26) finds that γ^o shows an initial decrease with $|m|$ followed by an increase for large $|m|$ values; this unusual result cannot be given a simple interpretation.

Wiggins' work (27) on HF broadening by Ar, Kr, and Xe in the fundamental (0 → 1) and overtone (0 → 2) bands has yielded some interesting and unusual results; in each case γ^o for lines in 0 → 2 band is much larger than for lines in the 0 → 1 band. In the case of Ar, γ^o decreases with increasing $|m|$ in both bands in a manner consistent with our present model, but we are unable to account for the differences in the magnitudes of γ^o observed in the two bands. In the case of Kr, variation of γ^o with $|m|$ in the 0 → 1 band is what would be anticipated, but in the 0 → 2 band, γ^o shows an initial decrease between $|m| = 1$ and $|m| = 5$ and an increase in the range $|m| = 5$ to $|m| = 8$. For Xe broadening of HF, γ^o is nearly constant for all lines observed in the 0 → 1 band but increases monotonically with increasing $|m|$ in the 0 → 2 band. These unusual effects cannot be interpreted in terms of a simple model.

CRITICISM OF PROPOSED MODEL

The collision-model that we have employed cannot in any sense be regarded as a complete theory but is rather an approximation comparable with the RDBB approximation. We have applied energy and angular-momentum conservation principles to a single class of hard collisions. We have assumed (1) that these collisions provide the only $|m|$-dependent contribution $\phi(|m|)\gamma_D$ to line broadening and (2) that, except for resonant dipole effects, all other types of collisions combine to provide an $|m|$-independent contribution γ_A to line broadening.

Having verified that, in many cases, our model can be applied with fair success, we must now consider the nature of the various types of diabatic processes thus far ignored. Simple consideration of detailed balance between the rotational and translational energy distributions for hard collisions indicates that the rate at which molecules return to a given rotational level J from all higher levels J' is equal to the rate at which they leave the level by the processes considered earlier; these downward transitions to level J thus serve to maintain the equilibrium population of the level against depletion by the upward transitions considered thus far. Since we have adjusted $\phi(|m|)$ and γ_D for collision-induced transitions between J and upper levels J' to match the observed values, we must conclude that all other types of diabatic collisions must combine to give the same contribution to γ for all lines.

Detailed-balance considerations indicates that this is impossible for hard collisions of the type considered thus far. Broadening due to transitions of this type from a given level J to all lower rotational levels ranges from 0 for J = 0 to a maximum for intermediate values of J and to small values for large J-values. Detailed-balance considerations indicate that the effect of upward transitions from all lower levels to a given J is to maintain its population. Thus, in order to fulfill completely the requirements for the proposed model it is necessary to have one or more diabatic processes that would combine with the effects of transitions between J levels and lower levels produced by hard collisions to cause equal broadening for all lines.

Although it would be difficult to meet this requirement exactly, it is possible that soft diabatic collisions involving translational resonance phenomena producing transitions between adjacent or nearly adjacent rotational states could partially meet the requirement. In a collision of this type (19,20) the impact parameter is larger than the radius for hard collisions, the duration τ of the collision is such that $|E_{J'}-E_J| \simeq h/2\pi\tau$, and the total translational energy involved in the collision is large compared with $|E_J-E_{J'}|$; transitions $J \rightarrow J'$ and $J' \rightarrow J$ are equally probable. The cross sections for transitions of this type are greatest for low values of J and J'. Thus, their effects increase γ significantly for small $|m|$ but less significantly for intermediate $|m|$ and negligibly for large values of $|m|$. Although we have introduced translational resonance in an ad hoc fashion, it is interesting to note that its introduction would account for the slight failures of our model in accounting for the large observed value of γ^o for $|m| = 1$ and the slightly low observed values of γ^o for the largest values of $|m|$ when we have established γ_A and γ_D on the basis of lines for intermediate values of $|m|$.

In the light of these considerations, we may therefore re-interpret (9) as follows: The term $\phi(|m|)\gamma_D$ gives a measure of line broadening due to hard collisions raising molecules from a given rotational level to higher levels. The line broadening associated with the term γ_A includes not only adiabatic collisions but also (1) diabatic hard collisions in which molecules leave a given rotational level for lower levels

and (2) diabatic soft collisions. In order for our model to work perfectly, γ_A should be constant for all lines; actually, the effects of soft collisions are greatest for lines of small $|m|$ and negligible for very large values of $|m|$. Therefore, for CO, HCl, and CO_2, if we adjust γ_A and γ_D for a best fit for the values of γ observed for intermediate $|m|$, calculated values of γ should become progressively too large as $|m|$ increases to very large values. We can therefore predict increasingly lower values of γ as measurements are extended beyond their present range and further into the extreme wings of the bands.

Although the present model accounts for nearly all of Smith's results (26) for line broadening in the HF fundamental; we cannot interpret his results for UF_6 and MoF_6. The differences between γ^o values in the HF fundamental and overtone bands noted by Wiggins (27) would indicate a dependence on the vibrational state of the absorbing molecule that we have omitted, since it is not needed for CO and HCl. Even if we included such a vibrational parameter, the unusual properties of Kr and Xe in collisional broadening of HF lines would remain unexplained.

Although the ultimate theoretical treatment of molecular collisions in terms of parameters calculated from first principles seems difficult of attainment , considerable theoretical progress is being made at present in treatments of collisional line broadening in terms of parameters based on independent experimental measurements. Any complete theory must yield the absolute rather than the relative cross sections for various processes. Meanwhile, it is possible that the agreement between observed values of γ and values of γ based on our adjusted parameters γ_A, γ_D, and $\phi(|m|)$ may not be entirely fortuitous. We hope that the greatly oversimplified treatment presented here may, like Benedict's RDBB approximation, give some insight into some of the important collision processes involved in spectral line broadening.

The results of the present study should also emphasize the importance of considerations of detailed balance between the quantized rotational energy states of the absorbing molecules and the unquantized translational energy states of the mixture of gases; to regard the translational states as a mere energy reservoir or thermal bath seems inadvisable. Except for the effects of rotational resonance in self-broadening, direct energy transfers between the rotational states of the absorbing molecules and the rotational states of diatomic and polyatomic broadeners would appear to be unimportant. With the possible exception of HF, there is little evidence that vibrational relaxation contributes significantly to collisional line broadening of the infrared lines of diatomic absorbers.

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LEGENDS FOR FIGURES

Figure 1. The function $P_J(b)$ expressed in arbitrary units for various rotational energy levels J as a function of impact parameter b in Angstrom units. Panel A applies to CO collisions with He and D_2; Panel B applies to CO collisions with Xe.

Figure 2. The function $P_J = \int_0^{b_0} P_J(b)db$ normalized to unity at $J = 0$ for various values of b_0 as a function of rotational quantum number J. Panel A applies to CO-H_2 collisions; Panel B applies to collisions of CO with D_2 or He; Panel C applies to CO-Xe collisions.

Figure 3. Line half-width parameter γ^o in 0.01 cm^{-1}/atm as a function of line number $|m|$ in the CO fundamental vibration-rotation band. Observed values are shown as filled circles; calculated values are shown by crosses and were computed from relation (9) on the basis of fitted parameters $\gamma^o{}_A = 3.8\ cm^{-1}/atm$, $\gamma^o{}_D = 4.7\ cm^{-1}/atm$, and $b_o = 1.8$ Å.

Figure 4. Collision cross sections for broadening of CO absorption lines by monatomic gases in Panel A and by diatomic gases in Panel B. The cross sections $\sigma_{CO,B}$ for various broadening gases are

expressed in 10^{-16} cm^2 and are plotted as a function of line number $|m|$ in the CO fundamental.

Figure 5. Observed and calculated half-width parameters γ^o in 0.01 cm^{-1}/atm for HCl self-broadening as a function of line number $|m|$; observed values are shown as circles and calculated values based on relation (10) as crosses. Panel A gives results for the HCl fundamental; calculated values are based on the following fitted parameters expressed in 0.01 cm^{-1}/atm:

$\gamma^o_A = 6.27$, $\gamma^o_D = 5.74$, $\gamma^o_{RD} = 77.4$.

Panel B gives results for the first overtone; calculated values are based on the following fitted parameters expressed in 0.01 cm^{-1}/atm:

$\gamma^o_A = 8.23$; $\gamma^o_D = 9.06$; and $\gamma^o_{RD} = 61.1$.

Figure 6. Comparison of observed and calculated values of foreign-gas line broadening parameters γ^o in 0.01 cm^{-1}/atm; observed values are shown as circles and calculated values as crosses, and are plotted as a function of line number $|m|$ in the HCl fundamental. The observed values are those of Babrov, Ameer, and Benesch (11). The calculated values are based on relation (9) with the following fitted parameters expressed in 0.01 cm^{-1}/atm:

Broadener	H_2	He	D_2	Ne	N_2	CO	O_2	Ar	CO_2
γ^o_A	~0	1.40	1.72	0.64	~0	0.34	0.01	~0	~0
γ^o_D	7.67	0.77	4.16	1.81	10.1	12.1	0.38	5.59	17.0
b_o	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0 Å

Table I

Observed (0) and Calculated (C) Values of γ^o for CO Lines Broadened by Various Gases in units of 0.01 cm^{-1}/atm.

Table I

Line Number $\lvert m \rvert$	He		Ne		Ar		Kr		Xe		H_2		D_2		N_2	
	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C
1	4.79	4.75	3.91	3.89	7.04	6.48	7.48	7.22	8.93	8.35	7.49	7.12	6.45	6.27	8.12	8.00
2	4.68	4.75	3.85	3.80	6.65	6.19	6.94	6.80	8.00	7.91	7.15	7.12	6.34	6.27	7.76	7.69
3	4.66	4.75	3.74	3.76	6.14	5.94	6.46	6.43	7.30	7.39	7.00	7.12	6.30	6.26	7.21	7.40
4	4.64	4.75	3.58	3.70	5.69	5.70	5.92	6.13	6.80	7.06	6.93	7.12	6.15	6.24	6.84	7.13
5	4.60	4.75	3.54	3.63	5.34	5.51	5.56	5.84	6.39	6.68	7.00	7.11	6.10	6.21	6.55	6.90
6	4.58	4.74	3.49	3.59	5.08	5.31	5.20	5.60	6.00	6.36	6.95	7.09	6.05	6.17	6.32	6.66
7	4.55	4.74	3.44	3.55	4.85	5.14	4.91	5.36	5.66	6.08	6.92	7.06	6.00	6.13	6.12	6.45
8	4.55	4.73	3.44	3.49	4.72	4.98	4.72	5.12	5.47	5.82	6.90	7.01	5.95	6.09	6.02	6.25
9	4.55	4.73	3.46	3.44	4.63	4.84	4.56	4.92	5.29	5.61	6.90	6.99	5.92	6.04	5.94	6.07
10	4.61	4.72	3.45	3.44	4.56	4.72	4.50	4.73	5.13	5.40	6.87	6.99	5.90	6.00	5.84	5.93
11	4.67	4.72	3.45	3.35	4.46	4.61	4.43	4.60	4.98	5.19	6.86	6.94	5.87	5.95	5.76	5.75
12	4.68	4.72	3.42	3.32	4.44	4.50	4.34	4.45	4.85	5.01	6.90	6.90	6.85	5.92	5.72	5.66
13	4.66	4.72	3.39	3.30	4.38	4.39	4.25	4.30	4.73	4.84	6.95	6.85	5.84	5.88	5.66	5.49
14	4.71	4.71	3.33	3.28	4.35	4.30	4.19	4.19	4.65	4.69	6.90	6.81	5.83	5.86	5.60	5.39
15	4.70	4.71	3.26	3.26	4.31	4.22	4.14	4.04	4.57	4.57	6.78	6.78	5.83	5.82	5.51	5.29
16	4.69	4.70	3.22	3.23	4.23	4.13	4.07	3.93	4.52	4.45	6.82	6.72	5.78	5.80	5.45	5.21
17	4.67	4.70	3.18	3.21	4.14	4.06	4.00	3.82	4.50	4.36	6.84	6.69	5.74	5.76	5.38	5.11
18	4.68	4.69	3.20	3.19	4.07	3.98	3.90	3.71	4.37	4.25	6.81	6.64	5.76	5.71	5.24	5.02
19	4.69	4.69	3.13	3.18	4.00	3.93	3.79	3.66	4.24	4.17	6.74	6.61	5.75	5.68	5.10	4.94
20		4.69				3.89				4.08		6.58		5.63		4.86
γ_A^o	4.61		2.76		2.64		1.91		2.05		5.46		4.83		3.15	
γ_D^o	0.142		1.13		3.84		5.31		6.30		1.66		1.44		4.85	
b_o	1.3Å		1.8Å		2.5Å		2.8Å		3.0Å		1.4Å		1.3Å		1.5Å	

Table II

Observed (O) and Calculated (C) Values of γ^{o} of CO Lines Broadened by Various Gases in units of 0.01 cm^{-1}/atm.

Table II

Line Number [m]	CO_2		CH_4		n-pentane		n-hexane		CF_4		SF_6		NO		HCl		SO_2		NH_3	
	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C	O	C
1	8.47	8.29	7.82	8.02	11.45	11.80	12.36	12.70	7.10	7.29	7.42	7.34	6.12	6.41	8.33	8.04	10.6	10.80	11.00	10.50
2	7.75	7.90	7.80	7.72	11.49	11.35	11.78	12.19	6.67	6.98	7.15	7.05	6.15	6.19	7.46	7.85	10.5	10.26	9.70	10.14
3	7.35	7.54	7.68	7.40	11.13	10.88	11.82	11.67	6.44	6.68	6.84	6.72	6.13	5.99	7.25	7.67	9.89	9.60	8.84	9.80
4	7.11	7.22	7.30	7.11	10.90	10.49	11.73	11.23	6.30	6.42	6.41	6.51	6.00	5.82	7.10	7.51	9.47	9.10	8.38	9.44
5	7.01	6.94	7.11	6.86	10.44	10.14	-	10.82	6.07	6.18	6.35	6.26	5.78	5.67	7.24	7.37	9.18	8.60	8.30	9.10
6	6.44	6.65	6.70	6.64	9.90	9.80	11.02	10.44	6.09	5.96	5.94	6.07	5.44	5.52	6.96	7.23	8.51	8.16	7.62	8.83
7	6.09	6.41	6.54	6.40	9.65	9.53	10.96	10.14	5.99	5.78	5.77	5.89	5.50	5.39	6.90	7.12	7.79	7.81	7.38	8.5[illegible]
8	6.10	6.18	6.24	6.24	9.33	9.27	10.97	9.84	5.61	5.60	5.50	5.72	5.41	5.27	6.80	7.00	7.44	7.41	7.26	8.36
9	5.81	5.99	6.10	6.04	9.32	9.02	10.75	9.57	5.40	5.44	5.38	5.60	5.29	5.16	6.88	6.91	7.15	7.06	7.38	8.11
10	5.64	5.81	5.97	5.88	9.18	8.83	9.65	9.35	5.49	5.31	5.33	5.46	5.16	5.07	6.90	6.82	7.00	6.77	7.23	7.91
11	5.36	5.65	5.87	5.71	8.91	8.65	9.80	9.10	5.50	5.19	5.31	5.35	5.14	4.97	6.98	6.75	6.35	6.48	7.27	7.71
12	5.22	5.49	5.66	5.57	8.79	8.55	9.71	8.92	4.92	5.05	5.15	5.22	5.21	4.90	6.84	6.66	6.38	6.25	7.31	7.53
13	5.10	5.34	5.63	5.45	8.93	8.35	9.38	8.72	-	4.94	5.16	5.12	5.09	4.81	7.00	6.60	6.20	6.00	7.42	7.39
14	5.32	5.20	5.55	5.32	8.27	8.21	9.06	8.55	4.71	4.82	5.19	5.03	5.04	4.75	6.87	6.53	5.64	5.81	7.29	7.24
15	5.20	5.08	5.42	5.21	8.29	8.00	8.66	8.39	4.82	4.74	5.07	4.94	4.79	4.68	6.71	6.46	5.67	5.60	7.09	7.09
16	4.95	4.95	5.36	5.11	8.29	7.84	8.56	8.25	4.84	4.68	5.30	4.90	4.81	4.63	6.90	6.41	5.86	5.41	7.57	6.99
17	4.92	4.84	4.87	5.02	7.82	7.72	7.44	8.10	4.47	4.59	5.03	4.83	4.57	4.57	6.49	6.39	4.92	5.23	7.62	6.87
18	4.61	4.71	4.53	4.96	7.56	7.60	7.20	7.98	4.32	4.50	4.99	4.78	4.38	4.52	6.16	6.34	4.68	5.09	7.27	6.74
19	4.48	4.64	4.41	4.89	7.39	7.50	6.86	7.85	4.22	4.42	4.92	4.71	4.04	4.48	5.89	6.29	4.64	4.91	6.85	6.66
20	4.73	4.60	4.57	4.79	7.05	7.41	6.93	7.75	4.10	4.36	4.68	4.64	4.11	4.44	5.85	6.23	4.65	4.78	6.76	6.57
Y_A^o	2.74		3.10		5.40		5.48		3.02		3.38		3.48		5.31		1.87		4.43	
Y_D^o	5.55		4.92		6.40		7.22		4.27		3.96		2.93		2.73		8.93		6.07	
b_o	2.0Å		2.0Å		2.8Å		2.8Å		2.8Å		3.0Å		2.5Å		2.0Å		2.0Å		1.8Å	

Table III

Half-Width Parameter γ^{o} for Self-Broadening of the HCl Fundamental at 300^{o}K; γ^{o} is expressed cm^{-1}/atm.

Line Number $\|m\|$	Observed γ^{o}	Calculated γ^{o} RDBB*	Present Model
1	0.218	0.15	0.203
2	0.223	0.20	0.236
3	0.249	0.23	0.255
4	0.246	0.22	0.248
5	0.227	0.19	0.220
6	0.186	0.15	0.181
7	0.153	0.11	0.146
8	0.127	0.075	0.117
9	0.106	0.05	0.098
10	0.090	0.035	0.086
11	0.084	0.03	0.079
12	0.083	0.03	0.075
13	0.066	0.03	0.073

*These values were computed by Benedict on the basis of a billiard ball cross section based on viscosity measurements; closer agreement could be obtained by adjustment of this parameter.

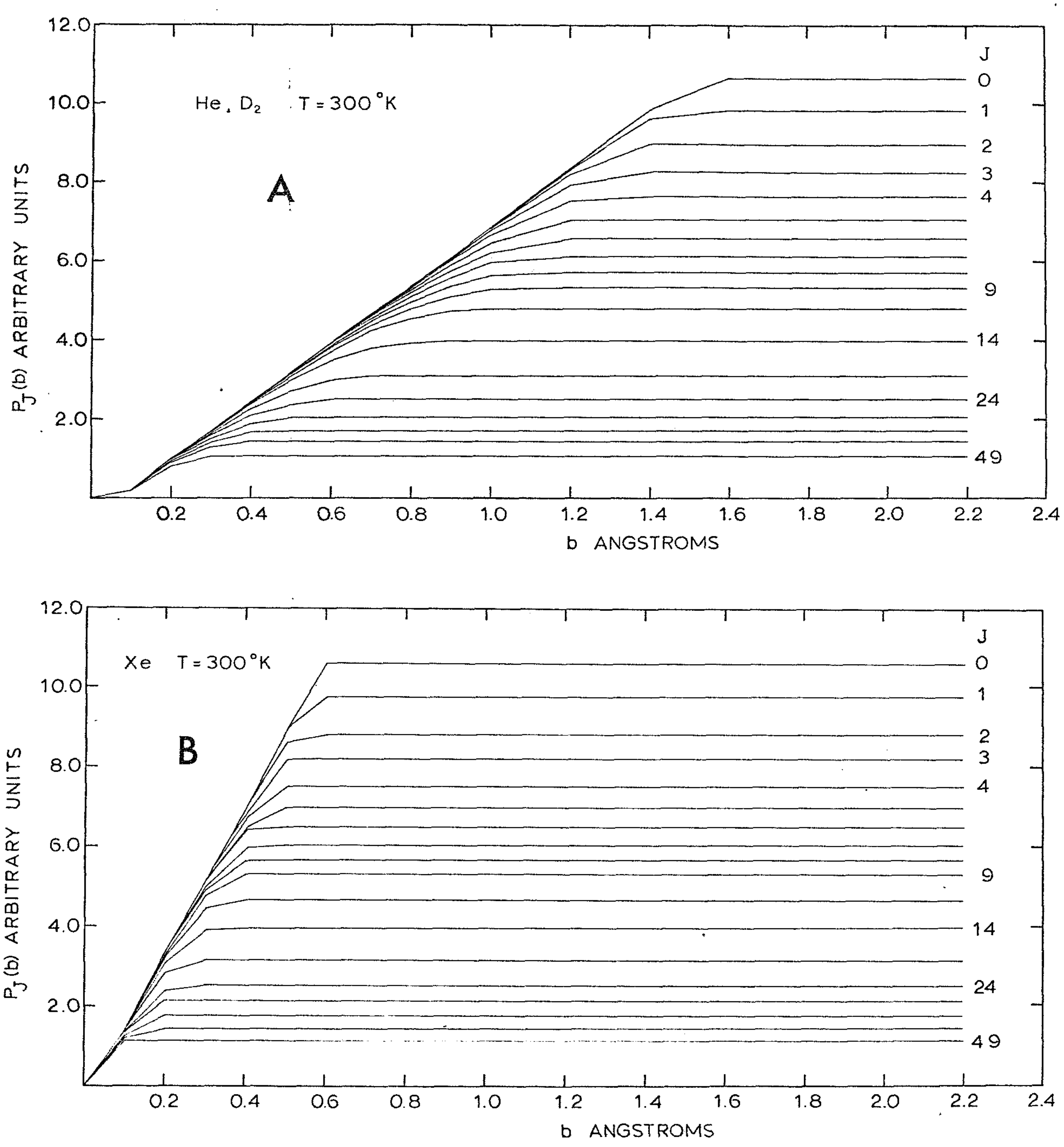
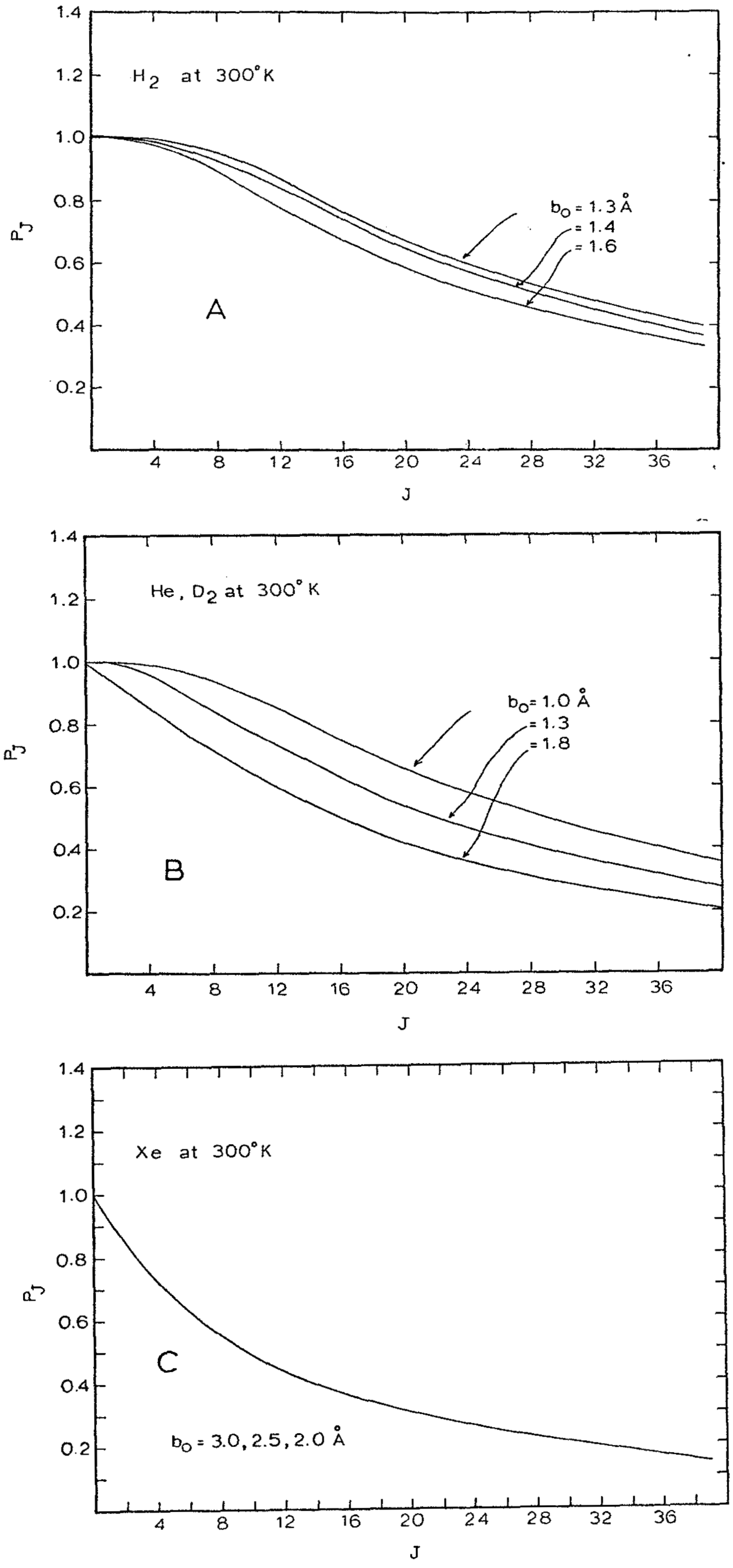

A
He, D₂ T = 300°K
J
0
1
2
3
4
9
14
24
49
$P_J(b)$ ARBITRARY UNITS
b ANGSTROMS
0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4
2.0 4.0 6.0 8.0 10.0 12.0
B
Xe T = 300°K
J
0
1
2
3
4
9
14
24
49
$P_J(b)$ ARBITRARY UNITS
b ANGSTROMS
0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4
2.0 4.0 6.0 8.0 10.0 12.0

Fig. 1



1.4
1.2
1.0
0.8
0.6
0.4
0.2
P_J
H_2 at 300°K
b_0 = 1.3 Å
= 1.4
= 1.6
A
4
8
12
16
20
24
28
32
36
J
1.4
1.2
1.0
0.8
0.6
0.4
0.2
P_J
He, D_2 at 300° K
b_0 = 1.0 Å
= 1.3
= 1.8
B
4
8
12
16
20
24
28
32
36
J
1.4
1.2
1.0
0.8
0.6
0.4
0.2
P_J
Xe at 300°K
C
b_0 = 3.0, 2.5, 2.0 Å
4
8
12
16
20
24
28
32
36
J

Fig. 2

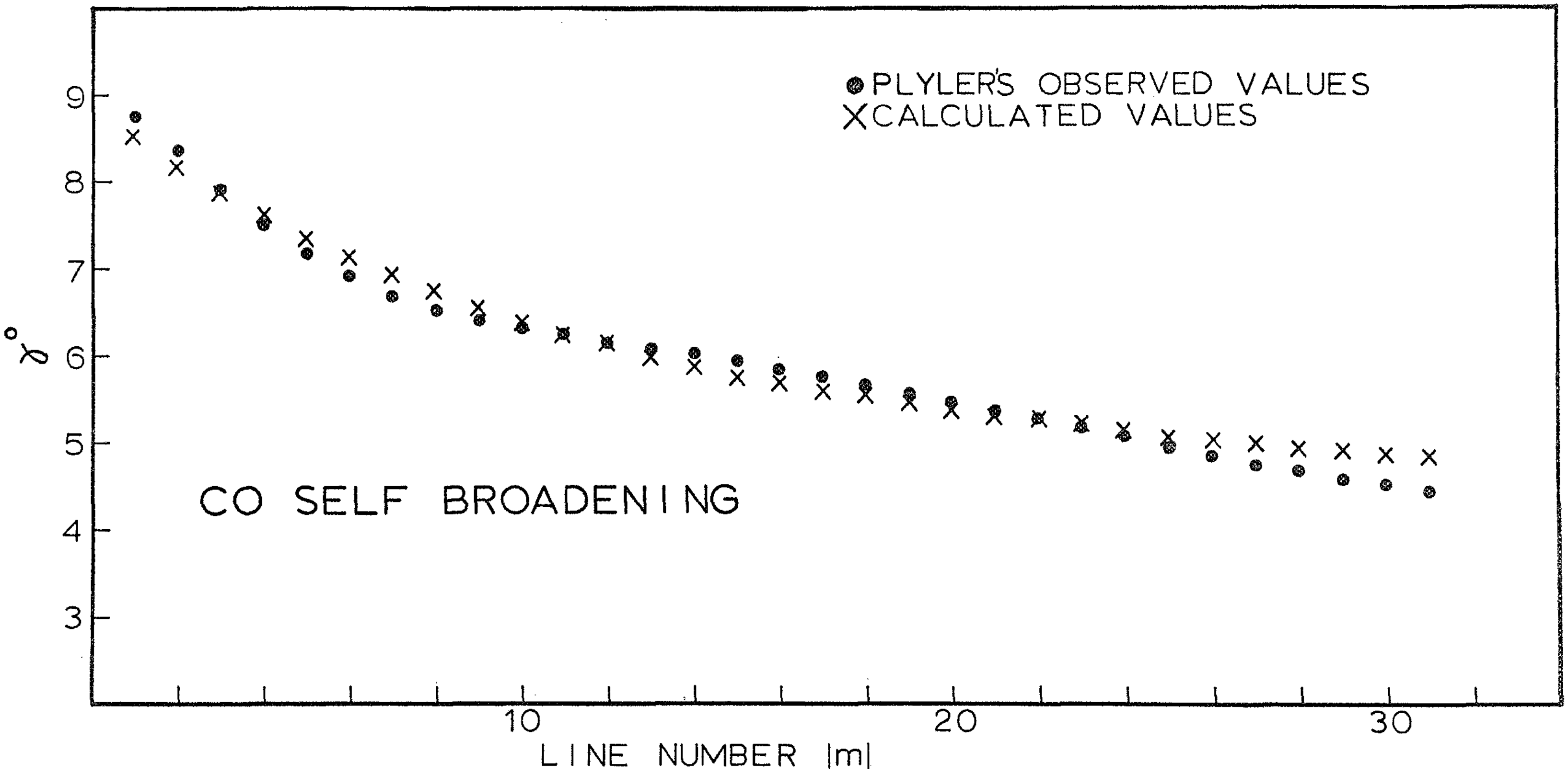

● PLYLER'S OBSERVED VALUES
X CALCULATED VALUES
CO SELF BROADENING
γ°
9
8
7
6
5
4
3
10
20
30
LINE NUMBER |m|

Fig. 3

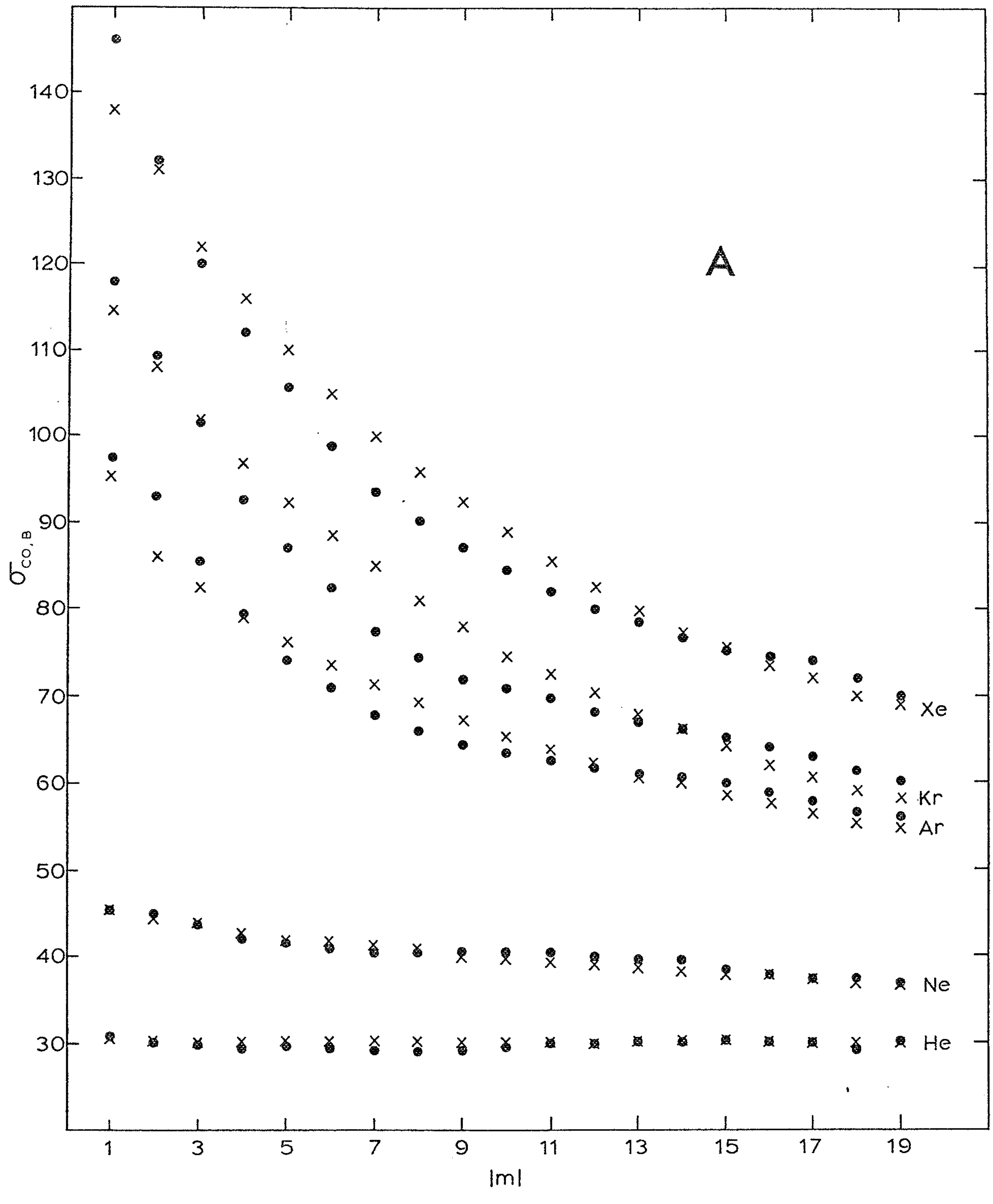

A
σ_CO,B
|m|
140
130
120
110
100
90
80
70
60
50
40
30
1
3
5
7
9
11
13
15
17
19
Xe
Kr
Ar
Ne
He

Fig. 4

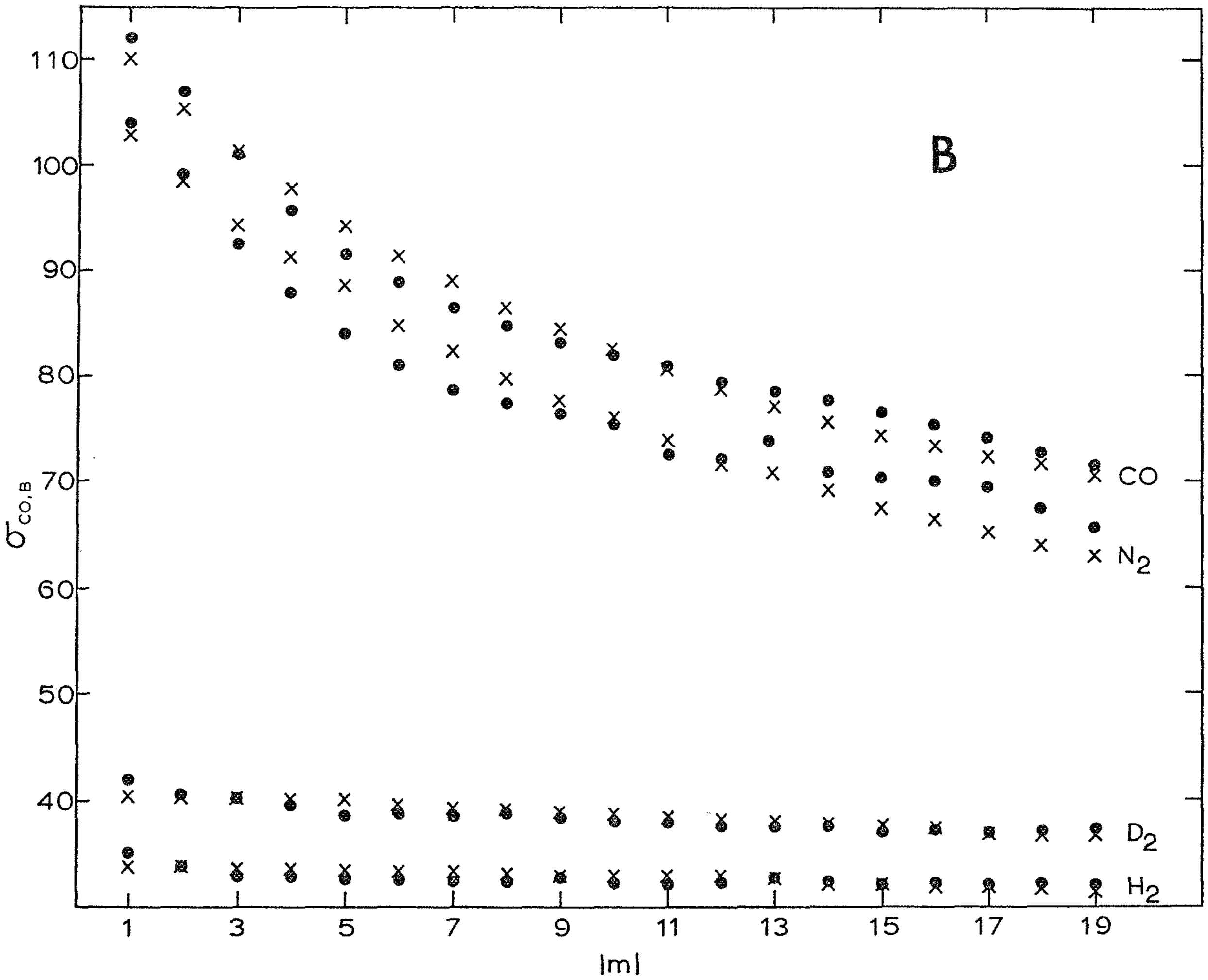
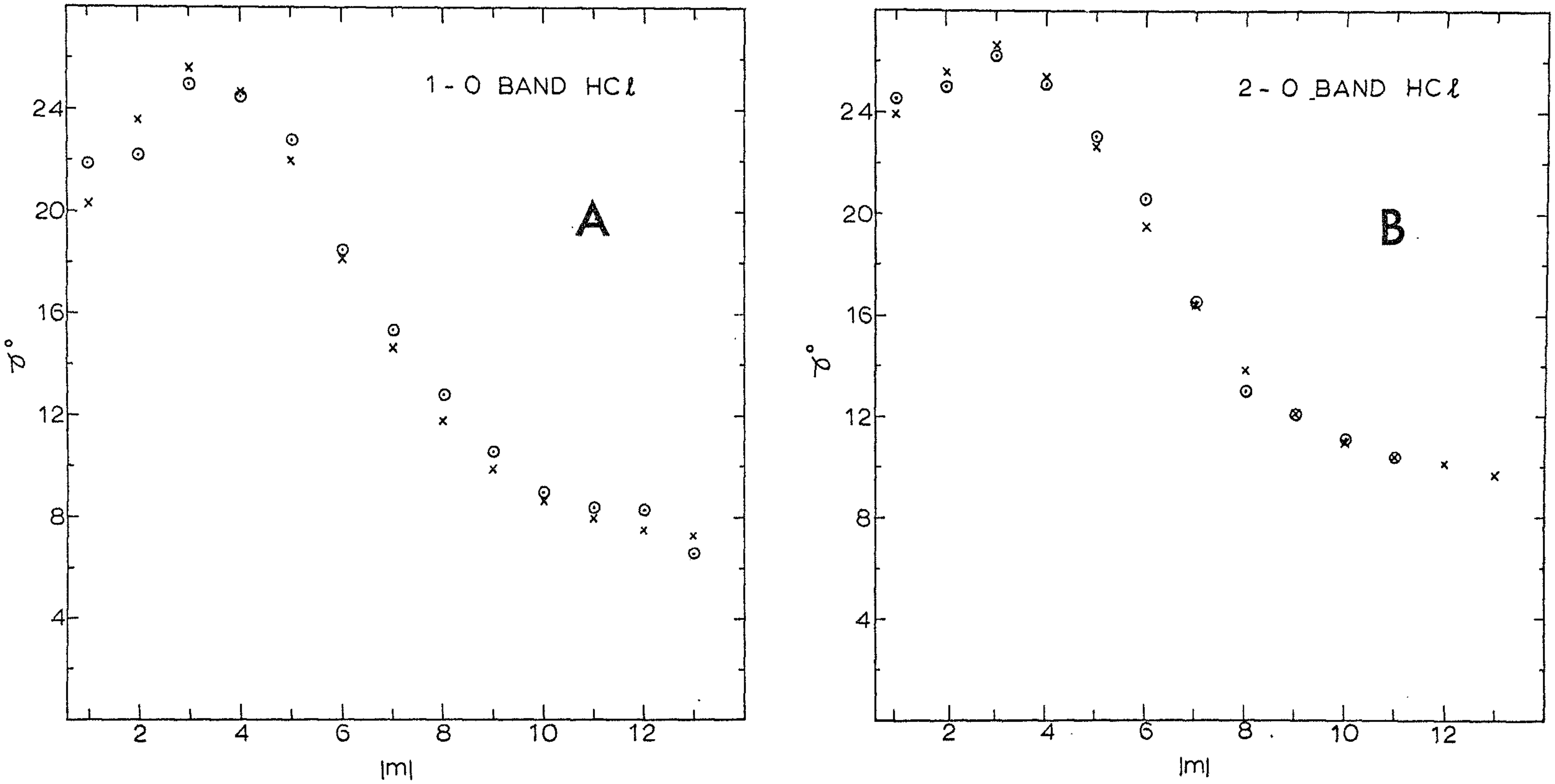
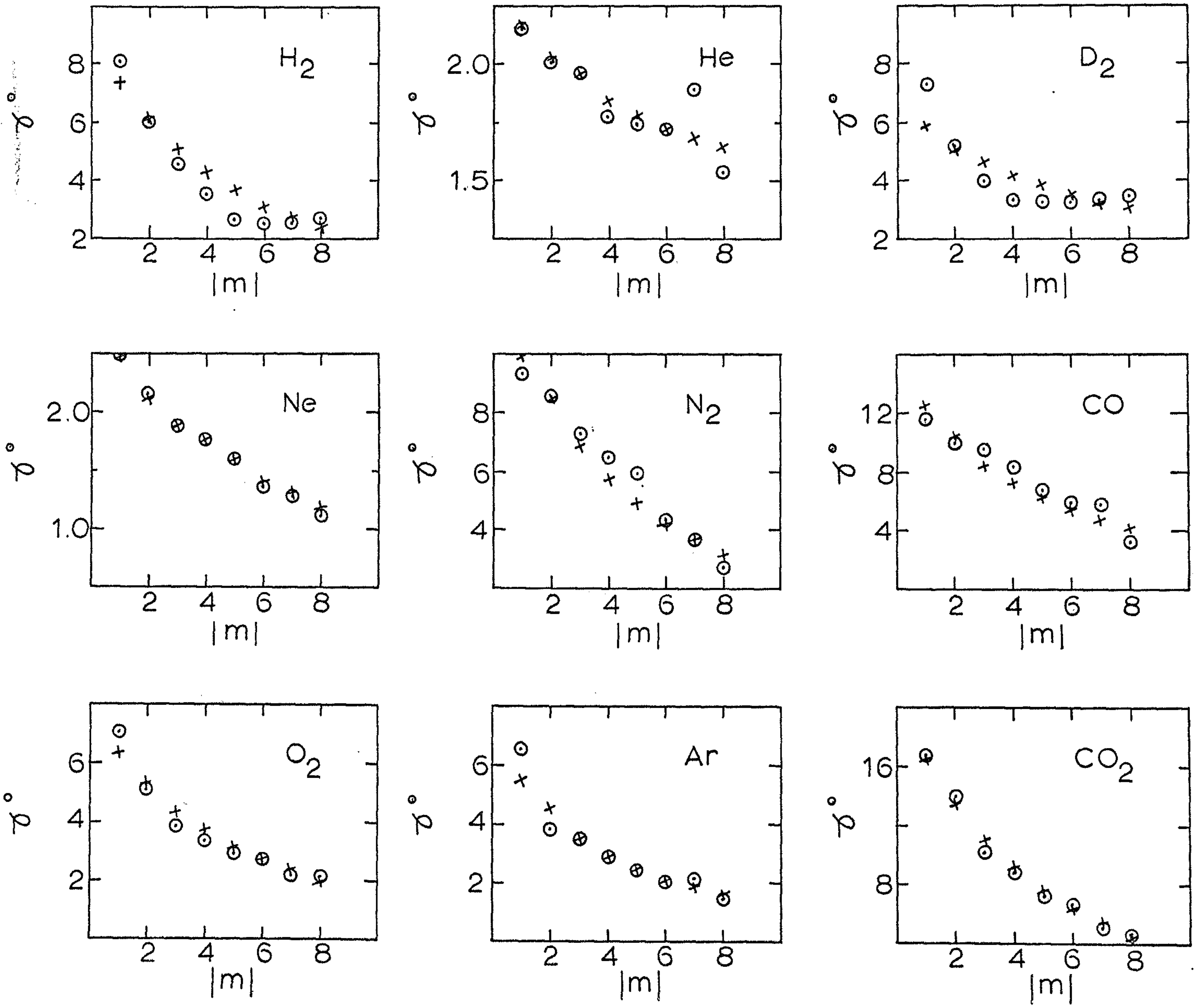

B
110
100
90
80
70
60
50
40
$\sigma_{CO,B}$
1
3
5
7
9
11
13
15
17
19
|m|
CO
N_2
D_2
H_2

Fig. 4


1 - 0 BAND HCℓ
A
2 - 0 BAND HCℓ
B
ρ°
24
20
16
12
8
4
2
4
6
8
10
12
|m|


H2
He
D2
Ne
N2
CO
O2
Ar
CO2
ρ°
|m|
2
4
6
8
1.5
2.0
1.0
12
16