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CLASSICAL SCATTERING CALCULATIONS FOR DIATOMIC MOLECULES

A General Procedure and Application to the Microwave Spectrum O_2

U.S.
DEPARTMENT
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JULY 1972

BOULDER
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FOREWORD

The work described in this report was done as part of a research program on quantitative millimeter wave spectroscopy of atmospheric oxygen. The project was partially supported by NASA Langley Research Center under Order No. AAFE, L58-506; and the computer time used in this research was provided by the National Center for Atmospheric Research which is sponsored by the National Science Foundation.

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[*] A cooperative effort of the National Oceanic and Atmospheric Administration and the University of Colorado.

CLASSICAL SCATTERING CALCULATIONS FOR DIATOMIC MOLECULES

A General Procedure and Application to the Microwave Spectrum of O_2

Uri Mingelgrin

ABSTRACT

Many properties of gaseous systems such as electromagnetic absorption and emission, sound dispersion and absorption, etc. may be elucidated if the nature of collisions between the particles in the system is understood. In this report, a procedure for the calculation of the classical trajectories of two interacting diatomic molecules will be described. The dynamics of the collision will be assumed to be that of two rigid rotors moving in a specified potential. The actual outcome of a representative sample of many trajectories at 298K was computed, and the use of these values at any temperature for calculations of various molecular properties will be described. Calculations performed for the O_2 microwave spectrum are given to demonstrate the use of the procedure described.

Key words: Classical scattering, line shape, collision cross sections, O_2 microwave spectrum, O_2 self broadening, O_2 spectrum foreign gas broadening.

1. INTRODUCTION

The elucidation of properties of an ensemble of particles in equilibrium requires the knowledge of ensemble averages, rather than the time development of the individual particles, over long periods of time. In addition, many properties of molecules in a gaseous system can be described by the impact approximation (Anderson, 1949) in the pressure range where the molecules are unperturbed except for the very short duration of binary collisions. To describe a trajectory of a molecule during such a binary collision, one needs to define the colliding molecule's initial conditions such as relative velocity, angular momenta, etc., and then to solve the equations of motion assuming some intermolecular potential. One may, therefore, choose a statistical sample of initial conditions for the various possible collisions and then solve the proper equations of motion. Once a set of initial and final conditions for a sample of trajectories is given, cross sections and expectation values for various variables can be derived which can then be used for calculations of the various relaxation phenomena and other properties. For example, the microwave spectrum, the rotational Raman spectrum and sound absorption by O_2 were computed from the data derived from such a statistical set of collisions (to be published, also see section 3).

Section 2 of this report will describe how a representative sample of collisions is calculated, while section 3 will demonstrate the use of such data in calculation of various properties. A description of a program which performed the trajectory calculations is given in section 2.3.

2. THE CLASSICAL TRAJECTORY CALCULATIONS

The collision between two diatomic molecules was assumed to be between two rigid rotators moving in a specified potential. This approximation will hold when:

a) the duration of practically all collisions is much longer than the vibrational period, so that (in analogy with the Born-Oppenheimer approximation) the vibrational motion can be approximately averaged in each intermolecular distance to give essentially two rigid rotors.

b) the total energy associated with the rotational and relative motion is lower for most collisions than the energy difference between the vibrational levels.

c) the energy differences between the rotational levels are significantly smaller than the energy difference between the vibrational levels.

When conditions b and c hold, vibrational transitions may be neglected. All three conditions are met by O_2 , N_2 and many other diatomic molecules up to temperatures higher than room temperature.

2.1 Solution of the Equation of Motion

To determine the trajectory of two colliding rotors it is necessary to solve the appropriate equations of motion. This can be done after the interaction potential between the two rotors is defined. For example, the potential chosen for the O_2-O_2 calculations consists of a 4-point exponential repulsion and of an attractive, angle dependent London dispersion potential (London, 1942):

$$V = \sum_{\substack{i=1,2\\ j=1,2}} V_o e^{-ar_{ij}} - \frac{C}{R^6}\Big\{1 + \Gamma\left(P_2(\cos\theta_1) + P_2(\cos\theta_2)\right) + \Delta\Big[\frac{3}{2}\left(\sin\theta_1 \sin\theta_2 \cos(\varphi_1 - \varphi_2) - 2\cos\theta_1 \cos\theta_2\right)^2 - \frac{3}{2}\left(\cos^2\theta_1 + \cos^2\theta_2\right)\Big]\Big\} \tag{1}$$

where V_o , a , C , Γ and Δ are potential parameters obtained by fit to virial coefficient, spectroscopic data and theoretical calculations (Mingelgrin, 1972). None of the parameters was adjusted to fit the microwave spectrum the calculation of which is described in section 3. The values of the potential parameters used are:

V_o = 48838 eV

a = 5.3883 A^{-1}

C = 48.108 eVA^6

Γ = .229

Δ = .052

The r_{ij} are the distances between four centers of repulsion, two on each molecule. In this work the r_{ij} were taken as the distances between the nuclei of one O_2 molecule and the nuclei of the other O_2 molecule. In addition, θ_1 and θ_2 are the angles between either molecule and the intermolecular axis, φ_1-φ_2 is the angle between the projections of both molecules on a plane perpendicular to the intermolecular axis and P_2 represents the second Legendre polynomial.

The coordinate system chosen to describe the motion of the rotors is as follows. The relative motion of the two rotors is described in a Cartesian coordinate system with the initial vector of relative motion defining the Z axis. The axis perpendicular to it in the plane of motion is the Y axis. The X axis is thus perpendicular to the plane of motion. This coordinate system was used and is described in detail by Karplus et al. (1965). The internal motion of the rotors is described in spherical polar coordinates. The axes defining the internal motion are parallel to those defining the relative motion. Using this coordinate system, Hamilton's equations of motion (Goldstein, 1950) are solved in the scattering program described below. The equations of motion are

$$\frac{\partial H}{\partial pj} = \dot{q}_j \tag{2a}$$

$$\frac{\partial H}{\partial q_j} = -\dot{p}_j \tag{2b}$$

where q_j are the specified coordinates and p_j are their conjugate momenta, $\dot{q}_j$ and $\dot{p}_j$ denote derivatives with respect to time. H is the Hamiltonian of the system. In terms of the chosen coordinate system, the Hamiltonian is defined as

$$H = \sum_{j=1}^{3} \frac{p_j^2}{2\mu} + \sum_{i=1}^{2} \frac{1}{2I_i}\left(P_{\theta_i}^2 + \frac{P_{\varphi_i}^2}{\sin^2\theta_i}\right) + V(\underset{\sim}{r}) \tag{2c}$$

where μ is the reduced mass for the relative motion; p_j the conjugate momenta of the Cartesian relative coordinates; θ_i and φ_i the angles defining the spherical polar coordinates of rotor i , φ_i being the azimuthal angle: I_i is the moment of inertia of rotor i, and $V(\underset{\sim}{r})$ the potential defined in equation 1. Finally, P_{θ_i}, P_{φ_i} are the appropriate conjugate momenta.

The solutions of the above defined equations of motion were done by a variable step Nordsieck integration scheme (Nordsieck, 1962). The trajectory is considered complete when the intermolecular distance is larger than the initial intermolecular distance. The initial intermolecular distance, in turn, is defined for each individual trajectory by the program scattering described below and is generally 20-26 a.u. The governing relation for determination of the initial intermolecular distance is:

$$R = \frac{26}{P^{(.1)}} \text{ a.u.} \tag{3}$$

where R is the initial intermolecular distance and P is the magnitude of the initial relative momentum in atomic units. The change in the variables of the motion upon passing a fixed distance during the collision will have some inverse relation to the relative momentum. The actual relation (eq. 3) is an empirical one derived from test runs of a sample of 27 trajectories so that the difference between the value of any component of the linear and angular momenta at the chosen R and at 35 a.u. is less than 3×10^{-3} a.u. It is then assumed that the trajectory will approximate well a collision with $R \to \infty$.

As is evident from equation 2c, there is a singularity in the Hamiltonian at $\theta_i = 0$. This singularity is not of a physical origin and thus can be removed for a given trajectory simply by changing the coordinate system. A 180° rotation of all the vectors defining the initial conditions about the line connecting the centers of mass of both rotors is performed when the calculations fail because of this apparent singularity. In this way an equivalent collision which will not pass through the previously encountered singularity is obtained. The internal Cartesian coordinates, the components of the angular momenta of the rotors and the Cartesian relative conjugate momenta are transformed in a straightforward way. The spherical coordinates and momenta used in the program are then calculated. The relative coordinates are not changed by the rotation.

The program in its current version calculates, in addition to the variables of the motion, the classical rotational phase shifts for both rotors, defined as the angular change in the position of the rotor in the rotation plane during a collision (Gordon, 1966). This quantity is not well defined in non-instantaneous collisions. Before a collision the rotor rotates in some plane. After the collision is over, the rotor rotates again in some plane, different in general from the original one. In an instantaneous collision, the rotor will change its plane of rotation at a point where the initial and final rotational planes intersect. If no phase change would have occurred in the collision, the rotor will rotate up to the instant of collision in the initial angular frequency and following that instant in the final angular frequency. At some time t after such a collision without a phase shift, the position of the rotor in the rotation plane is well defined. The angle at time t between the above defined position and the actual position of the rotor is the classical rotational phase shift. If the collision is not instantaneous, and during the collision both points of intersection of the initial and final planes of rotation are passed one or more times, the classical phase shift is not well defined. The procedure adapted for defining the classical phase shift is as follows. The time of closest approach in a collision is determined. Then, the two apparent phase shifts were calculated by assuming the rotor changed planes of rotation at both times of intersection of the initial and final rotational planes nearest to the time of closest approach. These two apparent phase shifts are designated as ν_1 and ν_2 . The difference between the two points of intersection of the initial and rotational plane is, of course, π radians. If we call the angles between the position of the rotor, if it had rotated up to the time of closest approach in the initial angular frequency and the points of intersection of the initial and final rotational planes, β_1 and β_2 , then the weighted average values of the various functions of the phase shift $(F(\nu))$ are given by

$$F(\nu) = F(\nu_1)\left(\frac{\beta_2}{\pi}\right) + F(\nu_2)\left(\frac{\beta_1}{\pi}\right)$$

2.2. Statistical Sampling and the Effect of Temperature

To obtain a representative sample of trajectories, a procedure formulated by Conroy was used (Conroy, 1967); a Conroy case II for non-periodic variables with his parameters for 12 variables and 1861 points was utilized. Conroy's procedure for multivariable sampling selects sampling points so that each variable is sampled uniformly along its range. For periodic variables one period is sampled. For non-periodic variables a transformation must be applied to let the range of the variable be 0 to 1. For every variable a parameter k_x, which is the ratio between some odd integer smaller than the sample size and the number of points is defined. The sample size is chosen to be some large prime number. The values of a variable (x_j) sampled may be selected by a number of schemes. In the case of "Conroy case II" the values selected are:

$$x_j = j \cdot k_x - e_j \qquad j = 1, 2, \ldots, \ell \tag{4}$$

where ℓ is the sample size and e_j is an integer chosen so that x_j falls between -1, 1. The absolute value of x_j is then taken. Conroy demonstrated that one set of points selected by such a procedure will optimize the sampling. The actual parameters k_x chosen were selected by Conroy for various numbers of variables and sample sizes by trial and error to minimize the error in a test integral. The test integral was such as to maximize the error in integration. The 12 variables chosen to completely define the initial conditions of a collision are: the absolute values of the angular momenta of both rotors; the impact parameter; the initial relative speed; the angles φ_1 , φ_2 , θ_1, θ_2 defined above; the conjugate momenta P_{θ_1} and P_{θ_2} ; and the signs of P_{φ_1} , P_{φ_2} . The number of trajectories (1861) yields a sample of 3722 collision outcomes if both colliding rotors are identical, as in the case studied (O_2-O_2 collisions).

As mentioned above, the initial values of the sampled variables had to be transformed so that the sampling range will be 0 to 1 . In the case of the angular momenta, a cutoff was selected so that the maximum rotational quantum number (J_{max}) was 25; namely: $K_{max} = \hbar\sqrt{25(25+1)}$, where K is the rotational angular momentum. The initial rotational angular momenta allowed were only those which correspond to the odd rotational quantum numbers. The actual selection of the rotational angular momenta of the two rotors is as follows:

let

$$Q_{(J)} = \sum_{N=1,3,\ldots,J} (2N+1)e^{-B^{o}N(N+1)/kT} \qquad (5a)$$

and

$$P_{(J)} = \frac{Q_{(J)}}{Q(J_{max})} \qquad (5b)$$

where B^o is the rotational constant.

The range of $P_{(J)}$ is 0 to 1 . The variable sampled by the Conroy procedure is $P_{(J)}$. All points in the range 0-1 that fell between $P_{(J-2)}$ and $P_{(J)}$ (or 0 and P(1) for J=1) were assigned to the rotational angular momentum $K = \hbar\sqrt{J(J+1)}$. This procedure will sample J according to its Boltzmann distribution. Note that although the trajectories were classical, the selected initial angular momenta were properly quantized as only odd rotational quantum numbers are allowed for O_2 .

For the sampling of the velocity and impact parameters at a fixed temperature, a procedure developed by R. G. Gordon (unpublished) was used. Consider a cross-section of the form

$$= \int_0^\infty dV \int_0^\infty dB < f(V, B) > G(B)\, G(V) \qquad (6)$$

where f(V, B) is a function of an individual trajectory. The function f(V, B) may be any function which depends on the trajectory. For example, table 1 gives a matrix whose elements are the corresponding functions f(V, B) needed for the calculation of the O_2 microwave spectrum at any density and temperature (see section 3). The variable

	$-\omega_-$	$-\omega_+$	0_-	0_+	$+\omega_+$	$+\omega_-$
$-\omega_-$	$\delta_{fi}-P_{fi}\cos^4\frac{1}{2}\alpha\cos\alpha$	$P_{fi}\sin^4\frac{1}{2}\alpha\cos\alpha$	$-\frac{1}{2}P_{fi}\cos^2\frac{1}{2}\alpha\sin^2\alpha$	$-\frac{1}{2}P_{fi}\sin^2\alpha\frac{1}{2}\sin^2\alpha$	$-\frac{1}{2}P_{fi}\cos^2\frac{1}{2}\alpha\sin^2\alpha$	$-\frac{1}{2}P_{fi}\sin^2\frac{1}{2}\alpha\sin^2\alpha$
$-\omega_+$	$P_{fi}\sin^4\frac{1}{2}\alpha\cos\alpha$	$\delta_{fi}-P_{fi}\cos^4\frac{1}{2}\alpha\cos\alpha$	$-\frac{1}{2}P_{fi}\sin^2\frac{1}{2}\alpha\sin^2\alpha$	$-\frac{1}{2}P_{fi}\cos^2\frac{1}{2}\alpha\sin^2\alpha$	$-1\frac{1}{2}P_{fi}\sin^2\frac{1}{2}\alpha\sin^2\alpha$	$-\frac{1}{2}P_{fi}\cos^2\frac{1}{2}\alpha\sin^2\alpha$
0_-	$-\frac{1}{2}P_{fi}\cos^2\frac{1}{2}\alpha\sin^2\alpha$	$-1\frac{1}{2}P_{fi}\sin^2\frac{1}{2}\alpha\sin^2\alpha$	$\delta_{fi}-P_{fi}\cos^4\frac{1}{2}\alpha\cos\alpha$	$P_{fi}\sin^4\frac{1}{2}\alpha\cos^2\alpha$	$-\frac{1}{2}P_{fi}\sin^2\frac{1}{2}\alpha\sin^2\alpha$	$-\frac{1}{2}P_{fi}\cos^2\frac{1}{2}\alpha\sin^2\alpha$
0_+	$-\frac{1}{2}P_{fi}\sin^2\frac{1}{2}\alpha\sin^2\alpha$	$-\frac{1}{2}P_{fi}\cos^2\frac{1}{2}\alpha\sin^2\alpha$	$P_{fi}\sin^4\alpha\frac{1}{2}\cos\alpha$	$\delta_{fi}-P_{fi}\cos^4\frac{1}{2}\alpha\cos\alpha$	$-\frac{1}{2}P_{fi}\cos^2\frac{1}{2}\alpha\sin^2\alpha$	$-\frac{1}{2}P_{fi}\sin^2\frac{1}{2}\alpha\sin^2\alpha$
$+\omega_+$	$-\frac{1}{2}P_{fi}\cos^2\frac{1}{2}\alpha\sin^2\alpha$	$--\frac{1}{2}P_{fi}\sin^2\frac{1}{2}\alpha\sin^2\alpha$	$-\frac{1}{2}P_{fi}\sin^2\alpha\frac{1}{2}\sin^2\alpha$	$-\frac{1}{2}P_{fi}\cos^2\alpha\frac{1}{2}\sin^2\alpha$	$\delta_{fi}-P_{fi}\cos^4\frac{1}{2}\alpha\cos\alpha$	$P_{fi}\sin^4\frac{1}{2}\alpha\cos\alpha$
$+\omega_-$	$-\frac{1}{2}P_{fi}\sin^2\frac{1}{2}\alpha\sin^2\alpha$	$-\frac{1}{2}P_{fi}\cos^2\frac{1}{2}\alpha\sin^2\alpha$	$-\frac{1}{2}P_{fi}\cos^2\frac{1}{2}\alpha\sin^2\alpha$	$-\frac{1}{2}P_{fi}\sin^2\frac{1}{2}\alpha\sin^2\alpha$	$P_{fi}\sin^4\frac{1}{2}\alpha\cos\alpha$	$\delta_{fi}-P_{fi}\cos^4\frac{1}{2}\alpha\cos\alpha$

TABLE 1: MATRIX OF INTEGRANDS FOR THE MATRIX OF CROSS-SECTIONS FOR THE MICROWAVE SPECTRUM OF O_2

α in table 1 is the angle of reorientation of the rotational angular momentum in a collision and P_{fi} is the probability of transfer in a particular collision from rotational state i to rotational state f . The angular brackets in equation 6 indicate average overall initial conditions other than relative velocity and the impact parameter. Here, V is the relative velocity, B the impact parameter. G(B) and G(V) are the probability functions for a collision to occur with the variables V and B for bimolecular collisions.

$$G(B) = 2\pi B \tag{7a}$$

$$G(V) = \frac{4\pi}{\bar{V}} \left(\frac{\mu}{2\pi kT}\right)^{3/2} V^3 e^{-\left(\frac{\mu V^2}{2kT}\right)} \tag{7b}$$

where $\bar{V}$ is the mean relative velocity, k is the Boltzmann constant, T the absolute temperature, and μ the reduced mass for the collision.

The transformation used to change the integration range from 0 - ∞ to the desired range of 0 - 1 will now be described. Define the unnormalized weights

$$\omega(V) = V^2 e^{-K_V(\mu V^2/2kT)} \tag{8a}$$

$$\omega(B) = (1+K1_B e^{\left(\frac{B^2}{K2_B R_M^2}\right)})^{-1}(K2_B R_M^2)^{-1} \tag{8b}$$

where K_V , $K1_B$, $K2_B$ are dimensionless parameters and R_M was selected to be the position of the minimum in the spherically averaged intermolecular potential. These parameters were selected so that $\frac{< f(V, B) >}{\omega(V)\omega(B)}$ is approximately constant throughout the integration range, thus improving the sampling (see equation 11). The normalized weights are now defined as

$$U(X) = \frac{\omega(X)}{\int_0^\infty \omega(X) G(X)\, dX} \qquad (9)$$

where X represents V or B . Now if we use the transformation

$$dA(X) = U(X) G(X)\, d(X) \qquad (10)$$

the integration limits are 0 - 1 . We can now use Conroy's procedure to define values of A(V) and A(B) in the range 0 - 1 and then extract the appropriate values for V and B . Integral (6) is evaluated now from the sum

$$\Sigma = \sum_{V,B} \frac{< f(V, B) >}{U(V)\, U(B)} \quad . \qquad (11)$$

A sample calculation for deriving such an integral will be demonstrated in section 3.

The distribution functions for V and the rotational angular momenta are temperature dependent. Thus, the sampling described above is valid for one temperature only. However, over a wide range of temperatures it is possible to utilize the trajectory calculations for the reference temperature (298°K) by using appropriate conversions. Define

$$W_{VB}(T_1) = (U(B)\,U(V,T_1))^{-1} \tag{12}$$

then

$$W_{VB}(T_2) = \frac{W_{VB}(T_1)\,U(V,T_1)}{U(V,T_2)} \tag{13}$$

The value of a term in the sum (11) at given values of V and B , and temperature T_2 is now

$$\frac{W_{VB}(T_1) < f(V,B) > U(V,T_1)}{U(V,T_2)} \tag{14}$$

In the Conroy procedure used, the values of V defining the terms of the sum of equation (11) were selected at fixed intervals in the function A(V) (equation (10)) so that, at the reference temperature T_1 , the integral (6) can be evaluated by the sum in equation (11) using the sample of V values directly. At an arbitrary temperature, however, if we use the V values selected at T_1, we need to modify the sum for a proper estimate of the integral. For a large enough sample we have

$$\Delta A(V, T_2) = \frac{dA(V, T_2)}{dV} \Delta V = \frac{dA(V, T_2)}{dV} \left(\frac{dA(V, T_1)}{dV} \right)^{-1} \Delta A(V, T_1) \qquad (15)$$

From equation (10) we obtain

$$\Delta A(V, T_2) = \frac{U(V, T_2) G(V, T_2)}{U(V, T_1) G(V, T_1)} \Delta A(V, T_1) \quad . \qquad (16)$$

At the arbitrary temperature T_2 the necessary cross section can now be expressed as

$$\sum (T_2) = \sum_{V, B} \frac{W_{VB}(T_1) < f(V, B) > G(V, T_2)}{G(V, T_1)} \qquad (17)$$

It is now necessary to properly evaluate the average $< f(V, B) >$ at an arbitrary temperature using the same sample of rotational angular momenta.

This is a straightforward procedure. If we define the distribution function of the angular momenta

$$G(J) = \frac{(2J+1)e^{-B^{o}J(J+1)/kT}}{\sum\limits_{J=1,\,3,\,\ldots,\,Jmax} (2J+1)e^{-B^{o}J(J+1)/kT}} \qquad (18)$$

where J is the rotational quantum number of the perturbing molecule and B^{o} the rotational constant, the average at an arbitrary temperature T_2 will be obtained by evaluating the function $f(V, B, J)$ at the J values selected for the distribution at the reference temperature T_1 and multiplying by the factor

$$\frac{G(J, T_2)}{G(J, T_1)} \quad . \qquad (19)$$

Finally, at the arbitrary temperature the integral in equation 6 will be calculated from

$$\sum(T_2) = \sum_{i=1}^{N_J} \frac{W_{V_iB_i}(T_1)G\,(V_i, T_2)\,G(J_i, T_2)\,f(V_i, B_i, J_i)}{G(V_iT_1(G(J_i, T_1)} \qquad (20)$$

where summation is over all trajectories with the same initial angular momentum for the absorbing molecule and N_J is the number of such trajectories. Note that the cross sections are averaged over the angular momenta of the perturbing molecule only, since in the case of the microwave spectrum of O_2 and many other properties (see for example section 3), these are the necessary averages. Averages for both molecules' angular momenta can be treated similarly, simply by summing overall values of the rotational angular momenta of both molecules using the proper Boltzmann factors. For example, equation (20) will have to be multiplied by the factor

$$\frac{G(J_i^r, T_2)}{G(J_i^r, T_1)}$$

where J_i^r indicate the rotational quantum number of the radiator and the sum will be over all trajectories.

2.3. Description of Program and Output[1]

The 4-body trajectory calculations described above are executed by a classical scattering program fashioned after a reactive scattering program written by K. Morokuma and L. Pedersen. The present

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[1] A list of the program described below as well as the output for a complete set of trajectories at 298°K can be obtained on request from the ITS MM Wave Transmission Spectroscopy Section. (See Table 3 for sample output and text for output description.

program is written by the author for the CDC 6600 and 7600 computers. An average trajectory calculation takes 4 seconds on the CDC 6600. Reference will be made to the actual variables and subroutines' names to simplify the understanding of the program listing for those interested in obtaining it.

The following items will be described:

a. A list of subroutines and their functions is given in table 2.

b. The input to the program. A list of the input appears in table 4. The subprogram and statement numbers of the format statements according to which the input variables are read also appear in table 4. A sample input appears in figure 5.

c. A description of the way the program executes a trajectory calculation.

d. The program output. A sample of the punch output is given in table 3. A list of the printed output parameters is given in table 6.

The program input consists of a set of 5 cards per set of trajectories followed by two cards per trajectory. A sample of the input is given in table 5. The input variables, definitions, and the location and statement number of the associated format statements are listed in table 4. The input includes some options regarding the form of output, the conditions for the set of trajectories and data which

TABLE 2

The subroutines of the scattering program and their functions.

Subroutine Name	Entry	Purpose
ZINIT	-------	To define initial coordinates, momenta, and error and step size parameters for the Nordsieck integrator.
"	ZNITY	To redefine initial conditions if a singularity is encountered in the trajectory path.
ZDIFFE	-------	Nordsieck integrator for the solution of the equations of motion.
ZEVAL	-------	Calculates time derivatives of coordinates and momenta at every step on trajectory path.
ZQUNO	-------	To read input data for the set of trajectories to be calculated, as well as for each individual trajectory. To determine the initial angular momenta of the two rotors.
ZOUPUT	-------	Defines all printed output.
ZEVR	-------	Calculates rotational energy of rotors.

Continuation of Table 2

ZVECPR	-------	Calculation initial and final components of the angular momenta vectors of rotors and relative motion, final velocity and kinetic energy.
XIT	-------	Special exit in case of program failure (e.g. due to defective input).
ZVIBR	-------	Calculate initial magnitude of linear momentum of rotor.
ZENERG	-------	Defines value of potential energy at each integration step.
"	ZNERGY	Defines various constants and potential parameters.

$W_{VB}(A^2)$	cos α	K_i ($\hbar$ UNITS)	K_f ($\hbar$ UNITS)	cos ν	sin ν	cos2ν	sin2ν	V (ATOMIC UNITS x10^3)
158.93715	.99961	13.49074	13.53075	.99933	.03653	.99733	.07302	.34605
158.93715	.99953	11.48913	11.35973	.99877	-.04693	.99509	-.09372	.34605
117.94579	.52239	9.48683	8.11743	.96970	-.09560	.88163	-.17547	.17402
117.94579	.96985	13.49074	14.31397	.99306	-.06840	.97241	-.13462	.17402
48.14532	.89148	11.48913	10.97377	.90667	.41831	.64494	.75645	.24181
48.14532	.02324	1.41421	10.14999	.53824	.83685	-.41153	.89091	.24181
69.20689	.48740	3.46410	4.75765	.78536	-.28521	.27591	-.29386	.18138
69.20689	.01545	11.48913	11.94856	.96058	.27717	.84549	.53228	.18138
375.47485	.70792	11.48913	13.82554	.80255	.57418	.29416	.90492	.13134
375.47485	.59653	15.49193	10.63735	.72209	-.58191	.07789	-.74776	.13134
49.39711	.47082	5.47723	6.31178	-.25519	-.93748	-.76469	.45144	.22106
49.39711	.23843	15.49193	16.42517	.97393	.21222	.89740	.41129	.22106
64.17044	.42345	3.46410	9.78082	-.81785	.55448	.34379	-.89120	.19150
64.17044	.32687	9.48683	3.65920	.61095	.25457	-.23164	.46623	.19150
441.65430	-.59535	13.49074	6.15585	.86501	.30548	.55230	.64920	.11350
441.65430	.74765	7.48331	4.84457	.86422	.14471	.49652	.28583	.11350
101.42239	.85721	13.49074	10.98014	.97042	-.07955	.89049	-.12823	.25734
101.42239	-.16402	15.49193	10.36226	.83583	-.29736	.51406	-.30705	.25734
89.96001	.83654	15.49193	13.56175	.19500	.96655	-.87333	.36125	.22830
89.96001	-.42541	3.46410	5.76833	-.72921	.67899	.06469	-.99425	.22830
58.43559	-.30825	9.48683	8.25630	.98187	-.08806	.93048	-.16174	.35495
58.43559	.97037	1.41421	15.19725	.54801	.77299	-.22340	.77658	.35495

TABLE 3: A SAMPLE OF TRAJECTORY OUTPUT AT REFERENCE TEMPERATURE 298°K (SEE DEFINITION OF SYMBOLS IN TEXT SECTION 2.3).

determine the initial conditions of individual trajectories. The conditions fixed for the set of trajectories are: The weights of the four atoms, the maximum integration time allowed per trajectory, a parameter defining the initial intermolecular distance, the number of trajectories per set, the temperature and the highest rotational quantum number allowed. The variables defining the initial conditions of a trajectory were listed in the text (section 2. 2) and the actual input data per trajectory are given in input cards 6 and 7 as listed and defined in table 4.

The basic features of the actual execution of a set of trajectory calculations will now be described. First, the necessary input for a set of trajectories is read. Next the various reduced masses (array W) are defined from the masses of the four atoms (array WP) in the main program. Subroutine ZINIT is then called. ZINIT calls in turn subroutine ZQUNO where the array XU(N, II) is defined. This is the array of the functions P(J) defined in equation (5b) for both rotors. The determination of individual trajectories starts at this point. ZINIT is called again. It in turn calls ZQUNO where the input data for the individual trajectories are read and the quantum numbers J(array JAB) of the rotational angular momenta for both rotors are determined. Upon returning to ZINIT the input data are used to define the initial coordinates and conjugate momenta (the arrays QI -- the array of the

TABLE 4

The scattering program input

Card #	Variable	Variable Definition	Location of read Statement and Format Statement Number	Comments
1	ISPST (*)^1	Set ISPST = 1	MAIN 103	KK is a bookkeeping parameter and may be arbitrarily defined
	TAN (*)			
	KK	File number for a given set of trajectories		
2	WP (4)^2	Weights of the four atoms (in grams)	MAIN 101	One molecule consists of atoms 1 and 2; the other of atoms 3, 4
3	TMAX	Maximum allowed integration time (in atomic units)	MAIN 699	D=RSHELL/P$^{\cdot 1}$ where P is the initial relative linear momentum and D is the initial intermolecular distance
	RSHELL	Determines initial intermolecular distance (in atomic units)		

Continuation of Table 4

4	IDTL	Back integration and detailed output option	MAIN 105	IDTL=0 No detail, no back integration (unless integration time exceeds 220, 000 a. u.) IDTL=1 No detail, back integration IDTL=2 Detail, no back integration IDTL=3 Detail, back integration
	KTRJ	Number of trajectories per file		
	DT (*)[3]			
	NSTEP	Details of trajectory printed every n-th step		
	ISTEP	Punched intermediate output option		ISTEP=0 No intermediate punched output ISTEP=1 Punch position of 4 atoms in center of mass system every n-th step
5	L(*)	Set L = 0	ZQUNO 1	NVAB was defined as the vibrational quantum number , not applicable to rigid rotors model, and has to be set to 0
	NVAB (2)(*)	Set NVAB(1)=NVAB(2)=0		
	BMAX (*)			
	TEMP	Absolute temperature		
	JMAX(2)	Maximum rotational quantum number for both rotors		

Continuation of Table 4

6	V	Initial relative velocity (in atomic units)	ZQUNO 2	φ and θ are the spherical polar coordinates as defined in text. W_{VB} is the weight factor as defined in text Cards 6 and 7 repeat once per trajectory
	BIMP	Impact parameter (in atomic units)		
	APHI (2)	φ_1 , φ_2 (range 0-2π)		
	ATHET (2)	θ_1 , θ_2 (range 0-π)		
	VBWT	W_{VB}(in A^2)		
7	X(6)	X(1) , X(2) determine magnitude of initial rotational angular momenta (range 0-1) X(3), X(4) determine conjugate momenta of θ_1 , θ_2 (range -1 to +1) X(5), X(6) determine conjugate momenta of φ_1 , φ_2 (range 0-1)	ZQUNO 3	Actual variables are determined from the six constants in subroutines ZQUNO (angular momenta) and subroutine ZINITS Cards 6 and 7 repeat once per trajectory

---

[1] (*) denotes a variable not used in this version.

[2] number in parenthesis denotes an array with the indicated number of elements.

[3] DT defined as the maximum step size in the Nordsieck integration is presently computed in subroutine ZINIT for each trajectory.

TABLE 5

Sample Input*

```
 1   NOT   0
       2.6556E-23     2.6556E-23     2.6556E-23     2.6556E-23
   800000.      26.000
0  520 800.00000     10   0
0          0          0     7.000   298.000   25   25
 0.0003747037  10.3994713  2.9154129  3.9856281  0.6811652  2.9398556  541.2844238
 0.6708758  0.8659286-0.6491089  0.2428741  0.9669552  0.4860287
```

---

[*] Last two lines are repeated once per trajectory

Table 6: The printed output*

Line #	Variable	Location of Write Statement	Description
1-2	KK	MAIN (statement 116)	Prints title and variable KK (defined in table 4)
3-6	WP	MAIN (statement 119)	Defined in table 4
7	R SHELL	"	"
8	TMAX	"	"
9	KTRJ	"	"
10	L	ZQUNO (statement 999)	"
11	TEMP	ZQUNO	"
12	JMAX	"	"
13	APHI (1) ATHET (1) X(3) X(5) APHI (2) ATHET (2) X(4) X(6)	ZINIT	"

*This is the standard output for a successful trajectory. Error messages (e.g. for too long trajectories) will also be printed.

Table 6 Continuation

Line #	Variable	Location of Write Statement	Description
14	RS2	ZINIT (statement 38)	RS2 = square of the initial intermolecular distance
	DT		DT = maximum step size in the Nordsieck procedure
	ERROR		ERROR = error parameter for the Nordsieck procedure
	VBWT		VBWT = defined in table 4 and text
15	KK	ZOUPUT	KK = defined in table 4
	NO		NO = sequential number of the trajectory in the set
	AN(I, 1) I=1, 2, 3		AN(I, 1) = x, y and z components of the initial rotational angular momentum of rotor 1 ($\hbar$ units)
	ANS(1)		ANS(1) = magnitude of the initial rotational angular momentum of rotor 1 ($\hbar$ units)
	AT(1)		AT(1) = initial rotational energy of rotor 1 (atomic units)
	JAB(1)		JAB(1) = initial rotational quantum number of rotor 1
16	AN(I, 2)I=1, 2, 3	ZOUPUT	The variables for rotor 2 corresponding to those defined in line 15 for rotor 1
	ANS(2)		
	AT(2)		
	JAB(2)		

Table 6 Continuation

Line #	Variable	Location of Write Statement	Description
17	URS(3) ANS(3) AT(3) AP(3)	ZOUPUT	URS(3) = initial relative velocity in a.u. $\times 10^2$ ANS(3) = initial angular momentum associated with relative motion ($\hbar$ units) AT(3) = initial kinetic energy associated with relative motion (a.u.) AP(3) = initial potential energy (a.u.)
18	AN(I, 4) I=1, 2, 3 ANS(4) ATOT	ZOUPUT	AN(I, 4) = x, y, z components of the initial total angular momentum of system ($\hbar$ units) ANS(4) = magnitude of initial total angular momentum ($\hbar$ units) ATOT = total energy in a.u.
19	Q	ZOUPUT	Q = Array of initial Cartesian coordinates of the system in the order: X, Y, Z of rotor 1, X, Y, Z of rotor 2, X, Y, Z of relative motion
20	P	ZOUPUT	P = Array of initial conjugate momenta of the system in the order: conjugate momenta of φ, θ and R (spherical coordinates) of rotor 1, of rotor 2, and of X, Y, Z (Cartesian coordinates) of relative motion

Table 6 Continuation

Line #	Variable	Location of Write Statement	Description
21	JCAS T R	ZOUPUT	JCAS = variables not used in present version (fixed as 1) T = collision time a.u. R = array of six final internuclear distances (a.u.) R(1) and R(2) are the bond-lengths of rotor 1 and rotor 2 respectively
22	Q	ZOUPUT	Q = array of final Cartesian coordinates of system in a.u. (see line 19 for order)
23	AM(I, 1) I=1, 2, 3 AMS(1) ET(1) EFJ(1)	ZOUPUT (statement 78)	AM, AMS, ET, EFJ are the arrays for the final state corresponding to AN, ANS, AT, JAB for the initial state (see lines 15, 16). EFJ is the array of "apparent rotational quantum numbers" namely $K(J) = \hbar\sqrt{EFJ(J)(EFJ(J)+1)}$ where K is the rotational angular momentum and J is either 1 or 2
24	AM(I, 2) I=1, 2, 3 AMS(2) ET(2) EFJ(2)	ZOUPUT (statement 78)	

Table 6 Continuation

Line #	Variable	Location of Write Statement	Description
25	VR(I , 3) I=1, 2, 3 VRS(3) AM(I , 3) I=1, 2, 3 AMS(3) ET(3) EP(3)	ZOUPUT	VRS, AMS, ET, EP are the arrays for the final state corresponding to URS, ANS, AT, AP for the initial state (see line 17) AM(I, 3) = the X, Y, Z components of the final angular momentum associated with the relative motion. VR(I, 3) are the X, Y, Z components of the final relative velocity (a.u. x 10^2)
26	THATA(1) PHI(1) AM(I, 4) I=1, 2, 3 AMS(4) ETOT	ZOUPUT	THATA(1), PHI(1) are the two scattering angles. THATA(1) defines the angle between the initial and final relative velocity vector. PHI(1) defines the direction of the component of the final relative velocity perpendicular to the initial velocity. AM(I, 4), AMS(4), ETOT are the variables for the final state corresponding to AN(I, 4), ANS(4), ATOT for the initial state (see line 18)
27	DIFF1 DIFF2 DIFF3 DIFF4 DIFF5	MAIN	These variables are used for conservation tests. DIFF1, DIFF2, DIFF3 = The magnitude of the difference between the X, Y and Z components of the initial and final total angular momentum respectively x 10^4 DIFF4 = the magnitude of the difference between the initial and final magnitude of the total

Table 6 Continuation

	Line #	Variable	Location of Write Statement	Description
				angular momentum x 10^4 DIFF5 = magnitude of the difference between the final and initial energy x 10^8
only for trajectories in which back integration is performed	28	T	MAIN (statement 182)	T = time of back integration (a.u.)
	29	Q	"	Q = array of final Cartesian coordinates for back integration (see line 19)
	30*	P	"	P = array of final conjugate momenta for back integration (see line 20)

*lines 1-12 appear once per set of trajectories. All other lines appear once per trajectory.

Cartesian coordinates of the system and PI-- the array of the spherical conjugate momenta for the internal motion and the Cartesian conjugate momenta for the relative motion). The parameters necessary for the Nordsieck integration (DT and ERROR) and the initial intermolecular distance ($\sqrt{\mathrm{RS2}}$) are also defined in ZINIT. As stated above, spherical polar coordinates are used for the internal motion of the rotors in solving the equations of motion. However, for some purposes, the Cartesian coordinates are preferable. This is the reason for defining the array QI above. The internal Cartesian coordinates will also be defined at each integration step.

Finally, the various components of the energy and angular momenta are calculated after a call to subroutines ZVECPR. Upon returning to the main program the subroutine ZOUPUT is called to print the properties of the initial state. At this point the initial state of the collision is completely defined. The solution of the equations of motion follows. At every step of the integration the subroutine ZDIFFE is called. Here the Nordsieck scheme is executed. ZDIFFE calls subroutine ZEVAL. In ZEVAL, the time derivatives of the momenta and coordinates (the array DZ) are defined at every step. These derivatives are obtained through partial derivatives of the Hamiltonian with respect to the coordinates and momenta (see eq. (2)). To get the above derivatives, the value of the potential at each step of the integration is needed. The value of the potential is defined in subroutine ZENERG. ZENERG is called by ZEVAL every integration step. In ZENERG the potential (eq. (1)) is defined in terms of the distances between the four atoms of the system (array R). Although the potential is in terms of the actual interatomic distances, the distance between the repulsion centers on a molecule is not necessarily the bond length of the molecule but is rather an adjustable parameter. In other words, for calculation of the repulsive potential an apparent bond length is introduced. For the O_2 calculations, however, the centers of repulsion were assumed to be at the nuclear sites.

ZENERG defines the potential of interaction and the user may replace ZENERG by another subroutine supplying any potential he chooses as long as it is in terms of the distances between atoms. ZENERG has to supply also the derivative of the potential with respect to the internuclear distances. The subroutine ZEVAL, before calling ZENERG, defines the internuclear distances from the present coordinates of the system.

After ZDIFFE performs an integration step the main program checks if the trajectory has terminated. If not, the integration is continued. If the integration approaches the apparent singularity (eq. (2c)), variable IDUD is set to 0 and the entry ZNITY in subroutine ZINIT is called. There, the rotation defined in section 2.1 is applied.

If the singularity is approached again the trajectory is cancelled. (About 1% of the trajectories had to be cancelled due to either two consecutive approaches to the singularity or any other reason, see below.)

After the integration of the equations of motion is completed, the output quantities are calculated and printed or punched. The final rotational angular momenta are defined in ZVECPR, as were the initial rotational angular momenta. The angles of reorientation of the angular momenta and the rotational phase shifts are defined in the main program.

Every trajectory which was longer than 220000 a.u. (T.GT. 220000) or had more than 1400 steps (IBKIN,GT.1400) is back integrated to ascertain the success of the numerical forward integration. There is an option IDTL (defined in the input list table 4), which allows back integration and detailed print for every trajectory. In the production runs, back integration was performed only for trajectories which obeyed the above restrictions in trajectory time and number of steps. Back integration is performed by setting the time T=0 , reversing the signs of all final momenta and solving the equation of motion through calls to ZDIFFE. The back integration is set to be of the same length of time as the forward integration and it should then terminate at the initial coordinates of the forward integration. The final momenta should be the negative of the initial momenta of the forward integration. After the final coordinates and momenta of the back integration are printed, the calculation of the next trajectory starts through a call to ZINIT for the definition of the initial conditions of the new trajectory and integration of the equations of motion as described for the previous trajectory.

Tables 4 and 6 define the input and the printed output variables. Between them they define most key variables and thus no further list of variables is supplied. In addition, comments in the body of the program listing give further details. Some variables defined in the program are not used in the current version. These were defined for various purposes in the past and were not removed as they might be useful again in the future. Table 4 includes a few such variables marked with an asterisk. All calculations in the program are done in atomic units.

The program output consists of printed and punched portions. The printed output gives details of the initial and final variables of the motion and the integration time. This printed output enables a check of the conservation of the components of the angular momenta as well as energy. In the printed output the coordinates printed are the Cartesian coordinates while the momenta are the spherical polar conjugate momenta for the internal motion and the Cartesian conjugate momenta for the relative motion. In addition, the results of the back integration are printed. A successful integration is determined by proper conservation of the constants of the motion and successful back integration. A successful back integration was taken to mean that no coordinate or momentum, after back integration, differs by more than 2×10^{-2} a.u. from its initial value. Any trajectory which failed in integration was repeated with tighter integration parameters. As mentioned above, about 1% of the trajectories were not accepted due to repeated failures of the integration from any cause. Table 6 describes the printed output.

The punched output (a sample of which is reproduced in table 3) includes the initial and final properties of each collision necessary for the calculation of various properties and cross sections (e.g. Gordon, 1968). The properties included in the punched output are: $W_{VB}(T_1)$ -- defined in section 2.2; $\cos\alpha$ -- the cosine of the angular change in the orientation of the rotational angular momentum vector of a rotor in the collision; K_i -- the initial angular momentum; K_f -- the final angular momentum; $\cos\nu$, $\sin\nu$, $\cos 2\nu$, $\sin 2\nu$, which are the average values of the sine and cosine of the classical rotational phase shift (ν) and of 2ν respectively, and V the relative initial velocity. The cosines and sines of both ν and 2ν are given since the values for these trigonometric functions are averages of two possible values as defined in the end of section 2.1. The averages for 2ν cannot be derived directly from the averages for ν (e.g. $F(\nu) = \cos 2\nu$)

Since there are in the case of O_2-O_2 collisions two identical molecules per collision, each trajectory yields 2 sets of output. These appear in the two consecutive cards (or lines in table 3) with the same value for $W_{VB}(T_1)$. In converting to different temperatures, it is the rotational angular momentum of the perturbing molecule in a set of two colliding molecules which corresponds to $G(J_i T)$ in equation (20).

3. USE OF THE PROGRAM: O_2 CALCULATIONS

The general usefulness of the data derived from the above program for a set of individual trajectories is in the fact that different properties can be calculated after the most complicated and computer-time consuming calculations, (namely the four-body trajectory calculations) are done. Expressions for various cross sections necessary for the elucidation of a number of properties are given by Gordon (1968 and 1967). The expressions in this section (equations (21)-(23)) are also derived in these last references. The calculations performed on the O_2 molecule microwave spectrum are described in the following to demonstrate one use of the data derived from the above program.

The loss tangent can be defined as

$$\tan\delta(\omega) = \frac{4\pi n\omega}{3kT}\, \mathrm{Im}\, \underset{\sim}{d} \cdot (\underset{\approx}{\omega} - \underset{\approx}{\omega}_o - iv\rho\underset{\approx}{g})^{-1} \cdot \underset{\approx}{p} \cdot \underset{\sim}{d} = A \cdot \lambdabar \tag{21}$$

A is the absorption coefficient, $\lambdabar$ is the wavelength/2π , n is the number density of the absorbing molecule, ρ is the number density of the perturbing molecule, k is the Boltzmann constant and $\underset{\approx}{\omega}$ is the angular frequency of the radiation times the unity matrix. T is the absolute temperature, $\underset{\sim}{d}$ is a vector of all the magnetic dipole moment matrix elements, $\underset{\approx}{p}$ is a diagonal matrix of the probabilities of the various molecular states, v is the mean relative velocity and $\underset{\approx}{\sigma}$ is a relaxation matrix to be discussed below. All quantities except for $\underset{\approx}{\sigma}$ are well known. The diagonal elements of $\underset{\approx}{\sigma}$ have the following interpretation:

$$\begin{aligned} -\mathrm{Im}\,\rho v \sigma_{ii} &= \text{line shift} \\ \mathrm{Re}\,\rho v \sigma_{ii} &= \text{line width} \end{aligned} \qquad (22)$$

for line i . For the O_2 microwave spectrum the line shift parameter equals zero as $\underset{\approx}{\sigma}$ is a real matrix. One can express $\underset{\approx}{\sigma}$ as

$$\underset{\approx}{\sigma} = \bar{v}^{-1} \int_0^\infty 2\pi B\,dB < v(\underset{\approx}{1} - \underset{\approx}{S}) > \qquad (23)$$

where B is the impact parameter; v is the relative velocity; $\bar{v}$ is the mean relative velocity; $\underset{\approx}{S}$ is a collisional transfer matrix for a single collision; and the brackets indicate average overall collisions with the same impact parameter.

A matrix element of the $\underset{\approx}{S}$ matrix S_{ij} defines the amplitude transferred from spectral line j to spectral line i in a collision. (See Gordon, 1967, for the derivation and definition of the $\underset{\approx}{S}$ matrix. Note, however, that the above $\underset{\approx}{S}$ matrix does not define transitions between states as does the familiar scattering matrix.) The microwave spectrum of O_2 in the frequency region discussed below is a multiplet spectrum, and thus every line arises from transitions between states, both with the same molecular rotational quantum number. Hence, each line can be assigned to a rotational level. The elements of the $\underset{\approx}{S}$ matrix will be, therefore, a product of the probability of transition between the initial and final rotational level and another term defining the probability of transition between the various multiplet lines corresponding to each rotational level (Gordon, 1967). If we define f(V, B, J) in equation (20) to be $\delta_{ij} - S_{ij}$, equation (23) can be solved using equation (20) and the calculated set of trajectories (the trajectories are completed as defined in section 2.1). A submatrix of $\underset{\approx}{1} - \underset{\approx}{S}$ corresponding to the lines belonging to one rotational level of O_2 is reproduced in table 1 from Gordon (1967). The variable P_{fi} in table 1 is defined as probability of transfer in a particular collision from the initial rotational level i to some final rotational level f and α is defined as the angle of reorientation of the rotational angular momentum in a collision.

The final rotational angular momenta are not quantized due to the use of a classical scattering scheme. The scattering program described above does not quantize the final rotational angular momenta. For the sake of completeness the quantization procedure used for the O_2 calculations will now be described briefly.

The final apparent quantum number J is defined through the relation

$$K_f = \hbar\sqrt{J(J+1)}$$

where K_f is the actual final rotational angular momentum. Only odd rotational quantum numbers are allowed for O_2, making the difference between the quantum numbers of neighboring levels 2. After the collision, the molecule is assumed to have some probability of being in either of the two rotational levels with quantum numbers closest to J but not in any other rotational level. The probability of the molecule being after a collision in one of these two rotational levels with quantum number J_f is taken as

$$P_{fi} = 1 - \frac{\Delta J}{2} \qquad (24)$$

where ΔJ is the difference between J and J_f. Thus, equation (24) defines the variable P_{fi} above. P_{fi} is zero for all levels but the two with quantum numbers closest to J. The index i in P_{fi} refers to the initial rotational level in the collision which is well defined by the sampling procedure (see section 2.2).

A detailed discussion of the O_2 microwave computations and the comparison of experimental results to calculations are given by Mingelgrin (1972). Note that there are no adjustable parameters in this theory and that the potential parameters are derived from independent data (see section 2.1).

Some results[2] are given in figures 1-4 and tables 7 and 8. Table 7 gives the calculated line width parameters for the different lines and compares them to experimental results. There are two absorption lines, designated J+ and J- , per rotational level. The wide variation in the experimental results makes the comparison with them difficult. This points out the need for further study of the O_2 spectrum at low densities. Since the scattering calculations reported here are classical, the line width parameters for the lowest rotational level should have the largest error.

---

[2] A set of programs developed by R. G. Gordon's group at Harvard University designed to evaluate expressions of the form of equation (21) from results of scattering calculations, such as described above, was used to derive the following results.

TABLE 7

The Line Widths of the Pure O_2 Microwave Spectrum

(Temperature 298° - 300° K)

Lines (J±)	Half Width (MHz/mmHg)					
	This Work	B, A, S&G[d]	Z&M[a]	A, S&G[b]	A&G[e]	H&G[c]
1+	2.38			1.96	2.20	
1-	2.38					1.97
3+	2.36		1.96	1.71	2.23	2.07
3-	2.36	2.09	1.96	1.92		
5+	2.06		1.56		1.96	1.80
5-	2.06		1.60	1.86	1.99	
7+	2.11		1.68	2.05	1.92	
7-	2.11		1.70		1.82	2.01
9+	1.96		1.42		1.93	
9-	1.96		1.64	1.97	2.00	1.94
11+	1.96		1.60	1.97		
11-	1.96				1.97	
13+	1.92	0.87	1.54			
13-	1.92			1.88	1.86	
15+	1.72			1.77		
15-	1.72				1.99	
17+	1.74		1.50			
17-	1.74			1.76	1.82	
19+	1.59			1.58		
19-	1.59			1.62	1.91	
21+	1.61					
21-	1.61	0.83		1.26		
23+	1.53			1.26		
23-	1.53			1.49		

[a] R. W. Zimmerer and M. Mizushima, Phys. Rev. 121, 151 (1961).

[b] R. S. Anderson, W. V. Smith, W. Gordy, Phys. Rev. 87, 561 (1952).

[c] R. M. Hill and W. Gordy, Phys. Rev. 93, 1019 (1954).

[d] J. H. Burkhalter, R. S. Anderson, W. V. Smith, W. Gordy, Phys. Rev. 79, 651 (1950).

[e] J. O. Artman, *Absorption of Microwaves by Oxygen in the Millimeter Wavelength Region* (Columbia Radiation Laboratory, 1963); J. O. Artman and J. P. Gordon, Phys. Rev. 96, 1237 (1954).

TABLE 8

Selected Values for the Pure O_2 Absorption Coefficient at 298°K about the O_2 9+ line (db/km)

Density (torr) / Frequency (GHz)	1	5	10	20	40	100	150	200	304	450	620	760
60.6506	.00134	.0332	.132	.518	1.94	8.63	14.49	19.92	30.12	43.16	57.13	67.80
60.7506	.000895	.0222	.0887	.352	1.36	7.04	12.91	18.63	29.36	42.69	56.71	67.35
60.8506	.000871	.0216	.0863	.342	1.32	6.83	12.54	18.16	28.84	42.22	56.24	66.84
60.9506	.00129	.0319	.127	.497	1.84	7.97	13.30	18.42	28.56	41.77	55.72	66.26
61.0506	.00402	.0990	.386	1.40	4.12	10.46	14.66	18.98	28.37	41.33	55.18	65.64
61.1506	9.35	9.36	9.38	9.48	9.83	12.19	15.32	19.16	28.14	40.90	54.61	64.97

In figure 1, some experimental and calculated spectra are compared. Maryott and Birnbaum (1960) pointed out the problems associated with fitting a theoretical line shape generated by addition of Lorentzian lines with empirical parameters to higher pressure data (approximately 10 atmospheres and up). Despite the fact that no parameters were adjusted to fit the data, figure 1 demonstrates the good fit achieved by the present computations. This fit of calculation to experiment improves with decreasing pressure.

Figure 2 compares calculations to experimental determinations of the O_2 absorption in an O_2-Ar mixture. Here we have to calculate two kinds of interactions, O_2-O_2 and O_2-Ar . The O_2-Ar collisions were determined by an available rigid rotor-sphere scattering program. The O_2-Ar calculations are described by Mingelgrin (1972). The O_2-O_2 were determined with the help of the present program. The O_2-Ar calculations, although not completely derived by the program described above, were introduced to demonstrate the possibility of extending the calculations to gas mixtures such as the atmosphere. O_2-N_2 and other O_2-diatomic calculations can be made with the present program after very minor modifications. Then, cross sections for the O_2 microwave spectrum in gas mixtures can be derived.

The scattering calculations (equation (21)), using a complete relaxation matrix, introduce "interference" between lines. Namely, at densities where the individual lines overlap, the total line is narrower than predicted from Lorentzian lines addition. This "interference" should increase with pressure. Thus, the scattering calculations should give higher attenuation at the center of the band (~ 60 GHz) and lower attenuation at the wings. At low densities, where the individual lines are resolved, the two procedures should be equivalent. The equivalence of the two procedures at the low densities where the lines are resolved arises from the fact that the off diagonal elements in the $\underset{\approx}{g}$ matrix approach zero and equation (21) becomes equivalent to addition of Lorentzian lines.

Figures 3 and 4 compare results of the present calculations for the pure O_2 spectrum to results of addition of Lorentzian lines with the same line width parameters. The linear addition spectrum was computed by W. M. Welch, I. T. S. The densities are all in the range of densities existing in the atmosphere. It is evident that there is a significant difference between the two calculations. This difference is gradually declining as the pressure declines and the spectrum approaches the resolved O_2 spectrum. In figure 4 a comparison between the present calculations and addition of Lorentzian lines at .13 Atmospheres (100 torr) and 298° K is given. Even at this density the

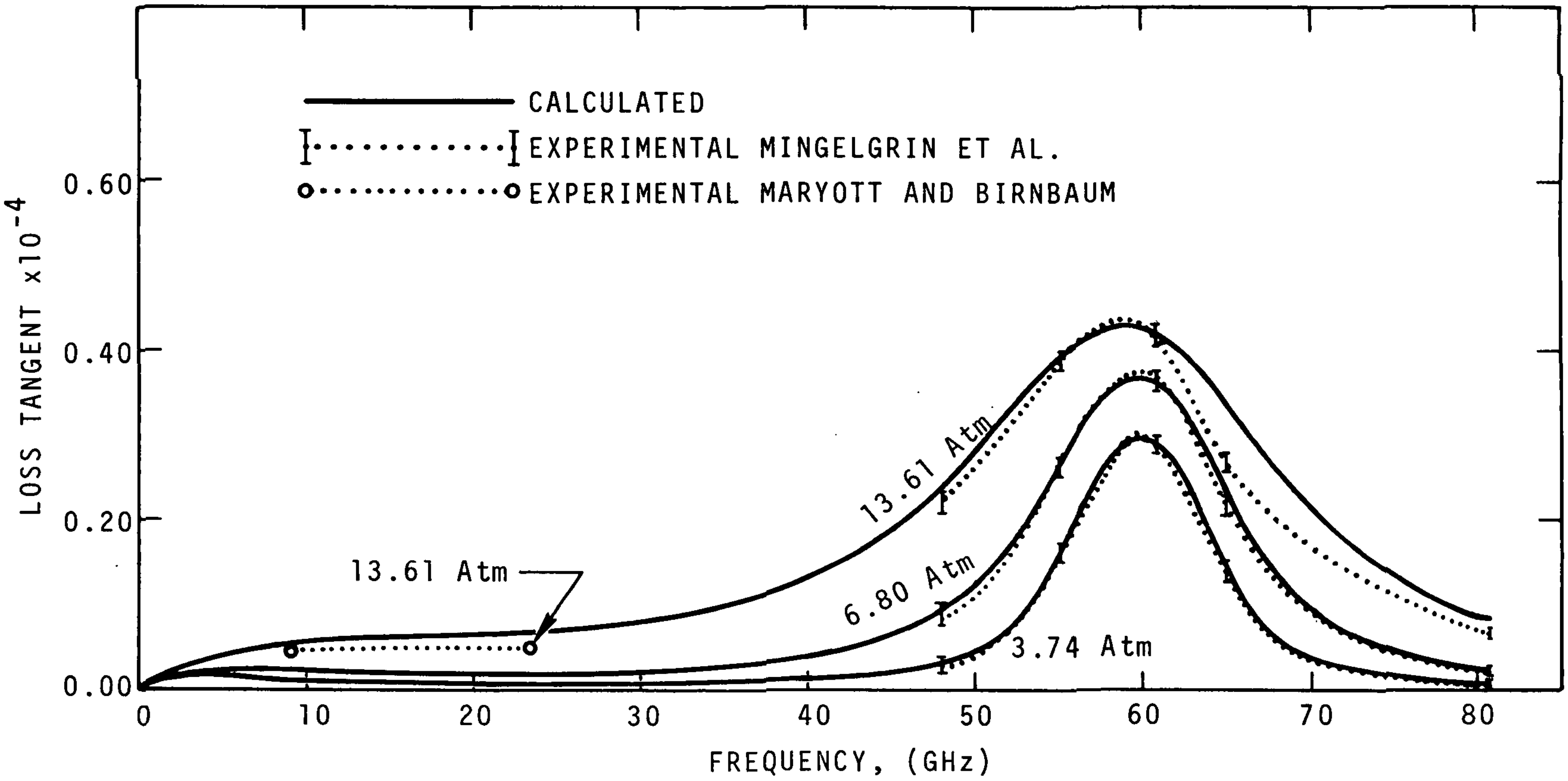

FIG. 1: EXPERIMENTAL VS. THEORETICAL LINE SHAPE OF PURE O_2 SPECTRUM. (298°K). I IS THE ACTUAL RANGE OF EXPERIMENTAL DETERMINATIONS, 7 DETERMINATIONS PER FREQUENCY-PRESSURE POINT

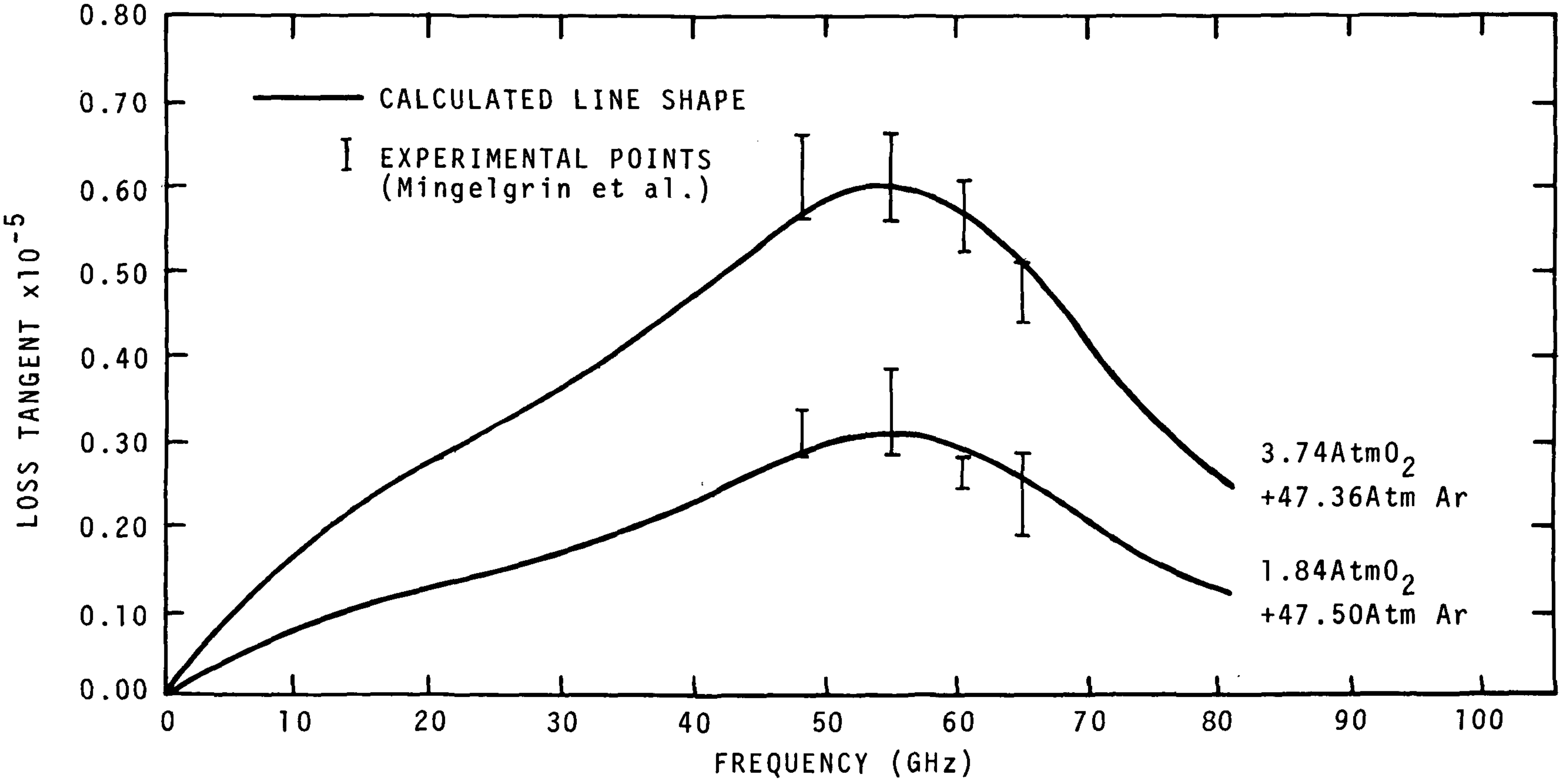

FIG. 2: EXP. VS. CALCULATED O_2 SPECTRUM IN O_2-Ar MIXTURES (298°K)
I IS THE ACTUAL RANGE OF EXPERIMENTAL DETERMINATIONS,
7 DETERMINATIONS PER FREQUENCY-PRESSURE POINTS.

two calculations differ. However, the difference is much smaller, as expected, than the difference at the higher pressures (see figure 3). Figure 4 demonstrates another fact of importance for applications. At densities where the spikes of the different lines are still prominent, the two calculations do not differ by a similar amount at neighboring frequencies. In general, the difference is larger at the peaks of the lines and the troughs between the lines and smaller in the intermediate frequencies.

The fit to experiment demonstrated in figure 1, especially at the lower density (3.74 Atmospheres), and the difference between the two methods of calculation described in figure 3 demonstrate the need for this more complex procedure for the purpose of determination of the O_2 spectrum in the atmosphere in accuracies sufficient for practical applications. One has to await experimental results for pure O_2 spectra in the pressure range of interest to unequivocally state that the scattering calculations represented in figure 3 give the good fit presumed. (Such measurements are presently being undertaken by the millimeter wave transmission spectroscopy section of ITS.) However, the fit in figure 1 and its improvement with decreased pressure suggest that the procedure does yield accurate spectra in the atmospheric pressure range.

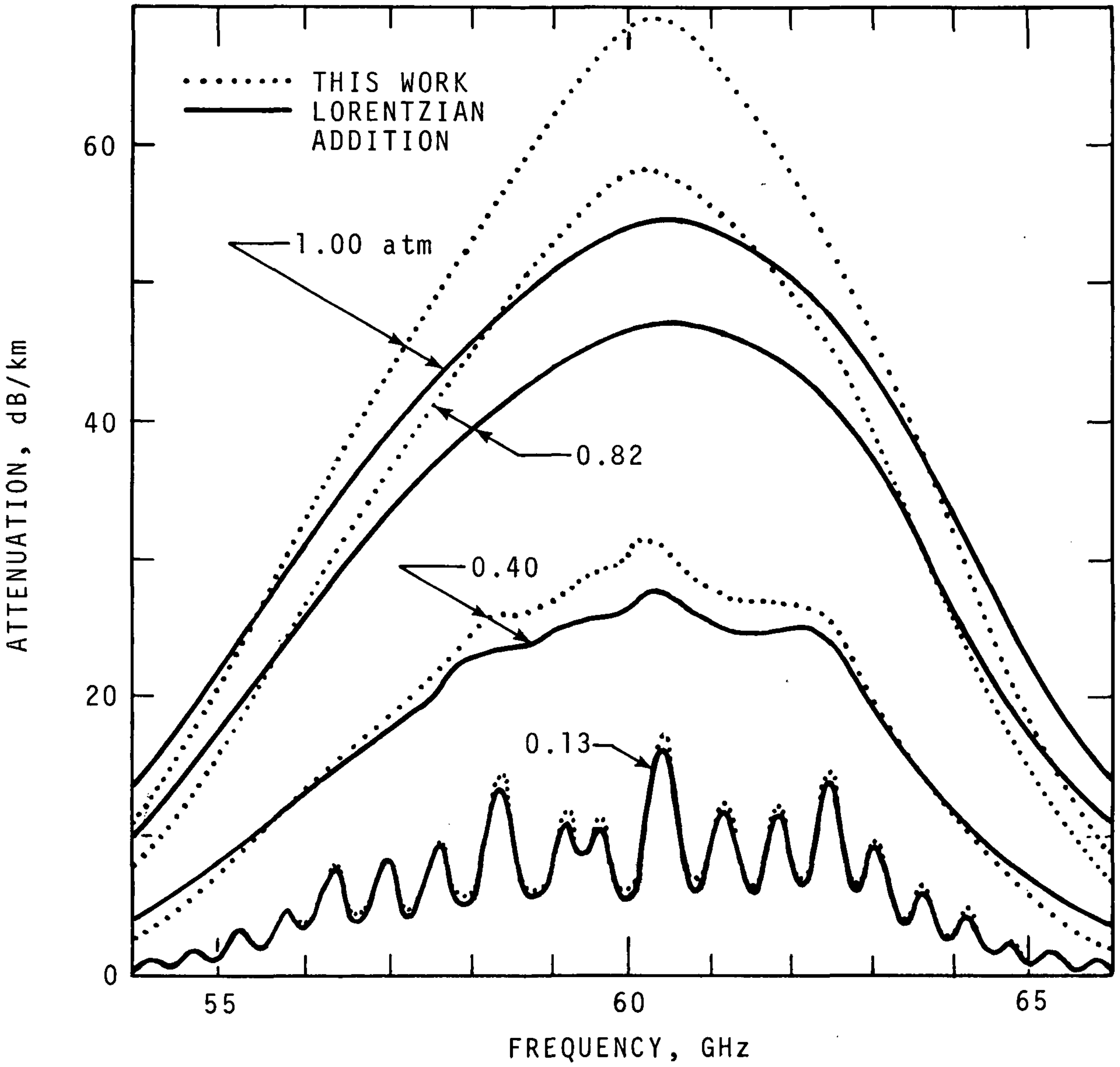

FIG. 3: COMPARISON OF COMPUTATIONS-SCATTERING CALCULATIONS VS. ADDITION OF LORENTZIAN LINES. (PURE O_2 AT 298°K)

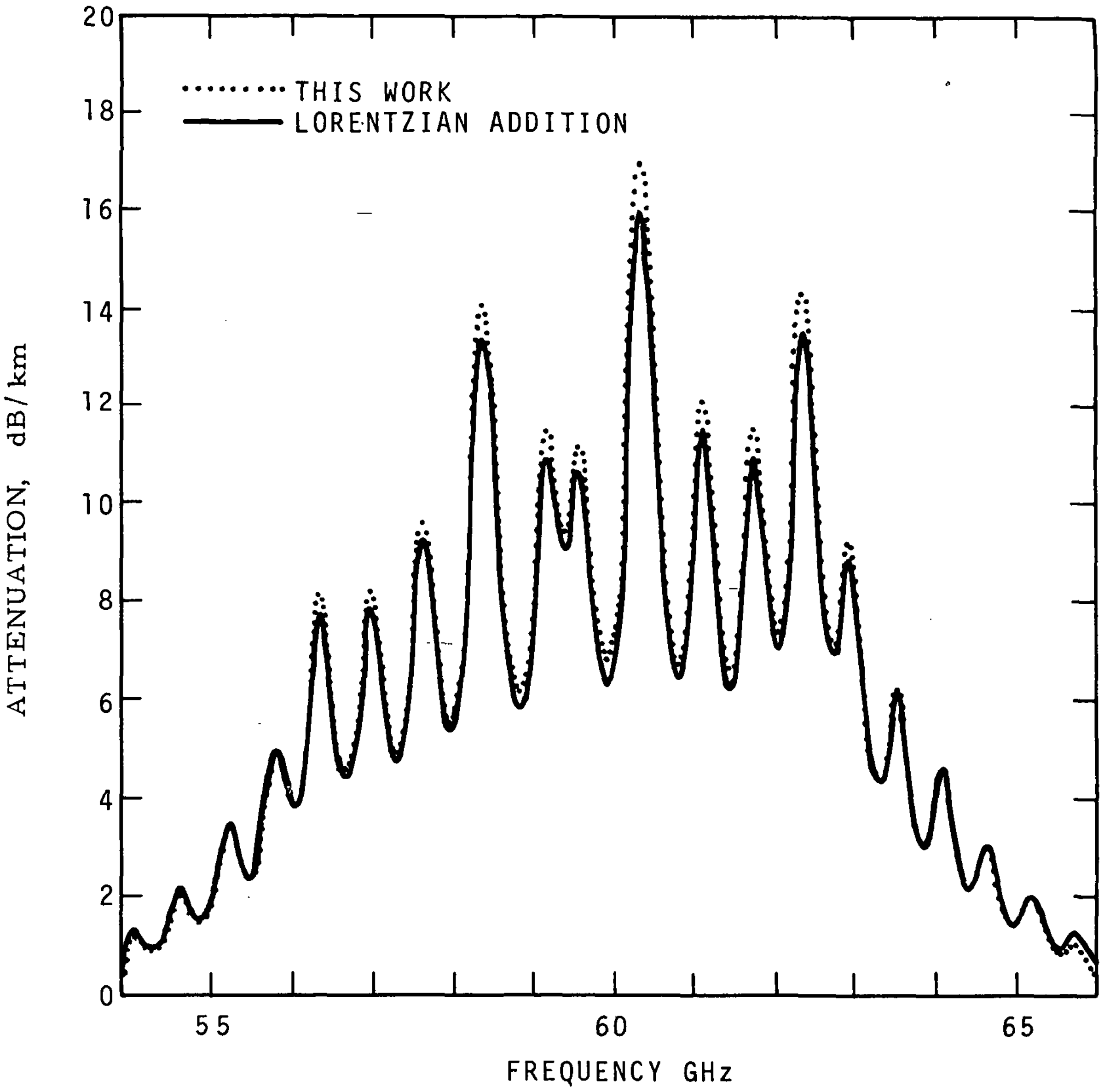

FIG. 4: SCATTERING VS. LORENTZIAN LINES ADDITION CALCULATIONS (PURE O_2 AT 298°K AND 0.13 atm)

It may seem that the equivalent of the scattering procedure can be achieved by adding Lorentzians with pressure dependent shift and width parameters. This is exactly so, except that the procedure described here does not rely on an empirical fit. As such, the method is universal and enables calculations of complete frequency or density profiles. Empirical fit of pressure dependent width and shift parameters will depend on the accuracy of available measurements and will be applicable only to a small range of conditions as determined by the experimental points to which the parameters are fitted.

Finally, the dispersion spectrum of O_2 at the microwave region can be easily computed using the same information and programs used for computation of the absorption spectrum. The real part of the refractive index at frequency ω $(n(\omega))$ can be obtained from the relation

$$n(\omega) - n(o) = \frac{-2\pi n\omega}{3kT} \, \mathrm{Re} \, \underset{\sim}{d}(\underset{\approx}{\omega} - \underset{\approx}{\omega}_o - iv\rho\underset{\approx}{\sigma})^{-1} \; \underset{\approx}{P} \; \underset{\sim}{d} \tag{25}$$

where all symbols have the same meaning as in equation (21). Equation (25) is discussed more fully in a forthcoming paper by the author. This equation may not apply at sufficiently high density, but it certainly holds for all pressures around and below 1 Atmosphere at 298°K. Some results of dispersion calculations are given in figures 5 and 6.

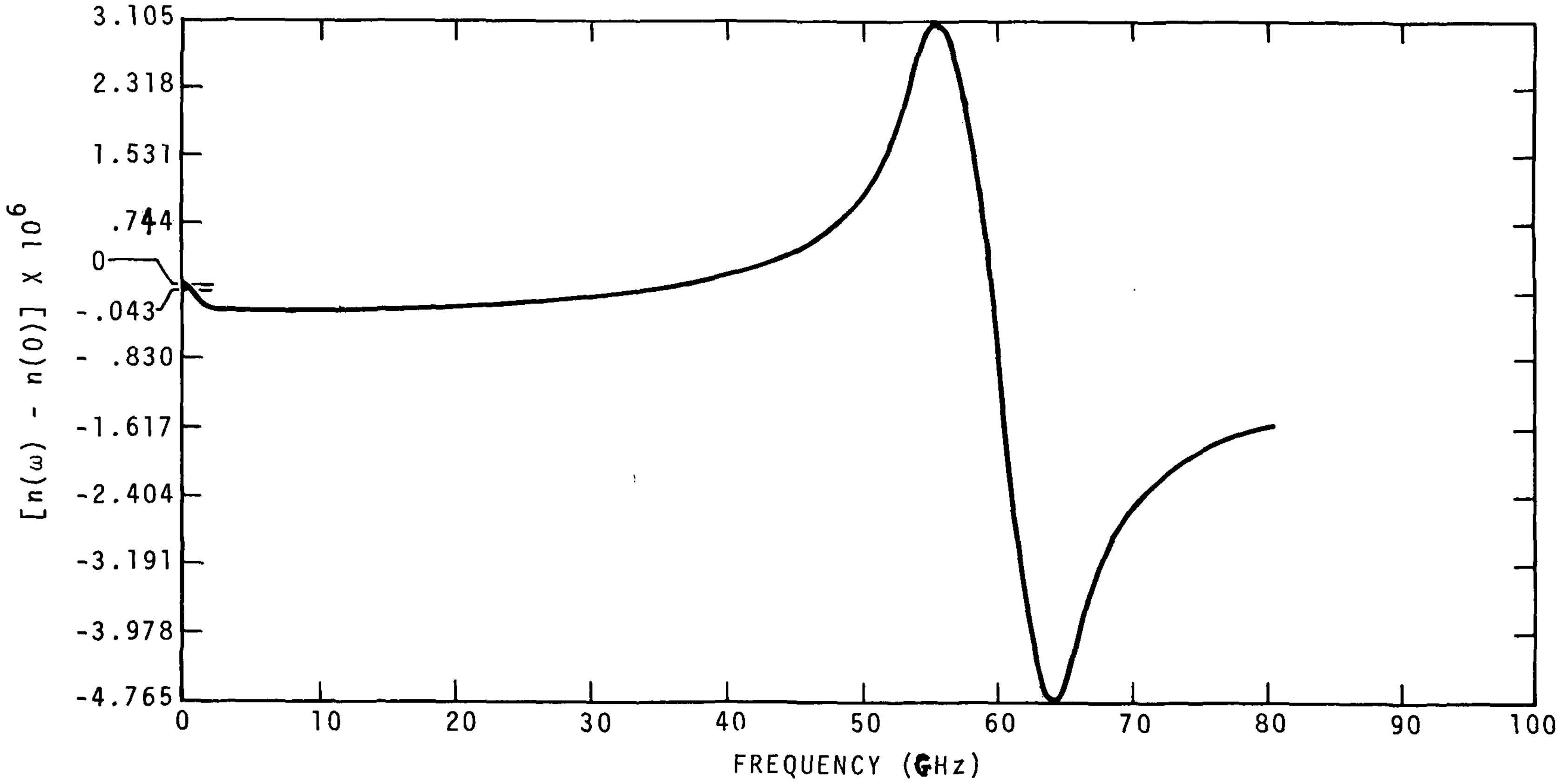

FIG. 5: THE CALCULATED DISPERSION SPECTRUM OF O_2 UP TO 80 GHz AT 1 Atm AND 298°K. ($n(\omega) - n(0)$, WHERE $n(\omega)$ IS THE REAL PART OF THE REFRACTIVE INDEX AT FREQUENCY ω.)

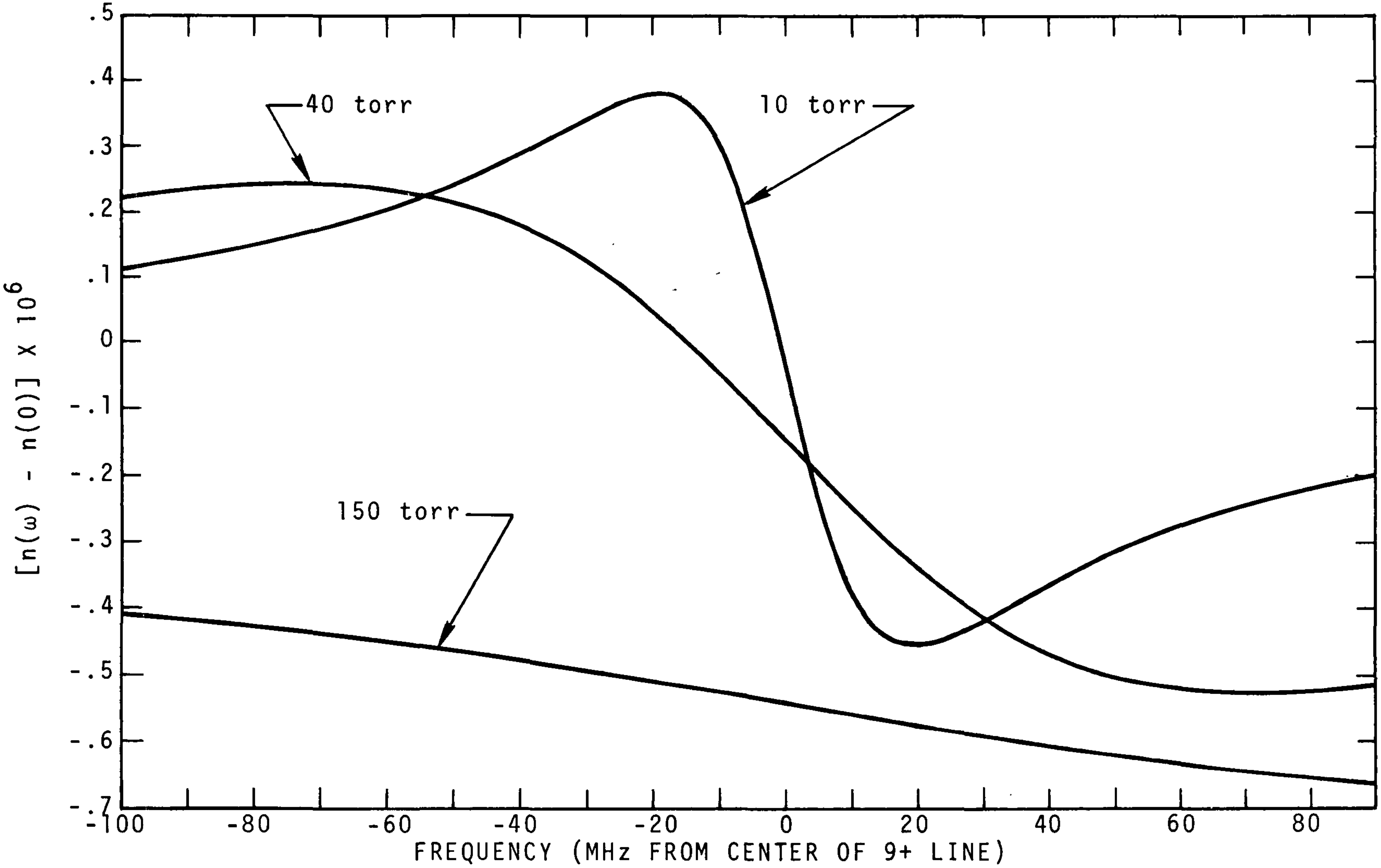

FIG. 6: THE CALCULATED DISPERSION SPECTRUM OF O_2 ABOUT THE 9+ LINE AT VARIOUS DENSITIES AT 298°K. ($n(\omega) - n(0)$, WHERE $n(\omega)$ IS THE REAL PART OF THE REFRACTIVE INDEX **AT** FREQUENCY ω.)

Zeeman splitting was neglected in all the computations. This, however, will affect the calculations at 298°K and pressures above 5 torr only negligibly for magnetic field strengths below or around .5 Gauss which is approximately the strength of the earth's magnetic field (Liebe and Welch, 1972).

4. ACKNOWLEDGMENTS

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