

Hansen Laboratory of Physics Report No. 1812, Stanford University, 1969 (unpublished); and G. A. Massey and A. E. Siegman, *IEEE J. Quantum Electron.* **QE-6**, 500 (1970).

<sup>4</sup>T. S. Moss, G. J. Burrell, and A. Hetherington, *Proc. Roy. Soc. (London)* **A308**, 125 (1968).

<sup>5</sup>Most of the historic experiments are cited in the papers of P. Zeeman, e.g., P. Zeeman, *Proc. Roy. Acad. Sci. Amsterdam* **17**, 445 (1914); P. Zeeman, *Nature* **113**, 838 (1924).

<sup>6</sup>C. Møller, *Nuovo Cimento Suppl.* **6**, 381 (1957).

<sup>7</sup>J. L. Anderson, *Principles of Relativity Physics* (Academic, New York, 1967), p. 189.

<sup>8</sup>E. J. Post, *Rev. Mod. Phys.* **39**, 475 (1967); E. O. Schultz-DuBois, *IEEE J. Quantum Electron.* **QE-2**, 299 (1966).

<sup>9</sup>A coordinate system fixed with the nonrotating earth

is, of course, not an inertial system either. Taking the next step by inclusion of the orbiting earth, we expect a diurnal peak-to-peak modulation of  $\Delta f_R$  of 0.13 Hz in the setup presented.

<sup>10</sup>A. T. Zavodny, thesis (Oklahoma State University, 1970) (unpublished).

<sup>11</sup>W. W. Rigrod, *Bell System Tech. J.* **44**, 907 (1965).

<sup>12</sup>M. Born and E. Wolf, *Principles of Optics*, 2nd ed., (Pergamon, New York, 1964) Sec. 1.6.5.

<sup>13</sup>It may also be noted that the dispersion term in gases at  $0.63 \mu$  is a very small fraction of the drag coefficient. For comparison,  $(\lambda/n)(dn/d\lambda)[1 - (1/n^2) - (\lambda/n)(dn/d\lambda)]^{-1} = 0.0006, 0.0013, 0.025, 0.065$  in He, N<sub>2</sub>, SiO<sub>2</sub> (silica), CCl<sub>4</sub>, respectively.

<sup>14</sup>In the fitting process, equal weight is given to all data points, and the  $f_m$  data are treated as exact, since the errors in  $\Delta f_B$  are usually large compared to  $\delta f_m$ .

## Pressure Broadening of the O<sub>2</sub> Microwave Spectrum

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A general expression for the calculation of pressure broadening for vibrational-rotational lines is derived in the strong-collision model. Classical trajectories and a peaking approximation are used to calculate a unitary scattering operator avoiding perturbation expansions, impact-parameter cutoffs, and straight paths. The latter approximations are not expected to be good when short-range potentials dominate the collision interaction. Use of intermolecular-potential parameters determined from thermodynamics and a simple theory of dispersion forces for O<sub>2</sub> calculations gave excellent agreement with experimental data on the magnitude, temperature, and quantum-number dependence of the linewidth parameter.

In an earlier paper,<sup>1</sup> hereafter referred to as I, a theory for pressure broadening in a strong-collision model was developed. General formalisms<sup>2,3</sup> give expressions for the width and shift in terms of matrix elements of the scattering operator for binary collisions integrated over the impact parameter. The scattering operator, a time-ordered exponential of a phase integral for the interaction potential, is generally evaluated in a perturbation expansion. The justification for this procedure is that the main contribution to the integral over impact parameter occurs when the phase integral is smaller than unity. The same arguments are used to justify straight-path trajectories and hard-sphere impact-parameter cutoffs for evaluation of the phase integral. However, for collisions between neutral atoms or molecules it frequently happens that a large contribution to the integral over impact parameter occurs when the phase integral is on the order of, or larger than unity. In such a case, the integral over impact parameter from zero to the hard-sphere cutoff (extrapolation formulas are used for S-matrix elements) are comparable to or even larger than the integral over

large impact parameters where the perturbation expansion and straight-path approximation are valid. In this paper the scattering operator is calculated to all orders and the phase integral is evaluated using curved trajectories determined by a Lennard-Jones (LJ) potential; avoiding any hard-sphere cutoffs or arbitrary extrapolation formulas. This procedure is described for general vibrational-rotational lines with the microwave spectrum of O<sub>2</sub> presented as an example. Oxygen is a good candidate for testing the theory; it is a nonpolar molecule with a very short interaction range; a large body of experimental line shape data exists; and the intermolecular potential has been partially determined by thermodynamic measurements. While many of the approximations used in this calculation are very well suited to oxygen, all of them are generally applicable to any pressure broadening process where strong collisions dominate.

### I. LINE SHAPE

The spectral distribution of power emitted or absorbed by a gas,  $P(\omega)$  is given as

$$P(\omega) = NF(\omega)(4\omega^4/3c^3), \quad (1)$$

where  $N$  is the number of radiators in the gas and  $F(\omega)$  is a quantity called the spectrum or line shape. Under the impact approximation the spectrum is<sup>2</sup>

$$F(\omega) = (-1/\pi) \text{Im Tr} [\vec{d}(\omega - L_0 + i\Lambda)^{-1} \rho \vec{d}], \quad (2)$$

where the trace is taken over the unperturbed internal states of the radiator. The operator  $\vec{d}$  is just the radiators' dipole moment,  $\rho$  is the density operator for the radiators' internal states, and  $L_0$  is the Liouville operator which is diagonal on the unperturbed internal states with eigenvalues corresponding to transition frequencies. The relaxation operator  $\Lambda$  is not in general diagonal and, when two or more transitions occur with frequency separations on the order of their half-widths, the contribution of off diagonal elements of  $\Lambda$  to the spectrum can become significant. Baranger has shown<sup>3</sup> that if the intermolecular potential is ro-

tationally invariant (i. e., no external fields) the equation for the spectrum is considerably simplified. The degenerate  $m$  dependence is accounted for and the spectrum is given by a trace over an  $m$  independent or "reduced" line space

$$F(\omega) = (-1/\pi) \text{Im Tr} [d^2(\omega - l_0 + i\lambda)^{-1} \rho]. \quad (3)$$

In the classical-path approximation, matrix elements of  $\lambda$  are obtained by averaging over the impact parameter  $b$  and the velocity  $v$ :

$$\lambda = \int_0^\infty nvf(v)\lambda'(v)dv, \quad (4a)$$

$$\lambda'(v) = 2\pi \int_0^\infty b\lambda''(b,v)db, \quad (4b)$$

where  $n$  is the perturber density and  $f(v)$  is Maxwellian velocity distribution. The matrix elements of  $\lambda''(b,v)$  in the reduced-line space of symmetric rotors are given by

$$\begin{aligned} & \langle (aJ_a K_a, \alpha J_\alpha K_\alpha | | \lambda'' | | bJ_b K_b, \beta J_\beta K_\beta) \rangle \\ &= \delta_{J_a J_b} \delta_{J_\alpha J_\beta} \delta_{K_a K_b} \delta_{K_\alpha K_\beta} - \sum_{\substack{\mu M_a M_b \\ M_\alpha M_\beta}} (-1)^{J_a + J_b - M_a - M_b} \begin{pmatrix} J_a & 1 & J_\alpha \\ -M_a & \mu & M_\alpha \end{pmatrix} \begin{pmatrix} J_b & 1 & J_\beta \\ -M_b & \mu & M_\beta \end{pmatrix} \\ & \times \langle aJ_a K_a M_a | S | bJ_b K_b M_b \rangle \langle \alpha J_\alpha K_\alpha M_\alpha | S | \beta J_\beta K_\beta M_\beta \rangle^*, \quad (5) \end{aligned}$$

where  $a, b, \alpha,$  and  $\beta$  denote sets of other quantum numbers (i. e., vibration, other angular momenta). A general form for the intermolecular potential which is a good approximation for many molecular collisions is

$$V = (\eta'_0 + \hat{\eta}_0) V_0(r) + \eta'_1 V_1(r) \hat{f}(\chi, \theta, \varphi), \quad (6)$$

where  $r$  is the magnitude of the intermolecular separation and  $\chi, \theta, \varphi$  are the Euler angles which orient the radiator with respect to the perturber. The terms  $\eta'_0, \eta'_1, V_0(r),$  and  $V_1(r)$  are scalars while  $\hat{f}(\chi, \theta, \varphi)$  operates only on rotational states and  $\hat{\eta}_0$  operates on vibrational states. We use a classical path approximation with perturber trajectories determined by the central potential,  $\eta'_0 V_0(r)$  which gives rise to scattering in a plane; thus  $\chi$  and  $\varphi$  are unchanged by the collision.

In Paper I it was shown how the unitarity (exponential form) of the scattering operator can be retained by introducing a projection operator  $\mathcal{P}$  and a strong-collision "peaking" approximation. The projection operator will only couple states for which the frequency corresponding to their energy separations is much less than the inverse of the collision duration time. In most cases this has the effect of "diagonalizing" the scattering operator on vibrational states and matrix elements of exponential terms are simply calculated as the exponential of

matrix elements. The "peaking" approximation replaces the time-dependent  $\theta$  by a constant  $\theta_0$  which can be chosen to retain the correct value for the phase integral. This eliminates time-ordering restrictions and leaves a simple form for the scattering operator which can be expanded as a series of rotation matrix elements,

$$\begin{aligned} S &= \exp \{ -i [K_0 \mathcal{P} \hat{\eta}_0 + K_1 \eta'_1 \mathcal{P} \hat{f}(\chi_0, \theta_0, \varphi_0)] \} \\ &= \exp [ -i K_0 \langle \mathcal{V} | \hat{\eta}_0 | \mathcal{V} \rangle ] \sum_{JKN} \tau_{KN}^J \hat{\mathcal{D}}_{KN}^J(\chi_0, \theta_0, \varphi_0) \\ &= S^{\mathcal{V}} \sum_{JNKM} \tau_{KN}^J \hat{\mathcal{D}}_{KM}^J(\chi_N, \theta_N, \varphi_N) \mathcal{D}_{MN}^J(\chi_b, \theta_b, \varphi_b), \quad (7) \end{aligned}$$

where the vibrational contribution is treated as diagonalized by  $\mathcal{P}$ . The rotation from molecule-fixed to space-fixed axes explicitly displays the terms which depend on the angles of molecular orientation,  $\chi_N, \theta_N, \varphi_N$  and so operate on rotational states, and scalar terms which depend on collision variables,  $\chi_b, \theta_b, \varphi_b$ . The constants  $K_0$  and  $K_1$  are integrals of  $V_0$  and  $V_1$  over classical trajectories. The angles  $\chi_b, \varphi_b$  are not affected by a collision in a central field, while  $\theta_b$  is the polar angle at closest approach in a coordinate system where the impact axis is parallel to the figure axis. The calculation of  $K_0, K_1,$  and  $\theta_b$  as functions of  $b, v$  is a simple application of classical orbit relations which were

discussed in Paper I. The expansion above is a very general result which will be evaluated on symmetric rotor basis functions to obtain a general expression for the relaxation matrix. Reduction of the general expression for simpler specific cases will be demonstrated later. Matrix elements of the scattering operator can be written in the form

$$\begin{aligned} & \langle aJ_a K_a M_a | S | bJ_b K_b M_b \rangle \\ &= \sum_{J_1 M_1} (-1)^{M_a} \begin{pmatrix} J_a & J_1 & J_b \\ -M_a & M_1 & M_b \end{pmatrix} \\ & \times \sum_{N_1 K_1} \mathfrak{D}_{M_1 N_1}^{J_1}(\chi_b, \theta_b, \varphi_b) S_{K_1 N_1}^{J_1, \nu a}(aJ_a K_a, bJ_b K_b), \end{aligned} \quad (8)$$

where

$$\begin{aligned} & S_{K_1 N_1}^{J_1, \nu a}(aJ_a K_a, bJ_b K_b) \\ &= (-1)^{K_a} [(2J_a + 1)(2J_b + 1)]^{1/2} \begin{pmatrix} J_a & J_1 & J_b \\ -K_a & K_1 & K_b \end{pmatrix} \end{aligned}$$

$$\begin{aligned} & ((aJ_a K_a, \alpha J_a K_\alpha | | \lambda' | | bJ_b K_b, \beta J_b K_\beta)) = \delta_{J_a J_b} \delta_{J_\alpha J_\beta} \delta_{K_a K_b} \delta_{K_\alpha K_\beta} + (-1)^{J_a + J_b} \sum_{J_1} \frac{(-1)^{J_1}}{(2J_1 + 1)} \begin{Bmatrix} J_a & J_\alpha & 1 \\ J_\beta & J_b & J_1 \end{Bmatrix} \\ & \times \sum_{\substack{M_1 N_1 K_1 \\ N_2 K_2}} \mathfrak{D}_{M_1 N_1}^{J_1*}(\chi_b, \theta_b, \varphi_b) \mathfrak{D}_{M_1 N_1}^{J_1}(\chi_b, \theta_b, \varphi_b) S_{K_1 N_1}^{J_1, \nu a}(aJ_a K_a, bJ_b K_b) S_{K_2 N_2}^{J_1, \nu \alpha*}(\alpha J_\alpha K_\alpha, \beta J_\beta K_\beta). \end{aligned} \quad (11)$$

In most cases the intermolecular potential only depends on two angles  $\theta$ ,  $\varphi$ , and the expansion of the scattering operator can be made with a  $\delta_{N_0}$  and for some important cases (linear molecules and nonpolar perturbers) the potential depends only on the polar angle  $\theta$  and the expansion can be made with  $\delta_{K_0} \delta_{N_0}$ . These  $\delta$  functions can be introduced directly giving rise to the following sequence of simplifications in the general result:

$$\begin{aligned} & \sum_{\substack{M_1 N_1 K_1 \\ N_2 K_2}} \mathfrak{D}_{M_1 N_1}^{J_1*}(\chi_b, \theta_b, \varphi_b) \mathfrak{D}_{M_1 N_1}^{J_1}(\chi_b, \theta_b, \varphi_b) S_{K_1 N_1}^{J_1, \nu a}(\alpha J_a K_a, bJ_b K_b) S_{K_2 N_2}^{J_1, \nu \alpha*}(\alpha J_\alpha K_\alpha, \beta J_\beta K_\beta) \\ & \xrightarrow{\delta_{N_0}} \sum_{K_1 K_2} S_{K_1 0}^{J_1, \nu a}(aJ_a K_a, bJ_b K_b) S_{K_2 0}^{J_1, \nu \alpha*}(\alpha J_\alpha K_\alpha, \beta J_\beta K_\beta) \\ & \xrightarrow{\delta_{K_0}} S_{00}^{J_1, \nu a}(aJ_a K_a, bJ_b K_b) S_{00}^{J_1, \nu \alpha*}(\alpha J_\alpha K_\alpha, \beta J_\beta K_\beta). \end{aligned} \quad (12)$$

For linear molecules a simplification occurs in Eq. (9), when  $K_a$  and  $K_b$  are set to zero,

$$\begin{aligned} & S_{K_1 N_1}^{J_1, \nu a}(aJ_a, bJ_b) \\ &= 4\pi S^{\nu a} \begin{pmatrix} J_a & J_1 & J_b \\ 0 & 0 & 0 \end{pmatrix} \langle aJ_a | | \mathfrak{D}^{J_1} | | bJ_b \rangle \tau_{0N_1}^{J_1} \delta_{K_1 0}, \end{aligned} \quad (13)$$

where linear rotor basis states are implied. In general, the expansion coefficients are calculated from the orthogonality relation for rotation matrix

$$\times S^{\nu a} \langle aJ_a | | \mathfrak{D}^{J_1} | | bJ_b \rangle \tau_{K_1 N_1}^{J_1}. \quad (9)$$

The reduced matrix element,  $\langle aJ_a | | \mathfrak{D}^{J_1} | | bJ_b \rangle$  does not depend on  $M$ 's or  $K$ 's and mainly serves the purpose of allowing for coupled representations. Substituting this form into Eq. (5), noting that  $S_{K_1 N_1}^{J_1, \nu a}$  does not depend on  $M_a$  or  $M_b$  and using the following identity,

$$\begin{aligned} & \sum_{\mu M_\alpha M_\beta} (-1)^{M_\alpha + M_\beta} \begin{pmatrix} J_a & 1 & J_\alpha \\ -M_a & \mu & M_\alpha \end{pmatrix} \begin{pmatrix} J_b & 1 & J_\beta \\ -M_b & \mu & M_\beta \end{pmatrix} \\ & \times \begin{pmatrix} J_\alpha & J_2 & J_\beta \\ -M_\alpha & M_2 & M_\beta \end{pmatrix} \\ &= (-1)^{J_2 + 1} \begin{pmatrix} J_a & J_2 & J_b \\ -M_a & M_2 & M_b \end{pmatrix} \begin{Bmatrix} J_a & J_\alpha & 1 \\ J_\beta & J_b & J_2 \end{Bmatrix}, \end{aligned} \quad (10)$$

and the orthogonality of 3- $J$  symbols, gives a general expression for the reduced relaxation operator,

elements,

$$\begin{aligned} & \tau_{KN}^J = [(2J + 1)/8\pi^2] \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} \mathfrak{D}_{KN}^J(\chi_0, \theta_0, \varphi_0) \\ & \times S(\chi_0, \theta_0, \varphi_0) d\chi_0 \sin d\theta_0 d\varphi_0. \end{aligned} \quad (14)$$

The case of expansion in Legendre polynomials was developed in detail in Paper I. The treatment of vibration as diagonal, although representing the most common case, is not general. Accidental degeneracy of overtones in different modes and

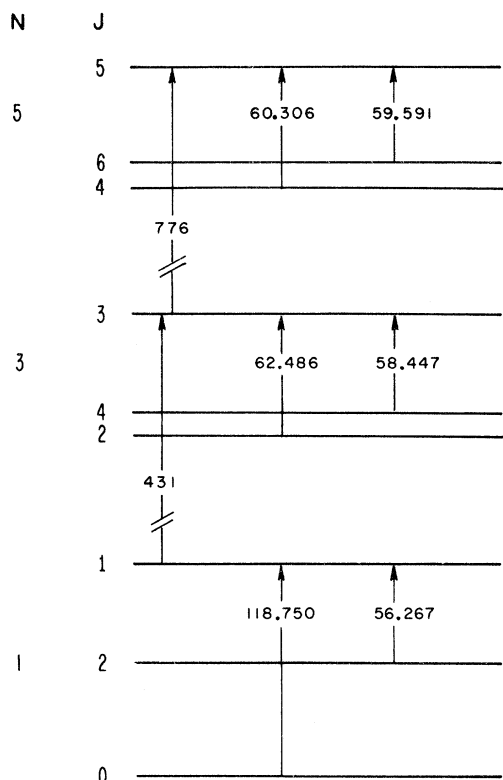


FIG. 1. Microwave absorption spectrum in the 60 GHz region. The allowed magnetic transition ( $\Delta V = \pm 1$ ) are indicated by the solid arrows.

strong coupling of degenerate modes with rotation can require more complicated analysis. In these cases it is necessary to expand the scattering operator in a series of products of rotation matrix elements and Hermite polynomials for the normal modes involved.

## II. O<sub>2</sub> MOLECULE

The oxygen molecule is paramagnetic in its ground electronic state,  ${}^3\Sigma_g^-$ . The total electronic spin  $S=1$  is coupled to the internuclear axis and the spin-rotational Hamiltonian is given as<sup>4</sup>

$$H = B\vec{N}^2 + (2\lambda/3)(3S_z^2 - \vec{S}_z) + \mu\vec{N} \cdot \vec{S}, \quad (15)$$

where  $\vec{N}$  is the end-over-end rotational angular momentum. The constants  $B$ ,  $\lambda$ , and  $\mu$  have been determined<sup>5</sup> by least-squares fitting microwave transition frequencies to a formula derived from Eq. (15).

Since the oxygen (16) nuclei contain an even number of nucleons, the total wave function for the oxygen molecule has an even parity under exchange of its identical nuclei.<sup>6</sup> The Born-Oppenheimer approximation gives the total wave function as a product of nuclear, electronic, vibrational, and rotational parts. The nuclear and vibrational wave

functions are even under exchange while the electronic wave function is odd which requires odd parity for the rotational wave functions. Rotational states formed by the direct coupling of pure rotational, and spin angular momenta

$$|NSJM\rangle = (-1)^{N-S-M} \sum_{M_N M_S} (2J+1)^{1/2} \\ \times \begin{pmatrix} S & N & J \\ M_S & M_N & -M \end{pmatrix} |NM_N\rangle |SM_S\rangle \quad (16)$$

are sufficiently accurate for line-shape calculations. These states are odd under exchange only for odd values of  $N$ . The energies of the levels are determined roughly by the value of  $N$ , since  $BN(N+1)$  is much larger than  $\lambda$  for values of  $N$  greater than unity. Each of these levels is in fact a triplet corresponding to values of the total angular momentum,  $J$  of  $N$  and  $N \pm 1$ . Magnetic dipole transitions (denoted  $N_{\pm}$ ) are allowed between  $J = N \pm 1$  initial states and the  $J = N$  final state as shown in Fig. 1. These transitions give rise to the microwave absorption spectrum in the 60-GHz region.

Table I summarizes measurements of the linewidth parameter  $\gamma_{N_{\pm}}/P$  at 300°K. Discrepancies among the values reported are so large that least-squares fitting for  $N$  quantum-number dependence is not very meaningful. Trends within each experiment show a decrease in linewidth as  $N$  varies from 1 to 5 but show no systematic variation as  $N$  increases beyond 5. With the exception of the  $1_{\pm}$

TABLE I. Linewidth parameter  $\gamma/P$  (MHz/Torr for  $T=300^\circ\text{K}$ .)

| Lines <sup>a</sup> | Refs. |      |      |      |      |      |      |
|--------------------|-------|------|------|------|------|------|------|
|                    | 11    | 12   | 7    | 13   | 14   | 15   | 16   |
| 1 <sub>+</sub>     |       |      | 2.20 | 1.96 | 1.38 |      |      |
| 3 <sub>+</sub>     | 1.96  | 2.07 | 2.23 | 1.71 | 1.10 |      | 1.74 |
| 5 <sub>+</sub>     | 1.56  | 1.80 | 1.96 | 1.86 |      |      | 1.61 |
| 7 <sub>+</sub>     | 1.68  |      | 1.92 | 2.05 |      |      | 1.62 |
| 9 <sub>+</sub>     | 1.42  |      | 1.93 |      |      |      | 1.67 |
| 11 <sub>+</sub>    | 1.60  |      |      | 1.97 |      |      | 1.46 |
| 13 <sub>+</sub>    | 1.54  |      |      |      | 0.99 | 0.87 |      |
| 15 <sub>+</sub>    |       |      |      | 1.77 |      |      |      |
| 17 <sub>+</sub>    | 1.50  |      |      |      |      |      |      |
| 19 <sub>+</sub>    |       |      |      | 1.58 |      |      |      |
| 21 <sub>+</sub>    |       |      |      |      |      |      |      |
| 23 <sub>+</sub>    |       |      |      | 1.26 |      |      |      |
| 1 <sub>-</sub>     |       | 1.97 |      |      |      |      |      |
| 3 <sub>-</sub>     | 1.96  |      |      | 1.92 | 1.41 | 2.09 |      |
| 5 <sub>-</sub>     | 1.60  |      | 1.99 |      |      |      | 1.86 |
| 7 <sub>-</sub>     | 1.70  | 2.01 | 1.82 |      | 1.10 |      | 1.43 |
| 9 <sub>-</sub>     | 1.64  | 1.94 | 2.00 | 1.97 | .83  |      | 1.39 |
| 11 <sub>-</sub>    |       |      | 1.97 |      | 1.34 |      |      |
| 13 <sub>-</sub>    |       |      | 1.86 | 1.87 |      |      |      |
| 15 <sub>-</sub>    |       |      | 1.99 |      | 1.89 |      |      |
| 17 <sub>-</sub>    |       |      | 1.82 | 1.76 |      |      |      |
| 19 <sub>-</sub>    |       |      | 1.92 | 1.62 |      |      |      |
| 21 <sub>-</sub>    |       |      |      | 1.26 |      | 0.83 |      |
| 23 <sub>-</sub>    |       |      |      | 1.29 |      |      |      |

<sup>a</sup> $N_+$  means  $J=N+1 \rightarrow J=N$  transition, while  $N_-$  means  $JM_N-1 \rightarrow J=N$  transition.

lines where experimental data is scarcest, no systematic difference occurs between  $N_{\pm}$  lines. The following is a summary of the data for the linewidth parameter for resolved (low pressure) O<sub>2</sub> lines at 300° (symbols are from Fig. 4):

- 1<sub>+</sub>, (●) 2.20, 1.96, 1.38 MHz/Torr;  
 1<sub>-</sub>, (□) 1.97 MHz/Torr ;  
 3<sub>±</sub>, (○) 1.81 MHz/Torr (average of 10 points);  
 N<sub>±</sub>, (△) 1.64 MHz/Torr (average of 49 points)  
 for  $N \geq 5$  ;

where 1 Torr equals 133.3224 N/m<sup>2</sup>. No experiment reported a line shift and only one experiment (Hill and Gordy)<sup>7</sup> reported measurements of line width at different temperatures. The ratio of linewidths at 90°K to linewidths at 300°K was 2.8 ± 0.1.

### III. CALCULATION

A simple theory of dispersion forces<sup>8</sup> for linear nonpolar molecules predicts a contribution,  $V_{\text{DIS}}$  to the intermolecular potential,

$$V_{\text{DIS}} = \frac{3}{4} h\nu r^{-6} [ \alpha^2 + \frac{1}{3} \alpha(\alpha_{\parallel} - \alpha_{\perp}) P_2(\cos\theta) + \dots ] . \quad (17)$$

$\nu$  is the resonance frequency (lowest allowed electronic transition);  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  are components of the polarizability tensor parallel and perpendicular to the internuclear axis and  $\alpha$  is the average polarizability,  $\frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$ .

It is known that repulsive exchange terms also contribute to the intermolecular potential. However, for molecules as complex as O<sub>2</sub> quantitative descriptions of these terms are not possible. The empirical LJ potential where an  $r^{-12}$  term represents exchange has been used with some success in kinetic theory,

$$V_{\text{LJ}}(r) = 4 [ (\sigma/r)^{12} - (\sigma/r)^6 ] . \quad (18)$$

Interpreting the  $r^{-6}$  term as arising from dispersion the intermolecular potential is written as

$$V(r) = \epsilon_0 V_{\text{LJ}}(r) + \epsilon_1 V_{\text{LJ}}(r) P_2(\cos\chi) + \dots , \quad (19)$$

where  $\epsilon_0$  and  $\sigma$  can be determined by kinetic theory from viscosity and second-virial-coefficient measurements. The ratio  $\epsilon_1/\epsilon_0$  is determined by comparison of Eqs. (17) and (19),

$$\epsilon_1/\epsilon_0 = (\alpha_{\parallel} - \alpha_{\perp})/3\alpha . \quad (20)$$

The scalar term,  $\epsilon_0 V_{\text{LJ}}(r)$  contributes to the broadening indirectly by determining the collision trajectories. The hyperelliptic orbit integrals which result from the polynomial form of  $\epsilon_0 V_{\text{LJ}}$  constitute a significant numerical simplification. However, the angle-dependent term,  $V_1 = \epsilon_1 V_{\text{LJ}}$ , appears explicitly in the scattering operator and with only a

very slight complication in the numerical calculations an exponential representation for the exchange term can be substituted by an approximation due to Hill,<sup>9</sup>

$$4 [ (\sigma/r)^{12} - (\sigma/r)^6 ] \rightarrow 828\,000 e^{-r/0.0826\sigma} - 4.5(\sigma/r)^6 . \quad (21)$$

For the case of O<sub>2</sub>, self-broadening thermodynamic measurements<sup>9</sup> give values for  $\epsilon_0/k$  of 113.2°K, for  $\sigma$  of 3.433 Å and a ratio  $\epsilon_1/\epsilon_0$  of 0.2389.

In practice the value of  $\epsilon_1$  was treated as an adjustable parameter. This form for the intermolecular potential is used for numerical integration of  $K_1$  and  $\theta$ , after a change of variables removes the apparent singularity at  $r_0$ . It should be noted that the LJ potential can give rise to orbiting, resulting in very long collision times. This is a clear violation of the basic assumption of the impact theory, but it has been shown<sup>10</sup> that orbiting cannot occur for velocities such that

$$\mu v^2/8\epsilon_0 > 0.2 . \quad (22)$$

This restriction prevents the use of a Gauss-Hermite quadrature rule for performing the velocity average [Eq. (4a)], but would only impose a fundamental restriction on the calculation at cryogenic temperatures. The integration is performed analytically by least-squares fitting of  $v\lambda'(v)$  to a polynomial of the thermal velocity variable  $\mathcal{F} \equiv \pi m v^2/16k$ :

$$v\lambda'(v) = \frac{P}{T} \sum_{n=0}^N C_n \mathcal{F}^n . \quad (23)$$

The density  $n$  is given by the ideal gas law as  $P/KT$  and the average in Eq. (4a) integrates analytically,

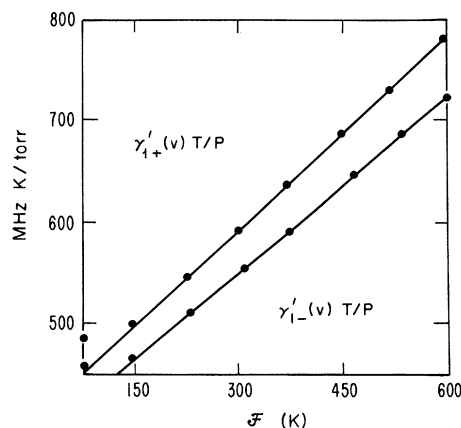


FIG. 2. Plot of  $v\gamma_{1\pm}' T/P$  vs the thermal velocity  $\mathcal{F}$  ( $\pi m v^2/16k$ ). The solid lines denote the linear least-squares fit to  $v\gamma_{1\pm}' T/P$ .

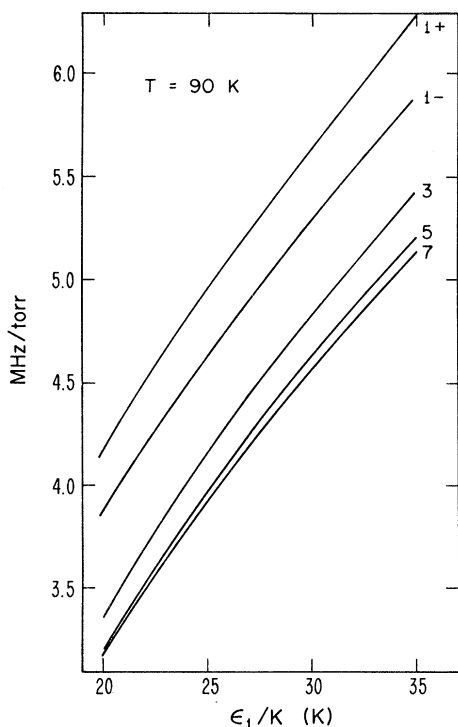


FIG. 3. Linewidth parameter  $\gamma_{N_{\pm}}^0(\gamma_{N_{\pm}}/P)$  vs potential parameter  $\epsilon_1$ , at  $T=90^\circ\text{K}$ . Plots are for  $N_{\pm}=1_{\pm}, 3_{\pm}, 5_{\pm}$  and  $7_{\pm}$ .

$$\lambda^0 \equiv \frac{\lambda}{P} = \frac{C_0}{T} + \frac{3\pi}{8} C_1 + \frac{5\pi^2}{64} C_2 T + \dots \quad (24)$$

The integral (4b) over the impact parameter is performed using a 40-point extended Simpson's rule.

#### IV. RESULTS

The rotationless microwave transitions of  $\text{O}_2$  occur in pairs characterized by quantum numbers  $S=1$ ,  $N_a=N_b=N_{\alpha}=N_{\beta}=J_a=J_b=N$ ,  $\nu_a=\nu_b=0$ , while  $J_{\alpha}$  and  $J_{\beta}$  can assume values of  $N\pm 1$ . The vibrational contributions cancel, and since the potential contains only a second-order Legendre polynomial the scattering operator is expanded in even ordered Legendre polynomials. Denoting the diagonal elements of the relaxation matrix by  $\gamma_{N_{\pm}}$  (width and shift for low pressure, resolved lines), a very simple form is obtained,

$$\begin{aligned} \gamma_{N_{\pm}}(b, v) &= \langle (N, N\pm 1) | \lambda'' | (N, N\pm 1) \rangle \\ &= 1 + \sum_J \frac{1}{(4J+1)} \begin{Bmatrix} N & N\pm 1 & 1 \\ N\pm 1 & N & 2J \end{Bmatrix} \\ &\quad \times | S_{00}^{2J}(\pm) |^2, \end{aligned} \quad (25)$$

where for the coupled representation

$$\begin{aligned} | S_{00}^{2J}(\pm) |^2 &= (2N+1)^3 (2N+1\pm 2) \begin{Bmatrix} N & N & 1 \\ N & N & 2J \end{Bmatrix} \\ &\times \begin{Bmatrix} N & N\pm 1 & 1 \\ N\pm 1 & N & 2J \end{Bmatrix} \begin{Bmatrix} N & 2J & N \\ 0 & 0 & 0 \end{Bmatrix}^2 | \tau_{00}^{2J} |^2. \end{aligned} \quad (26)$$

It can be seen that  $\gamma_{N_{\pm}}$  is real, giving zero line shift. This agrees with present experimental results for resolved lines in which no line shift is observed.  $\gamma_{N_{\pm}}$  is averaged over velocity and impact parameter to obtain the linewidth parameter. Figure 2 is a plot of  $v\gamma_{N_{\pm}}(v)T/P$  vs  $\mathfrak{F}$  (thermal velocity proportional to  $v^2$ ), where the solid line represents a linear least-squares fit. The coefficients obtained are used in Eq. (24) to obtain the temperature dependence for the linewidth parameter  $\gamma^0$ . This procedure is accurate if the deviation from the fit is small in the region where the Maxwellian distribution is large. For values of  $\mathfrak{F}$  below  $150^\circ$  the linear fit underestimates the computed result. For  $T=300^\circ\text{K}$  this region is not heavily weighted and the error is unimportant. However, for  $T=90^\circ\text{K}$  it is expected that this procedure will underestimate the linewidth parameter. The ratio,  $\gamma^0(90^\circ\text{K})/\gamma^0(300^\circ\text{K})$  was calculated to be 2.5 for all lines which is slightly less than the experimentally observed ratio of 2.8.

The linewidth parameter (half-width divided by pressure)  $\gamma_{N_{\pm}}^0$  is plotted against  $\epsilon_1/K$  in Figs. 3

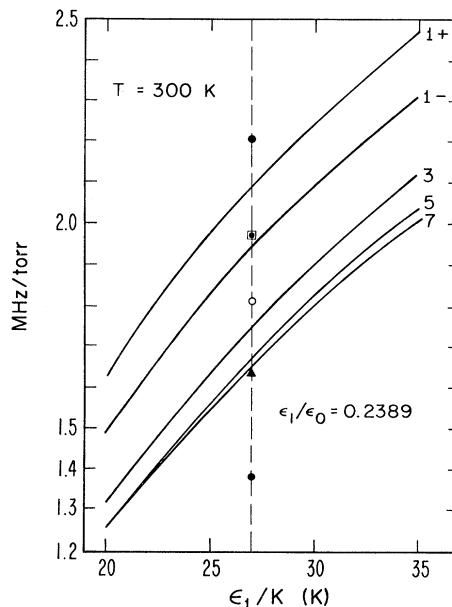


FIG. 4. Linewidth parameter  $\gamma_{N_{\pm}}^0(\gamma_{N_{\pm}}/P)$  vs potential parameter  $\epsilon_1$ , at  $T=300^\circ\text{K}$ . Plots are for  $N_{\pm}=1_{\pm}, 3_{\pm}, 5_{\pm}$  and  $7_{\pm}$ . The experimental data are represented by  $\bullet$  for  $1_{\pm}$ ,  $\square$  for  $1_{-}$ ,  $\circ$  for  $3_{\pm}$ , an average of 10 points, and  $\triangle$  for  $N_{\pm}$  ( $N \geq 5$ ), an average of 49 points. See Table I.

and 4. Figure 3 is for  $T = 90^\circ\text{K}$  while Fig. 4 is for  $300^\circ\text{K}$  and the points marked represent the experimental data summarized in Sec. II. The dashed line in Fig. 4 is the value for  $\epsilon_1$  determined by the simple theory of dispersion forces which is in excellent agreement with most of the measurements.

The excellent agreement of these results with the resolved line data on linewidth magnitude, temperature, and quantum-number dependence in-

dicates the importance of using a strong-collision model when large values of the phase integral are important. Straight-line perturber trajectories, series expansion of the scattering operator and impact parameter cutoffs are likely to be invalid approximations in such a case. Expansion of the scattering operator in spherical harmonics and the use of curved trajectories, while generally a more complicated procedure is straightforward and for the case of linear molecules, simple.

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<sup>1</sup>T. A. Dillon, E. W. Smith, J. Cooper, and M. Mizushima, *Phys. Rev. A* **2**, 1839 (1970).

<sup>2</sup>U. Fano, *Phys. Rev.* **131**, 259 (1963). Note: In Fano's notation  $iA = \langle m \rangle$ .

<sup>3</sup>M. Baranger, *Phys. Rev.* **111**, 502 (1958).

<sup>4</sup>M. W. P. Strandberg, *Microwave Spectroscopy* (Wiley, New York, 1954), pp. 75-80.

<sup>5</sup>M. Mizushima and R. M. Hill, *Phys. Rev.* **93**, 745 (1954).

<sup>6</sup>G. Herzberg, *Spectra on Diatomic Molecules* (Van Nostrand, New York, 1950), p. 130.

<sup>7</sup>R. M. Hill and W. Gordy, *Phys. Rev.* **93**, 1019 (1954).

<sup>8</sup>A. D. Buckingham, in *Advances in Chemical Physics* **XII**, edited by J. O. Herschfelder (Interscience, New York, 1967), pp. 107-142.

<sup>9</sup>J. O. Herschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 207.

<sup>10</sup>J. O. Herschfelder, R. B. Bird, and E. L. Spatz, *J. Chem. Phys.* **16**, 968 (1948).

<sup>11</sup>R. W. Zimmerman and M. Mizushima, *Phys. Rev.* **121**, 152 (1961).

<sup>12</sup>J. O. Artman and J. P. Gordon, *Phys. Rev.* **96**, 1237 (1954).

<sup>13</sup>R. S. Anderson, W. V. Smith, and W. Gordy, *Phys. Rev.* **87**, 561 (1952).

<sup>14</sup>B. V. Gokhale and M. W. P. Strandberg, *Phys. Rev.* **84**, 844 (1951).

<sup>15</sup>J. H. Burkhalter, R. S. Anderson, W. V. Smith, and W. Gordy, *Phys. Rev.* **79**, 651 (1950).

<sup>16</sup>L. F. Stafford, and C. W. Tolbert, *J. Geophys. Res.* **68**, 3431 (1963).

## Convergence of the $1/Z$ Expansion\*

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Lower bounds to the convergence radii of the  $1/Z$  expansions are reported for some low-lying states of the isoelectronic series of the helium and lithium atom. It is proven for the first time that the  $1/Z$  expansion converges for the ground state of the helium atom. The investigation of the  $1^2S$  and  $1^2P_u$  states of the lithium atom indicated poor convergence properties of the  $1/Z$  expansion for systems with more than two electrons. The Brillouin-Wigner perturbation expansion of the ground state of the helium atom is shown to converge if  $1/(Z - \sigma)$  is used as perturbation parameter for  $\sigma = 0.34$ .

### I. INTRODUCTION

Different kinds of perturbation theoretical approaches have been used extensively in the quantum-mechanical treatment of electronic wave functions and energies of small atoms. Since the perturbation equations cannot be solved explicitly in this case, one has to use approximate methods of evaluation, e. g., variational techniques. Most commonly used is the Hylleraas-Knight-Scheer (HKS) variational perturbation method<sup>1,2</sup> which has been successfully applied to treat the Rayleigh-Schrödinger

perturbation expansion (RSPE)<sup>3-5</sup> and the Brillouin-Wigner perturbation expansion (BWPE)<sup>6</sup> of several electronic states of first-row atoms.

In connection with the use of the HKS method or a related technique we meet two problems of principal interest. (a) Since the variational perturbation procedure yields only an approximation to the  $n$ th-order wave function and energy, it is important to establish error bounds for these quantities. (b) A rigorous justification for the use of perturbation theory itself must be given, i. e., to prove the convergence of the usually unknown exact perturbation