

THE ROLE OF HIGHER-MULTIPOLAR AND REPULSIVE FORCES IN THE CALCULATION OF COLLISION-BROADENED LINE-WIDTHS OF LINEAR MOLECULES*

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Abstract—Collision-broadened line widths in CO–CO₂ and CO–O₂ collisions have been calculated by incorporating interactions due to octopoles and hexadecapoles and short range repulsive interactions into Anderson's theory. It is shown how these higher-order interactions can be manipulated to yield good agreement with experimental data. A critical evaluation of this totally empirical manipulation suggests that a thorough revision of the theory is required for all but simple dipole–dipole interactions. In the process of the evaluation, the values of the multipole moments are discussed.

INTRODUCTION

THE COLLISION-BROADENING theory of ANDERSON,⁽¹⁾ in the expanded version of TSAO and CURNUTTE,⁽²⁾ has enjoyed much popularity in recent years. The popularity should be attributed not so much to the accuracy or usefulness of the theory but to the almost routine manner in which one can employ the theory to calculate the line widths in collisions influenced by electrostatic, induction and dispersion interactions. It is reflected, for instance, in the recent extensions^(3–6) of the theory. At the present time, the framework of Anderson's theory has been stretched by HIRONO⁽⁵⁾ so far as to include hexadecapole–dipole and hexadecapole–quadrupole interactions, and by us in the present paper to include octopole–hexadecapole and hexadecapole–hexadecapole interactions. A critical review of the theory, prior to the work which considers octopolar interactions,^(3,4) has been presented by BIRNBAUM,⁽⁷⁾ in which he has pointed out that the theory is not accurate enough to determine, for instance, quadrupole moments of molecules. Birnbaum's skepticism, which we share, appears to have had little effect on an ever increasing number of authors^(8–16) employing Anderson's theory. In view of Birnbaum's review, it is not at all surprising, though quite distressing, to find two or more values for the quadrupole moment of a molecule in a single paper.^(9,12–15) Exceedingly large estimates of octopole moments have also been the result of the application of the theory.^(3,4,6,9,11) As the results of the present work will demonstrate in the following sections, the theory can also be manipulated to yield values of hexadecapole moments that may be far removed from true values in order to match experimental data on line widths. Unfortunately, however, these higher moments do not appear to be obtainable by a direct measurement such as the induced bi-refringence method due to BUCKINGHAM,⁽¹⁸⁾ which yielded unambiguous estimates for quadrupole moments of homopolar and weakly-polar heteropolar molecules. While Anderson's theory involves certain disputable assumptions

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(see below), the technique of Buckingham is free from doubtful approximations. We shall engage in a more complete discussion on the values of the quadrupole moments in the last section of this paper.

An extensive compilation of the intermolecular potentials and interruption functions ($S_2(b)$ sums) has been given by ROBERT *et al.*⁽¹⁷⁾ for electrostatic, induction and dispersion interactions between linear molecules. Their compilation is to be appended to include the work of Refs. (3)–(6) and the present paper in order to gain a perspective on how far the theoretical framework, originally due to Anderson, has been stretched. Anderson's original work was intended primarily to include long range interactions for which the impact approximation, of which the straight line trajectory is an essential part, holds within reason. When the interacting molecules are not dipolar, the accuracy of the straight path must be carefully examined before one can rely completely on the theoretical predictions of line-width. It is not an easy task to include the true nature of the trajectory into a line width computation. TIPPING and HERMAN⁽¹⁹⁾ have offered an alternative, which is another straight-line trajectory that may be considered as 'the short-range counterpart' of Anderson's straight path approximation which applies for long-range collisions. One may define the term 'long-range collision' to mean such collisions for which Anderson's geometry of the collision is valid.⁽²⁰⁾ Below, we shall address ourselves to the influence of the curvature of the trajectory on the line width; and, in the process, a wrong impression that has been created in some recent papers^(8,9) will be corrected. The so-called improvement proposed by TIPPING and HERMAN,⁽¹⁹⁾ and supposed^(8,9) to present 'a more realistic representation' of the collision, is, in reality, another straight-path approximation that may be just as different from the true trajectory as the simple representation invoked by Anderson. As far as we know, the problem of the curvature of trajectories as it enters into the calculation of an *optical cross section* has not been solved successfully. NIELSEN and GORDON⁽²⁰⁾ have presented an interesting discussion of this problem recently.

It is clear from the above discussion that the approach we have taken in the present paper, by employing an extended version of Anderson's theory, is a negative one. That is, we wish to emphasize, before we proceed with the line-width computation, that we aim to examine the inadequacies of the theory rather than suggest improvements, which can be accomplished only if one abandons the basic framework in favor of more realistic representation of facts to describe collisions of range shorter than those envisioned by Anderson. In this respect, perhaps, it is not being fair to Anderson to attribute the failures of the recent theoretical exercises^(3–16) to the inadequacies of Anderson's theory.

In the following sections, we examine closely the computation of line widths in CO–CO₂ and CO–O₂ collisions for three compelling reasons. Firstly, Bouanich's recent calculations⁽⁹⁾ exhibit the maximum discrepancy between theoretical and experimental line widths of CO in these two cases among all the types of collisions he has considered. Secondly, these two molecules, being homopolar and linear, are perfect examples for studying the influence of hexadecapole moment on line width. Finally, Buckingham's direct measurement of quadrupole moments has been more severely disputed^(9,12,16) in the case of CO₂ and O₂ than for any of the other molecules that he has investigated.

CALCULATION OF LINE WIDTHS IN CO-CO₂ AND CO-O₂ COLLISIONS

The intermolecular potentials of electrostatic forces upto the quadrupole–quadrupole term, first order and second-order anisotropic dispersion forces, and of induction forces have been summarized along with the corresponding interruption functions by Robert *et al.*⁽¹⁷⁾

Similar expressions for octopolar interactions may be found in Refs. (3) and (4). The so-called ‘cross-terms’ involving octopole moments derived in Ref. (6) have little significance in the present study.

a. *Hexadecapolar contributions to interruption functions*

A straight-forward application of method indicated in Ref. (2) and the general expression given by GRAY⁽²¹⁾ for the multipolar interaction energy leads to the following interruption functions for hexadecapolar interactions:

(i) *Dipole–hexadecapole interaction*

$$S_2(b) = \frac{256}{945} \left(\frac{\mu_1 \Phi_2}{\hbar v} \right)^2 \frac{1}{b^{10}} \left\{ \sum_{J_2'} H(J_2, J_2') \left[\sum_{J_i'} D(J_i, J_i') f_4(k) + \sum_{J_f'} D(J_f, J_f') f_4(k) \right] \right\}; \quad (1)$$

(ii) *Quadrupole–hexadecapole interaction*

$$S_2(b) = \frac{256}{189} \left(\frac{\theta_1 \Phi_2}{\hbar v} \right)^2 \frac{1}{b^{12}} \left\{ \sum_{J_2'} H(J_2, J_2') \left[\sum_{J_i'} Q(J_i, J_i') f_5(k) + \sum_{J_f'} Q(J_f, J_f') f_5(k) \right. \right. \\ \left. \left. - 2[(2J_i + 1)(2J_f + 1)Q(J_i, J_i)Q(J_f, J_f)]^{1/2} W(J_i J_f J_i J_f; 12) f_5(k) \right] \right\}; \quad (2)$$

Hexadecapole–quadrupole interaction

$$S_2(b) = \frac{256}{189} \left(\frac{\Phi_1 \theta_2}{\hbar v} \right)^2 \frac{1}{b^{12}} \left\{ \sum_{J_2'} Q(J_2, J_2') \left[\sum_{J_i'} H(J_i, J_i') f_5(k) + \sum_{J_f'} H(J_f, J_f') f_5(k) \right. \right. \\ \left. \left. - 2[(2J_i + 1)(2J_f + 1)H(J_i, J_i)H(J_f, J_f)]^{1/2} W(J_i J_f J_i J_f; 14) f_5(k) \right] \right\}; \quad (3)$$

(iii) *Octopole–hexadecapole interaction*

$$S_2(b) = \frac{2048}{441} \left(\frac{\Omega_1 \Phi_2}{\hbar v} \right)^2 \frac{1}{b^{14}} \left\{ \sum_{J_2'} H(J_2, J_2') \left[\sum_{J_i'} O(J_i, J_i') f_6(k) + \sum_{J_f'} O(J_f, J_f') f_6(k) \right] \right\}; \quad (4)$$

(iv) *Hexadecapole–hexadecapole interaction*

$$S_2(b) = \frac{1024}{81} \left(\frac{\Phi_1 \Phi_2}{\hbar v} \right)^2 \frac{1}{b^{16}} \left\{ \sum_{J_2'} H(J_2, J_2') \left[\sum_{J_i'} H(J_i, J_i') f_7(k) + \sum_{J_f'} H(J_f, J_f') f_7(k) \right. \right. \\ \left. \left. - 2[(2J_i + 1)(2J_f + 1)H(J_i, J_i)H(J_f, J_f)]^{1/2} W(J_i J_f J_i J_f; 14) f_7(k) \right] \right\}. \quad (5)$$

In equations (1)–(5), μ , θ , Ω and Φ are, respectively, the dipole, quadrupole, octopole and hexadecapole moments as defined by STOGRYN and STOGRYN.⁽²²⁾ b is the impact parameter which, when equal to b_0 or less, represents a collision that interrupts the radiative process completely; that is, $S(b_0) = 1$. $k = (b/\hbar v)(\Delta E_{i,J_2}$ or $\Delta E_{f,J_2})$ is the energy exchange parameter defined in terms of the mean relative velocity of the colliding pair and the net rotational energy

exchanged $\Delta E_{i,J_2}$ (or $\Delta E_{f,J_2}$) during the collision. The collisional -transition probabilities are defined in terms of the corresponding Clebsch–Gordon coefficients:

$$\begin{aligned} D(J, J') &\equiv (J100/J'0)^2, \Delta J = \pm 1; \\ Q(J, J') &\equiv (J200/J'0)^2, \Delta J = 0, \pm 2; \\ O(J, J') &\equiv (J300/J'0)^2, \Delta J = \pm 1, \pm 3; \\ H(J, J') &\equiv (J400/J'0)^2, \Delta J = 0, \pm 2, \pm 4. \end{aligned}$$

The ‘ off-resonance ’ functions $f_4(k)$ and $f_5(k)$ are the same as those given in Refs. (3) and (4). The functions $f_6(k)$ and $f_7(k)$ have never been considered before and so we give them below:

$$f_6(k) = (2^6 6!)^{-2} k^{14} [K_7^2 + 14K_6^2 + 91K_5^2 + 364K_4^2 + 1001K_3^2 + 2002K_2^2 + 3003K_1^2 + 1716K_0^2] \quad (6)$$

and

$$f_7(k) = (2^7 7!)^{-2} k^{16} [K_8^2 + 16K_7^2 + 120K_6^2 + 560K_5^2 + 1820K_4^2 + 4368K_3^2 + 8008K_2^2 + 11440K_1^2 + 6435K_0^2]. \quad (7)$$

Both the functions have been normalized such that $f_6(0) = f_7(0) = 1$. It should be noted that equations (1) and (2) above are essentially the same as equations (7) and (19) of HIRONO⁽⁵⁾ if one observes that q (Ref. 5) = 2θ (Ref. 22).

b. Interruption functions for repulsive interactions

It can safely be stated that very little is known about the repulsive forces that exist between two linear molecules. Our current understanding of the nature of these forces is purely qualitative and goes no farther than to be able to say (a) that these forces are of extremely short range which come into prominence when the intermolecular separation R is equal to or less than its value at the depth of the potential well, and (b) that these forces probably vary as R^{-n} where n is very large ($n \geq 12$), or being, exchange forces, have probably an exponential [$\exp(-\text{const. } R)$] variation with R . In other words, whatever we know about repulsive potentials is purely empirical. NIELSEN and GORDON⁽²⁰⁾ have presented a detailed discussion of most of the empirical potentials that abound the literature. For the purpose of our present study we have selected the potential which resembles the repulsive part of equation (11) of Ref. (19):

$$V_r(R, \theta) = V_o(R)[1 + a_1 R^{-1} P_1(\cos \theta) + a_2 P_2(\cos \theta)] \quad (8)$$

with the isotropic part $V_o(R)$ being the repulsive part of the Lennard–Jones potential and θ is the orientation of the CO molecule with respect to \vec{R} . The constant a_1 may be identified as the ratio $6d/\sigma$ given by TIPPING and HERMAN⁽¹⁹⁾ if d is the displacement between the electrical and dynamical centers in the CO molecule and σ is the Lennard–Jones parameter for the colliding pair. BOUANICH⁽⁹⁾ has stated that an experimental estimate of $d = 0.21 \text{ \AA}$ exists and that it is due to FRIEDMAN and KIMEL.⁽²³⁾ We have used this value of d . The value of the constant a_2 has been treated as though it were an adjustable parameter. There exists no rationale behind the choice of this potential. It is merely an extension of the isotropic LENNARD–JONES potential to include anisotropic terms, where one assumes the same angle-dependence for the repulsive forces as for the (attractive) dispersion forces.⁽¹⁸⁾

The $P_1(\cos \theta)$ term in equation (8) and the $P_1(\cos \theta)$ term in the attractive (dispersion) potential, both of which are identified by the subscript (7-13) P_1 on $S_2(b)$ below, give rise to the following interruption function:

$$[S_2(b)]_{7-13P_1} = \frac{75}{8} \pi^2 \left(\frac{\varepsilon d}{\hbar v} \right)^2 \left(\frac{\sigma}{b} \right)^{12} \left\{ \sum_{J_i'} D(J_i, J_i') \left[g_3(k) - \frac{231}{80} \left(\frac{\sigma}{b} \right)^6 g_{7,13P_1}(k) \right. \right. \\ \left. \left. + \frac{53361}{25600} \left(\frac{\sigma}{b} \right)^{12} g_{13P_1}(k) \right] + (i \rightarrow f) \right\}, \quad (9)$$

where

$$g_{7,13P_1}(k) = \frac{e^{-2k}}{155925} [2k^9 + 45k^8 + 504k^7 + 3630k^6 \\ + 18270k^5 + 65835k^4 + 168210k^3 + 292005k^2 + 311850k + 155925], \\ g_{13P_1}(k) = \frac{e^{-2k}}{108056025} [2k^{12} + 72k^{11} + 1296k^{10} + 15330k^9 + 131985k^8 + 866880k^7 \\ + 4432680k^6 + 17701740k^5 + 54573750k^4 + 126214200k^3 + 207181800k^2 \\ + 216112050k + 108056025];$$

$g_3(k)$ has already been evaluated in Ref. (24) and reproduced in Ref. (17). In the above, the term designated by $(i \rightarrow f)$ is to be obtained by replacing i by f everywhere in the preceding term.

The $P_2(\cos \theta)$ terms in the dispersion and repulsive interactions contribute the following terms to the interruption function:

$$[S_2(b)]_{6-12P_2} = \frac{189\pi^2}{10240} \left(\frac{U_1 U_2}{U_1 + U_2} \frac{\alpha_1 \alpha_2 \gamma_1}{\hbar v} \right)^2 \\ \frac{1}{b^{10}} \left[\sum_{J_i'} Q(J_i, J_i') g_1(k) + \sum_{J_f'} Q(J_f, J_f') g_1(k) + B g_1(0) \right] \\ - \frac{378\pi^2}{5120} \cdot \frac{U_1 U_2}{U_1 + U_2} \cdot \frac{\alpha_1 \alpha_2 \gamma_1 \cdot a_2 \varepsilon \sigma^{12}}{(\hbar v)^2} \\ \cdot \frac{1}{b^{16}} \left[\sum_{J_i'} Q(J_i, J_i') g_{6-12P_2}(k) + \sum_{J_f'} Q(J_f, J_f') g_{6-12P_2}(k) + B g_{6-12P_2}(0) \right] \\ + \frac{783216\pi^2}{10485760} \left(\frac{\varepsilon \sigma^{12} a_2}{\hbar v} \right)^2 \\ \cdot \frac{1}{b^{22}} \left[\sum_{J_i'} Q(J_i, J_i') g_{12P_2}(k) + \sum_{J_f'} Q(J_f, J_f') g_{12P_2}(k) + B g_{12P_2}(0) \right], \quad (10)$$

where

$$B = -2[(2J_i + 1)(2J_f + 1)Q(J_i, J_i)Q(J_f, J_f)]^{1/2} \times W(J_i J_f J_i J_f; 12).$$

The quantity $g_1(k)$ was evaluated in Ref. (25) and reproduced in Ref. (17) and the functions $g_{6-12P_2}(k)$ and $g_{12P_2}(k)$ are defined as follows:

$$g_{6-12P_2}(k) = \frac{e^{-2k}}{45360} [2k^9 + 36k^8 + 330k^7 + 1974k^6 + 8343k^5 + 25560k^4 + 56700k^3 + 88830k^2 + 90720k + 45360]$$

and

$$g_{12P_2}(k) = \frac{e^{-2k}}{33041925} [2k^{12} + 60k^{11} + 912k^{10} + 9210k^9 + 68445k^8 + 393120k^7 + 1786680k^6 + 6467580k^5 + 18474750k^4 + 40483800k^3 + 64297800k^2 + 66083850k + 33041925].$$

In equation (10), U and α are the ionization potential and the mean polarizability, respectively, while γ_1 is a measure of the anisotropy in the polarizability of the absorbing molecule. ε and σ are the Lennard–Jones parameters for the colliding pair.

Once all the terms in the expression for the total interruption function, $S_2(b)$, are known, the *partial collision cross-section*, σ_{ifJ_2} , is evaluated by using the equation

$$\sigma = \pi b_0^2 + \int_{b_0}^{\infty} 2\pi b db S_2(b) \quad (11)$$

where b_0 is determined by the condition $S_2(b_0) = 1$. It follows that

$$\sigma = \pi b_0^2 \{1 + S_2(b_0) \text{ terms with } f_n(k) \text{ and } g_n(k) \text{ replaced by } F_n(k_0) \text{ and } G_n(k_0)\}. \quad (12)$$

The functions $F_n(k_0)$, for n from 1–5 are defined in Refs. (2)–(4). The functions $G_1(k_0)$ and $G_3(k_0)$ are given by Krishnaji and Srivastava.^(24,25) $F_6(k_0)$, $F_7(k_0)$, $G_{7-13P_1}(k_0)$, $G_{13P_1}(k_0)$, $G_{6-12P_2}(k_0)$ and $G_{12P_2}(k_0)$ are given below:

$$F_6(k_0) = (2^6 6!)^{-2} k_0^{14} [K_8 K_6 + 14 K_7 K_5 + 91 K_6 K_4 + 364 K_5 K_3 + 1001 K_4 K_2 + 2002 K_3 K_1 + 3003 K_2 K_0 - K_7^2 - 14 K_6^2 - 91 K_5^2 - 364 K_4^2 - 1001 K_3^2 - 2002 K_2^2 - 1287 K_1^2 - 1716 K_0^2],$$

$$F_7(k_0) = (2^7 7!)^{-2} k_0^{16} [K_9 K_7 + 16 K_8 K_6 + 120 K_7 K_5 + 560 K_6 K_4 + 1820 K_5 K_3 + 4368 K_4 K_2 + 8008 K_3 K_1 + 11440 K_2 K_0 - K_8^2 - 16 K_7^2 - 120 K_6^2 - 560 K_5^2 - 1820 K_4^2 - 4368 K_3^2 - 8008 K_2^2 - 5005 K_1^2 - 6435 K_0^2],$$

$$G_{7-13P_1}(k_0) = \frac{e^{-2k_0}}{1247400} [16k_0^8 + 296k_0^7 + 2700k_0^6 + 15540k_0^5 + 60690k_0^4 + 162540k_0^3 + 289170k_0^2 + 311850k_0 + 155925],$$

$$G_{13P_1}(k_0) = \frac{e^{-2k_0}}{108056025} [2k_0^{11} + 61k_0^{10} + 930k_0^9 + 9285k_0^8 + 66990k_0^7 + 364455k_0^6 + 1517040k_0^5 + 4806900k_0^4 + 11311650k_0^3 + 18753525k_0^2 + 19646550k_0 + 9823275],$$

$$G_{6-12P_2}(k_0) = \frac{e^{-2k_0}}{45360} [2k_0^8 + 30k_0^7 + 225k_0^6 + 1074k_0^5 + 3510k_0^4 + 8010k_0^3 + 12645k_0^2 + 12960k_0 + 6480].$$

$$G_{12P_2}(k_0) = \frac{e^{-2k_0}}{66083850} [4k_0^{11} + 102k_0^{10} + 1314k_0^9 + 11193k_0^8 + 69732k_0^7 \\ + 332982k_0^6 + 1242486k_0^5 + 3616515k_0^4 + 8017380k_0^3 \\ + 12819870k_0^2 + 13216770k_0 + 6608385].$$

The collision-broadened line width, γ_{if}° ($\text{cm}^{-1}\text{atm}^{-1}$), is related to the *partial collision cross-section*, σ_{if, J_2} , by

$$\gamma_{if}^\circ = \frac{n\bar{v}}{2\pi c} \sum_{J_2} \rho_{J_2} \sigma_{if, J_2}.$$

Here n is the number density of perturbers per an atmosphere of pressure, \bar{v} is the mean relative speed of the colliding pair and is set equal to the mean thermal speed of the particle with the reduced mass M of the colliding pair, c is the velocity of light and ρ_{J_2} is the fractional Boltzmann population of rotational levels in the ground vibrational level of the perturbing molecule. In what follows, the subscript ‘ if ’ identifying the broadened spectral line is replaced by m , where m equals $J + 1$ in the R -branch and $-J$ in the P -branch.

It is often suggested that replacing $n\bar{v}\sigma_m$, where $\sigma_m \equiv \sum_{J_2} \rho_{J_2} \sigma_{mJ_2}$, by $\langle nv\sigma_m \rangle$, which is an average over a Maxwell–Boltzmann distribution of v , is an improvement. Though it certainly is more correct than assuming all collisions to be occurring at the mean thermal speed, the difference between ‘velocity averaged’ and ‘average velocity’ results is often within experimental error. Furthermore, in view of the inconclusive information on the collisional trajectory, multipole moments and the form of the intermolecular potentials that is fed into the theoretical formulation, the advantage to be gained in velocity averaging is, more often than not, offset by the other errors in the computation. In the present paper, we shall ignore the velocity averaging aspect and simply use $\bar{v} = (8kT/\pi M)^{1/2}$. The various molecular constants that entered the calculation of the line width are given in Table 1 and the results of the computation are presented in Figs. 1–6.

Table 1. Molecular constants used in the line-width computations

	CO	CO ₂	O ₂	Reference
$\mu(D)$	0.112	0	0	22
$\theta(D\text{\AA})$	*	*	0.4	22
$\Omega(D\text{\AA}^2)$	*	0	0	
$\Phi(D\text{\AA}^3)$	*	*	*	
$B(\text{cm}^{-1})$ ground state	1.923	0.39	1.445	
$B(\text{cm}^{-1})$ excited state	1.905			
$D(\text{cm}^{-1})$	0.618×10^{-5}	0.135×10^{-6}	0.491×10^{-5}	
$\alpha(\text{\AA}^3)$	1.950	2.650	1.600	33
$\gamma = \frac{\alpha_{\parallel} - \alpha_{\perp}}{3\alpha}$	0.167	0.257	0.237	33
U (ergs)	0.224×10^{-10}	0.248×10^{-10}	0.200×10^{-10}	34
$\varepsilon/k(^{\circ}\text{K})$	100	190	100	33
$\sigma(\text{\AA})$	3.76	4.10	3.52	33

* See the figures for values used for these constants.

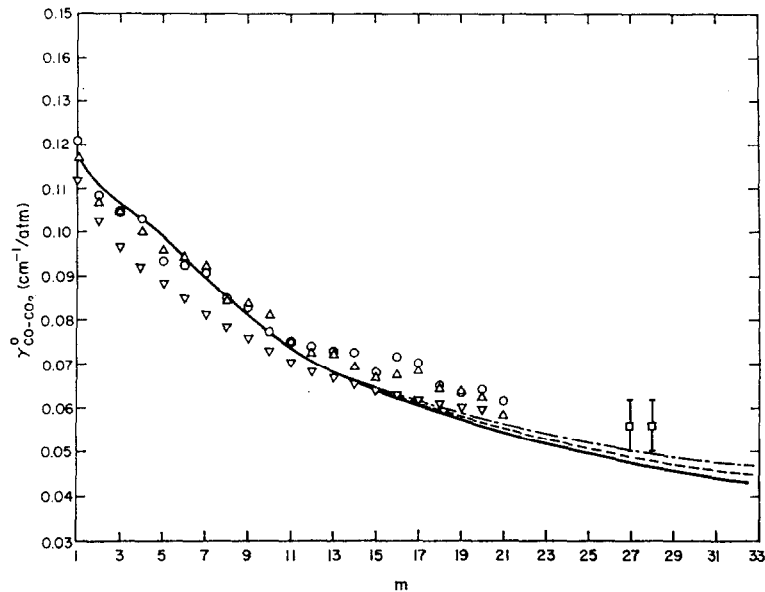


Fig. 1. CO_2 -broadened line widths of CO. Experimental points: ∇ —Ref. (26); \circ —Ref. (27), direct measurement; \triangle —Ref. (27), peak measurement; \square —Ref. 32. Theoretical computations with $\Theta_{\text{CO}} = 20 \text{ D \AA}$, $\Omega_{\text{CO}} = 4 \text{ D \AA}^2$, $\Phi_{\text{CO}} = 13 \text{ D \AA}^3$, $\Theta_{\text{CO}_2} = 3.6 \text{ D \AA}$ and $\Phi_{\text{CO}_2} = 26 \text{ D \AA}^3$. Both attractive (dispersion) and repulsive interactions with $P_1(\cos \theta)$ and $P_2(\cos \theta)$ dependence have been considered with $a_2/\gamma_{\text{CO}} = 1$ (—), 15 (---) and 25 (— · —).

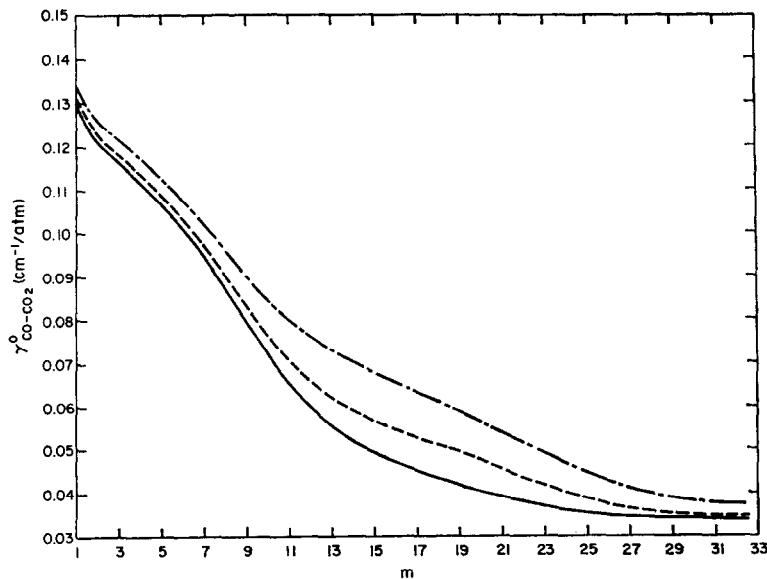


Fig. 2. Computed line widths in CO-CO_2 collisions with $\Theta_{\text{CO}} = 2.5 \text{ D \AA}$, $\Theta_{\text{CO}_2} = 4.3 \text{ D \AA}$; — $\Omega_{\text{CO}} = 0$; --- $\Omega_{\text{CO}} = 3 \text{ D \AA}^2$; — · — $\Omega_{\text{CO}} = 6 \text{ D \AA}^2$. $P_1(\cos \theta)$ - and $P_2(\cos \theta)$ -dependent dispersion and repulsive forces have been considered.

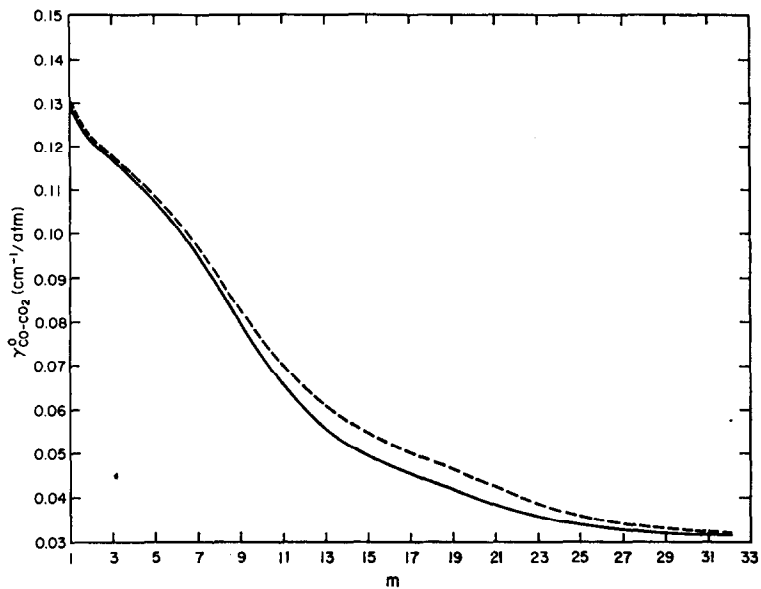


Fig. 3. Computed line-widths in CO-CO₂ collisions with $\Theta_{CO} = 2.5 \text{ D \AA}$, $\Theta_{CO_2} = 4.3 \text{ D \AA}$, $\Omega_{CO} = 0$; — $\Phi_{CO} = \Phi_{CO_2} = 0$, - - - $\Phi_{CO} = 9 \text{ D \AA}^3$ and $\Phi_{CO_2} = 20 \text{ D \AA}^3$. $P_1(\cos \theta)$ - and $P_2(\cos \theta)$ -dependent dispersion and repulsive interactions have also been considered.

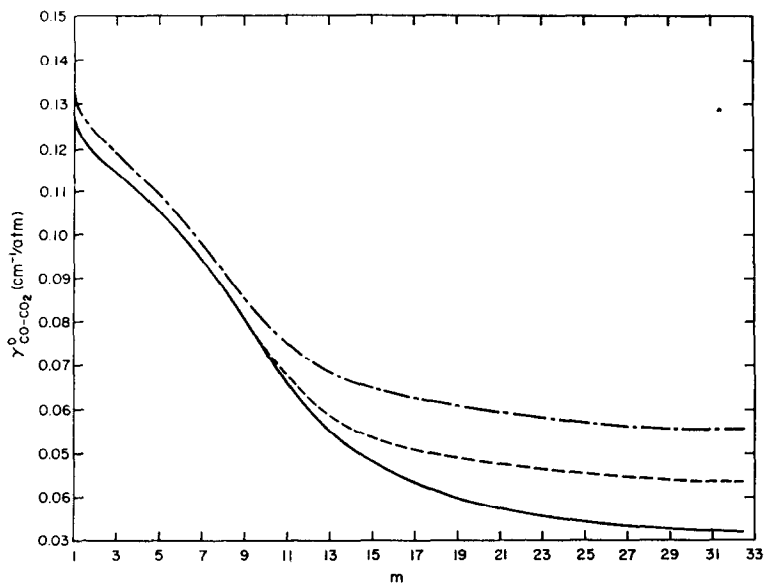


Fig. 4. Effect of the parameter a_2 of equation (8) on line widths in CO-CO₂ collisions. — $a_2 = \gamma_{CO}$; - - - $a_2 = 25 \gamma_{CO}$; - · - $a_2 = 90 \gamma_{CO}$. Dispersion terms with $P_1(\cos \theta)$ -, $P_2(\cos \theta)$ - and $P_3(\cos \theta)$ -dependence considered according to Ref. (17).

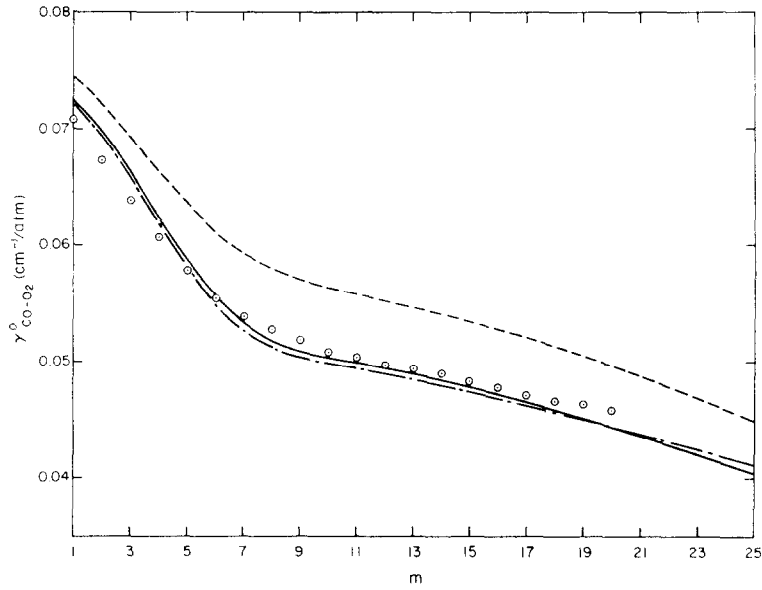


Fig. 5. CO-O₂ line widths. \odot —experimental [Ref. (26)], computed line widths with $\Theta_{\text{CO}} = 2.5 \text{ D \AA}$ and $\Theta_{\text{CO}_2} = 0.4 \text{ D \AA}$ and considering dispersion and repulsive interactions; — $\Phi_{\text{CO}} = \Phi_{\text{O}_2} = 9 \text{ D \AA}^3$ and $\Omega_{\text{CO}} = 0$; -·- $\Phi_{\text{CO}} = \Phi_{\text{O}_2} = 7 \text{ D \AA}^3$ and $\Omega_{\text{CO}} = 4 \text{ D \AA}^2$; ----- $\Phi_{\text{CO}} = \Phi_{\text{O}_2} = 13 \text{ D \AA}^3$ and $\Omega_{\text{CO}} = 0$.

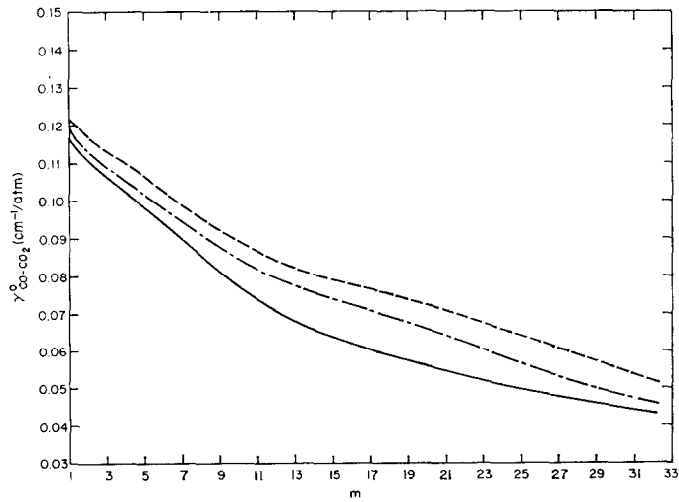


Fig. 6. Effects of curvature of trajectory on computed line widths for CO-CO₂ collisions: $\Theta_{\text{CO}} = 2.0 \text{ D \AA}$, $\Omega_{\text{CO}} = 4 \text{ D \AA}^2$, $\Phi_{\text{CO}} = 13 \text{ D \AA}^3$, $\Theta_{\text{CO}_2} = 3.6 \text{ D \AA}$ and $\Phi_{\text{CO}_2} = 26 \text{ D \AA}^3$: — curvature not considered [Refs. (1), (2)]; ----- [Ref. (19)]; -·- [Ref. (8)].

DISCUSSION OF RESULTS AND CRITICAL APPRAISAL OF THE THEORY

With the aid of Figs. 1–6, we may make several observations. We shall discuss the results obtained in CO–CO₂ collisions first. In Fig. 1, we compare the results of three computations with the experimental data of BOUANICH and BRODBECK⁽²⁶⁾ and of TOTH.⁽²⁷⁾ Toth has given two sets of data based upon ‘direct’ (circles) and ‘peak’ (triangles) measurements, both of which are plotted in Fig. 1. While Toth’s data show the scatter that is inevitable, from a statistical point of view, even in a most carefully performed experiment, the data of Bouanich and Brodbeck appear to have been smoothed out. The disparity between the data of the two papers is outside the limits of error allowed by Toth. The data of TUBBS and WILLIAMS,⁽²⁸⁾ which are not significantly different from Toth’s data, are not shown in Fig. 1 to avoid crowding. The most immediate conclusion that can be drawn from this figure is that good agreement between theoretical and experimental line width data can be achieved if one chooses a proper set of parameters, $\Theta(\text{CO})$, $\Theta(\text{CO}_2)$, $\Omega(\text{CO})$, $\Phi(\text{CO})$, $\Phi(\text{CO}_2)$ and of a_2 , which appears in the repulsive potential. Furthermore, there does not exist a unique set of these parameters. This is partly because the effect of each parameter does not simply reflect a term or terms in the interaction potential whose influence is more pronounced over a select range of values of m ; see Figs. 2, 3 and 4. If the effect of increasing the octopole moment of CO were to increase the calculated line widths for $11 \leq m \leq 25$ (Fig. 2) and bring about better agreement with experimental data, without altering the half-widths at lower m , which are determined by a usually empirically-determined value of the quadrupole moment (and dispersion energy), one could arrive at a meaningful estimate for $\Omega(\text{CO})$. However, as is evident from Figs. 2, 3 and 4, where the effects of increasing the parameters $\Omega(\text{CO})$, $\Phi(\text{CO})$ and $\Phi(\text{CO}_2)$, and a_2 , respectively, is illustrated, the determination of these parameters can, by no means, be unique. Thus, in essence, we have a choice between the empirical philosophy that is prevalent in many of the recent papers^(6, 8–16) or an objective philosophy which takes the relevant molecular properties as constants and involves an objective line-width calculation. We subscribe to the second point of view. To further emphasize this manner of thinking, we now consider the determination of quadrupole moments of CO₂ and O₂. By reading some of the recent papers,^(8–16) we get the erroneous impression that quadrupole moments of CO, CO₂, N₂, O₂, and N₂O have not been established. On the other hand, the work of BUCKINGHAM and collaborators,^(18, 29) which is meticulously compared by STOGRYN and STOGRYN⁽²²⁾ with all of the other available methods of determining these molecular constants, convinces us that they have been accurately and unambiguously determined experimentally. The induced bi-refringence technique developed by Buckingham is a direct method of measurement. Being an optical method, it can be considered quite precise in so far as the determination of the anisotropy of the refractive index of a gas, which is the quantity that is measured directly, is concerned. With very few assumptions, which are well justified, the measured anisotropy in the refractive index, $n_{xx} - n_{yy}$, which is produced by a precisely known applied orienting field (F_{xx}), is related to the molecular quadrupole moment Θ and to the hyperpolarizability B of a homopolar (or weakly polar) linear molecule.⁽¹⁸⁾

$$n_{xx} - n_{yy} = \frac{4\pi N F_{xx}}{15} \left[\frac{15}{2} B + \frac{\alpha_{\parallel} - \alpha_{\perp}}{kT} \Theta \right],$$

where N is the number density of molecules and T is the temperature. Values of the anisotropy of polarizability $\alpha_{\parallel} - \alpha_{\perp}$ and of the hyperpolarizability B are needed before Θ can be obtained. $\alpha_{\parallel} - \alpha_{\perp}$ has been measured accurately by BRIDGE and BUCKINGHAM.⁽³⁰⁾

BUCKINGHAM and DISCH⁽²⁹⁾ have argued in a most convincing manner that the contribution from B is indeed within the experimental error of measuring $n_{xx} - n_{yy}$, if not negligible.* Their argument is as follows. For Ar and SF₆, the term containing the quadrupole moment being already zero, the observed small anisotropy in the refractive index, for the same experimental conditions as for CO₂, must be attributed to the hyperpolarizability B . SF₆ has a much larger polarizability than CO₂ and, therefore, the effect produced by B of SF₆ may be considered as an upper bound for the case of CO₂. This upper bound was found to be within 10 per cent. BUCKINGHAM and DISCH⁽²⁹⁾ have estimated that the contribution of the B term will have to be less than 5 per cent, which is within their experimental error. It is obvious, therefore, that the value, used in Figs. 1 and 6, due to BOUANICH,⁽⁹⁾ of $\Theta(\text{CO}_2) = 3.6 \text{ D } \text{\AA}$ is lower than the value of $\Theta = 4.3 \text{ D } \text{\AA}$ determined by BUCKINGHAM and DISCH⁽²⁹⁾ by a margin larger than the 10 per cent mentioned above. Similarly, the disparity between the value of $\Theta(\text{CO}) = 2.0 \text{ D } \text{\AA}$, due to BOUANICH,⁽⁹⁾ used in Figs. 1 and 6, and the value $2.5 \text{ D } \text{\AA}$ given in Ref. (18) is too large to be acceptable. The value used in Ref. (9) for $\Theta(\text{N}_2) = 1.8 \text{ D } \text{\AA}$ is also much larger than the value $1.5 \text{ D } \text{\AA}$ measured by Buckingham. But it is really the value of the quadrupole moment of O₂ which is arrived at by Bouanich⁽⁹⁾ and by YAMAMOTO and CATTANI⁽¹⁶⁾ by employing the Anderson–Tsao–Curnutte theory, that troubles us the most. It can be argued that the value $0.4 \text{ D } \text{\AA}$ given by Buckingham, being rather low in magnitude, could be sensitive to the neglected contribution of the hyper-polarizability B of oxygen. Therefore, we have computed the line widths of CO broadened by O₂ in this paper and the self-broadened line widths of O₂ in the microwave elsewhere,⁽³¹⁾ using the value of $0.4 \text{ D } \text{\AA}$ for $\Theta(\text{O}_2)$ and considering higher multipolar and anisotropic dispersion and repulsive interactions. We present in Fig. 5 the results of the former computation. The anisotropic dispersion interaction term is evaluated using $3U_1U_2\alpha_1\alpha_2/2(U_1 + U_2)$ and not by replacing it with the empirical $4\epsilon\sigma^6$. Though we cannot place much trust in the rather approximate treatment of the quadrupole–hexadecapole, octopole–hexadecapole, hexadecapole–quadrupole, hexadecapole–hexadecapole and the repulsive interactions, the main thrust of our calculation is to argue that the value $0.4 \text{ D } \text{\AA}$ for the quadrupole moment of oxygen is consistent with a calculation similar to that of Bouanich and of Yamamoto and Cattani. That is, by not including interactions due to shorter range forces than quadrupole–quadrupole forces, which must be done for a molecule with a rather low quadrupole moment. Bouanich, and Yamamoto and Cattani, were led to the rather large value of $\Theta(\text{O}_2)$. From the description given above of the induced bi-refringence method, on account of the hyperpolarizability term, the values reported by BUCKINGHAM⁽¹⁹⁾ can only be larger, though not by a large margin.† On the other hand, the quadrupole moments required to yield the best fit of Anderson’s theory to experimental line width data are, in some cases, smaller (CO, CO₂, H₂ etc.) and are, in other cases, larger (N₂, O₂, N₂O, etc.) than Buckingham’s values. This is clearly one unacceptable aspect of the theory (see below).

Next, we wish to comment upon the semi-empirical treatment^(8–11) of the dispersion energy that is currently in use. The authors referred to have made a practice of replacing by $4\epsilon\sigma^6$ the quantity $3U_1U_2\alpha_1\alpha_2/2(U_1 + U_2)$, which appears in the rigorous expression for the dispersion energy, when the latter is treated as the second-order perturbation energy of a pair of interacting molecules in Unsöld–London approximation.⁽¹⁸⁾ There exists, of course,

* See also A. D. BUCKINGHAM and M. J. JAMIESON, *Molec. Phys.* **22**, 117 (1971)

† It is desirable to have his measurements repeated at different temperatures, thereby, providing a means of eliminating the constant B term.

no rationale whatsoever in the substitution mentioned above. This empirical ploy is a direct consequence of identifying the isotropic term of the first-order (R^{-6}) dispersion energy with the attractive part of the empirical Lennard-Jones potential. Since the single term in the Lennard-Jones potential is expected to approximate all of the isotropic terms in a complete expression for the dispersion energy, it is not surprising that $4\epsilon\sigma^6$ is often larger than $3U_1U_2\alpha_1\alpha_2/2(U_1 + U_2)$, a fact that is appealing when a larger dispersion contribution is desired⁽⁸⁻¹¹⁾ in the computation of line widths.

In this paper, as the title indicates, we have introduced hexadecapolar and repulsive interactions. These interactions arise at relatively shorter range than dipole-dipole or even quadrupole-quadrupole forces. Hence, one seriously doubts the straight line trajectories employed in deriving the interruption functions given in this paper. TIPPING and HERMAN⁽¹⁹⁾ have proposed a 'realistic physical approximation' for considering the curvature of the 'true' trajectories in grazing collisions. Their proposal, in essence, is to replace the straight line trajectory employed by Anderson, according to which $R(t) = (b^2 + v^2t^2)^{1/2}$ by another, for which $R(t) \simeq (r_c^2 + v_c^2t^2)^{1/2}$. The latter represents a linear trajectory that is tangential to the true trajectory at the closest distance of approach r_c , where the relative velocity of collision has the value v_c . The values of r_c and v_c can be solved in terms of b and v only if the isotropic part of the interaction potential is well understood throughout the collision. Employing the Lennard-Jones potential is at best empirical and its validity is as questionable as the simple asymptotic picture assumed by Anderson. It is clear that the true trajectory would maintain, in the course of the collision, a posture that is intermediate to the two straight paths mentioned above. For grazing collisions, at $t \rightarrow \pm \infty$, the trajectory would asymptotically assume the trajectory formulated by Anderson and, at $t = 0$, that suggested by Tipping and Herman. The effect of these two limiting trajectories on the line width computation, in which multipolar interactions are pronounced, in vivid contrast with HCl-Ar collisions considered by Tipping and Herman, is shown by the top and bottom curves in Fig. 6. The middle curve reflects an empirical suggestion made by BOUANICH^(8,9) to bring about agreement with experimental data. Since he offers no justification for it, we shall not venture an interpretation of his scheme. It is known that the order of the multipoles that determine the line width increases progressively with the rotational quantum number m . Thus, Anderson's approximation, which is justified for long-range dipole-dipole forces, may be acceptable for low m , while the picture presented by Tipping and Herman may be closer to reality for large m , at which repulsive interactions are quite important (see Fig. 4). It would greatly destroy the simplicity of the calculation, if one were to introduce all the information about a trajectory, assuming it is known, into a line width computation. On the other hand, one may use both of the straight line trajectories simultaneously in a calculation; that is, use the Anderson trajectory for longer range multipolar interactions and the Tipping and Herman trajectory for shorter range multipolar, dispersion and repulsive forces. It is obvious that the $S_2(b)$ sums for a Tipping and Herman trajectory are the same as for an Anderson trajectory provided one replaces $b^2 + v^2t^2$ by $r_c^2 + v_c^2t^2$.

Figure 2 shows the effect the assumed values of the octopole moment of CO have on the line width computation. In view of the discussion earlier on the quadrupole moments, we have used Buckingham's values. The value of the octopole moment, as defined by STOGRYN and STOGRYN,⁽²²⁾ is taken to be 0, 3.1 and 6.2 D Å². BOUANICH⁽⁹⁾ has used the results of Ref. (4) and a value of 4 D Å². The contributions arising from the octopole moment of CO, if it is as large as 4 D Å², can be substantial. On account of the large cloud of doubt that looms over the accuracy of the theory when the quadrupole moments are taken to be

the values given by Buckingham (compare results in Fig. 2 with the experimental data in Fig. 1), we are hardly in a position to derive a value for the octopole moment of CO based upon either the present work or the work of Ref. (9). A similar comment may also be made regarding the octopole moments derived in Refs. (6) and (11). Though it is dangerous to draw conclusions on the properties of one molecule based upon our understanding of another, it is, however, interesting to compare the cases of CO and N₂. Both have the same number of positive and negative charges. CO is heteropolar with a very small dipole moment ($\mu = 0.112\text{D}$) while N₂, being homopolar, has all of its odd multipole moments equal to zero. Since the quadrupole moments of CO and N₂ are comparable to each other (2 D Å and 1.8 D Å) in Bouanich's estimates, is it reasonable to assume an octopole moment as large as 4 D Å² for CO? A similar question may also be raised by comparing the cases of N₂O and CO₂. Can N₂O really have the large octopole moment suggested by Boulet *et al.*?⁽¹¹⁾ We cannot offer any answers to these questions, but, nevertheless, such questions may serve as useful guidelines.

Figure 3 serves to point out that the effect of hexadecapolar interactions may be important for $9 \leq m \leq 25$. Our present calculations involving hexadecapole moments are by no means conclusive and, hence, cannot be used for making any inferences on their magnitudes. The values we have used to obtain the results shown in Figs. 1, 3 and 5 are, at best, plausible upper bounds.

In CO-CO₂ collisions, as indicated by the two experimental points⁽³²⁾ at $m = 27$ and 28 in Fig. 1, the line widths remain larger than $0.056 \text{ cm}^{-1} \text{ atm}^{-1}$ at high values of m . Also, they decrease much more slowly with increasing m than do the theoretical line widths, when all the interactions, attractive as well as repulsive, are taken into account in a manner described in the preceding pages. Setting the empirical coefficient a_2 of the $P_2(\cos \theta)$ term in the repulsive potential equal to $(\alpha_{\parallel} - \alpha_{\perp})/3\alpha$ of CO, which multiplies a similar term in the (attractive) dispersion potential, in a generalization of Lennard-Jones potential, serves for a first guess at its value (solid curve in Fig. 1). The effect of increasing a_2 is shown in both Figs. 1 and 4. An exceedingly large value of $a_2 = 90(\alpha_{\parallel} - \alpha_{\perp})/3\alpha$ is required (Fig. 4), to match experimental line width data for $m = 27$, if one were to avoid any kind of a 'cut-off' approximation. The conventional 'cut-off' would have to be with $b_{\min} = 4.8 \text{ Å}$. Except to serve as 'a catch all parameter' for all the short range repulsive and attractive forces, b_{\min} would not have any recognizable physical significance. On the other hand, the large value of a_2 , which is a direct consequence of replacing potentially strong collisions by weak collisions, is as meaningless as the cut-off assumption. By weak collisions, we mean those collisions described by the asymptotic straight line trajectory proposed by Anderson and used throughout this paper. Repulsive collisions do not fall under that category. Typically, an interaction is pronounced predominantly repulsive only when the intramolecular separation becomes less than its value at the depth of the potential well. It should be concluded, therefore, that the existing formulation of the theory cannot be used successfully in the study of repulsive forces.

Aside from some of the doubtful assumptions mentioned in the preceding pages, it is becoming increasingly apparent⁽³⁻¹⁶⁾ that Anderson's theory can be applied with any degree of success only if the experimental line widths are known *a priori*. Using what are considered to be the most reliable estimates for the quadrupole moments has led to results that severely disagree with experimental line widths. Thus, the theory cannot be used to obtain reliable half-width information for molecules which have not been studied experimentally or for lines that cannot be measured in a laboratory. The temperature dependence of line widths, which may not always be possible to deduce in a laboratory at low tempera-

tures that are of planetary or astrophysical interest, cannot also be deduced reliably by the theory unless, as it seems, the experimental data are some how known *a priori*. The popular appeal of Anderson–Tsao–Curnutte theory is, therefore, hardly justified, since the choice between theoretical data and experimental data, when both are available, is an obvious one.

REFERENCES

1. P. W. ANDERSON, *Phys. Rev.* **76**, 647 (1949).
2. C. J. TSAO and B. CURNUTTE, *JQSRT* **2**, 41 (1962).
3. G. D. T. TEJWANI and P. VARANASI, *J. chem. Phys.* **55**, 1075 (1971).
4. G. YAMAMOTO and M. HIRONO, *JQSRT* **11**, 1537 (1971).
5. M. HIRONO, *J. Phys. Soc. Japan* **35**, 871 (1973).
6. P. ISNARD, C. BOULET and A. LEVY, *JQSRT* **13**, 1433 (1973).
7. G. BIRNBAUM, *Adv. chem. Phys.* **12**, 487 (1967).
8. J. P. BOUANICH and C. HAEUSLER, *JQSRT* **12**, 695 (1972).
9. J. P. BOUANICH, *JQSRT* **13**, 953 (1973).
10. C. BOULET, E. ARIE, J. P. BOUANICH and N. LACOME, *Can. J. Phys.* **50**, 2178 (1972).
11. C. BOULET, N. LACOME and P. ISNARD, *Can. J. Phys.* **51**, 605 (1973).
12. G. YAMAMOTO, M. TANAKA and T. AOKI, *JQSRT* **9**, 371 (1969).
13. G. YAMAMOTO and T. AOKI, *JQSRT* **12**, 227 (1972).
14. M. HIRONO, *J. phys. Soc. Japan* **26**, 1479 (1969).
15. R. TOH, *J. molec. Spectrosc.* **40**, 605 (1971).
16. Y. YAMAMOTO and M. CATTANI, *Can. J. Phys.* **51**, 2329 (1973).
17. D. ROBERT, M. GIRAUD and L. GALATRY, *J. chem. Phys.* **51**, 2192 (1969).
18. A. D. BUCKINGHAM, *Adv. chem. Phys.* **12**, 107 (1967).
19. R. H. TIPPING and R. M. HERMAN, *JQSRT* **10**, 881 (1970).
20. W. B. NIELSEN and R. G. GORDON, *J. chem. Phys.* **58**, 4131 (1973).
21. C. G. GRAY, *Can. J. Phys.* **46**, 135 (1968).
22. D. E. STOGRYN and A. P. STOGRYN, *Molec. Phys.* **11**, 371 (1966).
23. D. FRIEDMAN and S. KIMEL, *J. chem. Phys.* **43**, 3925 (1965).
24. KRISHNAJI and S. L. SRIVASTAVA, *J. chem. Phys.* **42**, 1546 (1965).
25. KRISHNAJI and S. L. SRIVASTAVA, *J. chem. Phys.* **41**, 2266 (1965).
26. J. P. BOUANICH and C. BRODBECK, *JQSRT* **13**, 1 (1973).
27. R. TOH, *J. molec. Spectrosc.* **949**, 100 (1974).
28. L. D. TUBBS and D. WILLIAMS, *J. opt. Soc. Am.* **62**, 423 (1972).
29. A. D. BUCKINGHAM and R. L. DISCH, *Proc. R. Soc.* **273A**, 275 (1963).
30. N. J. BRIDGE and A. D. BUCKINGHAM, *Proc. R. Soc.* **295A**, 334 (1966).
31. S. SARANGI and P. VARANASI, *JQSRT* (to be published).
32. S. SARANGI, Ph. D. Thesis, S.U.N.Y., Stony Brook (1974).
33. J. O. HIRSCHFELDER, C. F. CURTISS and R. B. BIRD, *Molecular Theory of Gases and Liquids*. Wiley, New York (1964).
34. R. C. WEAST (Ed.) *Handbook of Chemistry and Physics*. Chemical Rubber Company, Cleveland, Ohio (1969).