Microwave Collision Diameters II. Theory and Correlation with Molecular Quadrupole Moments*

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Observed microwave collision diameters are interpreted as arising exclusively from transitions induced during the collision. Collision diameters greater than kinetic theory values arise from dipole-dipole or dipole-quadrupole interactions. The former case affords a quantitative test of the theory. In the latter case measurements of collision diameters yield quadrupole moment measurements which are correlated with molecular structure.

INTRODUCTION

THE line widths of microwave spectra at low pressures can be described adequately by the concept that collisions initiate and terminate the molecular radiation or absorption. The Fourier analysis of the resulting wave trains gives a Lorentz or resonance type variation in intensity of absorption with frequency[1] with the half-power half-width $\Delta \nu$ of the absorption line related to the mean time τ between collisions by

$$\Delta \nu = 1/2\pi\tau. \tag{1}$$

Although the collision time is in general shorter than would be derived from kinetic theory cross sections, it is useful to define a cross section σ for microwave collisions by

$$\tau = 1/n\bar{v}\sigma, \tag{2}$$

where $\bar{v}$ is the relative velocity of impact.†† The problem then arises of evaluating σ in terms of the known intermolecular forces.

A number of partially contradictory, partially complementary theories of pressure broadening exist.[2-4] Their applicability to microwave spectra has so far been tested almost exclusively by Bleaney and Penrose's data on the self-broadening of the ammonia inversion spectrum centered near 24,000 megacycles.[2] While all theories manage to explain these data reasonably well, extension of the data to include the variation in line width with temperature serves to eliminate one of the theories.[5] These and other considerations finally lead to a verification of Anderson's theory of impact

broadening. A simplified version of this theory is then applied to the broadening of ammonia absorption lines by polar symmetric tops, polar linear molecules, and non-polar linear molecules with permanent quadrupoles. The self-broadening of polar linear molecules is also analyzed. Less extensive data and more qualitative analysis are presented for the broadening of the ammonia lines by asymmetric tops and spherical tops.

ELEMENTARY IMPACT THEORY

The simplest form of impact theory states that a radiation interrupting collision between two molecules occurs whenever their interaction energy, governed by their distance of separation r (center to center), exceeds a certain, perhaps arbitrarily assigned, quantity. When applied to the self-broadening of ammonia, a single interaction energy, W, of 2 to 3×10^{-16} erg (depending on the assumptions made in averaging the collisions) yields the observed cross sections for all the lines.[2] As these cross sections vary by a factor of almost three, the agreement between theory and experiment is quite good. Furthermore, the best figure for the interaction energy corresponds to W/hc equal to 1 cm^{-1}, almost exactly the energy separation of the inversion doublets. This coincidence of interaction energy with doublet separation implies that every microwave collision redistributes the relative population of the inversion doublets —a conclusion already experimentally confirmed by data on the saturation effect[6] where a high energy density of microwave radiation at the resonance frequency is observed to disturb the thermal distribution of the inversion doublet state. Indeed, in interpreting this saturation data, it is necessary to assume that, to the accuracy of the experimental data, every "line broadening" collision is also an energy redistributing collision.‡

Bleaney and Penrose's theory is formulated on a "hard ellipsoid" assumption in which the collision

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[1] J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. **17**, 227 (1945).
†† $\bar{v} = [\bar{v}_1{}^2 + \bar{v}_2{}^2]^{\frac{1}{2}}$ where $\bar{v}_1$ and $\bar{v}_2$ are the mean velocities of the two molecules involved in the collision.
[2] B. Bleaney and R. P. Penrose, Proc. Phys. Soc. LX, 540 (1948).
[3] H. Margenau, Phys. Rev. **76**, 121 (1949).
[4] P. W. Anderson, Phys. Rev. **76**, 647 (1949).
[5] R. Howard and W. V. Smith, Phys. Rev. **77**, 840 (1950).

[6] R. Bleaney and R. P. Penrose, Proc. Phys. Soc. LX, 83 (1948); R. L. Carter and W. V. Smith, Phys. Rev. **73**, 1053 (1948); Robert Karplus, Phys. Rev. **73**, 1120 (1948); R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1948).
‡ Margenau however considers this coincidence of the interaction energy at the collision radius with the doublet separation to be a weak point in the elementary impact theory (see reference 3).

radius is assumed independent of the impact velocity. As the interaction energy varies with r^{-3} this assumption seems unreasonable, and is, indeed, found to be experimentally invalid,[5] since the observed cross section varies with v^{-1}. The elementary theory also ignores rotational resonance interactions which are shown by Anderson to be important for molecules whose component K of total angular momentum J along the symmetry axis is low. When the theory is modified in these respects, it becomes indistinguishable from Anderson's theory.[4]

STATISTICAL THEORY

A radically different approach to the line breadth problem is the statistical theory.[3] The idea here is, essentially, to analyze an instantaneous picture of the molecular distribution in space. A given radiating or absorbing molecule will have its energy levels perturbed by interactions with neighbor molecules. At low pressures the interaction will be predominantly with one nearest neighbor. If the frequency shift $v-v_0$ is weighted according to the probabilities of the appropriate intermolecular distances, it is found that the intensity varies inversely as $(v-v_0)^2$. The assumptions made in this derivation are known to break down near $v=v_0$, so that the mathematical infinity here is not serious. A quantitative agreement with the experimental data for ammonia is obtained by assuming that the true intensity distribution near $v-v_0$ is given by a resonance type curve

$$I(v)=C\frac{\Delta v}{(v-v_0)^2+\Delta v^2} \qquad (3)$$

and normalizing (3) to agree with the statistically derived expression in the wings of the curve. Inasmuch as (3) has been derived as a specific result of the impact theory, this step would seem to constitute a mathematical acceptance of the impact theory in the face of a physical denial of it. There is clearly no mechanism explaining saturation effects inherent in the statistical theory. We should note, however, that the theory predicts line widths independent of molecular velocities, in agreement with observation.[5] Fortunately, the more rigorous version of the impact theory also yields line widths independent of molecular velocity.

RIGOROUS IMPACT THEORY

A rigorous quantum mechanical treatment of collision broadening in the microwave region, with particular emphasis on the ammonia problem, has been given by Anderson.[4] We shall merely summarize his results and indicate where simplifications are possible.

In essence, a "collision" occurs in either of two limiting cases. If the collision perturbation induces transitions between states j and k, with a total probability a_{jk} integrated over the path of the perturbing molecule, then if $|a_{jk}|=\frac{1}{2}$, a collision has occurred,

TABLE I.

Broadening gas (2)	Temperature	μ_2 Static Debye units	$\bar{\mu}_2$	Arbitrary $P/\Delta v$	$\frac{T\Delta v}{\bar{\mu}_2 P}$
NH$_3$	300°K	1.44	0.78	1±0.02	385
NH$_3$	195°K	1.44	0.775	0.66±0.02	396
CHCl$_3$	300°K	0.95	0.57	1.33±0.04	396
CH$_3$Cl	300°K	1.87	0.47	1.83±0.02	349

with complete interruption of radiation.¶ This is the non-adiabatic case. On the other hand, even if no transitions are caused, the energy levels j and k will be displaced by the perturbing molecule. If the two displacements are not equal, the radiation frequency will vary continuously during a collision. Although both before and after the impact $v=v_0$, there will be a phase shift in the emitted radiation. Weisskopf assumed that if the magnitude of the phase shift is unity, a "collision" has occurred in the sense that an arbitrarily large phase shift is the equivalent of a complete interruption of radiation.[7] This is the adiabatic case.

It should be emphasized that the above development is historically in reverse—i.e., in optical spectra, non-adiabatic collisions are the exception—hence the necessity for a phase shift theory. An implication of this theory is that frequently these phase shifts do not average to zero so that there is an over-all frequency shift accompanying pressure broadening. We have seen in considering the ammonia example that in this case most collisions are non-adiabatic. Qualitative observations on saturation effects indicate that most microwave collisions are non-adiabatic. Furthermore, no microwave transition has shown a frequency shift accompanying line broadening at low pressures.[8] (The frequency shifts in ammonia at high pressures are another phenomenon of a much smaller order of magnitude than those predicted by the phase shift theory.) To be sure, no net shift would be expected for the best observed absorption —ammonia—even on the phase shift theory. On the other hand, for linear molecules, a frequency shift is predicted on this theory—but not observed. For these reasons, then, we shall ignore the phase shift terms in computing microwave collision broadening.

Anderson, in his rigorous theory, has made no assumption so crude as to merely set $|a_{jk}|$ equal to $\frac{1}{2}$ for a collision. Rather, he has averaged the contributions to line broadening arising from different impact parameters (distance of closest approach) b. The end result of this averaging, however, is to arrive at a collision cross section σ depending on the parameters of the problem in the same manner as with the crude assumption—only the constant of proportionality is slightly different. To

¶ We choose a value $|a_{jk}|=\frac{1}{2}$ rather than the apparently more logical choice $|a_{jk}|=1/\sqrt{2}$ (which populates both states equally). This yields eventual agreement with Anderson's rigorous theory, without the necessity of carrying an adjustable constant.

[7] V. Weisskopf, Zeits. f. Physik **75**, 287 (1932).

[8] R. Howard and W. V. Smith, Phys. Rev. **78**, 128 (1950).

TABLE II. Collision diameters (b) of NH_3 with various colliding molecules.

Colliding molecule (2)	μ_2 ($\times 10^{18}$)	$\bar{\mu}_2$ ($\times 10^{18}$)	$b \times 10^8$ microwave 3–3 line[a]	$b \times 10^8$ kinetic theory[b]	$Q \times 10^{16}$
NH_3	1.44[c]	0.775	13.8	4.43	
H_e	0	0	2.00	3.31	0
A	0	0	3.73	4.04	0
H_2	0	0	2.95	3.59	<0.10
N_2	0	0	5.54	4.09	0.27
O_2	0	0	3.86	4.02	<0.09
CO_2	0	0	7.59	4.46	0.65
COS	0.720[d]	0	7.56		0.61
CS_2	0	0	7.72		0.64
HCN	2.96[e]	0	10.0		1.6
ClCN	2.80[f]	0	11.9		2.4
CH_3Cl	1.87[g]	0.47	11.3	5.14	—
CH_2Cl_2	1.59[h]	0	10.3		1.5
$CHCl_3$	0.95[h]	0.57	13.7		—
CCl_4	0	0	7.20		0
SO_2	1.7[h]	0	10.4		1.6

[a] See reference 8 except for NH_3, which is from reference 2.
[b] E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938). (Value for CH_3Br used for CH_3Cl.)
[c] A. Van Itterbeek and K. de Clippelier, Physica **14**, 349 (1948).
[d] Dakin, Good, and Coles, Phys. Rev. **70**, 560 (1946).
[e] R. G. Shulman and C. H. Townes, Phys. Rev. **78**, 347 (1950).
[f] Townes, Holden, and Merritt, Phys. Rev. **74**, 1126 (1948).
[g] Dailey, Mays, and Townes, Phys. Rev. **76**, 136 (1949).
[h] P. Debye, *Polar Molecules* (Chemical Catalog Company, Inc., 1929).

arrive at a convenient working formula, then, we will consider the case of dipole-dipole broadening in an elementary fashion, comparing our results to Anderson's.

The transition probability a_{jk} is given by[9]

$$a_{jk} = -i \int \frac{H_{jk} \exp(-i\omega_{jk}t)}{\hbar} dt, \qquad (4)$$

where H_{jk} is the collision perturbation Hamiltonian (Anderson's $H_i = -iH_{jk}$), and $\omega_{jk} = (E_k - E_j)/\hbar$ is the unperturbed angular frequency. Anderson has shown that if $K = (b\omega_{jk})/v$ is less than unity, the exponential term can be set equal to one with only a few percent error. Since for the ammonia inversion spectrum at room temperature $K = 0.2$, and in general in the microwave region $K < 1$, this approximation is valid. When $K > 1$, as in most optical spectroscopy, non-adiabatic collisions are unimportant.

Anderson's Eq. (7) then yields for dipole-dipole broadening, ignoring rotational resonance terms which are important only for the special case of ammonia|| (and then only for low K values).

$$|a_{jk}| = \left(\frac{8}{9}\right)^{\frac{1}{2}} \left(\frac{\mu_1 \bar{\mu}_2}{b^2 v \hbar}\right).$$

[9] H. M. Foley, Phys. Rev. **69**, 616 (1946).
|| For other microwave transitions the population of rotational states differing by $J = 1$ from the "struck" molecules is usually too small to be important.

We have included an r.m.s. average over the polar and azimuthal angles with respect to the impact parameter b. μ_1 and $\bar{\mu}_2$ are the magnitudes of the components of the dipole moment along the angular momentum axis. An average of μ_2 over the states of the colliding molecule has been included. Setting (5) equal to $\frac{1}{2}$ and solving for $\sigma = \pi b^2$

$$\sigma = \frac{2\pi \mu_1 \bar{\mu}_2}{v\hbar} \left(\frac{8}{9}\right)^{\frac{1}{2}}. \qquad (6)$$

This expression may be compared with Anderson's Eq. (11), rewritten as

$$\sigma = \frac{2\pi \mu_1 \bar{\mu}_2}{v\hbar} \left(\frac{8}{9}\right)^{\frac{1}{2}} C, \qquad (7)$$

where C is a constant whose value, depending on the averaging assumption, lies between 1.11 and 0.885. Clearly to the accuracy of the theory, the simpler Eq. (6) is satisfactory. Substituting (6) in (1) and (2), then, for symmetric top dipole broadening

$$\Delta \nu = \frac{n \mu_1 \bar{\mu}_2}{\hbar} \left(\frac{8}{9}\right)^{\frac{1}{2}}. \qquad (8)$$

The final result is seen to be independent of the molecular velocity. Formula (8) however is not valid over extreme ranges of velocity, as at very low velocity the assumption $K < 1$ becomes invalid. Table I summarizes the experimental test of Eq. (8) for variations in temperature and foreign gas. The $NH_3$3, 3 line is chosen, both because it is the strongest and because, even for self-broadening, rotational resonance terms are negligible in this case. The last column of Table I, with n proportional to P/T, should be a constant for verification of the theory. It is seen to be constant to within ± 9 percent, which is about the combined inaccuracies of the experimental parameters (including dipole moments).

It should be stressed at this point that a general acceptance of Bleaney and Penrose's elementary impact theory has led to the assumption that the line breadth, for constant pressure, is inversely proportional to the square root of the temperature. Thus many of the "engineered" intensity formulas current in the literature give an incorrect temperature dependence. It is also evident that only for symmetric top dipole broadening, with its interaction energy proportional to the inverse cube of the distance, will the line breadth be strictly independent of the velocity. For dipole-quadrupole broadening, only a small error is introduced in neglecting the velocity dependence. When the colliding molecules obey "harder" force laws involving higher inverse powers of r, the line width approaches proportionality to $T^{-\frac{1}{2}}$ as in the elementary impact theory.

HIGHER ORDER INTERACTIONS

When the colliding molecule 2 possesses no permanent dipole moment, averaged over the rotational motion, a

number of interactions that can be neglected when dipole-dipole forces are prominent now must be considered. Firstly, if the colliding molecule is linear and polar, there is the Keesom alignment interaction, resulting from the tendency of two rotating dipoles to "lock in" their rotation to a common frequency. This interaction is small when the dipole moment is small as in OCS. For an experimental confirmation, the observed microwave collision diameters given in Table II differ negligibly among the molecules CO_2, CS_2, and OCS despite the fact that OCS is polar and the other two are not. For dipole moments greater than about 2×10^{-18} e.s.u., this interaction is no longer negligible. The moderate size of the ammonia dipole however makes the interaction somewhat smaller than for the case of self-broadening of the linear molecules discussed in a subsequent section.

A second possible interaction is that arising from the polarization of molecule 2 by the dipole of molecule 1. This interaction varies as $\cos^2\theta$, where θ is the angle which μ_1 makes with the distance of closest approach b. Since the period of a microwave oscillation is long compared with the duration of a collision, μ_1 may be considered stationary during the collision. The torque exerted on the dipole thus averages to zero over the collision and, as a first approximation, the interaction vanishes. By considering collision-induced transitions other than the pure inversion discussed above, Anderson[4] calculated some finite collision diameters which are, however, considerably smaller than either kinetic theory ones, or observed microwave values.**

DIPOLE-QUADRUPOLE BROADENING

From Table II, we observe that many microwave diameters greatly exceed the kinetic theory diameters, implying the operation of some long range forces. We suggest that the important interactions in these cases are between the ammonia dipole moment and the quadrupole moment Q of the colliding molecule. Since these interactions vary as the inverse fourth power of the radius, they can give rise to large collision diameters. We should note that collision broadening differs from Van der Waal's interactions in that the former, in the microwave region, involves only the anisotropic part of the interaction potential,[4] as the isotropic part cannot induce transitions. Thus, it is possible for the largely isotropic polarization energies to play so important a role in Van der Waal's forces that quadrupole contributions can be neglected[10] while, conversely, quadrupole interactions sometimes assume the major role in microwave collision broadening.

** Anderson has recently considered the interactions between the ammonia quadrupole moment (arising from the displacement of the dipole moment from the molecular center of gravity) and induced dipole moments. These interactions give close agreement with theory for argon, helium, hydrogen, and oxygen—with, however, slight disagreements suggesting the presence of quadrupole moments for oxygen and, less definitely, hydrogen (private communication).
[10] F. London, Zeits. f. Physik 63, 245 (1930).

If the colliding molecule 2 possesses no permanent dipole moment, averaged over the rotational motion, but does possess a permanent quadrupole moment†† Q, then the interaction energy of this quadrupole with a dipole is given by [11]

$$H = \tfrac{3}{4}\mu_1(Qe/r^4)[\cos\theta_1'(1-3\cos^2\theta_2') + 2\cos\theta_2'\sin\theta_2'\sin\theta_1'\cos(\phi_1'-\phi_2')], \quad (9a)$$

where θ_1', θ_2', ϕ_1', and ϕ_2' are the polar and azimuthal angles of dipole and quadrupole with respect to the r axis. In terms of the polar angles θ and ϕ with respect to the impact parameter b (constants of the motion), then

$$H = \tfrac{3}{4}\mu_1(Qe/r^4)\cos\psi[(1-3\cos^2\theta_2) + 2\cos\theta_2\sin\theta_2\sin\theta_1\cos(\phi_1-\phi_2) + 5\sin^2\psi\{\cos\theta_1(\cos^2\theta_2-\sin^2\theta_2\cos^2\phi_2) - 2\cos\theta_2\sin\theta_1\sin\theta_2\cos\theta_1\cos\phi_2\}] \quad (9b)$$

plus terms in $\sin\psi\cos\psi$. Here $r^2 = b^2 + \bar{v}^2t^2$; $\sin\psi = \bar{v}t/r$. Substituting (9b) in (4), integrating, and averaging the magnitude of the interaction over the angles yields‡‡

$$|a_{jk}| = \frac{0.42\mu Qe}{hb^3\bar{v}} \frac{1}{} = \frac{1}{2}. \quad (10)$$

For the ammonia 3,3 line, $Q = 2.09b^3\bar{v}$.

Quadrupole moments evaluated from the microwave values of b are given in Table II. The values appear to be consistent with the molecular structure, although an independent check from other physical data, unfortunately, is not possible in most cases. The self-broadening of HCN, ClCN, and OCS, however, furnish corroboratory evidence, as discussed in the next section.

SELF-BROADENING OF LINEAR MOLECULES

The self-broadening of linear molecules in the infrared region has been the subject of much experimental and theoretical investigation.[4,9,12] In this region, the important interactions are rotational resonance and second-order Keesom alignment forces. We have already seen that, except for the special case of ammonia self-broadening, rotational resonance is relatively unimportant in the microwave region owing to the scarcity of colliding molecules with low J values. The general formula for the alignment interactions may be specialized to the case where J_2 of the colliding molecule is much greater than J_1 of the radiating molecule. In

†† For a linear rotating molecule this is equal to $\tfrac{1}{2}$ the amount of the static molecule, and is perpendicular to the plane of the motion. Our Q is twice Margenau's Θ/e.
[11] H. Margenau, Rev. Mod. Phys. 11, 1 (1939).
‡‡ We note that with increasing "hardness" of the interaction, agreement between our simple assumptions and Anderson's averaging should become better. Since we have fitted our constants to agree with an inverse cube interaction, however, this means they will not agree quite so well with an inverse fourth power law, as is the case for dipole-quadrupole interactions. The over-all effect will be that our calculated Q values will be too small by a few percent. This error is approximately compensated by neglect of other interactions in computing Q.
[12] E. Lindhohn, Zeits. f. Physik 109, 223 (1938).

Table III. Calculated and observed microwave collision diameters for linear molecules.

Molecule	b microwave $\times 10^8$ [a]	b theoretical $\times 10^8$
OCS	8.6	6.3
ClCN	17.7	16.8
HCN	14.7	12.7

[a] Townes, Holden, and Merritt, Phys. Rev. **74**, 1113 (1948). Smith, Gordy, Simmons, and Smith, Phys. Rev. **75**, 260 (1949).

this case, the second-order interaction $\langle H_2 \rangle_{\text{Av}}$ is given by

$$\langle H_2 \rangle_{\text{Av}} = \tfrac{1}{3}(\mu^4/r^6 E_{J2}), \tag{11}$$

where E_{J2} is the average rotational energy of the colliding molecule $=kT=4.1\times10^{-14}$ erg. The interaction energy calculated from Eq. (11) may be compared with that from Eq. (9b) averaged to be $H=\tfrac{1}{3}(\mu_{jk}Qe/r^4)$. For OCS the dipole-quadrupole interaction at 7.5 angstroms is a factor of 18 greater than the alignment interaction. For HCN at 14 angstroms, the discrepancy is reduced to a factor of 2.6. For dipole moments of 3×10^{-18} or more the alignment interactions become predominant.

In Table III, experimental collision diameters (calculated from the published line widths) are compared with the theoretical ones from Eq. (10), using the dipole and quadrupole moments listed in Table II. The theoretical collision diameters are somewhat smaller than the observed values. We interpret this to mean that for low dipole moments the neglected higher order interactions are important, and for high dipole moments the Keesom alignment interactions are important. For HCN and ClCN however, the dipole-quadrupole interactions are a satisfactory first approximation to the interaction energy.

CORRELATION OF QUADRUPOLE MOMENTS WITH MOLECULAR STRUCTURE

In interpreting our quadrupole moment data, we shall visualize a non-rotating linear molecule as having point charges at the nuclei, and a uniform negative charge density ρ (depending on the bond) between the nuclei. Thus our observed Q value for the rotating molecule is equal to $\Theta/e=\sum \rho_i x_i^2$ for the stationary molecule, as compensating factors of two cancel in the definition of Q and the transition from linear to rotating molecule. For nitrogen, with $Q=0.27\times10^{-16}$ cm^2 (nuclear separation$=1.10$A) this model gives positive charges of $0.6e$ on each nitrogen nucleus—i.e., the distortion from spherical symmetry is equivalent to $0.4e$ per bond. Our upper bound for the quadrupole moments

of hydrogen and oxygen is about 0.1×10^{-16} cm^2—one-third the observed value for nitrogen. This bound is of the same magnitude as London's estimate[10] of Q for $H_2=0.08\times10^{-16}$ cm^2. Furthermore the small Q for oxygen suggests that its bond more closely resembles a single bond than a double bond.¶¶ This single bond hypothesis for oxygen was originally suggested by London in interpreting the paramagnetism and reactivity of oxygen.[13]

Interpretation of the quadrupole moments of CO_2 and CS_2 is a little more complex as the bond dipole moments of these molecules can also contribute to the quadrupole moment of the rotating molecule. The slight difference in electronegativity between carbon and sulfur should permit us to ignore the dipole moment contributions here however. Thus calculations similar to those for nitrogen, utilizing the C$-$S deparation of 1.55A, gives positive charges of $0.4e$ on each sulfur nucleus and $0.8e$ on the carbon nucleus—i.e., the distotion per bond is the same for CS_2 as for N_2. Lest we extrapolate this simple picture too far, however, we note that this model gives for hydrogen a Q of only 0.04×10^{-16} cm^2, a value consistent with our measurements, but only half the theoretical value. Also, we may note that calculations for CO_2 show approximate cancellation of the homopolar and the bond dipole contributions to the over-all quadrupole moment. Thus our present picture is to be considered as qualitative only, but the observed moments should serve as valuable checks on more quantitative theories.

It is possible to deduce from the observed quadrupole moments of simple molecules the homopolar quadrupole moment per bond. Our data indicates a proportionality of bond quadrupole moment to bond order N times the square of the bond length, so that

$$Q\cong0.07r^2N. \tag{12}$$

This relation gives quadrupole moments about a factor of five smaller than those proposed by Lassettre and Dean to explain internal rotation phenomena.[14]

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¶¶ The prevalent interpretation is that oxygen possesses essentially a double bond. Our quadrupole observations do not constitute a disproof of this picture, but do cast some doubt on it.
[13] F. London, Zeits. f. Physik **50**, 24 (1928).
[14] E. N. Lassettre and L. B. Dean, Jr., J. Chem. Phys. **17**, 317 (1949).