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Evaluation of Molecular Quadrupole Moments

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Knowledge of the molecular quadrupole moments may be used to propose a better model for the structure of the molecule and could also provide a crucial test for the accuracy of the trial wave functions that are used in other molecular calculations. A general survey of the different methods available for the evaluation of molecular quadrupole moments has been made and their relative merits and demerits have been discussed. It is suggested that the quadrupole moments determined by the microwave linewidth data are probably more reliable. The quadrupole moments of different molecules known to date have been tabulated.

CONTENTS

I. INTRODUCTION

The way a molecule interacts with another, has long been the subject of extensive investigations. The essential problem is to find the molecular interaction potential. For this purpose a molecule can be considered as a special case of a charge distribution, the total charge of the system being zero. The interaction potential is[1] electrostatic and can be expanded in terms of a set of parameters, characteristic of the particular distribution in question. These parameters are:

1. The total charge

$$q=\sum_i e_i\,,$$

2. The dipole moment

$$\mu=\sum_i e_i r_i\,,$$

3. The quadrupole moment

$$\theta_{\alpha\beta}=\tfrac{1}{2}\sum_i e_i(3r_{i\alpha}r_{i\beta}-r_i^2\delta_{\alpha\beta})\,,$$

··· etc. or, in general, 'the multipole moment of order n.' The potential expansion then has the general form

$$\phi=(q/r)+(\mu_\alpha r_\alpha/r^3)+(\theta_{\alpha\beta}/3r^5)(3r_\alpha r_\beta-r^2\delta_{\alpha\beta})+\cdots. \tag{1.1}$$

For a complete specification of the potential the parameters need be known beforehand. The total charge q, is always zero for a molecular charge distribution. The dipole moment μ can be measured fairly accurately by a number of methods.[2–5] The quadrupole moment $\theta_{\alpha\beta}$ can not be measured easily nor accurately. Most of the available methods involve certain assumptions and approximations whose validity is doubtful. A general survey of these methods is the main object of the present paper. Knowledge of molecular quadrupole moments is of interest not only because it helps in a better understanding of all the phenomena resulting from the interaction of the molecule with any other external system but also because it may be used to propose a better model for the structure of the molecule. Recently, Buckingham[6] has pointed out that if accurate values of the quadrupole moment were known, it would provide a crucial test for the accuracy of the trial wave functions that are used in other molecular calculations. All this makes the measurement of molecular quadrupole moments important in spite of the difficulties involved. The last review on Molecular Quadrupole Moments was published by Buckingham[1] in 1959. Since then a large amount of work has been done on the subject.

The molecular quadrupole moment is defined as[1]

$$\theta_{\alpha\beta}=\tfrac{1}{2}\sum_i e_i(3r_{i\alpha}r_{i\beta}-r_i^2\delta_{\alpha\beta})\,, \tag{1.2}$$

where $\delta_{\alpha\beta}=1$ if $\alpha=\beta$ and, $=0$ if $\alpha\neq\beta$ and where the summation is over all the charges in the molecule.

$\theta_{\alpha\beta}$ is thus a tensor having nine components. However, by a proper choice of the axes of reference all the off-diagonal terms $\theta_{\alpha\beta}(\alpha\neq\beta)$ can be made to vanish. Thus three principal axes x, y, and z are obtained such that only the following three components for which $\alpha=\beta$ survive:

$$\begin{aligned}\theta_{xx}&=\tfrac{1}{2}\sum_i e_i(3x_i^2-r_i^2),\\ \theta_{yy}&=\tfrac{1}{2}\sum_i e_i(3y_i^2-r_i^2),\\ \theta_{zz}&=\tfrac{1}{2}\sum_i e_i(3z_i^2-r_i^2).\end{aligned} \tag{1.3}$$

These are the three principal quadrupole moments of the molecule. However, Eqs. (1.2) and (1.3) show that

$$\theta_{\alpha\alpha}=\theta_{xx}+\theta_{yy}+\theta_{zz}=0$$

so that only two of these are independent.

If the distribution of the charges is considered to be continuous, the summation over discrete charges need to be replaced by an integration of the charge density $\rho(r)$ over the whole space. Thus

$$\begin{aligned}\theta_{xx}&=\tfrac{1}{2}\int(3x^2-r^2)\rho(r)\,d\tau,\\ \theta_{yy}&=\tfrac{1}{2}\int(3y^2-r^2)\rho(r)\,d\tau,\\ \theta_{zz}&=\tfrac{1}{2}\int(3z^2-r^2)\rho(r)\,d\tau.\end{aligned} \tag{1.4}$$

If the charge distribution is symmetrical about any axis, say z axis, then

$$\theta_{xx}=\theta_{yy}=-\tfrac{1}{2}\theta_{zz}=-\tfrac{1}{2}\theta \text{ (say)}. \tag{1.5}$$

The problem of evaluation of the molecular quadrupole moments can be attacked in many ways. A theoretical approach utilizes knowledge of the quantum-mechanical wave functions.

For experimental measurement a direct method is, in principle, possible. In this the energy of interaction of the molecule with an external electric field is measured. A simple electrostatic argument[1] shows that this energy consists of, besides other terms, a term depending only on the quadrupole moment $\theta_{\alpha\beta}$ of the molecule and the gradient $F_{\alpha\beta}'$ of the applied field at the center of the molecule. Thus if one can separate out the contribution of this term for known field-gradient values, the quadrupole moment comes out directly. But this method is not practicable because of the difficulties in producing sufficiently large field gradients over the size of the molecule. The largest gradients obtainable are of the order of 1000 esu while the quadrupole moment values are only of the order of 10^{-26} esu. Thus the contribution of the quadrupolar term is only about 10^{-23} ergs which is difficult to separate out from the rest of the interaction energy. Thus this direct method which can work well in the case of the dipole moments, fails in the present case.

However, a slight modification of this results in an elegant method, applicable to the molecules with anisotropic polarizability only. The application of an external electric field makes these molecules birefringent[7] and the amount of birefringence induced depends on the interaction of the molecule with the applied field. A method based on measuring the birefringence resulting due to the interaction proves to be practicable. This method was first suggested by Buckingham[6] in 1959 and has since been successfully applied to the case of the CO_2 molecule.[8]

The other method is to study the interaction between two molecules themselves. At a point a few angstroms from a polar molecule, the field gradient is $\sim 10^{14}$ esu whereas the field strength is only $\sim 10^{6}$ esu. Thus if a second molecule comes in this region, it will interact with the field of the first one giving rise to an interaction energy. The contribution of the quadrupolar term ($\theta_{\alpha\beta}F_{\alpha\beta}'\sim 10^{-12}$) to this energy then is of a comparable order of magnitude to the contribution of the dipolar term ($\mu F\sim 10^{-12}$). Thus molecular quadrupoles contribute significantly to intermolecular forces and this suggests that their indirect evaluation from a study of these forces should be practicable. These indirect methods are the ones that involve one or the other observable phenomenon to which the presence of a finite interaction between the gaseous molecules gives rise.

The principal methods for the evaluation of the molecular quadrupole moments can thus be listed as follows:

1. The Molecular Orbital Method.
2. The Induced Optical Birefringence Method.
3. The Second Virial Coefficient Method.
4. The Spectral Line-Broadening Method.
5. The Anisotropic Susceptibility Method.
6. The Dielectric Constant Method.
7. The Pressure-Induced Absorption Method.
8. The Bond Moments Method.

A few other methods, e.g., "the quadrupolar radiation method," "the macroscopic-quadrupole vibration method," etc. have also been proposed. But the investigations show that none of these can be regarded as practical methods for the evaluation of the molecular quadrupole moments having a wide applicability. A detailed survey of these will not be made here. For a brief discussion one may refer to the previous review.[1]

II. THE MOLECULAR ORBITAL METHOD

In the molecular orbital method one evaluates the nuclear and the electronic contributions to the molecular quadrupole moment, separately. For the nuclear contributions, a straightforward computation of the quadrupole moment components from Eqs. (1.3) is feasible because the charges in the different nuclei and their positions in reference to the origin (usually the center of mass of the molecule) are known.

For the electronic contributions, such a direct calculation is not possible because of the continually changing positions of the electrons so that their coordinates x_i, y_i, z_i, and r_i can not be uniquely defined. For such a case of a continuous charge distribution the quadrupole moment components are evaluated from Eqs. (1.4) with density $\rho(r)$ of the distribution given by

$$\rho(r)=e\sum_i |\phi_i(r)|^2, \tag{2.1}$$

where e is the electronic charge and ϕ_i is the wave function associated with the ith electron. The two center integrals, if any, involved in this evaluation may be taken from Coulson's paper.[9]

To determine the different wave functions ϕ_i use is made of the molecular orbital theory.[10,11] The self-consistent field molecular orbitals ϕ_i are usually determined in the linear combination of atomic orbitals approximation using one or more Slater-type orbitals[12] or Gaussian orbitals[13] as the basis for the linear combination.

It is sometimes more convenient and advantageous to use the method of equivalent orbitals developed by Lennard-Jones.[14,15] In this the set of molecular orbitals ϕ_i is transformed by the methods based on group theory to another set of orbitals which have the property of equivalence in the sense that they are interchangeable under the operations of the group. It is this set of equivalent orbitals which is used in Eq. (2.1) to calculate the charge density[16,17] and then the quadrupole moment components[17] from Eqs. (1.4).

III. THE INDUCED OPTICAL BIREFRINGENCE METHOD

Application of an external electric field F makes a fluid optically birefringent, that is to say, the fluid becomes doubly refracting having one value (say n_x) of the refractive index for light beams with electric vector parallel to F and another value (say n_y) for light beams with electric vector perpendicular to F. The difference (n_x-n_y) is known as the optical birefringence induced by the field F and is determined by the interaction of this field with the molecules of the fluid.

If the field is uniform, the interaction is that between the strength of the field and the permanent dipole moment as well as the polarizability anisotropy of the molecules. The resulting birefringence has been identified as the normal Kerr effect and is proportional to the square of the strength of the applied field[18]

$$(n_x-n_y)_F=KF^2. \tag{3.1}$$

However, if the field is inhomogeneous, an additional interaction between the gradient of the applied field and the quadrupole moment of the molecules will come up. This will result in an additional birefringence $(n_x-n_y)_{F'}$, which is proportional to the gradient of the applied field

$$(n_x-n_y)_{F'}=QF'. \tag{3.2}$$

The proportionality factor Q, for a dilute gas of axially symmetric molecules, is given by

$$Q=(4\pi N/15)[\tfrac{15}{2}B+(\theta/kT)(\alpha''-\alpha')], \tag{3.3}$$

where N is the number of molecules per unit volume, B is the quadrupole polarizability of the molecules, and α'' and α' are the polarizabilities parallel and perpendicular to the symmetry axis, respectively.

Thus if the component of the birefringence due to the gradient of the field could be separated out, the quadrupole moment can be evaluated from Eqs. (3.2) and (3.3).

Theory of the Method[6]

Consider a molecule whose position and orientation are described by a variable τ and suppose it is placed in an electrostatic potential field ϕ. Then its energy $u(\tau, \phi)$ can be expressed as

$$u(\tau,\phi)=\{u^0-\mu_\alpha F_\alpha-\tfrac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta-\tfrac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma-\tfrac{1}{24}\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta$$
$$-\tfrac{1}{3}\theta_{\alpha\beta}F_{\alpha\beta}'-\tfrac{1}{3}A_{\alpha:\beta\gamma}F_\alpha F_{\beta\gamma}'-\tfrac{1}{6}B_{\alpha\beta:\gamma\delta}F_\alpha F_\beta F_{\gamma\delta}'-\tfrac{1}{6}C_{\alpha\beta:\gamma\delta}F_{\alpha\beta}'F_{\gamma\delta}'-\cdots\}, \tag{3.4}$$

where u^0 is the energy of the molecule in the absence of the field, μ_α and $\theta_{\alpha\beta}$ are the permanent dipole and quadrupole moments of the molecule, F_α and $F_{\alpha\beta}'$ are the applied field strength and the field gradient, and the higher-order tensors denote the polarizabilities.

Differentiation of (3.4) with respect to F_α gives the total dipole moment μ_α^T of the molecule as

$$\mu_\alpha^T=\{\mu_\alpha+\alpha_{\alpha\beta}F_\beta+\tfrac{1}{2}\beta_{\alpha\beta\gamma}F_\beta F_\gamma+\tfrac{1}{6}\gamma_{\alpha\beta\gamma\delta}F_\beta F_\gamma F_\delta+\tfrac{1}{3}A_{\alpha:\beta\gamma}F_{\beta\gamma}'+\tfrac{1}{3}B_{\alpha\beta:\gamma\delta}F_\beta F_{\gamma\delta}'+\cdots\}e_\alpha^{\|}, \tag{3.5}$$

where $e_\alpha^{\|}$, $e_\beta^{\|}$, $\cdots$ denote unit vectors along the α, β, $\cdots$ component directions.

Differentiating (3.5) with respect to F_β, one gets

$$\partial\mu_\alpha^T/\partial F_\beta=\{\alpha_{\alpha\beta}+\beta_{\alpha\beta\gamma}F_\gamma+\tfrac{1}{2}\gamma_{\alpha\beta\gamma\delta}F_\gamma F_\delta+\tfrac{1}{3}B_{\alpha\beta:\gamma\delta}F_{\gamma\delta}'+\cdots\}e_\alpha^{\|}e_\beta^{\|}=\pi_{\alpha\beta}e_\alpha^{\|}e_\beta^{\|}, \tag{3.6}$$

where $\pi_{\alpha\beta}$ stands for the quantity within brackets. The quantity on the left-hand side describes the increase in moment μ_α^T per unit increase in the field F_β and is known as the "differential polarizability" associated with α and β directions. Similarly the differential polarizability associated with the perpendicular directions is $\pi_{\alpha\beta}e_\alpha^{\perp}e_\beta^{\perp}$, where $e_\alpha^{\perp}$, $e_\beta^{\perp}$, $\cdots$ denote the unit vectors at right angles to the α, β, $\cdots$ directions. The difference $\pi(\tau, \phi)$ between the two is

$$\pi(\tau,\phi)=[\alpha_{\alpha\beta}+\beta_{\alpha\beta\gamma}F_\gamma+\tfrac{1}{2}\gamma_{\alpha\beta\gamma\delta}F_\gamma F_\delta+\tfrac{1}{3}B_{\alpha\beta:\gamma\delta}F_{\gamma\delta}'+\cdots](e_\alpha^{\|}e_\beta^{\|}-e_\alpha^{\perp}e_\beta^{\perp}). \tag{3.7}$$

The difference (n_x-n_y) between the refractive indices for light beams with electric vectors along x and y then becomes

$$(n_x-n_y)=2\pi N\bar{\pi}, \tag{3.8}$$

where $\bar{\pi}$ is the average of $\pi(\tau, \phi)$ over all configurations τ, averaged with a Boltzmann-type weighting factor

$$\bar{\pi}=\int\pi(\tau,\phi)\exp[-u(\tau,\phi)/kT]\,d\tau\Big/\int\exp[-u(\tau,\phi)/kT]\,d\tau. \tag{3.9}$$

Since $\bar{\pi}$ depends on the applied field also, it can be expanded in terms of its value and the derivatives at $\phi=0$. Thus

$$\bar{\pi}=\left[(\bar{\pi})_{\phi=0}+\left\{\left(\frac{\partial\bar{\pi}}{\partial F}\right)_{\phi=0}F+\frac{1}{2}\left(\frac{\partial^2\bar{\pi}}{\partial F^2}\right)_{\phi=0}F^2+\cdots\right\}+\left\{\left(\frac{\partial\bar{\pi}}{\partial F_{xx}'}\right)_{\phi=0}F_{xx}'+\frac{1}{2}\left(\frac{\partial^2\bar{\pi}}{\partial F_{xx}'^2}\right)_{\phi=0}F_{xx}'^2+\cdots\right\}\right]. \tag{3.10}$$

Here the first term denotes the value of $\bar{\pi}$ in the absence of the applied field, the terms in the first bracket give the various order contributions from the field strength, those in the second bracket give the various order contributions from the gradient of the field and so on. In the second bracket the second-order term comes out to be zero so that for all moderate field gradients, only the first term in F_{xx}' need to be considered to describe the anisotropy due to the field gradients. Thus

$$(\bar{\pi})_{F_{xx}'}=(\partial\bar{\pi}/\partial F_{xx}')_{\phi=0}F_{xx}'. \tag{3.11}$$

Now Eq. (3.9) shows that

$$\left(\frac{\partial\bar{\pi}}{\partial F_{xx}'}\right)_{\phi=0}=\left\langle\frac{\partial\pi}{\partial F_{xx}'}\right\rangle_{\phi=0}-(kT)^{-1}\left\langle\pi\frac{\partial u}{\partial F_{xx}'}\right\rangle_{\phi=0}+(kT)^{-1}\langle\pi\rangle\left\langle\frac{\partial u}{\partial F_{xx}'}\right\rangle_{\phi=0}, \tag{3.12}$$

where $\langle\quad\rangle$ indicates an average over the configurations τ, averaged with a Boltzmann-type weighting factor.

Equation (3.7) shows that

$$\pi(\tau,0)=\alpha_{\alpha\beta}(e_\alpha^{\parallel}e_\beta^{\parallel}-e_\alpha^{\perp}e_\beta^{\perp})$$

which vanishes on averaging over all directions of $e_\alpha^{\parallel}$. Equation (3.12) thus reduces to

$$(\partial\bar{\pi}/\partial F_{xx}')_{\phi=0}=\langle\partial\pi/\partial F_{xx}'\rangle_{\phi=0}-(kT)^{-1}\langle\pi(\partial u/\partial F_{xx}')\rangle. \tag{3.13}$$

For an applied field such that $F_{xx}'=-F_{yy}'$ and $F_{zz}'=0$, one finds from Eq. (3.7) that

$$\langle\partial\pi/\partial F_{xx}'\rangle=\tfrac{1}{3}B_{\alpha\beta:\gamma\delta}\langle(e_\alpha^{\parallel}e_\beta^{\parallel}-e_\alpha^{\perp}e_\beta^{\perp})(e_\gamma^{\parallel}e_\delta^{\parallel}-e_\gamma^{\perp}e_\delta^{\perp})\rangle. \tag{3.14}$$

A simple trigonometrical analysis then shows that

$$\begin{aligned}\langle e_\alpha^{\parallel}e_\beta^{\parallel}e_\gamma^{\parallel}e_\delta^{\parallel}\rangle&=\langle e_\alpha^{\perp}e_\beta^{\perp}e_\gamma^{\perp}e_\delta^{\perp}\rangle=\tfrac{1}{15}(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})\\ \langle e_\alpha^{\parallel}e_\beta^{\parallel}e_\gamma^{\perp}e_\delta^{\perp}\rangle&=\langle e_\alpha^{\perp}e_\beta^{\perp}e_\gamma^{\parallel}e_\delta^{\parallel}\rangle=\tfrac{1}{30}(4\delta_{\alpha\beta}\delta_{\gamma\delta}-\delta_{\alpha\gamma}\delta_{\beta\delta}-\delta_{\alpha\delta}\delta_{\beta\gamma}),\end{aligned} \tag{3.15}$$

where $\delta_{\alpha\beta}=1$ if $\alpha=\beta$ and, $=0$ if $\alpha\neq\beta$. Substituting from equation (3.15) in Eq. (3.14) one finds

$$\langle\partial\pi/\partial F_{xx}'\rangle=\tfrac{1}{45}B_{\alpha\beta:\gamma\delta}[-2\delta_{\alpha\beta}\delta_{\gamma\delta}+3\delta_{\alpha\gamma}\delta_{\beta\delta}+3\delta_{\alpha\delta}\delta_{\beta\gamma}]. \tag{3.16}$$

From Eqs. (3.4) and (3.7) one has

$$[\pi(\partial u/\partial F_{xx}')]_{\phi=0}=-\tfrac{1}{3}\theta_{\gamma\delta}\alpha_{\alpha\beta}(e_\alpha^{\parallel}e_\beta^{\parallel}-e_\alpha^{\perp}e_\beta^{\perp})(e_\gamma^{\parallel}e_\delta^{\parallel}-e_\gamma^{\perp}e_\delta^{\perp})$$

and so

$$\langle\pi(\partial u/\partial F_{xx}')\rangle_{\phi=0}=-\tfrac{1}{45}\theta_{\gamma\delta}\alpha_{\alpha\beta}[-2\delta_{\alpha\beta}\delta_{\gamma\delta}+3\delta_{\alpha\gamma}\delta_{\beta\delta}+3\delta_{\alpha\delta}\delta_{\beta\gamma}]. \tag{3.17}$$

Substitution from Eqs. (3.16) and (3.17) into Eq. (3.13) then gives

$$(\partial\bar{\pi}/\partial F_{xx}')_{\phi=0}=\tfrac{2}{15}[B_{\alpha\beta:\alpha\beta}+(kT)^{-1}\theta_{\alpha\beta}\alpha_{\alpha\beta}]. \tag{3.18}$$

Equations (3.8), (3.11), and (3.18) then give the induced birefringence as

$$(n_x-n_y)_{F_{xx}'}=(4\pi N/15)F_{xx}'[B_{\alpha\beta:\alpha\beta}+(kT)^{-1}\theta_{\alpha\beta}\alpha_{\alpha\beta}]. \tag{3.19}$$

If the molecules are axially symmetric having a quadrupole moment θ and the polarizabilities α'' and α' along and at right angles to the symmetry axis, then Eq. (3.19) reduces to

$$(n_x-n_y)_{F_{xx}'}=(4\pi N/15)F_{xx}'[B_{\alpha\beta:\alpha\beta}+(\theta/kT)(\alpha''-\alpha')]. \tag{3.20}$$

{*Note added in the proof.* Buckingham and Pariseau [A. D. Buckingham and M. Pariseau, Trans. Faraday Soc. **62**, 1 (1966)] have given the quantum-mechanical derivation of an expression for (n_x-n_y) and its application to diatomic molecules. This treatment introduces two distinct modifications. One takes care of the different discrete rotational states of the molecule and results in a more complex temperature dependence than the simple T^{-1} law obtained classically. The other takes care of the nuclear motions and introduces the derivatives of the equilibrium separation quadrupole moment θ_e in the expression for (n_x-n_y). It may be noted that this makes the evaluation of quadrupole moment from this expression more difficult. It has also been observed that for CO_2 at room temperature these corrections are unimportant while for H_2 at room temperature they lead to a value of the birefringence about 75% of the classical value. At lower temperatures the corrections may become more important.}

For spherically symmetric molecules $B_{\alpha\beta:\alpha\beta}=\frac{15}{2}B$. For other molecules there are more than one quadrupole polarizability components and further simplification is difficult. However, for simplicity this quantity is replaced by $(15/2)B$ for the axially symmetric molecules also. Thus the birefringence due to the gradient of the field can, for the axially symmetric molecules, be written as

$$(n_x-n_y)_{F'_{xx}}=(4\pi N/15)F_{xx}'[\tfrac{15}{2}B+(\theta/kT)(\alpha''-\alpha')]. \tag{3.21}$$

Thus if the anisotropy $(\alpha''-\alpha')$ and the quadrupole polarizability B are known, measurements of the birefringence would lead to the molecular quadrupole moments from Eq. (3.21).

The details of the experimental method of measurement of the induced birefringence may be seen elsewhere.[8]

IV. THE SECOND VIRIAL COEFFICIENT METHOD

Many gases exhibit deviation from ideal gas behavior. This deviation is expressed in terms of the virial coefficients as[19]

$$\text{Deviation}=\left(\frac{PV}{RT}-1\right)=\frac{B}{V}+\frac{C}{V^2}+\frac{D}{V^3}+\cdots. \tag{4.1}$$

If there is no mutual interaction between the molecules, the gas behavior will be ideal and the coefficients $B, C, D, \cdots$ will all vanish. However, if a finite interaction exists, the coefficients are finite. If the magnitudes of these virial coefficients are known it should be possible to draw inferences about the interactions. In particular, if the explicit expression for the second virial coefficient B in terms of the interaction potential u is known one can calculate the leading unknown parameter of this potential. In most cases the molecular quadrupole moment θ is this parameter. A trial value of θ is used for calculating the value of B from the known expression. This value of B is compared with the measured B and the value of θ is adjusted such that the two B values agree.

Theory of the Method[20–22]

Second virial coefficient B is explicitly given in terms of interaction potential energy u by the equation

$$B(T)=\frac{N}{8\pi}\int_{\text{vol}}[1-\exp(-u/kT)]\,d\tau, \tag{4.2}$$

where N is the Avogadro number, k is the Boltzmann constant, T is the temperature of the gas, and $d\tau$ is a volume element.

Suppose that the potential u can be broken up into two parts as

$$u=u^0+u'. \tag{4.3}$$

Then Eq. (4.2) yields

$$B(T)=B_0(T)+\sum_{p=1}^{\infty}B_p(T), \tag{4.4}$$

where

$$B_0(T)=\frac{N}{8\pi}\int_{\text{vol}}[1-\exp(-u^0/kT)]\,d\tau,$$

$$B_p(T)=-\frac{N}{8\pi}\int_{\text{vol}}\frac{1}{p!}\left(-\frac{u'}{kT}\right)^p\exp(-u^0/kT)\,d\tau. \tag{4.5}$$

In an actual case of two interacting molecules the interaction potential u consists of a number of terms. Each term, in general, has a separation-dependent term multiplied by certain functions of angles θ_1, ϕ_1, and θ_2, ϕ_2. For convenience the potential u is expressed[20] such that the angular functions appear in the form of spherical harmonics

$$S_{lm}=\left[(2l+1)\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2}P_l^m(\cos\theta)\exp(im\phi). \tag{4.6}$$

The interaction potential u then has the form

$$u=\sum_{l_1l_2m}\xi^{l_1l_2m}(r)S_{l_1m}(\theta_1,\phi_1)S_{l_2m}(\theta_2,\phi_2), \tag{4.7}$$

where $\xi^{l_1l_2m}(r)$ incorporates in itself the radial dependence as well as the other constants not included in S_{l_1m} and S_{l_2m}. Since $S_{00}=1$, this reduces to

$$u=u^0+u',$$

where

$$u^0=\xi^{000}(r)$$

$$u'=\sum_{l_1l_2m}{}'\,\xi^{l_1l_2m}(r)S_{l_1m}(\theta_1,\phi_1)S_{l_2m}(\theta_2,\phi_2) \tag{4.8}$$

a prime over the summation sign indicating that the summation is over all the terms except the one for which $l_1=l_2=m=0$.

Thus u^0 is the term independent of the orientations θ and ϕ while u' becomes the orientation-dependent term. In Eq. (4.4) then one can interpret $B_0(T)$ as the contribution to the second virial coefficient from the orientation-independent or the so-called central forces, while $B_1(T)$, $B_2(T)$, $\cdots$ can be interpreted as first-order correction, second-order correction, $\cdots$ to second virial coefficient $B_0(T)$ when noncentral forces are present in addition to the central ones. If the noncentral forces are small, (u'/kT) will be small so that $B_3(T)$ and higher-order correction terms containing the third and higher powers of (u'/kT) can safely be neglected. The virial coefficient $B(T)$ then becomes

$$B(T)=B_0(T)+B_1(T)+B_2(T), \tag{4.9}$$

where $B_0(T)$, $B_1(T)$, and $B_2(T)$ are given by Eq. (4.5).

Equation (4.5) gives

$$B_0(T)=2\pi N\int_0^{\infty}[1-\exp(-u^0/kT)]r^2\,dr.$$

If the central force potential u^0 is taken to be the Lennard-Jones (12–6) potential[23]

$$u^0=4\epsilon[(r_0/r)^{12}-(r_0/r)^6], \tag{4.10}$$

then

$$B_0(T)=\tfrac{2}{3}\pi Nr_0^3F(T^*), \tag{4.11}$$

where

$$F(T^*)=3r_0^{-3}\int_0^{\infty}[1-\exp(-u^0/kT)]r^2\,dr \tag{4.12}$$

is known as the reduced second virial coefficient and has been tabulated by Hirschfelder *et al.*[24] as a function of $T^*=kT/\epsilon$.

For $B_1(T)$ one has from Eq. (4.5)

$$B_1(T)=\frac{2\pi N}{kT}\int_0^\infty r^2\langle u'\rangle_{\text{Av}}\exp(-u^0/kT)\,dr,$$

where $\langle u'\rangle_{\text{Av}}$ indicates a classical average of u' over all orientations. This will evidently consist of some inverse power of the separation r multiplied by some constants. One therefore takes it to be of the form

$$\langle u'\rangle_{\text{Av}}=-4\epsilon a(r_0/r)^n, \tag{4.13}$$

where the only two unknown parameters a and n are to be adjusted appropriately in any specific case. Substituting this above one gets

$$B_1(T)=-\tfrac{2}{3}\pi Nr_0^3(a/4)[H_n(y)/y^2], \tag{4.14}$$

where $y=2(\epsilon/kT)^{1/2}$ and $H_n(y)$ is the function

$$H_n(y)=12y^4r_0^{n-3}\int_0^\infty r^{-n}\exp(-u^0/kT)r^2\,dr. \tag{4.15}$$

This function has been tabulated by Buckingham and Pople.[22]

However, if several interactions are present simultaneously, $\langle u'\rangle_{\text{Av}}$ may have to be expressed as a sum of two or even more terms as

$$\langle u'\rangle_{\text{Av}}=-4\epsilon[a_1(r_0/r)^{n_1}+a_2(r_0/r)^{n_2}+\cdots]. \tag{4.16}$$

$B_1(T)$ then becomes

$$B_1(T)=-\tfrac{2}{3}\pi Nr_0^3\{\tfrac{1}{4}(a_1)[H_{n_1}(y)/y^2]+\tfrac{1}{4}(a_2)[H_{n_2}(y)/y^2]+\cdots\}. \tag{4.17}$$

For $B_2(T)$ one has from Eq. (4.5)

$$B_2(T)=-(N/16\pi^2k^2T^2)\int_{\text{vol}}u'^2\exp(-u^0/kT)\,d\tau.$$

This can similarly be expressed in terms of the average of u'^2. But in this case it is more convenient to use the form of u' obtained in Eq. (4.8). Substituting this and using standard properties of spherical harmonics

$$B_2(T)=-\frac{N\pi}{k^2T^2}\sum_{l_1l_2m}{}'\int_0^\infty r^2\exp(-u^0/kT)[\xi^{l_1l_2m}(r)]^2\,dr.$$

The radial function $\xi^{l_1l_2m}(r)$ consists of some inverse power of r multiplied by some constants. One therefore takes it to be of the form

$$\xi^{l_1l_2m}(r)=4\epsilon b(r_0/r)^s, \tag{4.18}$$

where the two unknowns b and s are to be adjusted appropriately in any specific case. Substituting this in the above expression for $B_2(T)$

$$B_2(T)=-\tfrac{2}{3}\pi Nr_0^3\,\tfrac{1}{8}\sum_{l_1l_2m}{}'b^2H_{2s}(y). \tag{4.19}$$

However, it is quite possible particularly when directional interactions of several types are being considered, that $\xi^{l_1l_2m}(r)$ may have to be expressed as a sum of two or even more terms as

$$\xi^{l_1l_2m}(r)=4\epsilon[b_1(r_0/r)^{s_1}+b_2(r_0/r)^{s_2}+\cdots]. \tag{4.20}$$

A substitution then gives $B_2(T)$ as

$$B_2(T)=-\tfrac{2}{3}\pi Nr_0^3\cdot\tfrac{1}{8}\sum_{l_1l_2m}{}'[b_1^2H_{2s_1}(y)+b_2^2H_{2s_2}(y)+\cdots+2b_1b_2H_{s_1+s_2}(y)+\cdots]. \tag{4.21}$$

Substituting from Eqs. (4.11), (4.17), and (4.21) in Eq. (4.9), the complete expression for the second virial coefficient $B(T)$ to the second order for a gas having a small noncentral force in addition to central one between its molecules, is

$$B(T)=\tfrac{2}{3}\pi Nr_0^3[F(T^*)-\{\tfrac{1}{4}(a_1)[H_{n_1}(y)/y^2]+\tfrac{1}{4}(a_2)[H_{n_2}(y)/y^2]+\cdots\}-\tfrac{1}{8}\sum_{l_1l_2m}{}'\{b_1^2H_{2s_1}(y)+b_2^2H_{2s_2}(y)+\cdots+2b_1b_2H_{s_1+s_2}(y)+\cdots\}], \tag{4.22}$$

where the central force is represented by Lennard-Jones potential [Eq. (4.10)] and the constants $a_1, n_1, b_1, s_1, \cdots$ specify noncentral forces. These constants are the only unknowns in Eq. (4.22) and need to be evaluated for noncentral forces of specific types.

Specific Cases

Dipole–Dipole Interaction

The potential for a dipole–dipole type interaction is[1]

$$u_{\mu\mu}'=(\mu^2/r^3)[2\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos(\phi_1+\phi_2)], \tag{4.23}$$

where μ is molecular dipole moment. To assign appropriate values to the constants $a_1, a_2, \cdots$ and $n_1, n_2, \cdots$ one has to find the average value of u'

$$\langle u_{\mu\mu}'\rangle_{\text{Av}}=\frac{\mu^2}{r^3}\int_0^\pi\int_0^\pi\int_0^{2\pi}\int_0^{2\pi}u'\sin\theta_1\sin\theta_2\,d\theta_1\,d\theta_2\,d\phi_1\,d\phi_2\Big/\int_0^\pi\int_0^\pi\int_0^{2\pi}\int_0^{2\pi}\sin\theta_1\sin\theta_2\,d\theta_1\,d\theta_2\,d\phi_1\,d\phi_2=0$$

which by comparison with Eq. (4.16) gives

$$a_1=a_2=\cdots=n_1=n_2=\cdots=0. \tag{4.24}$$

Similarly, for assigning proper values to the constants $b_1, b_2, \cdots$ and $s_1, s_2, \cdots$ one has to express u' in the form

(4.8) and then compare the nonvanishing $\xi^{l_1l_2m}(r)$ with Eq. (4.20). Suppose on expressing u' in the form (4.8) the only nonzero $\xi^{l_1l_2m}(r)$ are

$$\xi^{100}=x_1(\mu^2/r^3),\qquad \xi^{010}=x_2(\mu^2/r^3),\qquad \xi^{110}=x_3(\mu^2/r^3),\qquad \xi^{111}=\xi^{11-1}=x_4(\mu^2/r^3).$$

Then,

$$u'=(\mu^2/r^3)[x_1\sqrt{3}\cos\theta_1+x_2\sqrt{3}\cos\theta_2+3x_3\cos\theta_1\cos\theta_2+3x_4\sin\theta_1\sin\theta_2\cos(\phi_1+\phi_2)].$$

Comparing this with Eq. (4.23)

$$x_1=x_2=0,\qquad x_3=\tfrac{2}{3},\qquad x_4=\tfrac{1}{3}.$$

Thus the only nonzero $\xi^{l_1l_2m}(r)$ are

$$\xi^{110}=\tfrac{2}{3}(\mu^2/r^3),\qquad \xi^{111}=\xi^{11-1}=\tfrac{1}{3}(\mu^2/r^3). \tag{4.25}$$

In any other case also the average value of u' and the nonzero $\xi^{l_1l_2m}(r)$ can similarly be found out. The detailed computation for every case has not been attempted here. The results are reproduced below.

Dipole–Quadrupole Interaction

The interaction potential is[1]

$$u_{\mu\theta}'=(3\mu\theta/2r^4)[\{\cos\theta_1(3\cos^2\theta_2-1)+2\sin\theta_1\sin\theta_2\cos\theta_2\cos(\phi_1+\phi_2)\}$$
$$+\{\cos\theta_2(3\cos^2\theta_1-1)+2\sin\theta_1\sin\theta_2\cos\theta_1\cos(\phi_1+\phi_2)\}]. \tag{4.26}$$

The average of this vanishes. The nonzero $\xi^{l_1l_2m}(r)$ are

$$\xi^{120}=(\tfrac{3}{5})^{1/2}(\mu\theta/r^4),\qquad \xi^{210}=(\tfrac{3}{5})^{1/2}(\mu\theta/r^4),\qquad \xi^{121}=\xi^{12-1}=5^{-1/2}(\mu\theta/r^4),\qquad \xi^{211}=\xi^{21-1}=5^{-1/2}(\mu\theta/r^4). \tag{4.27}$$

Quadrupole–Quadrupole Interaction

The interaction potential is[1]

$$u_{\theta\theta}'=(3\theta^2/4r^5)[1-5\cos^2\theta_1-5\cos^2\theta_2+17\cos^2\theta_1\cos^2\theta_2+2\sin^2\theta_1\sin^2\theta_2\cos^2(\phi_1+\phi_2)$$
$$+16\sin\theta_1\sin\theta_2\cos\theta_1\cos\theta_2\cos(\phi_1+\phi_2)]. \tag{4.28}$$

The average of this is zero. The nonzero $\xi^{l_1l_2m}(r)$ are

$$\xi^{220}=\tfrac{6}{5}(\theta^2/r^5),\qquad \xi^{221}=\xi^{22-1}=\tfrac{4}{5}(\theta^2/r^5),\qquad \xi^{222}=\xi^{22-2}=\tfrac{1}{5}(\theta^2/r^5). \tag{4.29}$$

First–Order Induction Interaction

The potential for interaction of the dipole of one molecule with the dipole that it induces in the other is[25]

$$u_{\mu-\alpha\mu}'=-(\alpha\mu^2/2r^6)[(3\cos^2\theta_1+1)+(3\cos^2\theta_2+1)]. \tag{4.30}$$

The average of this over all orientations is

$$\langle u_{\mu-\alpha\mu}'\rangle_{\text{Av}}=-2\alpha\mu^2/r^6. \tag{4.31}$$

The nonzero $\xi^{l_1l_2m}(r)$ are

$$\xi^{000}=-2\alpha\mu^2/r^6,\qquad \xi^{020}=-5^{-1/2}(\alpha\mu^2/r^6),\qquad \xi^{200}=-5^{-1/2}(\alpha\mu^2/r^6). \tag{4.32}$$

Second–Order Induction Interaction

The potential for interaction of the quadrupole of one molecule with the dipole induced in the second by the dipole of the first plus that of the dipole of first molecule with the dipole induced in the second by the quadrupole of the first, is[25]

$$u'_{(\mu-\alpha\theta+\theta-\alpha\mu)}=-(12\mu\theta\alpha/r^7)(\cos^3\theta_1+\cos^3\theta_2). \tag{4.33}$$

The average value of this potential vanishes. The nonzero $\xi^{l_1l_2m}(r)$ are

$$\xi^{100}=\xi^{010}=-(12\sqrt{3}/5)(\mu\theta\alpha/r^7),\qquad \xi^{300}=\xi^{030}=-[24/5(7)^{1/2}](\mu\theta\alpha/r^7). \tag{4.34}$$

Third–Order Induction Interaction

The potential for interaction between the quadrupole of one molecule and the dipole induced by this quadrupole in the second molecule, is[1,25]

$$u_{\theta-\alpha\theta}'=-(9\alpha\theta^2/4r^8)[1-\cos^2\theta_1-\cos^2\theta_2+\tfrac{5}{2}\cos^4\theta_1+\tfrac{5}{2}\cos^4\theta_2]. \tag{4.35}$$

The average value of this is

$$\langle u_{\theta-\alpha\theta}'\rangle_{\text{Av}}=-3\alpha\theta^2/r^8. \tag{4.36}$$

The nonzero $\xi^{l_1 l_2 m}(r)$ are

$$\xi^{200}=\xi^{020}=-[12/7(5)^{1/2}](\alpha\theta^2/r^8), \qquad \xi^{400}=\xi^{040}=-\tfrac{3}{7}(\alpha\theta^2/r^8). \tag{4.37}$$

Anisotropic Dispersion Interaction

The potential for dispersion interaction is[26]

$$u_{\mathrm{dis}}'=-(1/r^6)[\{\tfrac{2}{3}A+\tfrac{5}{3}\mathrm{B}+\mathrm{B}'+\tfrac{8}{3}C\}+\{(A-B-B'+C)(\sin\theta_1\sin\theta_2\cos(\phi_1+\phi_2) \\ +2\cos\theta_1\cos\theta_2)^2+3(B-C)\cos^2\theta_1+3(B'-C)\cos^2\theta_2-\tfrac{2}{3}(A+B-2C)\}], \tag{4.38}$$

where

$$A=\tfrac{1}{4}(h)\alpha_1''\alpha_2''[\nu_1''\nu_2''/(\nu_1''+\nu_2'')], \qquad B=\tfrac{1}{4}(h)\alpha_1''\alpha_2'[\nu_1''\nu_2'/(\nu_1''+\nu_2')] \\ B'=\tfrac{1}{4}(h)\alpha_1'\alpha_2''[\nu_1'\nu_2''/(\nu_1'+\nu_2'')], \qquad C=\tfrac{1}{4}(h)\alpha_1'\alpha_2'[\nu_1'\nu_2'/(\nu_1'+\nu_2')], \tag{4.39}$$

where α_1'', α_1', are parallel and perpendicular components of the polarizability of first molecule and ν_1'', ν_1' are those of the fundamental frequency of oscillations for first molecule. α_2'', α_2' and ν_2'', ν_2' denote these quantities for second molecule.

For an isotropic molecule α'' and α' as well as ν'' and ν' are identical and the constants A, B, B', and C are all equal. In u_{dis}' then all the terms except those in the first curly brackets vanish. These can therefore be regarded as the isotropic part. This has already been accounted for by the inverse sixth-power term of Lennard-Jones potential.

The remaining anisotropic part of dispersion interaction potential thus becomes

$$u'_{\mathrm{anis\ dis}}=-(1/r^6)[(A-B-B'+C)\{\sin\theta_1\sin\theta_2\cos(\phi_1+\phi_2)+2\cos\theta_1\cos\theta_2\}^2 \\ +3(B-C)\cos^2\theta_1+3(B'-C)\cos^2\theta_2-\tfrac{2}{3}(A+B-2C)]. \tag{4.40}$$

The average value of this is zero. The nonzero $\xi^{l_1 l_2 m}(r)$ are

$$\xi^{200}=\xi^{020}=-(4/5^{1/2})\kappa\epsilon(r_0/r)^6, \qquad \xi^{220}=-\tfrac{12}{5}\kappa^2\epsilon(r_0/r)^6 \\ \xi^{221}=\xi^{22-1}=-\tfrac{8}{5}\kappa^2\epsilon(r_0/r)^6, \qquad \xi^{222}=\xi^{22-2}=-\tfrac{4}{5}\kappa^2\epsilon(r_0/r)^6, \tag{4.41}$$

where it has been assumed that $\nu''=\nu'=\nu$ and where use has been made of the fact that isotropic part is equal to the inverse sixth-power term of Lennard-Jones function.

In any specific case if more than one of these noncentral forces are present, the complete list of nonzero $\xi^{l_1 l_2 m}(r)$ should first be written out considering all the noncentral interactions present. It is only then that the constants b_1, b_2, $\cdots$ and s_1, s_2, $\cdots$ are evaluated by comparison with standard form [Eq. (4.20)] and substituted in Eq. (4.21) to get $B_2(T)$.

The details of experimental method of measurement of the virial coefficients may be seen elsewhere.[27–29]

V. THE SPECTRAL LINE-BROADENING METHOD

The causes of spectral linewidth are the following[30]:

1. Natural linewidth due to zero point energy.
2. Doppler broadening.
3. Wall collision broadening.
4. Saturation broadening.
5. Collision broadening.

Contributions of the first four causes in the microwave and infrared regions are either negligible or can be made extremely small by suitable choice of experimental conditions. Experimentally observed linewidths are thus due to the collisions among gas molecules. These collisions produce the interaction energy which perturbs the molecular energy levels causing the shift and the width of a spectral line. If other molecular parameters are known a suitable value of the quadrupole moment could be chosen to give the desired results.

Theory of the Method

Many theories[31–39] have been put forward to explain the linewidths in the microwave and infrared regions. But the one that has so far been most widely used is the Anderson theory. According to this the intensity $I(\omega)$ at any frequency ω in a broad line is given by[31,40]

$$I(\omega)=\mathrm{const}\times\frac{n v\sigma_r}{(\omega-\omega_{if}+n v\sigma_i)^2+(n v\sigma_r)^2}, \tag{5.1}$$

where σ_r and σ_i are, respectively, the real and imaginary parts of the collision cross section σ, n is the number of molecules per unit volume given by

$$n=9.68\times[p(\mathrm{mm\ Hg})/T(^\circ\mathrm{K})]\times10^{18}, \tag{5.2}$$

and where v is the average relative velocity of the two molecules given by

$$v=(8RT/M\pi)^{1/2}, \tag{5.3}$$

where R is the gas constant, T the temperature, and M the reduced mass of the system of two molecules.

Equation (5.1) shows that the half-intensity half-width of the line is

$$\Delta\nu=(nv/2\pi)\sigma_r. \tag{5.4}$$

The radiating molecule interacts with a large number of molecules passing at different distances from it. The number of molecules which pass at a distance b

is proportional to $2\pi b\, db$. Interactions with some of these may disturb the radiation completely, with others less completely, while with still others it may not disturb at all, depending upon their separation, their energy states, and upon the types of interactions involved. It is thus convenient to define a probability function $S(b)$ which specifies the probability that the interaction with a molecule in the rotational state J_2 passing from a distance b will disturb the radiation completely. Thus the effective number of collisions that do actually disturb the radiation is only $2\pi b\, dbS(b)$. This when integrated over all b gives the cross section for collisions with the molecules in the J_2 state

$$\sigma_{J_2}=\int_0^\infty 2\pi b\, dbS(b).$$

The function $S(b)$ can be expanded as[40]

$$S(b)=S_0(b)+S_1(b)+S_2(b)+\cdots,$$

where $S_0(b)$ is zero, $S_1(b)$ is an imaginary quantity, while $S_2(b)$ is a real quantity. Since we are interested in the real part alone, the partial cross section to the first order becomes

$$\sigma_{J_2}=\int_0^\infty 2\pi b S_2(b)\, db.$$

The function $S_2(b)$ has a very small value for large b and increases as b decreases till at $b=b_0$, $S_2(b_0)=1$. But as $S_2(b)$ is a probability function, a value greater than one makes no sense. So it is assumed that for $b=b_0$ to 0, $S_2(b)=1$. σ_{J_2} then becomes

$$\sigma_{J_2}=\pi b_0^2+\int_{b_0}^\infty 2\pi b S_2(b)\, db. \tag{5.5}$$

The cross section for the molecules in different rotational states is, in general, different and an average must be found for the effective collision cross section σ_r

$$\sigma_r=\sum_{J_2}\rho_{J_2}\sigma_{J_2}, \tag{5.6}$$

where ρ_{J_2} denotes the fraction of the molecules in the rotational state J_2 which for the case of linear molecules is given by[41]

$$\rho_{J_2}=(hcB/kT)(2J_2+1)\exp\{-(hcB/kT)J_2(J_2+1)\}, \tag{5.7}$$

where B is the rotational constant of the second molecule and other symbols have their usual significance.

The probability function $S_2(b)$ has been calculated in terms of the P matrices and is expressed as[40]

$$S_2(b)=\frac{1}{2}\left[\sum_{m_im_2}\frac{(J_im_iJ_2m_2\mid P^2\mid J_im_iJ_2m_2)}{(2J_i+1)(2J_2+1)}+\sum_{m_fm_2}\frac{(J_fm_fJ_2m_2\mid P^2\mid J_fm_fJ_2m_2)}{(2J_f+1)(2J_2+1)}\right]$$
$$-\sum_{m_im_i'm_fm_f'm_2m_2'M}\sum_{J_2'}\frac{(J_f1m_fM\mid J_im_i)(J_f1m_f'M\mid J_im_i')}{(2J_i+1)(2J_2+1)}\times(J_fm_fJ_2m_2\mid P\mid J_fm_f'J_2'm_2')(J_im_i'J_2'm_2'\mid P\mid J_i'm_iJ_2m_2), \tag{5.8}$$

where P is a matrix with its elements

$$(m\mid P\mid n)=\hbar^{-1}\int_{-\infty}^{+\infty}\exp(i\omega_{mn}t)(m\mid H_c(t)\mid n)\, dt. \tag{5.9}$$

The matrix P and the function $S_2(b)$ thus depend on the collision interaction Hamiltonian $H_c(t)$.

The forms of $S_2(b)$ and of σ_{J_2} obtained as a result of subsequent integration [Eq. (5.5)] have been worked out for interactions of different types. A detailed derivation is not attempted here but the results are reproduced below.

In the general case of two interacting molecules, the leading interactions are of the following types: the dipole–dipole, the dipole–quadrupole, the quadrupole–dipole, and the quadrupole–quadrupole representing electrostatic forces, first-order and second-order induction interactions, the dispersion forces, and the exchange forces.

The probability function is then[42–44]

$$S_2(b)=\{S_2(b)_{\mu_1\mu_2}+S_2(b)_{\mu_1\theta_2}+S_2(b)_{\theta_1\mu_2}+S_2(b)_{\theta_1\theta_2}\}+\{S_2(b)_{\mu_1\alpha_2\mu_1}+S_2(b)_{\mu_1\theta_1\alpha_2}\}+S_2(b)_{\mathrm{dis}}+S_2(b)_{\mathrm{exch}}. \tag{5.10}$$

The individual contributions $S_2(b)_{\mu_1\mu_2}, \cdots$ are[40,44–47]

$$S_2(b)_{\mu_1\mu_2}=A^4{}_{\mu_1\mu_2}b^{-4}\{\sum_{J_i'J_2'}D_1(J_iJ_i')D_2(J_2J_2')f_1(k)+\sum_{J_f'J_2'}D_1(J_fJ_f')D_2(J_2J_2')f_1(k)\}$$

$$S_2(b)_{\mu_1\theta_2}=A^6{}_{\mu_1\theta_2}b^{-6}\{\sum_{J_i'J_2'}D_1(J_iJ_i')Q_2(J_2J_2')f_2(k)+\sum_{J_f'J_2'}D_1(J_fJ_f')Q_2(J_2J_2')f_2(k)\}$$

$$S_2(b)_{\theta_1\mu_2}=A^6{}_{\theta_1\mu_2}b^{-6}\{\sum_{J_i'J_2'}Q_1(J_iJ_i')D_2(J_2J_2')f_2(k)+\sum_{J_f'J_2'}Q_1(J_fJ_f')D_2(J_2J_2')f_2(k)+B\sum_{J_2'}D_2(J_2J_2')f_2(k)\}$$

$$S_2(b)_{\theta_1\theta_2}=A^8{}_{\theta_1\theta_2}b^{-8}\{\sum_{J_i'J_2'}Q_1(J_iJ_i')Q_2(J_2J_2')f_3(k)+\sum_{J_f'J_2'}Q_1(J_fJ_f')Q_2(J_2J_2')f_3(k)+B\sum_{J_2'}Q_2(J_2J_2')f_3(k)\}$$

$$S_2(b)_{\mu_1\alpha_2\mu_1}=A^{10}{}_{\mu_1\alpha_2\mu_1}b^{-10}\{\sum_{J_i'}Q_1(J_iJ_i')g_1(k)+\sum_{J_f'}Q_1(J_fJ_f')g_1(k)+B\}$$

$$S_2(b)_{\mu_1\theta_1\alpha_2}=A^{12}{}_{\mu_1\theta_1\alpha_2}b^{-12}\{\sum_{J_i'}D_1(J_iJ_i')g_3(k)+\sum_{J_f'}D_1(J_fJ_f')g_3(k)\}$$

$$S_2(b)_{\text{dis}} = S_2(b)_{\text{dis}\,2} + S_2(b)_{\text{dis}\,4}$$

$$S_2(b)_{\text{dis}\,2} = A^{10}_{\text{dis}\,2} b^{-10} \{ \sum_{J_i'} Q_1(J_iJ_i') g_1(k) + \sum_{J_f'} Q_1(J_fJ_f') g_1(k) + B \}$$

$$S_2(b)_{\text{dis}\,4} = A^{10}_{\text{dis}\,4} b^{-10} \{ \sum_{J_i'J_2'} Q_1(J_iJ_i') Q_2(J_2J_2') g_2(k) + \sum_{J_f'J_2'} Q_1(J_fJ_f') Q_2(J_2J_2') g_2(k) + B \sum_{J_2'} Q_2(J_2J_2') g_2(k) \}$$

$$S_2(b)_{\text{exch}} = A^{\text{exp}}_{\text{exch}} b [1 - \tfrac{9}{4}(a/b) + \tfrac{165}{32}(a^2/b^2)] C_{J_iJ_f} \exp \{ -2[(b-d/a)] \}, \tag{5.11}$$

where

$$A^4_{\mu_1\mu_2} = \tfrac{4}{9}(\mu_1\mu_2/\hbar v)^2, \qquad A^6_{\mu_1\theta_2} = \tfrac{16}{45}(\mu_1\theta_2/\hbar v)^2$$

$$A^6_{\theta_1\mu_2} = \tfrac{16}{45}(\theta_1\mu_2/\hbar v)^2, \qquad A^8_{\theta_1\theta_2} = \tfrac{16}{25}(\theta_1\theta_2/\hbar v)^2$$

$$A^{10}_{\mu_1\alpha_2\mu_1} = (21\pi^2/640)(\alpha_2\mu_1^2/\hbar v)^2, \qquad A^{12}_{\mu_1\theta_1\alpha_2} = (27\pi^2/32)(\mu_1\theta_1\alpha_2/\hbar v)^2$$

$$A^{10}_{\text{dis}\,2} = \frac{84\pi^4}{10240} \left[\frac{\epsilon_1\epsilon_2}{\epsilon_1+\epsilon_2} \cdot \frac{(\alpha_1''-\alpha_1')\alpha_2}{hv} \right]^2, \qquad A^{10}_{\text{dis}\,4} = \frac{2236\pi^4}{1228800} \left[\frac{\epsilon_1\epsilon_2}{\epsilon_1+\epsilon_2} \frac{(\alpha_1''-\alpha_1')(\alpha_2''-\alpha_2')}{hv} \right]^2$$

$$A^{\text{exp}}_{\text{exch}} = \frac{256\pi}{5} \left(\frac{\gamma}{3+\gamma} \right)^2 a \left[(hv)^{-1} \left\{ kT + d^{-6} \left(\tfrac{1}{2}\pi\alpha_2\mu_1^2 + \frac{3\pi}{16} \frac{\epsilon_1\epsilon_2}{\epsilon_1+\epsilon_2} (2+\tfrac{1}{3}\gamma)\alpha_1\alpha_2 \right) \right\} \right]^2. \tag{5.12}$$

μ_1, μ_2, θ_1, and θ_2 are the dipole and quadrupole moments of the two molecules, ϵ_1 and ϵ_2 are their ionization energies, α_1'' and α_1' are, respectively, the parallel and perpendicular components of the polarizability of first molecule, α_2'' and α_2' are that for the second molecule, a and d are the range of exchange forces and the hardcore diameter, respectively, and $\gamma = (\alpha_1''-\alpha_1')/\alpha_1$.

$$C_{J_iJ_f} = Q_1(J_i, J_i) + Q_1(J_f, J_f) + B$$

$$B = (-1)^{J_i+J_f} 2[(2J_i+1)(2J_f+1) Q_1(J_i, J_i) Q_1(J_f, J_f)]^{1/2} W(J_iJ_fJ_iJ_f, 12), \tag{5.13}$$

where W is the Racah coefficient given by

$$W(J_iJ_fJ_iJ_f, 12) = (-1)^{2J}[(2J+5)(J+2)J(2J-1)]^{1/2}/[(J+1)(2J+1)(2J+3)]. \tag{5.14}$$

D_1, D_2, Q_1, and Q_2 are the dipolar and quadrupolar transition probabilities[48] given for the case of linear molecules, by

$$D(J, J+1) = \frac{J+1}{2J+1}, \qquad D(J, J-1) = \frac{J}{2J+1}, \qquad Q(J, J+2) = \frac{3}{2} \frac{(J+1)(J+2)}{(2J+1)(2J+3)}$$

$$Q(J, J-2) = \frac{3}{2} \frac{J(J-1)}{(2J-1)(2J+1)}, \qquad Q(J, J) = \frac{J(J+1)}{(2J-1)(2J+3)}. \tag{5.15}$$

The functions $f_1(k), f_2(k), f_3(k)$, $g_1(k)$, $g_2(k)$, and $g_3(k)$ are functions of $k = (2\pi c/v) b\Delta E$, ΔE being the sum of transition energies of the two molecules, defined and tabulated elsewhere.[40,44]

The partial collision cross section σ_{J_2} is obtained as[44]

$$\begin{aligned}
\sigma_{J_2} = \pi b_0^2 \Bigg[1 &+ A^4_{\mu_1\mu_2} b_0^{-4} \{ \sum_{J_i'J_2'} D_1(J_iJ_i') D_2(J_2J_2') F_1(k_0) + \sum_{J_f'J_2'} D_1(J_fJ_f') D_2(J_2J_2') F_1(k_0) \} \\
&+ A^6_{\mu_1\theta_2} b_0^{-6} \{ \sum_{J_i'J_2'} D_1(J_iJ_i') Q_2(J_2J_2') F_2(k_0) + \sum_{J_f'J_2'} D_1(J_fJ_f') Q_2(J_2J_2') F_2(k_0) \} \\
&+ A^6_{\theta_1\mu_2} b_0^{-6} \{ \sum_{J_i'J_2'} Q_1(J_iJ_i') D_2(J_2J_2') F_2(k_0) + \sum_{J_f'J_2'} Q_1(J_fJ_f') D_2(J_2J_2') F_2(k_0) + B \sum_{J_2'} D_2(J_2J_2') F_2(k_0) \} \\
&+ A^8_{\theta_1\theta_2} b_0^{-8} \{ \sum_{J_i'J_2'} Q_1(J_iJ_i') Q_2(J_2J_2') F_3(k_0) + \sum_{J_f'J_2'} Q_1(J_fJ_f') Q_2(J_2J_2') F_3(k_0) + B \sum_{J_2'} Q_2(J_2J_2') F_3(k_0) \} \\
&+ A^{10}_{\mu_1\alpha_2\mu_1} b_0^{-10} \{ \sum_{J_i'} Q_1(J_iJ_i') G_1(k_0) + \sum_{J_f'} Q_1(J_fJ_f') G_1(k_0) + \tfrac{1}{4}B \} \\
&+ A^{12}_{\mu_1\theta_1\alpha_2} b_0^{-12} \{ \sum_{J_i'} D_1(J_iJ_i') G_3(k_0) + \sum_{J_f'} D_1(J_fJ_f') G_3(k_0) \} \\
&+ A^{10}_{\text{dis}\,2} b_0^{-10} \{ \sum_{J_i'} Q_1(J_iJ_i') G_1(k_0) + \sum_{J_f'} Q_1(J_fJ_f') G_1(k_0) + \tfrac{1}{4}B \} \\
&+ A^{10}_{\text{dis}\,4} b_0^{-10} \{ \sum_{J_i'J_2'} Q_1(J_iJ_i') Q_2(J_2J_2') G_2(k_0) + \sum_{J_f'J_2'} Q_1(J_fJ_f') Q_2(J_2J_2') G_2(k_0) + B \sum_{J_2'} Q_2(J_2J_2') G_2(k_0) \} \\
&+ A^{\text{exp}}_{\text{exch}}\, a^3 b_0^{-2} \left(\frac{145}{32} - \frac{5}{4}\frac{b_0}{a} + \frac{b_0^2}{a^2} \right) C_{J_iJ_f} \exp \left\{ -2 \left(\frac{b_0-d}{a} \right) \right\} \Bigg],
\end{aligned} \tag{5.16}$$

where b_0 is such that $S_2(b_0)=1$, $k_0=(2\pi c/v)b_0\Delta E$ and where the functions $F_1(k_0)$, $F_2(k_0)$, $F_3(k_0)$, $G_1(k_0)$, $G_2(k_0)$, and $G_3(k_0)$ are the functions of k_0 defined and tabulated elsewhere.[40,44]

Method of Computation[42,43]

One calculates the average relative velocity v from Eq. (5.3). With this v and other known constants of the two molecules and an assumed value for the unknown constant, if any, the different A coefficients are evaluated from Eq. (5.12). Then for a given value of J_2 a trial value of b is taken and $S_2(b)_{\mu_1\mu_2}$, etc. are calculated from Eq. (5.11). If the value of the function $S_2(b)$ comes out to be different from unity, another value of b is taken and the calculations are repeated till $S_2(b)$ becomes unity. The corresponding value of b is b_0. With this b_0 then the partial collision cross section σ_{J_2} is evaluated from Eq. (5.16) using the known values of A coefficients and transition probabilities and the values of $F_1(k_0)$, $\cdots$ from the tables.

The value of σ_{J_2} is thus found for every J_2 starting right from $J_2=0$ and upto the value say $J_2^{\max}$ after which σ_{J_2} becomes independent of J_2. In practice the calculation of σ_{J_2} at five or six values of J_2 and a subsequent graphical interpolation for intermediate values of J_2, suffices. The average collision cross section σ_r is then evaluated from Eq. (5.6) in the following manner:

$$\sigma_r=\sum_{J_2=0}^{J_2^{\max}}\rho_{J_2}\sigma_{J_2}+\Big(1-\sum_{J_2=0}^{J_2^{\max}}\rho_{J_2}\Big)\sigma_{J_2^{\max}}. \tag{5.17}$$

The values of ρ_{J_2} needed here are calculated in advance from Eq. (5.7).

The half-intensity half-width $\Delta\nu$ is then calculated from Eq. (5.4), using known value of v and that of n from Eq. (5.2).

If any one of the constants of the two molecules, particularly if the quadrupole moment of any one molecule, be unknown the width is evaluated as explained above for several values of the quadrupole moment and a curve of linewidth vs quadrupole moment is drawn. The value corresponding to the measured width gives the best value of the quadrupole moment of the molecule.

The details of experimental method of measurement of microwave spectral linewidths may be seen elsewhere.[49–52]

Lineshift Method[53,54]

An investigation of the lineshifts in the microwave or infrared regions can also lead to the molecular quadrupole moments. Following the impact theory of Anderson, Eq. (5.1) directly gives the lineshift as

$$\delta\nu=-(nv/2\pi)\sigma_i\,, \tag{5.18}$$

where σ_i is the imaginary part of collision cross section averaged over all the rotational states J_2 of the perturbing molecules

$$\sigma_i=\sum_{J_2}\rho_{J_2}\sigma_{J_2}\,. \tag{5.19}$$

Since we are now interested in the imaginary part alone, the partial collision cross section σ_{J_2} is

$$\sigma_{J_2}=\pi b_0^2+\int_{b_0}^{\infty}2\pi bS_1(b)\,db, \tag{5.20}$$

where $S_1(b)$ is the leading imaginary term in the expansion of $S(b)$ and where it has been assumed that from $b=b_0$ to 0, $S_1(b)=1$, b_0 being such that $S_1(b_0)=1$.

The function $S_1(b)$ is expressed in terms of the P matrices [Eq. (5.9)] as follows[40]:

$$S_1(b)=i\bigg[\sum_{m_i,m_2}\frac{(J_im_iJ_2m_2\mid P\mid J_im_iJ_2m_2)}{(2J_i+1)(2J_2+1)}-\sum_{m_f,m_2}\frac{(J_fm_fJ_2m_2\mid P\mid J_fm_fJ_2m_2)}{(2J_f+1)(2J_2+1)}\bigg]. \tag{5.21}$$

The theoretical lineshift investigations have been carried out mainly in the infrared region only by a number of workers.[53,54] But the expressions for the function $S_1(b)$ and the collision cross section have so far been worked out only for the induction and dispersion interactions in an attempt to explain the shift of a dipolar line perturbed by rare gas molecules. However, the expressions for electrostatic interactions can be derived in a similar manner. Then if θ is the only unknown parameter, its value may be suitably chosen to fit the experimental lineshift data.

Recently, Kranendonk[55–57] has investigated the broadening of Raman lines and it appears that these investigations may also lead to molecular quadrupole moments. However, as the accuracy of Raman line measurements may not be very high, the values may probably not be very reliable.

VI. OTHER METHODS

The Anisotropic Susceptibility Method

The diamagnetic susceptibility of a molecule is, in general, anisotropic. For axially symmetric molecules the susceptibility χ'' along the symmetry axis and χ' at right angles to it are given by[58]

$$\chi'=(e^2/4mc^2)\sum_i(y_i^2+z_i^2)+\chi_{\mathrm{HF}}'$$
$$\chi''=(e^2/4mc^2)\sum_i(x_i^2+y_i^2), \tag{6.1}$$

where x_i, y_i, z_i are the coordinates of ith electron and the summation is over all the electrons in the molecule. χ_{HF}' is the contribution to χ' from the high-frequency matrix elements occurring in the theory of diamagnetic susceptibility. This contribution to χ'' is zero because of the symmetry of the Hamiltonian of the electrons about the molecular axis.

Equations (6.1) yield

$$e\sum_i (z_i^2-x_i^2)=(4mc^2/e)\{(\chi'-\chi'')-\chi_{\mathrm{HF}}'\}. \quad (6.2)$$

The left-hand side of this equation is identified as the electronic contribution to the molecular quadrupole moment and can be determined provided the anisotropy $(\chi'-\chi'')$ in diamagnetic susceptibility and the high-frequency contribution χ_{HF}' were known.

The anisotropy $(\chi'-\chi'')$ is determined[59] by studying the dependence of diamagnetic susceptibility on the orientation of molecular rotational angular momentum. Let χ_M represent the diamagnetic susceptibility of a molecule with rotational quantum number $J=1$ and with rotational magnetic quantum number equal to M. If θ be the angle between the applied field and the internuclear symmetry axis

$$\chi_M=\chi'\langle\sin^2\theta\rangle_M+\chi''\langle\cos^2\theta\rangle_M \quad (6.3)$$

where the angular brackets indicate an average over the state concerned. These averages have been evaluated for the three possible values of M and are[59]

$$\langle\sin^2\theta\rangle_{\pm1}=\tfrac{4}{5}, \qquad \langle\sin^2\theta\rangle_0=\tfrac{2}{5}$$

$$\langle\cos^2\theta\rangle_{\pm1}=\tfrac{1}{5}, \qquad \langle\cos^2\theta\rangle_0=\tfrac{3}{5}. \quad (6.4)$$

Substituting this in Eq. (6.3) one gets

$$(\chi'-\chi'')=\tfrac{5}{2}(\chi_{\pm1}-\chi_0). \quad (6.5)$$

The difference $(\chi_{\pm1}-\chi_0)$ has been measured by Ramsey[60] using molecular beam experiments. This gives the anisotropy $(\chi'-\chi'')$. Its value for a number of molecules is now available in literature.[61]

The high-frequency contribution χ_{HF}' has been shown[60] to be related to the rotational magnetic moment of the molecule. This can be measured by studying the radio-frequency spectrum of a molecular beam in a strong magnetic field.[60,62]

The structure of the molecules being known from other sources, the nuclear contribution to the molecular quadrupole moment is calculated directly from Eq. (1.3).

The Dielectric Constant Method

The dielectric constant of any real gas is determined both by the properties of isolated molecules and by the effects of molecular interactions. If the interactions are small, they can be neglected completely and the dielectric behavior of the gas is represented well by Clausius–Mossotti equation[4]

$$[(\epsilon-1)/(\epsilon+2)](n/v)=A, \quad (6.6)$$

where (n/v) is molar density of the gas and $A=4\pi\alpha/3$, α being average polarizability of the molecules.

However, for a real gas the effect of molecular interactions is fairly important and one has to consider the complete virial expansion of the Clausius–Mossotti function as[63]

$$\frac{\epsilon-1}{\epsilon+2}\frac{n}{v}=A+B\left(\frac{n}{v}\right)+C\left(\frac{n}{v}\right)^2+\cdots, \quad (6.7)$$

where the coefficients B, C, $\cdots$ are known as second, third, $\cdots$ dielectric virial coefficients. The second coefficient B incorporates the effects of pair interactions, the third one C that of the three body interactions and so on.

The second dielectric virial coefficient B has been calculated theoretically[64–67] considering the dipole moment induced in a molecule by the quadrupolar field of a neighboring molecule at the first one. Its value for a nonpolar gas of axially symmetric molecules is

$$B=\frac{16\pi^2N^2}{3kT}\alpha^2\theta^2(1+\tfrac{4}{5}\kappa^2)\int_0^\infty r^{-8}\exp\{-u(r)/kT\}r^2\,dr, \quad (6.8)$$

where N is the Avogadro number, κ and θ are, respectively, the polarizability anisotropy and the quadrupole moment of the molecules of the gas, and $u(r)$ is the pair interaction potential assumed purely radial in the theory.

Using a Lennard-Jones potential [Eq. (4.10)] for $u(r)$ one has

$$B=(\pi N\alpha/3y)^2\,(1+\tfrac{4}{5}\kappa^2)(\theta^2/\epsilon r_0^5)H_8(y), \quad (6.9)$$

where $H_n(y)$ is the function as defined in Eq. (4.15) and tabulated by Buckingham and Pople.[22]

The coefficient B may be evaluated experimentally also by[63,68] fitting the observed dielectric constant data into Eq. (6.7). Then if other molecular parameters occurring in Eq. (6.9) are known, the value of quadrupole moment θ may be chosen such that the two B values agree.

The Pressure-Induced Absorption Method

Transient dipoles may be induced in the molecules when perturbed by strong external fields or by intermolecular force fields. Thus nondipolar gases may also exhibit rotational absorption at high pressures. Such absorption has been observed in a number of gases.[69–73] The integrated intensity at moderate pressures increases as the square of the density indicating that the absorption is caused by the bimolecular force fields. The quadrupole field has a greater range than other possible force fields. In fact the pressure induced rotational absorption has so far been observed only in the quadrupolar gases such as CO_2, C_2H_4, etc. For gases like CH_4 and SF_6 having higher multipoles as their leading multipoles, the absorption is immeasurably small.[72]

Considering these quadrupole induced dipoles, Maryott and Birnbaum[71] have derived an expression for the loss factor in terms of pertinent molecular parameters. They obtain

$$\epsilon''=3(\epsilon_0-\epsilon_\infty)\omega\pi r_0\langle 1/v\rangle/28, \qquad (6.10)$$

where $(\epsilon_0-\epsilon_\infty)$ is the total contribution to the dielectric constant arising from quadrupole induced dipoles, ω is the angular frequency, r_0 is kinetic collision diameter, and $\langle 1/v\rangle$ is the Boltzmann average of the reciprocal of the relative velocity.

On introducing the molecular parameters and rearranging, Eq. (6.10) becomes[72]

$$\theta^2=\frac{7}{3\pi^{7/2}}\left(\frac{V_{\mathrm{STP}}{}^2}{N^{3/2}}\right)\left(\frac{\epsilon''}{\omega\rho^2}\right)\frac{(kT)^{3/2}}{\alpha^2 r_0 M^{1/2}}\Bigg/\int_0^\infty r^{-8}\exp\{-u(r)/kT\}r^2\,dr, \qquad (6.11)$$

where θ is the molecular quadrupole moment, α is the average polarizability of the molecules, N is the Avogadro number, M is the molecular weight, V_{STP} is the molar volume at 1 atm and 0°C, ρ is the density in Amagat units, and where $u(r)$ is the intermolecular potential assumed purely radial in the theory.

Using Lennard-Jones potential [Eq. (4.10)] for $u(r)$ one has

$$\theta^2=112\,\frac{V_{\mathrm{STP}}{}^2}{\pi^{7/2}N^{3/2}}\,\frac{\epsilon^2}{(kT)^{1/2}}\,\frac{r_0{}^4}{\alpha^2 M^{1/2}}\cdot\frac{1}{H_8(y)}\left(\frac{\epsilon''}{\omega\rho^2}\right), \qquad (6.12)$$

where $H_n(y)$ is the function as defined in Eq. (4.15) and tabulated by Buckingham and Pople.[22]

Thus if other molecular parameters were known, Eq. (6.12) could be used to evaluate molecular quadrupole moments from the measured absorptions at known values of the density and frequency.

The Bond Moments Method

Let us consider a molecule having several bonds with known multipole moments. Then an approximate distribution of the charges in the bonds can be obtained provided a suitable model for this is assumed. One assumes[74] a classical model in which each bond is supposed to consist of two $+e$ charges at each of the two nuclear positions and two circular charge rings each of radius r and charge $-e$ at distances say z_1 and z_2 from the center of the bond. The coordinates r, z_1, and z_2 are then to be found.

The contributions of the discrete positive charges to the bond moments are calculated directly and subtracted from the known moments to get the contributions μ, P, Ω, ϕ, ··· of the charge rings to the dipole-, quadrupole-, octopole-, hexadecapole-, ··· moments of the bond.

These are calculated directly also from Eq. (1.4). Thus

$$\mu=r(z_1+z_2)$$
$$P=e(z_1{}^2+z_2{}^2-r^2)$$
$$\Omega=e[z_1{}^3+z_2{}^3-\tfrac{3}{2}r^2(z_1+z_2)]. \qquad (6.13)$$

A simultaneous solution of these three equations gives the coordinates r, z_1, and z_2.

The contribution of the rings to the quadrupole moment θ of the molecule is then calculated from Eq. (1.4). The nuclear contribution is calculated directly from Eq. (1.3). The inner-shell electrons, if any, may be considered along with the appropriate nucleus.

VII. DISCUSSION

The Molecular Orbital Method

The molecular orbital method is, in principle, applicable to any type of molecule. There are no restrictions as regards the symmetry properties of the molecule. This makes it specially suitable and advantageous for asymmetric molecules like H_2O, NH_3, ··· for which so far it has not been possible to apply most of the other available methods. The method is a direct one starting from the microscopic standpoint of electronic charges and nuclei constituting the molecule. It has the credit of determining the magnitude as well as the sign of the molecular quadrupole moment.

This method is based on the knowledge of electronic wave functions which are determined by the considerations of energy of the molecule. But the energy of a molecule is not so sensitive to these wave functions as is the molecular quadrupole moment. The quadrupole moment values derived from these wave functions will therefore not be very reliable.

The determination of electronic wave functions involves evaluation of the multicenter Coulomb and exchange integrals between different electrons of the molecule. This becomes prohibitively tedious as the number of centers exceeds three or four. The applicability of the method is thus limited to smaller molecules only.

The Induced Optical Birefringence Method

This is a direct method determining the magnitude as well as the sign of the molecular quadrupole moment. It is applicable for the axially symmetric molecules only.

The measurement is essentially of the quantity $y=[\frac{15}{2}B+(\theta/kT)(\alpha''-\alpha')]$. Thus the values of the quadrupole polarizability B and the anisotropy $(\alpha''-\alpha')$ must be known before the quadrupole moment θ can be calculated. The value of B can be assessed by making the measurements over a range of temperatures and plotting y against $1/T$. For obtaining an appreciable range in y, a fairly large range of temperatures has to be covered. But there are practical difficulties in extending the temperature range upwards while at lower temperatures the low vapor pressure of most of the gases of interest presents practical difficulties. Thus an accurate assessment of B is rather difficult. It is then seen that for many molecules it contributes at most a few per cent only. The influence of B is therefore neglected completely. This neglect is justifiable for molecules with large values of the product $\theta(\alpha''-\alpha')$ but not for those with smaller values of this product. In many molecules, as for example in the H_2 molecule, the two terms in y being of opposite signs, cancel each other and a separation of the two by measurements over a range of temperatures becomes still more difficult. Thus the complications due to the quadrupole polarizability B render the method suitable only for those molecules for which the product $\theta(\alpha''-\alpha')$ is large and a fairly high vapor pressure is obtainable.

The anisotropy $(\alpha''-\alpha')$ is known for a large number of molecules. But an examination of the data shows that there exists much uncertainty about this factor. This introduces a corresponding ambiguity in the calculated quadrupole moment and constitutes the most serious drawback of the method.

The Second Virial Coefficient Method

This is an indirect method involving molecular interactions manifested in the form of an imperfection in the gas behavior. It determines only the magnitude of the quadrupole moment and gives no idea about its sign. It is applicable to axially symmetric molecules only.

In the theoretical treatment of the method, the directional part of the intermolecular potential is assumed to be small and $B_3(T)$ and higher-order terms are neglected. However, in the case of molecules having a large dipole moment and a high polarizability, this assumption is not quite justified and one must consider up to at least the $B_3(T)$ term in the expansion of $B(T)$.

Calculations show that in many cases the sensitivity of the second virial coefficient B to the quadrupole moment is poor. Small uncertainties in the measured B lead to much larger uncertainties in the calculated quadrupole moment of the molecule.

The experimental value of $B(T)$ is found from high-pressure p–v–t data which may extend up to 100 atm or even more. At such high pressures, apart from the changes in the polarizability and its anisotropy, a distortion in the shape of the molecules takes place. The quadrupole moment being highly sensitive to the shape of the molecular charge distribution, its value at such high pressures will be different from that for the normal molecules at low pressures of the gas.

The Spectral Line-Broadening Method

This is an indirect method depending on the use of Anderson theory and the experimentally determined width of the spectral lines in the microwave or infrared regions. Only the magnitude of the quadrupole moment can be determined by this process. So far this method has been used for axially symmetric molecules only. The difficulty with the asymmetric molecules is that the quadrupole transition probabilities in them are still not known.

In many polar molecules having a large dipole moment and polarizability (for example in the linear molecule BrCN[75]), the width of the line is not quite sensitive to the quadrupole moment and it is seen that small errors in the measured width lead to quite discouraging deviations in the calculated quadrupole moment of the molecule. This means that the self-broadening method is suitable only for those molecules which have a low value of the dipole moment. For nonpolar molecules the line of some other polar molecule as broadened by this nonpolar molecule is studied. In this case a change in the quadrupole moment changes the linewidth more than in the first case.

The experimental measurement of the linewidth in the microwave region can be done with a high degree of accuracy. The measurements are made at low pressures where the molecular charge distribution is not distorted. This constitutes a great advantage of the present method.

The microwave linewidth investigations are to be preferred over the infrared lineshift and Raman linewidth investigations because of higher experimental accuracy and reliability.

The Anisotropic Susceptibility Method

This is a very elegant and accurate method determining the nuclear and the electronic contributions to the quadrupole moment separately. Thus both the magnitude as well as the sign of the quadrupole moment are determined. Like most of the other methods this also is applicable for the axially symmetric molecules only.

The evaluation is based on an accurate determination of rotational magnetic moment by the high-precision molecular-beam resonance techniques. The experimental difficulties involved in this technique limit the applicability of this method.

The Dielectric Constant Method

This also is an indirect method and determines only the magnitude of the quadrupole moment. It applies strictly to axially symmetric molecules only. However, a more general treatment applicable to the molecules of lower symmetry also could be given.

The evaluation is based on the determination of second dielectric virial coefficient B, in the theoretical treatment of which the intermolecular potential is taken to be a purely radial L-J potential. For many nonpolar gases the orientation dependent quadrupole–quadrupole interaction is of considerable importance and needs to be considered. An approximate correction for this term gives[68] an additional $+ve$ contribution to B, thereby reducing the calculated quadrupole moment. The complex angular dependence of θ–θ interaction makes a very accurate treatment rather difficult.

The experimental determination of B is done through the deviations from Clausius–Mossotti equation. Since this effect is small at moderate pressures, very high precision measurements of the dielectric constant are essential. Further, appreciable deviations from the C–M behavior appear only at high pressures that may extend up to 100 atm or so. Because of the distortions in the molecular charge distributions at such high pressures, the quadrupole moment is likely to be different from that for the normal molecules.

The Pressure-Induced Absorption Method

This also is an indirect method determining only the magnitude of the quadrupole moment and is applicable to axially symmetric molecules only. Since this also makes use of the high-pressure data (appreciable absorption is induced only at high pressures), the derived quadrupole moment values are expected to be erroneous.

In the sensitivity and experimental accessibility these measurements offer definite advantages over direct studies of the dielectric constants.

For a more accurate evaluation one should study the induced absorption in the quadrupolar gas–foreign nonquadrupolar gas system and not in the pure quadrupolar gas system. This is because the large quadrupole–quadrupole interaction in the latter case changes the intermolecular potential appreciably from the assumed L-J potential. It is for this reason that the quadrupole moment values calculated with this potential for the pure gas are somewhat higher than those derived from the mixtures.[73] If pure gas is used, an allowance must be made for the θ–θ interaction which will reduce the calculated quadrupole moment.

The Bond Moments Method

This method evaluates the nuclear and the electronic contributions to the molecular quadrupole moment separately and, therefore, has the credit of determining its magnitude as well as the sign. It is applicable irrespective of the symmetry properties of the molecule and does not involve any tedious computational effort even for the larger molecules having a larger number of bonds. The method, however, does not account properly for the contribution of lone-pair electrons which in some molecules do contribute significantly.[17] Further, the simple model assumed for the charge distribution in the bonds appears too crude to give accurate molecular moments.

The bond moments to be used in the calculations are obtained either by the molecular orbital calculations or from the internal rotation data. If the complete MO calculations are to be done it would be better to compute the molecular moments directly rather than to compute first the bond moments and then to derive the molecular moments by the above method. The second method[76] is to interpret the measured "barrier to internal rotation" in terms of the interactions between the members of two groups of bonds in the same molecule and hence to derive the bond moments. This would give fairly accurate bond moments provided the assumption that the barrier arises from the bond–bond interaction is justified. It may be pointed out here that because of the effects of the environments on the bonds, the moments of a bond as such do not have a very precise significance. If the same bond occurs in several molecules, the calculation of its moments has to be done for each molecule and for each of its geometrical configurations.

VIII. LIST OF MOLECULAR QUADRUPOLE MOMENTS

Serial Nos.	Molecule	Quadrupole moment[a] $\times 10^{-26}$esu cm^2	Method	Reference
1.	H_2	0.60	Theoretical MO calculations	77
		0.78	Theoretical MO calculations	78
		0.34	Theoretical MO calculations	79
		0.626	Theoretical MO calculations	80
		0.64	Theoretical modified Schrödinger equation calculations	81
		0.95	Second virial coefficients	21
		0.52	Second virial coefficients	82
		0.3	Microwave line broadening—NH_3	83
		0.38±0.02	Microwave line broadening—NH_3	84
		0.63	Anisotropic susceptibility measurements	62
		0.6	Pressure-induced absorption	85
		1.0	Pressure-induced absorption	72

Serial Nos.	Molecule	Quadrupole moment[a] $\times 10^{-26}$ esu cm^2	Method	Reference
		2.45	Microwave line broadening—OCS	86
		0.82±0.10	Microwave line broadening—CHF$_3$	86
		1.23±0.25	Microwave line broadening—N$_2$O	86
	HD	3.25	Microwave line broadening—OCS	86
	D$_2$	3.1	Microwave line broadening—OCS	86
		1.02±0.07	Microwave line broadening—CHF$_3$	86
		1.33±0.25	Microwave line broadening—N$_2$O	86
2.	N$_2$	−2.55	Theoretical MO calculations	87
		−1.221	Theoretical MO calculations	88
		1.80	Second virial coefficients	21
		1.90	Second virial coefficients	82
		1.27	Crystal data	89
		1.2	Combined second virial coeff. and crystal data	90
		0.8	Microwave line broadening-NH$_3$	83
		0.80±0.02	Microwave line broadening-NH$_3$	84
		1.23	Microwave line broadening—H$_2$O	91
		1.4	Microwave line broadening—SO$_2$	92
		2.75±0.25	Microwave line broadening—OCS	44
		3.05	Microwave line broadening—OCS	86
		1.35±0.08	Microwave line broadening—CHF$_3$	86
		2.11±0.30	Microwave line broadening—N$_2$O	86
		1.64	Pressure-induced absorption	93
		1.0	Pressure-induced absorption	72
		1.5	Pressure-induced absorption	94
		1.5	Pressure-induced absorption	95
3.	O$_2$	0.50	Microwave line broadening—O$_2$	96
		1.90	Second virial coefficients	21
		0.19	Microwave line broadening—O$_2$	97
		1.13±0.12	Microwave line broadening—O$_2$	98
		0.43	Microwave line broadening—NH$_3$	83
		0.35±0.03	Microwave line broadening—NH$_3$	84
		0.41	Microwave line broadening—H$_2$O	99
		1.0±0.1	Microwave line broadening—OCS	100
4.	CO	−1.806	Theoretical MO calculations	88
		−1.97	Theoretical MO calculations	101
		2.81	Second virial coefficients	82
		1.71	Crystal data	89
		0.94	Microwave line broadening—NH$_3$	102
		1.60	Infrared line broadening	103
		2.0	Infrared line broadening	43
5.	CO$_2$	−8.5	Theoretical MO calculations	104
		−4.1	Induced optical birefringence	8
		5.73	Second virial coefficients	20

Serial Nos.	Molecule	Quadrupole moment[a] $\times 10^{-26}$esu cm^2	Method	Reference
		5.00	Second virial coefficients	21
		4.59	Second virial coefficients	82
		3.3	Second virial coefficients	29
		5.8	Second virial coefficients	105
		4.60	Crystal data	1
		5.29	Combined second virial coeff. and crystal data	90
		3.5	Refractivity virial coefficients	106
		1.8	Microwave line broadening—NH_3	83
		1.72 ± 0.14	Microwave line broadening—NH_3	84
		2.7	Microwave line broadening—SO_2	107
		3.95	Microwave line broadening—OCS	86
		2.81 ± 0.16	Microwave line broadening—CHF_3	86
		2.24 ± 0.30	Microwave line broadening—N_2O	86
		7.9 ± 1.0	Dielectric constants	66
		5.3	Dielectric constants	68
		5.9	Pressure-induced absorption	72
		5.2	Pressure induced absorption[77] (recalculation by Johnston and Cole[73])	68
		4.4	Pressure-induced absorption	73
6.	C_2H_2	3.0	Microwave line broadening—NH_3	102
		13.06 ± 0.11	Bond moments	74
7.	C_2H_4	3.92	Second virial coefficients	82
		1.32	Microwave line broadening—NH_3	102
		4.0	Dielectric constants	68
		2.6	Pressure-induced absorption	72
		4.24 ± 0.04	Bond moments	74
8.	C_2H_6	0.77	Microwave line broadening—NH_3	102
		0.3	Pressure-induced absorption	72
		1.72 ± 0.13	Bond moments	74
9.	C_6H_6	3.6	Microwave line broadening—NH_3	102
10.	OCS	1.47	Microwave line broadening—NH_3	83
		4.32	Microwave line broadening—OCS	108
		5.9	Microwave line broadening—OCS	109
		3.55	Microwave line broadening—OCS	42
		1.5 ± 0.25	Microwave line broadening—OCS	44
		1.0	Microwave line broadening—OCS	86, 100
11.	BrCN	10.1	Microwave line broadening—BrCN	108
		6.75 ± 4.0	Microwave line broadening—BrCN	75
12.	ClCN	3.3	Microwave line broadening—NH_3	73
13.	HCN	2.21	Microwave line broadening—NH_3	73
14.	HCl	3.96	Theoretical MO calculations	110
		3.75	Infrared line broadening	43

Serial Nos.	Molecule	Quadrupole moment[a] $\times 10^{-26}$ esu cm^2	Method	Reference
15.	HF	3.0	Infrared line broadening	43
16.	HI	6.0	Infrared line broadening	43
17.	BF	-4.382	Theoretical MO calculations	88
		-4.49	Theoretical MO calculations	101
18.	CH_3F	20	Dielectric studies	111
19.	NO	0.77	Microwave line broadening—NH_3	102
		2.9	Microwave line broadening—OCS	86
		0.93 ± 0.09	Microwave line broadening—CHF_3	86
		1.89 ± 0.30	Microwave line broadening—N_2O	86
20.	N_2O	1.63	Microwave line broadening—NH_3	102
		3.95 ± 0.20	Microwave line broadening—N_2O	86
21.	CH_2Cl_2	4.13	Microwave line broadening—NH_3	83
22.	CS_2	1.78	Microwave line broadening—NH_3	83
23.	SO_2	4.42	Microwave line broadening—NH_3	83
24.	H_2O	$\theta_{xx}=-0.907$ $\theta_{yy}=\ 0.694$ $\theta_{zz}=\ 0.213$ (Referred to Oxygen nucleus as origin)	Theoretical MO calculations (using the equivalent orbitals developed by Lennard-Jones)	17
		$\theta_{xx}=-1.149$ $\theta_{yy}=\ 0.755$ $\theta_{zz}=\ 0.394$	Theoretical MO calculations (using the wave function of Ellison and Shull[113])	112
		$\theta_{xx}=-1.304$ $\theta_{yy}=\ 0.940$ $\theta_{zz}=\ 0.364$	Theoretical MO calculations (using "bond orbital" wave function McWeeny and Ohno[114])	112
		$\theta_{xx}=-1.211$ $\theta_{yy}=\ 0.853$ $\theta_{zz}=\ 0.358$	Theoretical MO calculations (using McWeeny–Ohno's[114] configuration interaction bond orbital' wave functions with 7 configurations)	112
		$\theta_{xx}=-1.055$ $\theta_{yy}=\ 0.660$ $\theta_{zz}=\ 0.395$	Theoretical MO calculations (using McWeeny–Ohno's[114] "configuration interaction bond orbital wave functions" with 12 configurations)	112
		$\theta_{xx}=-1.228$ $\theta_{yy}=\ 0.868$ $\theta_{zz}=\ 0.360$	Theoretical MO calculations (using McWeeny–Ohno's[114] 'modified electron pair' wave functions)	112
		$\theta_{xx}=-1.143$ $\theta_{yy}=\ 0.729$ $\theta_{zz}=\ 0.414$	Theoretical MO calculations (using McWeeny–Ohno's[114] SCF LCAO wave functions)	112
		$\theta_{xx}=-1.61$ $\theta_{yy}=\ 1.35$ $\theta_{zz}=\ 0.26$	Theoretical MO calculations based on Rowlinson's empirical four-point-charge model[115]	112
25.	NH_3	$\theta_{xx}=\theta_{yy}=0.069$ $\theta_{zz}=-0.137$ (Referred to nitrogen nucleus as the origin)	Theoretical MO calculations (using the equivalent orbitals developed by Lennard–Jones)	17

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[a] Some of the values were recalculated to conform to the definition used here.

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