

# Determination of Molecular Quadrupole Moments from Viscosities and Second Virial Coefficients\*

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Gas viscosity data for nine quadrupolar molecules are analyzed using calculated collision integrals for the 12-6-5 potential. The parameters of the spherical component of the potential are obtained from the viscosity data, and then used in conjunction with second virial coefficient data to determine the quadrupole moments and "shape" parameters of the molecules. The quadrupole moments obtained are very reasonable, and further improvement along these lines will probably depend on a better understanding of the non-spherical components of the repulsive part of the potential.

## I. INTRODUCTION

THE potential energy of interaction between two polyatomic molecules is usually assumed to consist of a spherically symmetric component plus a contribution due to the asphericity of the molecular charge distribution. The latter contribution is conveniently divided into terms representing the classical electrostatic interaction between the two charge distributions, the anisotropy of the quantum-mechanical dispersion forces, and the "shape" of the molecular core (i.e., the anisotropy of the repulsive part of the potential). Parts of the potential contribute more significantly to some properties of the molecular gas than to others. For example, the viscosity of a quadrupolar gas can usually be adequately described by a potential function consisting only of the spherical component plus the contribution due to the quadrupole moments, whereas the second virial coefficient of the same gas depends significantly on all parts of the potential function.

Kielich<sup>1</sup> and Orcutt<sup>2</sup> have shown that reasonable values of molecular quadrupole moments could be obtained even by ignoring the effect of the quadrupole moment on the viscosity, and the effect of the shape component and of most of the higher-order anisotropy terms on the second virial coefficient.

It is the purpose of this paper to analyze the viscosity data for nine quadrupolar gases (N<sub>2</sub>, O<sub>2</sub>, NO, CO, F<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>O, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>) with the collision integrals for a 12-6-5 potential reported in the preceding paper, in order to obtain the parameters of the spherical component of the potential. These parameters are then used in conjunction with experimental second virial coefficients to determine the quadrupole moments and shape parameters of the molecules.

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<sup>1</sup> S. Kielich, *Acta Phys. Polon.* **20**, 433 (1961); *Physica* **28**, 511 (1962).

<sup>2</sup> R. H. Orcutt, *J. Chem. Phys.* **39**, 605 (1963); see also A. D. King, Jr., *ibid.* **42**, 2610 (1965).

## II. CALCULATIONS

### A. Analysis of Viscosity Data

The viscosity  $\eta$  is given by the formula

$$\eta = \frac{5}{16} [(\pi m k T)^{1/2} f_{\eta} / \pi \sigma_0^2 \langle \Omega^{(2,2)*} \rangle], \quad (1)$$

for which the collision integrals  $\langle \Omega^{(2,2)*} \rangle$  are tabulated in the preceding paper<sup>3</sup> on the assumption of fixed relative orientation per collision for a 12-6-5 potential model. The range and accuracy of the viscosity data and of the model itself do not justify allowing all three parameters ( $\epsilon_0$ ,  $\sigma_0$ ,  $q$ ) to be freely adjustable. Since viscosity is only weakly dependent on the value of the reduced quadrupole moment parameter  $q$ , the procedure adopted was to let the viscosity data determine  $\epsilon_0$  and  $\sigma_0$ , and let the second virial coefficient data determine  $q$ . This is an iterative procedure which converges very quickly. A value of  $q$  was first estimated from the definition

$$q = \frac{3}{2} \Theta^2 / \epsilon_0 \sigma_0^5, \quad (2)$$

with values of  $\epsilon_0$  and  $\sigma_0$  from the 12-6 potential and the value of the quadrupole moment  $\Theta$  taken from Orcutt's estimate<sup>2</sup> for N<sub>2</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and from Buckingham's summary<sup>4</sup> for O<sub>2</sub>, NO, N<sub>2</sub>O, and C<sub>2</sub>H<sub>2</sub>. For F<sub>2</sub> the value  $\Theta = 1.5 \times 10^{-26}$  esu was used. With a fixed value of  $q$ , Eq. (1) can be written in practical units as

$$\log(10^7 \eta / M^{1/2} T^{9/10}) = \log[f_{\eta} / (T^*)^{2/5} \langle \Omega^{(2,2)*} \rangle] - 2 \log \sigma_0 - \frac{2}{5} \log(\epsilon_0 / k) + 2.4263, \quad (3a)$$

$$\log T = \log T^* + \log(\epsilon_0 / k). \quad (3b)$$

Thus a plot of the experimental quantities

$$\log(10^7 \eta / M^{1/2} T^{9/10}) \text{ vs } \log T$$

<sup>3</sup> F. J. Smith, E. A. Mason, and R. J. Munn, *J. Chem. Phys.* **45**, 317 (1966), preceding paper.

<sup>4</sup> A. D. Buckingham, *Quart. Rev. (London)* **13**, 183 (1959).

should be superposable by translation of axes on a plot of the theoretical quantities

$$\log[f_\eta / (T^*)^{2/5} \langle \Omega^{(2,2)*} \rangle] \text{ vs } \log T^*.$$

The particular theoretical curve to use is determined by the previous choice of  $q$ . The amount of translation along the abscissa determines  $\epsilon_0/k$ , and the amount of translation along the ordinate determines  $\sigma_0$ . (In practice it was adequate to take the correction factor  $f_\eta$  equal to unity.)

The gas viscosity is insensitive enough to the quadrupole moment for a variation of  $\pm 0.25$  in the value of  $q$  to make only a slight difference in the values of  $\epsilon_0$  and  $\sigma_0$ , so that only a single iteration was usually needed. The parameters determined are listed in Table I.

### B. Second Virial Coefficients

The potential model used for the analysis of the second virial coefficient data was<sup>1,4,5</sup>

$$\varphi(r) = \varphi(\text{spherical}) + \varphi(\text{quadrupole}) + \varphi(\text{anisotropy}) + \varphi(\text{quad-ind dipole}) + \varphi(\text{shape}), \quad (4)$$

where

$$\varphi(\text{spherical}) = 4\epsilon_0[(\sigma_0/r)^{12} - (\sigma_0/r)^6], \quad (5a)$$

$$\varphi(\text{quadrupole}) = \frac{3}{4}(\Theta^2/r^6)[1 - 5c_1^2 - 5c_2^2 - 15c_1^2c_2^2 + 2(s_1s_2c - 4c_1c_2)^2], \quad (5b)$$

$$\varphi(\text{anisotropy}) = 4\epsilon_0(\sigma_0/r)^6[\kappa - \frac{3}{2}\kappa(1-\kappa)(c_1^2 + c_2^2) - \frac{3}{2}\kappa^2(s_1s_2c - 2c_1c_2)^2], \quad (5c)$$

$$\varphi(\text{quad-ind dipole}) = -\frac{9}{8}(\Theta^2\bar{\alpha}/r^8)(s_1^4 + s_2^4 + 4c_1^4 + 4c_2^4), \quad (5d)$$

$$\varphi(\text{shape}) = 4D\epsilon_0(\sigma_0/r)^{12}(3c_1^2 + 3c_2^2 - 2), \quad (5e)$$

in which  $\bar{\alpha} = \frac{1}{3}(\alpha_{||} + 2\alpha_{\perp})$  and  $\kappa = (\alpha_{||} - \alpha_{\perp})/3\bar{\alpha}$  are the mean polarizability and the anisotropy of the polarizability and the anisotropy of the polarizability, respectively,  $\alpha_{||}$  being the polarizability along the axis of symmetry and  $\alpha_{\perp}$  that perpendicular to it. The

quadrupole moment is defined by

$$\Theta = \sum e_i(z_i^2 - x_i^2),$$

where  $e_i$  is the  $i$ th element of charge and  $z_i$  and  $x_i$  are its coordinates in a system where the  $z$  axis is the symmetry axis and the origin is the center of mass. The non-coincidence of the center of mass and the center of charge affects the value of  $\Theta$  only for CO and N<sub>2</sub>O (which have nonzero dipole moments). The above definitions do not strictly apply to ethylene, which is not cylindrically symmetric; our values of  $\kappa$  and  $\Theta$  for ethylene are therefore estimates based on the assumption that the deviation from cylindrical symmetry of the molecule is not large enough to affect the results. There is no particular theoretical basis for the form of  $\varphi(\text{shape})$ ; it merely represents the leading term of an expansion in Legendre polynomials.<sup>5</sup> The quantity  $D$  is a dimensionless shape parameter. The angle-dependent quantities in Eqs. (5) are

$$s_1 = \sin\theta_1, \quad s_2 = \sin\theta_2, \\ c_1 = \cos\theta_1, \quad c_2 = \cos\theta_2, \quad c = \cos\phi, \quad (6)$$

where  $\theta_1$ ,  $\theta_2$ , and  $\phi$  are the usual angles describing the relative orientation of two linear molecules.

This potential is more elaborate than the 12-6-5 potential used in the analysis of the viscosity data, but this is not important for the following reasons.

<sup>5</sup> J. A. Pople, Proc. Roy. Soc. (London) **A221**, 508 (1954); A. D. Buckingham and J. A. Pople, Trans. Faraday Soc. **51**, 1173 (1955).

TABLE I. Potential parameters from viscosity data.

Gas	$q$	$\sigma_0$ (Å)	$\epsilon_0/k$ (°K)	Ref. for data
N <sub>2</sub>	0.5	3.702	87.5	a, b, c, d, e
O <sub>2</sub>	0.5	3.431	110.9	a, b, c, e
NO	1.0	3.474	115.1	a, b, c, e
CO	0.5	3.702	88.0	a, b, c
F <sub>2</sub>	0.5	3.621	114.8	f
CO <sub>2</sub>	1.0	3.819	218.8	a, b, c, d
N <sub>2</sub> O	0.5	3.802	235.5	a, b, c, e
C <sub>2</sub> H <sub>2</sub>	1.0	4.104	195.0	c, g, h
C <sub>2</sub> H <sub>4</sub>	0.5	4.218	201.8	a, g

<sup>a</sup> M. Trautz *et al.*, Ann. Physik **2**, 733, 737 (1929); **3**, 409 (1929); **7**, 409, 427 (1930); **9**, 981 (1931); **10**, 155 (1931); **11**, 606 (1931); **20**, 135 (1934).

<sup>b</sup> H. L. Johnston, and K. E. McCloskey J. Phys. Chem. **44**, 1038 (1940);

H. L. Johnston and E. R. Grilly, *ibid.* **46**, 948 (1942).

<sup>c</sup> R. Wobser and F. Müller, Kolloidchem. Beih. **52**, 165 (1941).

<sup>d</sup> V. Vasilescu, Ann. Phys. (Paris) **20**, 137, 292 (1945).

<sup>e</sup> C. J. G. Raw and C. P. Ellis, J. Chem. Phys. **28**, 1198 (1958); **30**, 574 (1959).

<sup>f</sup> E. Kanda, Bull. Chem. Soc. Japan **12**, 463 (1937).

<sup>g</sup> T. Titani, Bull. Chem. Soc. Japan **8**, 255 (1933).

<sup>h</sup> H. Adzumi, Bull. Chem. Soc. Japan **12**, 199 (1937).

Suppose anisotropy and shape terms were added to the 12-6-5 viscosity potential; for a given orientation they would merely cause small changes in the values of  $\epsilon_0$  and  $\sigma_0$ . To first order the collision integrals are linear in  $\epsilon_0$  and  $\sigma_0$  (but not in  $\Theta$ ), so that the effects of anisotropy and shape vanish on the subsequent averaging over orientations. The contribution of the  $r^{-8}$  quadrupole-induced-dipole term to the viscosity potential cannot be thus averaged away because there is no  $r^{-8}$  term in the 12-6-5 potential, so its presence in the virial calculations is, in principle, inconsistent. However, in view of the small effect the  $r^{-5}$  quadrupole term has on the viscosity, it seems safe to assume that the  $r^{-8}$  polarizability term would have negligible effect on

the viscosity and hence on the parameters  $\epsilon_0$  and  $\sigma_0$ . In short, we believe it is accurate to neglect the  $r^{-8}$  term in determining  $\epsilon_0$  and  $\sigma_0$  from viscosity, but not accurate to neglect it in calculating virial coefficients, although we must admit that this is an opinion and has not been proved.

If we define the reduced quantities

$$\alpha^* = \bar{\alpha}/\sigma_0^3, \quad \Theta^* = \Theta/(\epsilon_0\sigma_0^5)^{1/2}, \quad \gamma = 2(\epsilon_0/kT)^{1/2}, \quad (7a)$$

$$B^*(T) = B(T)/b_0, \quad b_0 = \frac{2}{3}\pi N_0\sigma_0^3, \quad (7b)$$

then the second virial coefficient according to this model can be written as an infinite series of terms<sup>1,5</sup>

$$\begin{aligned} B^*(T) = & B^*(12-6) + B^*(\text{quad}) + B^*(\text{anis}) \\ & + B^*(\text{quad-ind dipole}) + B^*(\text{shape}) \\ & + B^*(\text{quad} \times \text{anis}) + B^*(\text{quad} \times \text{shape}) \\ & + B^*(\text{anis} \times \text{shape}) + \text{higher-order cross terms}, \end{aligned} \quad (8)$$

where

$$B^*(12-6) = \gamma^{-2} [H_{12}(\gamma) - \frac{1}{2}H_6(\gamma)], \quad (9a)$$

$$B^*(\text{quad}) = -\frac{7}{3^2 2^6} (\Theta^*)^4 [H_{10}(\gamma) - \frac{1}{3^2 4^2} (\gamma\Theta^*)^2 H_{15}(\gamma) + \dots], \quad (9b)$$

$$B^*(\text{anis}) = \frac{1}{2^2 0^2} \kappa^2 (1 + \frac{1}{1^2 0^2} \kappa^2) H_{12}(\gamma) + \dots, \quad (9c)$$

$$B^*(\text{quad-ind dipole}) = -\frac{3}{1^2 6^2} \alpha^* (\Theta^*/\gamma)^2 [H_8(\gamma) - \frac{6}{3^2 5^2} (\gamma\Theta^*)^2 H_{13}(\gamma) + \dots], \quad (9d)$$

$$B^*(\text{shape}) = -\frac{1}{5^2} D^2 H_{24}(\gamma) + \dots, \quad (9e)$$

$$B^*(\text{quad} \times \text{anis}) = \frac{3}{1^2 0^2} (\kappa\Theta^*)^2 H_{11}(\gamma) + \dots, \quad (9f)$$

$$B^*(\text{quad} \times \text{shape}) = D(\gamma\Theta^*)^2 [\frac{3}{5^2 0^2} D H_{29}(\gamma) + \frac{1}{5^2 0^2} (\Theta^*)^2 H_{22}(\gamma) + \dots], \quad (9g)$$

$$B^*(\text{anis} \times \text{shape}) = -\frac{1}{5^2} \kappa D H_{18}(\gamma) + \dots. \quad (9h)$$

The  $H_k(\gamma)$  are functions tabulated by Buckingham and Pople.<sup>5</sup>

Nitric oxide, carbon monoxide, and nitrous oxide all have small dipole moments. This means that an additional term  $\varphi(\text{dipole})$  has to be added to the potential function

$$\varphi(\text{dipole}) = -(\mu^2/r^3)(2c_1c_2 - s_1s_2c), \quad (10)$$

where  $\mu$  is the dipole moment. This leads to a term  $B^*(\text{dipole})$  and more cross terms in the expression for the second virial coefficient. The term  $B^*(\text{dipole})$  was calculated to be negligible for NO, CO, and N<sub>2</sub>O, and the only cross term included was

$$B^*(\text{quad} \times \text{dipole}) = -\frac{1}{3^2 4^2} (\mu^* \Theta^*) H_8(\gamma) + \dots, \quad (11)$$

where  $\mu^* = \mu/(\epsilon_0\sigma_0^3)^{1/2}$ .

No data for the anisotropy of the polarizability of NO and F<sub>2</sub> were available so the second virial coefficients for these two gases were calculated for  $\kappa=0$  and for a plausible upper limit for  $\kappa$ . The two values of

TABLE II. Potential parameters for virial coefficient calculations.

Gas	$\alpha$ (Å <sup>3</sup> )	$\kappa$	$\mu$ (10 <sup>-18</sup> esu)	$\Theta$ (10 <sup>-26</sup> esu)	$D$
N <sub>2</sub>	1.73 <sup>a</sup>	0.176 <sup>a</sup>		2.05	+0.15
O <sub>2</sub>	1.59 <sup>a</sup>	0.239 <sup>a</sup>		1.48	+0.1
NO	1.72 <sup>a</sup>	(0, 0.20)	0.158 <sup>c</sup>	2.4, 2.2	+0.15
CO	1.97 <sup>a</sup>	0.168 <sup>a</sup>	0.13 <sup>c</sup>	2.43	+0.20
F <sub>2</sub>	1.28 <sup>b</sup>	(0, 0.15)		1.7, 1.4	0.0
CO <sub>2</sub>	2.925 <sup>a</sup>	0.257 <sup>a</sup>		4.10	-0.1
N <sub>2</sub> O	3.00 <sup>a</sup>	0.310 <sup>a</sup>	0.18 <sup>c</sup>	2.78	+0.05
C <sub>2</sub> H <sub>2</sub>	3.33 <sup>a</sup>	0.270 <sup>a</sup>		5.01	+0.3
C <sub>2</sub> H <sub>4</sub>	4.269 <sup>a</sup>	0.158 <sup>a</sup>		3.85	+0.1

<sup>a</sup> H. H. Landolt and R. Börnstein, *Zahlenwerte und Funktionen*, J. Bartels, Ed. (Springer-Verlag, Berlin, 1951), Pt. 3, pp. 510ff.

<sup>b</sup> E. U. Franck, *Naturwiss.* 41, 37 (1954).

<sup>c</sup> A. L. McClellan, *Tables of Experimental Dipole Moments* (W. H. Freeman and Co., San Francisco, Calif., 1963).

TABLE III. Comparison of experimental and calculated second virial coefficients.

N <sub>2</sub> <sup>a,b</sup>			O <sub>2</sub> <sup>a,c-h</sup>			CO <sub>2</sub> <sup>i-k</sup>		
T (°C)	B(T) (cm <sup>3</sup> /mole)		T (°C)	B(T) (cm <sup>3</sup> /mole)		T (°C)	B(T) (cm <sup>3</sup> /mole)	
	Exptl	Calc		Exptl	Calc		Exptl	Calc
76.8	+3.6	+3.5	34.9	-14.0	-13.2	602.0	+12.2	+4.2
-30.1	-17.6	-18.9	-46.9	-34.5	-35.9	334.0	-8.2	-20.3
-94.6	-48.0	-48.9	-99.9	-66.5	-65.2	192.1	-31.9	-33.7
-136.5	-87.8	-89.2	-136.3	-107.0	-103.0	68.7	-90	-96.6
-152.1	-113.0	-112.2	-162.3	-159.0	-151.9	-3.1	-155	-153.7
			-181.5	-217	-216.8	-30.8	-187	-188.9
C <sub>2</sub> H <sub>2</sub> <sup>a,k,l</sup>			NO <sup>m,n</sup>			F <sub>2</sub> <sup>f</sup>		
204.4	-42.8	-45.0	-0.8	-25.0	-29.0 <sup>o</sup>	-38.9	-32.0	-37.2 <sup>a</sup>
138.6	-66.1	-67.6	-38.3	-39.1	-42.8 <sup>o</sup>	-93.8	-66.0	-68.7 <sup>a</sup>
85.6	-92.1	-93.3	-93.4	-74.2	-76.9 <sup>o</sup>	-131.5	-109	-108.5 <sup>a</sup>
42.1	-123.0	-122.6	-131.1	-133.0	-122.1 <sup>o</sup>	-158.4	-160	-158.6 <sup>a</sup>
6.1	-157.0	-155.8	-145.7	-184.5	-149.9 <sup>o</sup>	-178.3	-225	-223.8 <sup>a</sup>
						-193.5	-388	-306.0 <sup>a</sup>
								-37.8 <sup>p</sup>
								-69.4 <sup>p</sup>
								-109.9 <sup>p</sup>
								-161.3 <sup>p</sup>
								-226.3 <sup>p</sup>
								-310.1 <sup>p</sup>
N <sub>2</sub> O <sup>r</sup>			CO <sup>t</sup>			C <sub>2</sub> H <sub>2</sub> <sup>u</sup>		
145.5	-59.5	-67.0	161.4	+11.2	+10.2	73.5	-97.5	-112.5
94.8	-82.9	-88.1	78.8	+1.5	+1.0	31.5	-144	-146.2
52.8	-109.4	-112.1	17.7	-10.0	-10.0	-3.3	-198	-185.4
17.5	-141.2	-139.3						

<sup>a</sup> L. Holborn and J. Otto, Z. Physik **33**, 1 (1925).

<sup>b</sup> A. Michels, H. Wouters, and J. de Boer, Physica **1**, 587 (1936).

<sup>c</sup> H. A. Kuypers and H. Kamerlingh Onnes, Leiden Commun. **165a**, (1923).

<sup>d</sup> G. P. Nijhoff and W. H. Keesom, Leiden Commun. **179b**, (1926).

<sup>e</sup> G. A. Bottomley, D. S. Massie, and R. Whytlaw-Gray, Proc. Roy. Soc. (London) **A200**, 201 (1950).

<sup>f</sup> D. White, J. H. Hu, and H. L. Johnston, J. Chem. Phys. **21**, 1149 (1953).

<sup>g</sup> A. Michels, H. W. Schamp, and W. de Graaff, Physica **20**, 1209 (1954).

<sup>h</sup> T. L. Cottrell, R. A. Hamilton, and R. P. Taubinger, Trans. Faraday Soc. **52**, 1310 (1956).

<sup>i</sup> A. Michels and C. Michels, Proc. Roy. Soc. (London) **A153**, 201 (1936).

<sup>j</sup> K. E. McCormack and W. G. Schneider, J. Chem. Phys. **18**, 1269 (1950).

<sup>k</sup> E. G. Butcher and R. S. Dadson, Proc. Roy. Soc. (London) **A277**, 448 (1964).

<sup>l</sup> A. Michels and M. Geldermans, Physica **9**, 967 (1942).

<sup>m</sup> H. L. Johnston and H. R. Weimer, J. Am. Chem. Soc. **56**, 625 (1934).

<sup>n</sup> B. H. Golding and B. H. Sage, Ind. Eng. Chem. **43**, 160 (1951).

<sup>o</sup>  $\kappa=0.20$ .

<sup>p</sup>  $\kappa=0$ .

<sup>q</sup>  $\kappa=0.15$ .

<sup>r</sup> L. J. Hirth and K. A. Kobe, J. Chem. Eng. Data **6**, 233 (1961).

<sup>s</sup> H. W. Schamp, Jr., E. A. Mason, and K. Su, Phys. Fluids **5**, 769 (1962).

<sup>t</sup> A. Michels, J. M. Lupton, T. Wassenaar, and W. de Graaff, Physica **18**, 121 (1952).

<sup>u</sup> G. A. Bottomley, C. G. Reeves, and G. H. F. Seiflow, Nature **182**, 596 (1958).

the quadrupole moment obtained thus represent probable upper and lower limits, respectively.

The parameters  $\Theta$  and  $D$  which give the best fit with experimental second virial coefficient data are listed in Table II, together with the other parameters used. Calculated values of the second virial coefficients are compared with values obtained from experimental data in Table III.

### III. DISCUSSION

#### A. Quadrupole Moments

Table IV lists values of the quadrupole moments obtained by Orcutt, values obtained by other methods since 1963, and a summary of previous values given by Buckingham.<sup>4</sup> Although the values obtained by the present method appear only slightly different from Orcutt's, it must be remembered that the quadrupole moment appears to the fourth power in the virial coefficient expression, so small changes in its value make an appreciable change in its contribution to the second virial coefficient. Moreover, Orcutt used only a

TABLE IV. Comparison of quadrupole moments ( $10^{-26}$  esu) from different sources.

Gas	This work	Bloom <i>et al.</i> <sup>a</sup>	Orcutt <sup>b</sup>	Buckingham <sup>c</sup>	Other
N <sub>2</sub>	2.05	1.70	1.90	1.5	1.60 <sup>d</sup> , 1.5 <sup>e</sup>
O <sub>2</sub>	1.48	0.92		0.3	0.70 <sup>d</sup>
NO	2.2-2.4	2.05		1	
CO	2.43	2.0	2.81	1	
F <sub>2</sub>	1.4-1.7				
CO <sub>2</sub>	4.1	4.85	4.59	3	3.43, <sup>d</sup> 4.1, <sup>f</sup> 4.4, <sup>g</sup> 5.8 <sup>h</sup>
N <sub>2</sub> O	2.78			2.5	
C <sub>2</sub> H <sub>2</sub>	5.01			3	
C <sub>2</sub> H <sub>4</sub>	3.85	4.25	3.92	1	

<sup>a</sup> M. Bloom, I. Oppenheim, M. Lipsicas, C. G. Wade, and C. F. Yarnell, J. Chem. Phys. **43**, 1036 (1965).

<sup>b</sup> R. H. Orcutt, J. Chem. Phys. **39**, 605 (1963).

<sup>c</sup> A. D. Buckingham, Quart. Rev. (London) **13**, 183 (1959).

<sup>d</sup> H. Feeny, W. Madigosky, and B. Winters, J. Chem. Phys. **27**, 898 (1957).

<sup>e</sup> J. A. A. Ketelaar and R. P. Rettschnick, Mol. Phys. **7**, 191 (1963); J. D. Poll, Phys. Letters **7**, 32 (1963).

<sup>f</sup> A. D. Buckingham and R. Disch, Proc. Roy. Soc. (London) **A273**, 275 (1963).

<sup>g</sup> A. A. Maryott and S. J. Kryder, J. Chem. Phys. **41**, 1580 (1964).

<sup>h</sup> A. D. King, Jr., J. Chem. Phys. **42**, 2610 (1965).

TABLE V. Comparison of the "rod likeness" of molecules.

Molecule	$l/w$	Molecule	$l/w$
H <sub>2</sub>	2.6	F <sub>2</sub>	2.0
N <sub>2</sub>	1.7	CO <sub>2</sub>	2.7
O <sub>2</sub>	1.9	N <sub>2</sub> O	2.6
NO	1.8	C <sub>2</sub> H <sub>2</sub>	1.6
CO	1.7	C <sub>2</sub> H <sub>4</sub>	1.7

few of the terms of Eq. (8) for  $B^*(T)$ ; it must be regarded as partly fortuitous that many of the terms he neglected tend to cancel each other. It is of interest that the value of  $\Theta$  obtained for CO<sub>2</sub> agrees very well with that obtained by Buckingham and Disch, which is probably the most reliable value listed in Table IV.

A completely self-consistent calculation would have either included the  $r^{-8}$  term of Eq. (5d) in the viscosity potential or excluded it from the virial coefficient potential. The former alternative we believe would have negligible effect on the determined  $\epsilon_0$  and  $\sigma_0$  and hence  $\Theta$ ; the effect of the latter alternative on the calculated quadrupole moments is small but not negligible. For example,  $\Theta$  would be changed from 4.1 to 4.3 for CO<sub>2</sub> and from 2.0 to 2.2 for N<sub>2</sub>.

### B. Shape Parameters

In order to keep the  $\epsilon_0(\sigma_0/r)^{12}$  repulsive term in the over-all potential positive, the shape parameter  $D$  must lie between  $-0.25$  and  $+0.50$ .<sup>5</sup> A negative  $D$  corresponds to a platelike molecule and a positive  $D$  to a rodlike one. All our molecules are actually rodlike, but  $D < 0$  for CO<sub>2</sub>. One way of estimating the "rod-likeness" of different molecules is to compare their ratios of length ( $l$ ) to width ( $w$ ), as calculated from the

known molecular geometries and the van der Waals radii of the peripheral atoms, as shown in Table V.

Recently Roberts<sup>6</sup> has found  $D = \frac{1}{2}(0.375)$  for the repulsive field of H<sub>2</sub> probed by an He atom. On the basis of this result and the above values of  $l/w$ , one might expect that  $D$  should be roughly 0.2 for CO<sub>2</sub> and N<sub>2</sub>O and 0.1 for the other molecules. Comparing these values with those in Table II, we see that the shape model of Eq. (5e) seems to be reasonable for the less elongated molecules N<sub>2</sub>, O<sub>2</sub>, NO, F<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub>, but to break down for the two elongated molecules CO<sub>2</sub> and N<sub>2</sub>O and to need larger than expected values for CO and C<sub>2</sub>H<sub>2</sub>. For CO, the second virial coefficient data are available only at high reduced temperatures where the small influence of all the noncentral terms makes the curve-fitting process very subjective. For C<sub>2</sub>H<sub>2</sub>, both the viscosity and the second virial coefficient data cover such a small temperature range that an unambiguous choice of parameters is difficult. The discrepancies for CO<sub>2</sub> and N<sub>2</sub>O, however, probably represent a real failure of the model.

In summary, it appears that reasonable estimates of molecular quadrupole moments can be obtained from viscosity and second virial coefficient data. Improvement of the present estimates will require improvement of the potential model used; the least satisfactory component of this model appears to be the shape term used to describe the anisotropy of the repulsion. Even with a relatively crude shape function, however, reasonable values of quadrupole moments can be obtained if the virial coefficient data extend to low enough temperatures.

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<sup>6</sup> C. S. Roberts, Phys. Rev. **131**, 203 (1963).