

SHORT COMMUNICATIONS

ON THE ESTIMATION OF THE QUADRUPOLE MOMENT OF CARBON DISULPHIDE

By H. P. HUNG† and T. H. SPURLING†‡

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In a recent review, Parsonage¹ commented that the value of the quadrupole moment of carbon disulphide (9.23×10^{-26} e.s.u.) deduced from an analysis of second virial coefficient data² seemed to be too large. This is not unlikely since the quadrupole-quadrupole interaction term was the only orientation dependent term included in the intermolecular potential function used for the analysis. A more reliable model is one in which the asphericity of the molecular charge distribution includes terms representing the classical electrostatic interaction between two polarizable charge distributions, the anisotropy of the quantum mechanical dispersion forces, and the anisotropy of the repulsive part of the potential. This model has been used to obtain values of molecular quadrupole moments for nine gases from an analysis of their gaseous viscosity and second virial coefficient data.³ Details of the function (which includes a Lennard-Jones 12-6 central potential) and expressions for the second virial coefficient for it can be found in ref.³

When the procedure used by Spurling and Mason³ is applied to the available gas viscosity and second virial coefficient data for carbon disulphide it is found that the parameters deduced from the viscosity data ($\sigma = 4.364 \text{ \AA}$, $\epsilon/k = 514^\circ\text{K}$, $\Theta = \pm 6.1 \times 10^{-26}$ e.s.u. cm²) predict values of the second virial coefficient *more negative* than the experimentally determined values and do so even if a zero value of the quadrupole moment is used. Thus the two sets of experimental data are inconsistent with each other or else the intermolecular force model is unsatisfactory for carbon disulphide.

In this note we assume that the second virial coefficient data are reliable and examine the effect that a variation of the form of the central part of the potential function has on the determined value of the quadrupole moment.

The two potential models which we use for the least mean square analysis of the second virial coefficient data can be summarized in the equation:

$$\begin{aligned} \phi(r, \theta_1, \theta_2, \phi) = & \phi(\text{spherical}) + \phi(\text{quadrupole}) + \phi(\text{anisotropy}) \\ & + \phi(\text{quadrupole-induced dipole}) + \phi(\text{shape}) \end{aligned} \quad (1)$$

where

$$\phi(\text{spherical}) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \quad (2a)$$

† Department of Chemistry, University of Tasmania, P.O. Box 252C, Hobart, Tas. 7010.

‡ Present address: Division of Applied Chemistry, CSIRO Chemical Research Laboratories, P.O. Box 4331, Melbourne, Vic. 3001.

¹ Parsonage, N. G., *Rep. Prog. Chem. (A)*, 1967, **64**, 57.

² Bottomley, G. A., and Spurling, T. H., *Aust. J. Chem.*, 1967, **20**, 1789.

³ Spurling, T. H., and Mason, E. A., *J. chem. Phys.*, 1967, **46**, 322.

$$\text{or} \quad = (3^{3/2}/2)\epsilon[(\sigma/r)^{18} - (\sigma/r)^6] \quad (2b)$$

$$\begin{aligned} \phi(\text{quadrupole}) &= \frac{3}{4}(\Theta^2/r^5)[1 - 5C_1^2 - 5C_2^2 - 15C_1^2C_2^2 \\ &\quad + 2(S_1S_2C - 4C_1C_2)^2] \end{aligned} \quad (3a,b)$$

$$\begin{aligned} \phi(\text{anisotropy}) &= 4\epsilon(\sigma/r)^6[\kappa - \frac{3}{2}\kappa(1-\kappa)(C_1^2 + C_2^2) \\ &\quad - \frac{3}{2}\kappa^2(S_1S_2C - 2C_1C_2)^2] \end{aligned} \quad (4a)$$

$$\text{or} \quad = (3^{3/2}/2)\epsilon(\sigma/r)^6[\kappa - \frac{3}{2}\kappa(1-\kappa)(C_1^2 + C_2^2) - \frac{3}{2}\kappa^2(S_1S_2C - 2C_1C_2)^2] \quad (4b)$$

$$\phi(\text{quadrupole-induced dipole}) = -\frac{9}{8}(\Theta^2\bar{\alpha}/r^8)(S_1^4 + S_2^4 + 4C_1^4 + 4C_2^4) \quad (5a,b)$$

$$\phi(\text{shape}) = 4D\epsilon(\sigma/r)^{12}(3C_1^2 + 3C_2^2 - 2) \quad (6a)$$

$$\text{or} \quad = (3^{3/2}/2)D\epsilon(\sigma/r)^{18}(3C_1^2 + 3C_2^2 - 2) \quad (6b)$$

in which $\bar{\alpha}$ is the mean polarizability, κ the anisotropy of polarizability, D is a dimensionless shape parameter, and $S_1 = \sin \theta_1$, $S_2 = \sin \theta_2$, $C_1 = \cos \theta_1$, $C_2 = \cos \theta_2$, and $C = \cos \phi$ where θ_1 , θ_2 , and ϕ are the usual angles describing the relative orientation of two linear molecules. Θ is the quadrupole moment and is defined by $\Theta = \sum e_i(z_i^2 - x_i^2)$, where e_i is the i th element of the 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 centre of mass.³

The second virial coefficient for the model represented by the equations (1), (2a), (3a), (4a), (5a), and (6a) (which we shall call the "12-6" model) have been calculated previously³ and we will not reproduce the equations here. For the model represented by equations (1), (2b), (3b), (4b), (5b), and (6b) the second virial coefficient is as follows:

$$\begin{aligned} B^*(T) &= B^*(18-6) + B^*(\text{quad}) + B^*(\text{anis}) + B^*(\text{quadrupole-induced dipole}) + B^*(\text{shape}) \\ &\quad + B^*(\text{quad} \times \text{anis}) + B^*(\text{anis} \times \text{shape}) + B^*(\text{quad} \times \text{shape}) + \text{higher order} \\ &\quad \text{cross terms} \end{aligned}$$

where

$$B^*(18-6) = y^{\frac{1}{2}}[I_{18}(y) - \frac{1}{3}I_6(y)]$$

$$B^*(\text{quad}) = -\frac{14}{405}y^2(\Theta^*)^4I_{10}(y) + \frac{32}{6615 \times 3^{\frac{1}{2}}}y^{7/2}(\Theta^*)^6I_{15}(y) + \dots$$

$$B^*(\text{anis}) = -\frac{1}{60}y^2\kappa^2(2 + \frac{19}{5}\kappa^2)I_{12}(y) + \dots$$

$$B^*(\text{quadrupole-induced dipole}) = -4\alpha^*(\Theta^*)^2[3^{5/2}y^{\frac{1}{2}}I_8(y) - \frac{4}{315}\kappa(\Theta^*)^2I_{13}(y) + \dots]$$

$$B^*(\text{shape}) = -\frac{2}{15}y^2D^2I_{36}(y) + \dots$$

$$B^*(\text{quad} \times \text{anis}) = \frac{4}{75}y^2(\Theta^*)^2\kappa^2I_{11}(y) + \dots$$

$$B^*(\text{quad} \times \text{shape}) = 8y^{7/2}(\Theta^*)^2D \left[\frac{2}{567}(\Theta^*)^2I_{28}(y) + \frac{1}{25 \times 3^{3/2}}DI_{41}(y) + \dots \right]$$

$$B^*(\text{anis} \times \text{shape}) = -\frac{2}{15}y^2\kappa DI_{24}(y) + \dots$$

and the $I_k(y)$ functions are defined as follows:

$$I_k(y) = 18\sigma^{k-3}y \int_0^\infty r^{-k} \exp(\phi_{\text{L-J } 18-6}/kT)r^2 dr$$

$$\phi_{\text{L-J } (18-6)} = (3^{3/2}/2)\epsilon[(\sigma/r)^{18} - (\sigma/r)^6]$$

$$\alpha^* = \bar{\alpha}/\sigma^3$$

$$\Theta^* = \Theta/(\epsilon\sigma^5)^{1/2}$$

$$y = 3(\epsilon/2kT)^{2/3}$$

$$B^*(T) = B(T)/b_0$$

$$b_0 = \frac{2}{3}\pi N_0\sigma^3$$

The potentials as written have four parameters (ϵ , σ , Θ , and D) for which independent values cannot be assigned. Rather than determine all four from virial coefficient data we assigned a value to D on the following basis.

TABLE 1
POTENTIAL PARAMETERS FOR CARBON DISULPHIDE

Type of Data	σ (Å)	ϵ/k (°K)	$10^{26}\Theta$ (e.s.u.)	D	$10^4\nu^2$
Liquid density ^a	4.218				
Second virial coefficients ^b					
(i) L-J 12-6 model	3.72	537.5	± 6.8	0.1	0.19
(ii) L-J 18-6 model	7.08	177.50	± 6.0	0.1	1.28

^a Weast, R. C., and Selby, S. M., "Handbook of Chemistry and Physics", 48th Edn, p. C-243. (Chemical Rubber Co.: Cleveland, Ohio, 1967.)

^b Bottomley, G. A., and Spurling, T. H., *J. phys. Chem.*, 1964, **68**, 2029.

The ratio of the length of the molecule to its width as calculated from its known molecular geometry and the van der Waals radii of its atoms is 1.8 compared to a value of 2.6 for H₂. Roberts⁴ found D for H₂ to be approximately 0.19 and so for CS₂, D should be approximately 0.1. The determined value of the quadrupole moment is not sensitive to the value of D .

Table 1 contains a summary of the results obtained from the least means fit analysis. In the table $\nu^2 = [1/(N-1)][\ln B(\text{calculated}) - \ln B(\text{experiment})]^2$, where N is the number of data points used.

It can be seen that the fit is not improved by changing the central potential from a Lennard-Jones 12-6 potential to a Lennard-Jones 18-6 potential. From this evidence and in view of Table 1 we conclude that an estimate of the quadrupole moment of carbon disulphide is $\pm 6.8 \times 10^{-26}$ cm².

⁴ Roberts, C. S., *Phys. Rev.*, 1963, **131**, 203.