

Determination of Molecular Structures from Rotational Spectra Measurements

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TABLE III. D_i/D_{lin} for the alkali halides studied by Barrow and Caunt.^a

Molecule	D_{lin} (in ev)	D_0 (in ev)	D_i (in ev)	D_i/D_{lin}
KF	3.4	5.0	5.7	1.7
RbF	3.6	5.4	6.0	1.7
RbCl	3.2	4.5	4.9	1.5
RbBr	2.9	4.0	4.7	1.6
RbI	2.6	3.4	4.4	1.7
CsF	3.7	5.5	5.8	1.6
CsCl	3.0	4.6	4.7	1.6
CsBr	2.9	4.1	4.5	1.6
CsI	2.2	3.4	4.1	1.9

^a See reference 14.

Recently, Barrow and Caunt¹⁴ have analyzed the electronic spectra of a number of alkali halides. The values of D_{lin} and D_i/D_{lin} calculated from their data are shown in Table III. The ratios are all close to 1.6. These ratios suffer because of the possibility of error in an empirical relationship used by Barrow and Caunt, and also because their values of ω_e and $\omega_e x_e$ were derived primarily from highly energetic vibrational levels rather than from those near equilibrium.

It seems very unlikely that errors in the values of D_i listed in Tables I, II, and III are large enough to alter appreciably the values of D_i/D_{lin} . For example, a value of $E=4.1$ ev rather than 3.6 ev for the fluorides lowers D_i/D_{lin} by only ~ 0.2 . Errors in D_{lin} are undoubtedly appreciable for the molecules shown in Tables II and III. However, it seems unlikely that these errors are sufficiently large to make $D_i/D_{lin} < 1$. On the contrary, Barrow and Caunt's analysis is likely to lead to a higher value of D_{lin} than an analysis based on vibrational data from near equilibrium.

¹ A. G. Gaydon, Proc. Phys. Soc. (London) **58**, 525 (1946).² A. H. Nielsen and E. A. Jones, J. Chem. Phys. **19**, 1117 (1951).³ A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Chapman and Hall Ltd., London, 1953).⁴ G. Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, Inc., New York, 1944).⁵ H. O. Pritchard, Chem. Rev. **52**, 529 (1953).⁶ E. Miescher, Helv. Phys. Acta **14**, 148 (1941).⁷ H. Levi, Dissertation (Berlin, 1934).⁸ R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) **A219**, 120 (1953).

Intermolecular Forces in Ethane*

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THE long-range attractive forces between ethane molecules are computed from optical dispersion data, and the short-range repulsive forces are estimated from second virial coefficients. The experimental second virial coefficients for C_2H_6 are those of Lambert and his co-workers.¹ The optical dispersion data are given by²

$$n-1 = \frac{8.485}{1.140 \cdot 10^{31} - \nu^2}$$

This equation yields a static polarizability of $4.39 \cdot 10^{-24}$ cm³, an oscillator strength of 7.80 and a resonance energy of 13.9 ev.

TABLE I. A comparison of the experimental and theoretical second virial coefficients on the basis of the hard sphere model.

Temperature °K	Experimental virial cm ³ /mole	Theoretical virial cm ³ /mole	Percent difference
223	-384	-380	1.0
283	-224	-226	-0.9
343	-141	-143	-1.4

TABLE II. A comparison of the experimental and theoretical second virial coefficients on the basis of a $1/R^{13}$ repulsive force.

Temperature °K	Experimental virial cm ³ /mole	Theoretical virial cm ³ /mole	Percent difference
223	-384	-347	9.6
283	-224	-226	-0.9
343	-141	-163	-15.6

Table I shows the results for the hard-sphere model:

$$V = -\left(\frac{323 \cdot 10^{-12}}{R^6} + \frac{880 \cdot 10^{-12}}{R^8}\right) \text{erg}, \quad R > 4.0 \text{ \AA};$$

$$V = \infty, \quad R < 4.0 \text{ \AA}.$$

R is the distance between the molecular centers in angstrom units.

The effect of a $1/R^{13}$ repulsive force is given in Table II for the potential

$$V = \frac{6.65 \cdot 10^{-7}}{R^{12}} - \left(\frac{323 \cdot 10^{-12}}{R^6} + \frac{880 \cdot 10^{-12}}{R^8}\right).$$

* This work was supported by the Research Corporation.

¹ Lambert, Roberts, Rowlinson, and Wilkinson, Proc. Roy. Soc. (London) **A196**, 113 (1949).² H. Lowery, Proc. Roy. Soc. (London) **A133**, 188 (1931).

Determination of Molecular Structures from Rotational Spectra Measurements

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WE wish to report a general method, particularly suited for digital computers, for determining structural parameters from the measured rotational constants of isotopically substituted asymmetric molecules. With this method, a set of structural parameter values is sought such that the moments of inertia calculated using this set are equal to the moments of inertia obtained from the spectra of the molecule. The following relationship is obtained for each of the moments of inertia:

$$I_k^j \text{ (measured)} - I_k^j \text{ (calculated)} = \sum_i \frac{\Delta I_k^j}{\Delta X_i} \Delta X_i,$$

I_k^j is the k th principal moment of inertia for isotopic species j , X_i is a structural parameter.

The coefficients, $\Delta I_k^j / \Delta X_i$, are determined by assuming a reasonable structure and then calculating the change in I_k^j for a given change in X_i , the other X_i 's being held constant. The resulting system of linear equations is solved for the ΔX_i 's which are then applied as corrections to the originally assumed structure. This process may be repeated if necessary; the number of iterations depending on the validity of the assumed structure. It should be noted that the solution may be "weak" unless the masses of the two isotopes are quite different. On the other hand, when the two isotopic masses differ appreciably, the isotopic bond parameter changes due to the zero-point vibrational effect are more noticeable. This can be taken into account by admitting the isotopic bond parameters as separate variables.

To illustrate this method, we have determined the structure of ethylene oxide (principally because of its similarity to ethylenimine on which we are working) using the microwave spectrographic measurements made by Cunningham, Boyd, Myers, Gwinn, and LeVan.¹ For our work the rotational constants reported by these workers were converted to principal moments of inertia using the latest values of the physical constants.² It should be noted that special methods can be developed for ethylene oxide or in similar cases where a number of symmetries are involved, and that our general method would be necessary for more complicated molecules.

TABLE I. The structure of ethylene oxide.

C—C distance	1.470 ₁₁ ±0.001 Å
C—O distance	1.435 ₂₇ ±0.001
C—H distance	1.083 ₈₂ ±0.002
C—D distance	1.083 ₇₈ ±0.001
H ₂ CC angle	158° _{6.2'} ±39'
D ₂ CC angle	158° _{6.6'} ±22'
HCH angle	116° _{15.2'} ±21'
DCD angle	116° _{30.1'} ±12'

Since ethylene oxide is an asymmetric rotor, nine moments of inertia (uncorrected for rotation-vibration interaction) are available from the three isotopic species, C₂H₄O, CC¹³H₄O, and C₂D₄O. The C—D distance and the DCD and D₂CC angles were not assumed equal to their hydrogen counterparts but the effect of deuterium substitution on the C—C and C—O distances and the effect of C¹³ substitution were neglected. The 9×8 system of equations was solved by the method of least squares on the ORDVAC and the resulting structure is given in Table I. The

TABLE II. Ethylene oxide principal moments of inertia.

	Measured ^a (amu Å ²)	Calculated (amu Å ²)
C ₂ H ₄ O		
<i>I</i> _a	19.8374 ±0.0005	19.8382
<i>I</i> _b	22.8530 ±0.0006	22.8514
<i>I</i> _c	35.8582 ±0.0015	35.8574
CC ¹³ H ₄ O		
<i>I</i> _a	19.9883 ±0.0004	19.9901
<i>I</i> _b	23.4069 ±0.0005	23.4098
<i>I</i> _c	36.5658 ±0.0013	36.5688
C ₂ D ₄ O		
<i>I</i> _a	24.7820 ±0.0009	24.7787
<i>I</i> _b	32.7055 ±0.0015	32.6964
<i>I</i> _c	43.7915 ±0.0027	43.7855

^a See reference 1.

moments of inertia calculated using this structure are presented in Table II. It was found necessary to give the structural parameters (Table I) to six significant figures in order to insure computational consistency, but of course these parameters are not known to such accuracy. The allowed deviations were determined on the assumption that the only source of error was in the measured values of the moments of inertia. From the results of a least squares inversion made by the ORDVAC on the linear system, the root mean square deviations were calculated and are listed in Table I. The physical constants and masses used throughout this work are given in Table III. The structure reported by

TABLE III. Physical constants^a and masses.^b

<i>h</i>	= 6.6252 ×10 ⁻²⁷ erg-sec
1/16O ¹⁶	= 1.659828 ×10 ⁻²⁴ g
H	= 1.008130 amu
D	= 2.014708 amu
C ¹²	=12.00382 amu
C ¹³	=13.007581 amu
C ¹⁶	=16.000000 amu

^a See reference 2.

^b See reference 1.

Cunningham *et al.*¹ agrees favorably with that presented here since Gwinn has pointed out an error in their paper changing the H₂—C—C angle to 158° 6'.

We wish to express our sincere thanks to Mr. G. Reitweiser for his invaluable help in running this problem on the ORDVAC.

¹ Cunningham, Boyd, Myers, Gwinn, and LeVan, J. Chem. Phys. **19**, 676 (1951).

² J. W. M. DuMond and E. R. Cohen, Revs. Modern Phys. **25**, 691 (1953).

Viscous Flow and the Constitution of Liquid Boron Trioxide

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CONTROVERSIAL views exist regarding the structure of liquid boron trioxide and the only structural interpretation of viscosity results¹ is erroneous. The purpose of this note is to rectify this error and to indicate the correct flow mechanism by the use of more recent data.^{2,3} According to the rate process theory,⁴ viscosity may be represented by

$$\eta = \left[\frac{Nh}{V} \exp(-\Delta S^*/R) \right] \exp(\Delta H^*/RT) \quad (1)$$

where ΔH^* , the energy of activation for flow, is experimentally obtainable from the plot of $\log \eta$ against $1/T$, the intercept of which gives ΔS^* , the entropy of activation, if V , the molar volume is known. The free energy of activation is evaluated from

$$\Delta F^* = \Delta H^* - T\Delta S^*. \quad (2)$$

The $\log \eta/1/T$ relationship for molten boron trioxide in Fig. 1 is best satisfied by a slight curve, indicative of an associated liquid. From the mp of 450° to 750°C, the best straight line yielded a value of 33 kcal/mole for ΔH^* . When flow occurs, the simplest unit which can maintain homogeneity of the liquid is B₂O₃. At 750°C its molar volume is 45 cc,² and ΔS^* is 4.0 cal/degree/mole. Thus from Eq. (2) ΔF^* at this temperature is 29 kcal/mole.

Recently, it has been shown that liquid boron trioxide vaporizes as monomeric B₂O₃ and that the latent heat of vaporization, ΔH_v , is 77.6 kcal/mole.⁵ The relationship

$$\Delta E_v/\Delta F^* = 2.45 \quad (3)$$

is obeyed for numerous substances including the associated liquids.⁴ ΔE_v , given by $(\Delta H_v - RT)$, is 75.6 kcal/mole and thus substituting in Eq. (3), ΔF^* is equal to 30.7 kcal/mole. Remarkable agreement is therefore obtained between the two values on the assumption that B₂O₃ constitutes the principal units of flow. This is analogous to water⁶ and liquid silica⁷ where H₂O and SiO₂ are the respective flow units.

Fajans and Barber¹ extended the $\log \eta/1/T$ plot to the solid glass region. By linear extrapolation back to higher temperatures,

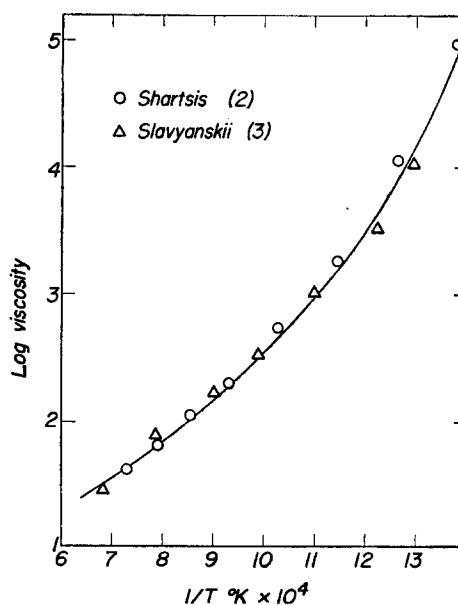


FIG. 1. Relation between log viscosity (poise) and the reciprocal of the absolute temperature for liquid B₂O₃.