

## Structure of Ethylene Oxide

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There are two objections to such an assumption: First, the molecule in ice has only four nearest neighbors compared to twelve in  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ , and  $\text{H}_2\text{Te}$  crystals. Second, as the critical data for non-hydrogen bonded molecules<sup>3</sup> listed in Table I illustrates, a non-hydrogen bonded water

TABLE I. Critical data for some non-hydrogen bonded molecules.

	Critical temperature degrees C	Critical density g/cm <sup>3</sup>
Ne	-228.7	0.484
CH <sub>4</sub>	-82.5	0.162
A	-122	0.531
HCl	51.4	0.42
PH <sub>3</sub>	51	0.30

would have a density at room temperature less than half that of actual water. The non-hydrogen bond energies in an  $\text{H}_2\text{S}$ -like ice might be considerably different from those in real ice, particularly if the closer approach of nearest neighbors in real ice makes the repulsive energy large.

If we assume that at absolute zero the simple equation

$$E = a/r^3 + b/r^6 - c/r^{12} \quad (1)$$

applies, where  $a$ ,  $b$ , and  $c$  are arbitrary constants,  $E$  is the energy of sublimation, and  $r$  is the intermolecular distance, we can calculate the dipole energy in ice by a method which eliminates the sources of error mentioned above. In our equation  $a/r^3$  is the dipole energy,  $b/r^6$  is the London energy, and  $c/r^{12}$  is the repulsive energy. We shall consider that the dipole energy is the sum of the energies of the two hydrogen bonds of the molecule.

The derivative of Eq. (1) with respect to  $r$  must be equal to zero for a stable crystal, and  $E$  can be calculated from known data to be 10.9 kcal. at absolute zero. We need only estimate the London energy to determine both the dipole and repulsive energies. We will find the London energy between a pair of nearest neighbors in a hypothetical non-polar ice and make a sixth power correction for a change of intermolecular distance to that in real ice.

TABLE II. Heats of sublimation and density at 0°K.

	Heat of sublimation kcal./mole	Density of solid g/cm <sup>3</sup>
Ne	0.4	1.44
CH <sub>4</sub>	(2.6)	—
N <sub>2</sub>	1.5	1.03
O <sub>2</sub>	2.0	1.43
A	1.8	1.60

In Table II are listed approximate heats of sublimation<sup>4</sup> and density<sup>5</sup> data for non-polar substances near 0°K. From these data we estimate that the density of hypothetical twelve-coordinated, non-polar water would be about  $1.3 \pm 0.2$  g/cm<sup>3</sup> and the energy of sublimation,  $1.5 \pm 0.5$  kcal. at absolute zero. Since the dipole energy would be zero, we solve the energy equation and its derivative equation directly, finding  $3 \pm 1$  kcal. for the London energy of a non-polar water. A consideration of the geometry of a close-packed crystal indicates that the London energy per molecule is 7.227 times that binding the molecule to one nearest neighbor.<sup>6</sup> By a similar calculation one finds that in a real ice crystal the London

energy is approximately 2.5 times that between two nearest neighbors. A close-packed crystal of density  $1.3 \pm 0.2$  g/cm<sup>3</sup> would have a nearest neighbor distance of  $3.2 \pm 0.2 \text{ \AA}$  compared to  $2.75 \text{ \AA}$  for real ice of density 0.948.<sup>7</sup> The London energy in actual ice is then  $3.0(3.2/2.75)^6 \times (2.5/7.2) = 2.6 \pm 1.5$  kcal. Introducing this value into our two equations we find the repulsive energy in real ice to be  $4.5 \pm 0.5$  kcal. and the total dipole energy,  $12.8 \pm 1$  kcal. Since there are two hydrogen bonds per molecule of ice, the dipole energy per bond is  $6.4 \pm 0.5$  kcal.

We conclude that repulsive forces make an important contribution to the energy of ice and that the dipole energy per hydrogen bond is about 2 kcal. per mole greater than previously estimated.

<sup>1</sup> L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1944), p. 304.

<sup>2</sup> R. W. Taft, Jr. and H. H. Sisler, *J. Chem. Ed.* **24**, 175-181 (1947).

<sup>3</sup> *International Critical Tables*, Vol. III, p. 248.

<sup>4</sup> F. R. Bichowsky and F. D. Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

Values corrected to absolute zero.

<sup>5</sup> *International Critical Tables*, Vol. I, p. 103; neon and argon values from K. Clusius, *Zeits. f. physik. Chemie* **B31**, 459 (1936).

<sup>6</sup> J. E. Jones and A. E. Ingham, *Proc. Roy. Soc. A* **107**, 636 (1925).

<sup>7</sup> N. E. Dorsey, *Properties of Ordinary Water Substance* (Reinhold Publishing Corporation, New York, 1940), p. 466.

## Structure of Ethylene Oxide

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THE moments of inertia of ethylene oxide have recently been reported.<sup>1</sup> In order to calculate the bond distances, deuterated ethylene oxide has been prepared, and its microwave spectrum has been measured. The values of the rotational parameters for the zero rotational level are:  $(a-c)/2 = 4427.5 \pm 0.5$  mc,  $\kappa = -0.11615 \pm 0.00010$ , and  $(a+c) = 31,943 \pm 1$  mc. The transitions observed are listed in Table I with the values of  $(a-c)/2$  calculated assuming  $\kappa = -0.11615$ . The uncertainty of  $\kappa$  has very little effect on the uncertainty of the moments of inertia because of the small value of  $\kappa$ . The recent values of the physical constants<sup>2</sup> have been employed, necessitating a small revision of the moments of inertia of  $\text{C}_2\text{H}_4\text{O}$ . The values for both molecules are given in Table II.

Since the moments of inertia are very sensitive to the bond distances, it is possible to calculate distances which

TABLE I. Spectrum of  $\text{C}_2\text{D}_4\text{O}$ .

Transition	Frequency	$\left(\frac{a-c}{2}\right)$ (calc.)	$\Delta$
0 <sub>0</sub> -1 <sub>0</sub>	31,943 mc	—	—
2 <sub>-1</sub> -2 <sub>1</sub>	26,565	4427.5	0.0
3 <sub>-2</sub> -3 <sub>-1</sub>	24,055	4427.9	+0.4
3 <sub>-1</sub> -3 <sub>0</sub>	33,285	4427.9	+0.4
3 <sub>0</sub> -3 <sub>2</sub>	35,341	4427.7	+0.2
3 <sub>1</sub> -3 <sub>1</sub>	29,080	4427.9	+0.4
4 <sub>-2</sub> -4 <sub>0</sub>	21,664	4427.8	+0.2
5 <sub>-1</sub> -5 <sub>1</sub>	24,668	4427.7	+0.2
5 <sub>1</sub> -5 <sub>1</sub>	39,592	4427.7	+0.2
6 <sub>-2</sub> -6 <sub>0</sub>	28,495	4427.5	0.0
8 <sub>-2</sub> -8 <sub>0</sub>	35,068	4427.1	-0.4

TABLE II. Moments of inertia.

C <sub>2</sub> H <sub>4</sub> O		
$I_A$	$32.917 \times 10^{-40}$	g-cm <sup>2</sup>
$I_B$	$37.920 \times 10^{-40}$	g-cm <sup>2</sup>
$I_C$	$59.500 \times 10^{-40}$	g-cm <sup>2</sup>
C <sub>2</sub> D <sub>4</sub> O		
$I_A$	$41.123 \times 10^{-40}$	g-cm <sup>2</sup>
$I_B$	$54.271 \times 10^{-40}$	g-cm <sup>2</sup>
$I_C$	$72.667 \times 10^{-40}$	g-cm <sup>2</sup>

are uncertain by less than  $\pm 0.0001A$ . However, the moments of inertia measured are those of the zero vibrational level, and introduction of a different isotope alters the zero-point energies and may change the effective positions of the atoms. The uncertainty of the bond distance obtained has been estimated<sup>3</sup> as less than 0.01A in OCS. In the case of ethylene oxide, the molecular dimensions are determined by five parameters, so that with six moments of inertia it is possible to remove one of the assumptions about the relative positions of the hydrogen and deuterium atoms. If we assume the direction of the C-H bond does not change, a C-D bond length can be calculated. The bond distances so calculated have an uncertainty which is unknown, but less than 0.01A. They are given in Table III.

It should be noted that although six variables were solved for, it is impossible to obtain equally valid results by making a large change in one and compensating small changes in the other five. The height of the hydrogen atoms above the plane of the molecule is in each case determined directly by the difference between  $(I_A + I_B)$  and  $I_C$ . (The sign of  $\kappa$  was determined by this relationship because, when  $\kappa$  is small, the Stark coefficients vary only slightly in going from  $+\kappa$  to  $-\kappa$ , making assignment from the observed Stark effect difficult. If  $\kappa$  were positive, the C-D distance would be 8 percent smaller than the C-H distance, whereas for negative  $\kappa$  the distance increases by only 0.16 percent.) The two values of  $I_B$  then determine the C-C distance and one component of the C-H distance, and of  $I_A$  determine the distance of the oxygen atom from the C-C bond and the other component of the C-H distance. Each pair of solutions is unique.

It is interesting to note that the normal C-C bond distance is 1.54A and the C-O distance is 1.44A. In ethylene oxide, the C-O distance is nearly 1.44A, while the C-C distance is 0.07A shorter than the normal bond. This seems to indicate that nearly all the strain required to form the C-O-C ring is taken up in the C-C bond.

Three further lines of the C<sub>2</sub>H<sub>4</sub>O spectrum have been

TABLE III.

C-O distance	1.4363A
C-C distance	1.4728A
C-H distance	1.0802A
C-D distance	1.0819A
H-C-H angle	116° 51'
H <sub>2</sub> -C-C angle	158° 5'
Derived	
C-O-C angle	61° 41.2'
O-C-C angle	59° 9.4'
H <sub>2</sub> -CO angle	142° 45.6'

observed. They are in complete agreement with the previously observed spectrum and are given in Table IV. The value predicted<sup>1</sup> for the 4<sub>2</sub>-4<sub>4</sub> transition was somewhat low because of a numerical error in the calculated energy of the 4<sub>4</sub> level.

Data differing from ours on ethylene oxide have been published.<sup>4</sup> The discrepancy between our results and those of Shulman, Dailey, and Townes is of the same order of magnitude as the internal consistency of their data as shown in Table V.

TABLE IV. Additional lines for C<sub>2</sub>H<sub>4</sub>O.

Transition	Frequency	$\left(\frac{a-c}{2}\right)$ (calc.)	$\Delta$
2 <sub>-1</sub> -2 <sub>1</sub>	34,158	5693.0	+0.1
4 <sub>2</sub> -4 <sub>4</sub>	34,150	5692.7	-0.2
4 <sub>2</sub> -4 <sub>0</sub>	41,581	5692.5	-0.4
8 <sub>2</sub> -8 <sub>4</sub>	43,398	5689.6	-3.3

TABLE V. Data of Shulman, Dailey, and Townes on C<sub>2</sub>H<sub>4</sub>O.

Transition	Frequency	$\left(\frac{a-c}{2}\right)$ (calc.) assuming $\kappa = 0.395$	$\Delta$
2 <sub>-2</sub> -2 <sub>0</sub>	24,948	5744.4	—
3 <sub>-1</sub> -3 <sub>1</sub>	23,614	5727.2	- 17.2
3 <sub>1</sub> -3 <sub>3</sub>	23,160	5611.7	-132.7
4 <sub>0</sub> -4 <sub>2</sub>	24,855	5685.9	- 58.5

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<sup>1</sup> G. L. Cunningham, W. I. LeVan, and William D. Gwinn, Phys. Rev. **74**, 1537 (1948).

<sup>2</sup> J. W. M. DuMond and E. R. Cohen, Rev. Mod. Phys. **20**, 82 (1948).

<sup>3</sup> C. H. Townes, A. N. Holden, and F. R. Merritt, Phys. Rev. **74**, 1113 (1948).

<sup>4</sup> R. G. Shulman, B. P. Dailey, and C. H. Townes, Phys. Rev. **74**, 846 (1948).

## Vibrational Spectrum of Diiodoacetylene

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RAMAN frequencies and semiquantitative relative intensities have been obtained for diiodoacetylene in alcohol and acetone solutions. The results are compared in Table I with the previous Raman data of Glockler and Morrell<sup>1</sup> and with the infra-red data of Emschwiller and Lecomte.<sup>2</sup> The Raman frequencies agree rather well in the two investigations except that in the present work a value of 2099 cm<sup>-1</sup> was obtained for the second line in the 2100-cm<sup>-1</sup> region which Glockler and Morrell observed but did not measure. This line was measured on three separate plates as 2098, 2098, and 2101 cm<sup>-1</sup> and is visible on the microphotometer tracing in the paper by Glockler and Morrell. Also, no coincidences in Raman and infra-red frequencies were observed in the region for which the infra-red frequencies were determined by Emschwiller and Lecomte (650-1450 cm<sup>-1</sup>).