

## On the Assignment of the $\delta\pi$ , $\nu_2\pi$ Frequencies in Ethylene Molecule

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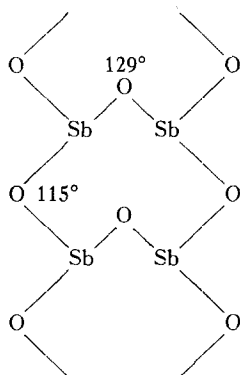
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### Polymorphism of Antimony Trioxide and the Structure of the Orthorhombic Form

Vapor density measurements indicate that antimony trioxide vapor below 1000°C consists principally of  $\text{Sb}_4\text{O}_6$  molecules. These molecules also have been shown to be present in the crystalline cubic form of this compound<sup>1</sup> which is stable below 570°C.<sup>2</sup> Crystal structure analysis of the high temperature orthorhombic modification which can be obtained as a metastable phase at room temperature, however, leads to a structure of an entirely different type in which such molecules have lost their identity.

The structure of this orthorhombic form as here reported can be considered as made up of double molecular chains of the following type:



with their axes parallel to the crystallographic  $c$  axis. Each antimony atom is at the expected distance, 2.00 to 2.02 Å, corresponding to electron pair binding<sup>3</sup> from three oxygen atoms of the double chain. Absence of such binding between the chains results in perfect cleavage parallel to them.

That the antimony oxygen binding is really of a directed type as would be expected from electron pair binding is further shown by the observed valence angles. The valence angles of oxygen atoms within a single chain are *ca.* 115° while the corresponding angles for those oxygen atoms connecting the single chains to form the double ones are about 129°. These values are similar to those found in other simple compounds containing oxygen, the variation being from about 100 to 130° where ring formation does not limit it. The antimony valence angles, which are 79, 92 and 100°, also have about the expected values.

Since transition of the cubic to the orthorhombic form involves destruction of  $\text{Sb}_4\text{O}_6$  molecules by rearrangement of electron pair bonds it might be expected to require considerable activation energy. This accounts for the slowness of the transition and the persistence of the orthorhombic form as a metastable phase.

The crystal structure is summarized as follows: space group  $Pccn-D_{2h}^{10}$ ,  $4\text{Sb}_2\text{O}_3$  in the unit of structure with  $a=4.92\text{Å}$ ,  $b=12.46\text{Å}$ ,  $c=5.42\text{Å}$ . Antimony and two-thirds of the oxygen atoms are in the general positions with  $x_{\text{Sb}}=0.044$ ,  $y_{\text{Sb}}=0.128$ ,  $z_{\text{Sb}}=0.176$ ,  $x_0=0.150$ ,  $y_0=0.05$ ,  $z_0=-0.14$ . The remaining oxygen atoms are on the two-fold axes at  $\frac{1}{4}\frac{1}{4}u$  with  $u_0=0.015$ . These parameter values

were determined on pure materials from intensity data alone without assumption of possible structure type.

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<sup>1</sup> Bozorth, J. Am. Chem. Soc. **45**, 1621 (1923).

<sup>2</sup> Roberts and Fenwick, J. Am. Chem. Soc. **50**, 2125 (1928).

<sup>3</sup> Pauling and Huggins, Zeit. f. Krist. **87**, 218 (1934).

### On the Assignment of the $\delta_{\pi s}$ , $\nu_{2\pi s}$ Frequencies in Ethylene Molecule

The assignment of the fundamental frequencies of  $\text{C}_2\text{H}_4$  has been given by a number of authors.<sup>1</sup> Of the five "parallel" vibrations  $\nu_{\pi s}$ ,  $\nu_{\pi a}$ ,  $\delta_{\pi s}$ ,  $\delta_{\pi a}$ ,  $\nu_{2\pi s}$ , one can be quite certain that  $\nu_{\pi s}=3019$  (Raman),  $\nu_{\pi a}=2988$  (infrared),  $\delta_{\pi a}=1444$  (infrared). For  $\delta_{\pi s}$  and  $\nu_{2\pi s}$ , there seem to be two possible choices. Sutherland and Dennison<sup>1</sup> assumed  $\delta_{\pi s}=1623$  (Raman),  $\nu_{2\pi s}=1342$  (Raman), while Mecke and others<sup>2</sup> favor the alternative  $\delta_{\pi s}=1342$ ,  $\nu_{2\pi s}=1623$ . As these two vibrations have the same symmetry character and enter symmetrically in any system of equations for the calculation of the force constants, it is not possible to decide between these two assignments from polarization data in the Raman effect or from the determinantal equations giving these frequencies. This can be done, however, by examining the transformation equations between the physical coordinates and the normal coordinates for these vibrations.

Following Sutherland and Dennison,<sup>2</sup> we shall introduce the coordinates  $x_1$  for the relative displacement along the  $\text{C}=\text{C}$  axis of the center of gravity of the two H atoms and the C atom in one  $\text{CH}_2$  group  $x_2$  for the similar displacement in the other  $\text{CH}_2$  group,  $x_0$  for the relative displacement between the two C atoms,  $q_1$ ,  $q_2$  for the relative displacements between the two H atoms in each group in the direction perpendicular to the  $\text{C}=\text{C}$  axis. These coordinates serve for describing the five vibrations whose frequencies are given by the determinantal equation

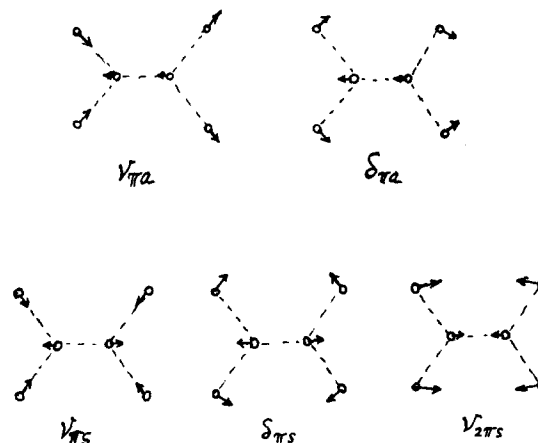


FIG. 1. "Parallel" vibrations of  $\text{C}_2\text{H}_4$ .

$$\begin{vmatrix} A\lambda - a & B\lambda & C\lambda & -d & 0 \\ B\lambda & A\lambda - a & C\lambda & 0 & -d \\ C\lambda & C\lambda & D\lambda - c & 0 & 0 \\ -d & 0 & 0 & \frac{C}{2}\lambda - b & 0 \\ 0 & -d & 0 & 0 & \frac{C}{2}\lambda - b \end{vmatrix} = 0, \quad (1)$$

where  $a$ ,  $b$ ,  $c$  and  $d$  are force constants defined in Sutherland and Dennison's paper, and

$$A = \frac{2m(m+M)}{2m+M}, \quad B = \frac{2m^2}{2m+M}, \quad C = m, \quad D = \frac{2m+M}{2}.$$

That their treatment of these vibrations is satisfactory is shown by the fact that the five observed frequencies satisfy quite well the relation which results on eliminating the four force constants among the five equations from (1). The modes of these vibrations are shown in Fig. 1.

To decide between the two assignments  $\begin{cases} \delta_{\pi s} = 1342 \\ \nu_{2\pi s} = 1623 \end{cases}$  and  $\begin{cases} \delta_{\pi s} = 1623 \\ \nu_{2\pi s} = 1342 \end{cases}$ , let us denote the normal coordinates by  $\xi_i$ ,  $i=1, 2, \dots, 5$ . The transformation equations between the coordinates  $x_1, x_2, x_0, q_1, q_2$  and these normal coordinates are then

$$x_1 = \Sigma c_{1i} \xi_i, \quad x_2 = \Sigma c_{2i} \xi_i, \quad x_0 = \Sigma c_{3i} \xi_i, \quad q_1 = \Sigma c_{4i} \xi_i, \quad q_2 = \Sigma c_{5i} \xi_i,$$

where  $c_{1i} \dots c_{5i}$  are proportional to the minors of the elements in any one row in the secular determinant (1) in which  $\lambda$  is given the value of the  $i$ th root, i.e., of the  $i$ th normal vibration. For the  $i$ th vibration, we have, except for a common factor of proportionality,

$$\begin{aligned} x_1 &= \begin{vmatrix} A\lambda_i - a & C\lambda_i & -d \\ C\lambda_i & D\lambda_i - c & 0 \\ -d & 0 & \frac{C}{2}\lambda_i - b \end{vmatrix} \xi_i, \\ x_2 &= -\lambda_i \left( \frac{C}{2}\lambda_i - b \right) \begin{vmatrix} B & C \\ C\lambda_i & D\lambda_i - c \end{vmatrix} \xi_i, \\ x_0 &= C\lambda_i \begin{vmatrix} B\lambda_i & A\lambda_i - a & -d \\ 1 & 1 & 0 \\ 0 & -d & \frac{C}{2}\lambda_i - b \end{vmatrix} \xi_i, \\ q_1 &= d \left( \frac{C}{2}\lambda_i - b \right)^{-1} x_1, \quad q_2 = d \left( \frac{C}{2}\lambda_i - b \right)^{-1} x_2. \end{aligned} \quad (2)$$

From these, the relative values of the coordinates  $x_1, x_2, x_0, q_1, q_2$  for the five fundamental frequencies can be obtained. The result is given in Table I. Consideration of the vibrational form of  $\delta_{\pi s}$  (Fig. 1) shows that  $x_1/x_0$  and  $x_2/x_0$  must be negative, while  $q_1/x_0, q_2/x_0$  must be positive. These relations are satisfied only by the frequency 1623  $\text{cm}^{-1}$ , while the relative displacements for the frequency 1342  $\text{cm}^{-1}$  are compatible with  $\nu_{2\pi s}$ , if the amplitudes of the H atoms are larger than those of the C atoms, and if on approaching together of the two  $\text{CH}_2$  groups the H atoms in each group are pushed apart a little, as shown in Fig. 1.

TABLE I. Relative displacements in the normal vibrations of  $\text{C}_2\text{H}_4$ .

	2988 $\text{cm}^{-1}$	1444 $\text{cm}^{-1}$	3060 $\text{cm}^{-1(3)}$	1623 $\text{cm}^{-1}$	1342 $\text{cm}^{-1}$
$x_0$	0	0	$\neq 0$	$\neq 0$	$\neq 0$
$x_1/x_2$	-1	-1	1	1	1
$q_1/q_2$	-1	-1	1	1	1
$x_1/x_0$ Or $x_2/x_0$	—	—	<0	<0	>0
$q_1/x_0$ Or $q_2/x_0$	—	—	<0	>0	<0
$x_1/q_1$	>0	<0	>0	<0	<0
assignment	$\nu_{\pi a}$	$\delta_{\pi a}$	$\nu_{\pi s}$	$\delta_{\pi s}$	$\nu_{2\pi s}$

But these are just what one would expect on purely mechanical considerations. Thus we are led to the assignment of Sutherland and Dennison, namely,  $\delta_{\pi s} = 1623$ ,  $\nu_{2\pi s} = 1342$  in contradiction to that of Mecke.

In view of this change, the values of the frequencies for  $\text{C}_2\text{H}_4$ , *cis*, *trans* and asymmetric  $\text{C}_2\text{H}_2\text{D}_2$ ,  $\text{C}_2\text{D}_4$  given in another article "On the Fundamental frequencies of  $\text{CH}_2$ ,  $\text{CHD}$ ,  $\text{CD}_2$ ,  $\text{CHCl}$ ,  $\text{CDCl}$  and *Cis* and *Trans*  $\text{C}_2\text{H}_2\text{D}_2$  and  $\text{C}_2\text{H}_2\text{Cl}_2$ "<sup>4</sup> should be interchanged. This does not, however, necessarily invalidate the usual assignment to the vibration  $\nu_{2\pi s}$  of frequencies in the region 1500–1600  $\text{cm}^{-1}$  in molecules in which one or more H atom is replaced by another atom or a group of atoms. The frequency of the vibration  $\nu_{2\pi s}$  depends not only on the force constant between the double bond carbon atoms, but also on the force constants and masses in the  $\text{CH}_2$ ,  $\text{CHX}$ , or  $\text{CX}_2$  group.

In Table I, the signs for the ratios  $x_1/q_1$  are obtained from Eq. (2) with the positive sign for  $d$ , i.e.,  $d = +1.46 \times 10^5$ . Consideration of Fig. 1 shows that the signs of  $x_1/q_1$  for all the five vibrations are just as expected. Thus we are led to choose the positive value for  $d$ , in agreement with the conclusion of Sutherland and Dennison based on a different reason.<sup>1</sup>

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<sup>1</sup> G. B. B. M. Sutherland and D. M. Dennison, Proc. Roy. Soc. A148, 250 (1935); R. Mecke, Zeits. f. physik. Chemie B17, 1 (1932); *Hand und Jahrbuch d. chem. phys.*, Bd. 9/11, 395 (1934); Bonner, J. Am. Chem. Soc. 58, 34 (1936).

<sup>2</sup> Sutherland and Dennison, Proc. Roy. Soc. A148, 250 (1935). Reference is made to this paper for the notation and values of the force constants used in this letter.

<sup>3</sup> It is found that a change of the value 3019 to 3060 is necessary in order to satisfy the relation (5) in Sutherland and Dennison's paper and hence to give consistent solution for the force constants.

<sup>4</sup> J. Chem. Phys. 5, 392 (1937).

## The Viscosity (or Fluidity) of Liquid or Plastic Monomolecular Films

Theories of the structure of monomolecular films are in an unsatisfactory state on account of a lack of knowledge of the change of properties of the films as the film pressure ( $f$ ) increases. A determination of the viscosity relations of the films would be of great value, not only to the theory, but also in connection with the phenomena of penetration of liquids into solids, and of the rate of spreading of films. Unfortunately the literature contains no values for the viscosity of liquid films. In the work reported here such vis-