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Robert N. Wiener and Eugene R. Nixon

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Infrared Spectrum of Solid Sulfur Dioxide

ROBERT N. WIENER* AND EUGENE R. NIXON
*Department of Chemistry, University of Pennsylvania,
 Philadelphia, Pennsylvania*
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X-RAY powder work¹ indicates that sulfur dioxide at 95°K has an orthorhombic unit cell with a probable space group C_{2v}^{17} . In this structure the two SO_2 molecules per lattice point each occupy sites of C_2 symmetry. According to the present theory,² the fundamental vibrations of A_1 species (ν_1 and ν_2) of the free molecule will each give rise to one infrared active A_1 component in the crystal, while the B_1 fundamental (ν_3) will be split by the crystalline field into a B_1 and a B_2 component, both infrared active. Experience shows combination modes seem to follow the same selection rules as the fundamentals.³

We have examined the infrared spectrum of polycrystalline films of sulfur dioxide with the results shown in Fig. 1 and in Table I, which also lists the gas frequencies.⁴ The single com-

TABLE I. Infrared frequencies of solid sulfur dioxide at -180°C .

Gas (cm^{-1})	Solid (cm^{-1})	Assignment
518	521	ν_2
	1142	$\nu_1 - \nu'$
1151	1147	ν_1
	1316	$\nu_3 - \nu''$
1361	1308 } 1330 }	ν_3
	2436 } 2460 }	$\nu_1 + \nu_3$

ponent of ν_2 and the two components of $\nu_1 + \nu_2$ are apparent in Fig. 1. In addition to the one component (1147 cm^{-1}) predicted for ν_1 , there is a weak shoulder band at about 1142 cm^{-1} and in the ν_3 region three peaks appear instead of the expected pair.

One possible cause for the appearance of extra peaks in infrared spectra of solids is spurious absorption due to reflection, but the peaks here seem to increase proportionately in intensity as the film thickness increases, a fact which argues strongly against reflection. We have not ruled out reflection effects on the high-frequency sides of the bands as the cause of the asymmetry of several of them. There remains the plausible explanation that the extra peaks are combinations involving two very low-frequency lattice modes. According to the selection rules, ν_1 may combine with the infrared active translational modes parallel to the C_2 axis and with the torsional oscillation modes about the C_2 axis,

while the torsions about axes perpendicular to C_2 and the translations perpendicular to C_2 may combine with ν_3 .

To test this latter interpretation, we have calculated several lattice frequencies on the basis of a simple electrostatic model. From the dipole moment of SO_2 ,⁵ it has been assumed that each oxygen atom carries a charge of $-0.23e$ and each sulfur $+0.46e$, and from the geometry given by the x-ray crystal structure, the potential energy for a given small displacement of one molecule in the field of its twelve nearest-neighbor molecules (held stationary) has been calculated. The potential function yields the corresponding force constant, which, with either the mass of the molecule or one of its moments of inertia,⁵ gives the frequency. For the torsional oscillation about the C_2 axis, we find a force constant of $7.6 \times 10^{-16}\text{ erg/rad}^2$ and a frequency of 2 cm^{-1} . The torsion about the molecular axis of least moment (in the plane of the molecule and perpendicular to C_2) has a force constant of $45 \times 10^{-16}\text{ erg/rad}^2$ and a frequency of 17 cm^{-1} . The translational modes turn out to have much lower frequencies. Now although the translations and torsions are coupled, our model suggests a torsional mode ν' near 2 cm^{-1} and another, labeled ν'' , near 17 cm^{-1} .

The assignment of the 1142 cm^{-1} peak as $\nu_1 - \nu'$ gives 5 cm^{-1} for ν' . The summation band $\nu_1 + \nu'$, which should appear at 1152 cm^{-1} and have the same intensity as $\nu_1 - \nu'$, may be buried in the spurious absorption previously mentioned. The most reasonable set of assignments for the ν_3 region are given in Table I. The second lattice torsion ν'' thus has a value of 14 cm^{-1} . Again the band $\nu_3 + \nu''$, which should fall at about 1343 cm^{-1} , may be masked by reflection effects.

* Present address: Department of Chemistry, Rutgers University, New Brunswick, New Jersey.

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New Terms in the Potential Function of the Y_2X_2 Molecule*

FRED L. KELLER AND ALVIN H. NIELSEN, *Department of Physics, The University of Tennessee, Knoxville*

AND

WAVE H. SHAFFER, *Department of Physics, The Ohio State University, Columbus, Ohio*

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A RE-EXAMINATION of the infrared spectrum of acetylene at high dispersion, recently concluded, disclosed several serious difficulties with regard to band assignments and consistency among the vibrational constants. These difficulties led to a re-examination of the paper, by Shaffer and Nielsen,¹ on the theory of the linear Y_2X_2 molecule. From this study it became apparent that several permitted terms had been omitted from the cubic and quartic portions of their expression for the potential energy; namely,

$$hc\beta_{345}q_3(r_4s_5 - r_5s_4), \quad hc \sum_{i=1}^2 \gamma_{i345}q_iq_3(r_4s_5 - r_5s_4), \quad hc\gamma'_{4455}(r_4s_5 - r_5s_4)^2$$

and $hc\gamma''_{4455}(r_4s_5 + s_4s_5)^2$, where the notation is the same as that in the original paper.

With the polar coordinate substitutions $r_4 = \rho_4 \cos \phi_4$, $r_5 = \rho_5 \cos \phi_5$, $s_4 = \rho_4 \sin \phi_4$ and $s_5 = \rho_5 \sin \phi_5$, these terms reduce to $hc\beta_{345}q_3\rho_4\rho_5$

$$\sin(\phi_5 - \phi_4), \quad hc \sum_{i=1}^2 q_iq_3\rho_4\rho_5 \sin(\phi_5 - \phi_4), \quad hc\gamma'_{4455}\rho_4^2\rho_5^2 \sin^2(\phi_5 - \phi_4),$$

and $hc\gamma''_{4455}\rho_4^2\rho_5^2 \cos^2(\phi_5 - \phi_4)$. It may, therefore, be seen that all the terms depend upon the phase angle between the degenerate vibrations $\bar{\nu}_4$ and $\bar{\nu}_5$, but as they have A_{1g} symmetry should be included in the potential energy expression.

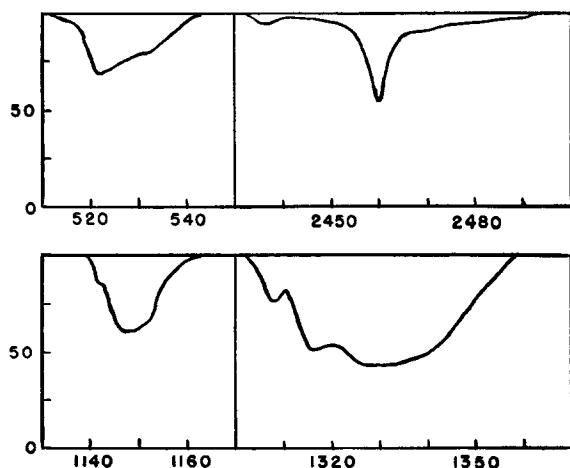


FIG. 1. Infrared absorption spectrum of solid sulfur dioxide at -180°C . Percent transmission vs cm^{-1} .

These new terms affect the energy of the molecule by contributing additional terms to the anharmonic constants x_{34} , x_{35} , and x_{45} given by Shaffer and Nielsen, and by introducing an entirely new constant X_{45} which is the coefficient of $(l_4 l_5 - 1)$. The revised expressions for x_{34} , x_{35} , and x_{45} are

$$x'_{34} = x_{34} + \frac{\beta_{345}^2 \omega_5 (\omega_3^2 + \omega_4^2 - \omega_5^2)}{2[(\omega_3 + \omega_4)^2 - \omega_5^2][(\omega_3 - \omega_4)^2 - \omega_5^2]},$$

$$x'_{35} = x_{35} + \frac{\beta_{345}^2 \omega_4 (\omega_3^2 + \omega_5^2 - \omega_4^2)}{2[(\omega_3 + \omega_4)^2 - \omega_5^2][(\omega_3 - \omega_4)^2 - \omega_5^2]},$$

$$x'_{45} = x_{45} + \frac{\beta_{345}^2 \omega_3 (\omega_4^2 + \omega_5^2 - \omega_3^2)}{4[(\omega_4 + \omega_5)^2 - \omega_3^2][(\omega_4 - \omega_5)^2 - \omega_3^2]} + \frac{1}{2}(\gamma'_{4455} + \gamma''_{4455}),$$

where the unprimed x_{34} , x_{35} , and x_{45} are the original expressions given by Shaffer and Nielsen. The new constant X_{45} has the form

$$X_{45} = \frac{\beta_{345}^2 \omega_3 \omega_4 \omega_5}{2[(\omega_4 + \omega_5)^2 - \omega_3^2][(\omega_4 - \omega_5)^2 - \omega_3^2]}.$$

Although the contributions to x_{34} , x_{35} , and x_{45} have no effect on the interpretation of the spectrum or on the experimental values previously obtained for them, the new constant X_{45} does affect the agreement between theory and experiment, the interpretation and assignment of the bands, and the values obtained for several of the other constants. The experimental value obtained for X_{45} is 4.91 cm^{-1} .

The new terms may also become important in special cases of accidental degeneracies. For example in C_2H_2 the bands $\tilde{\nu}_3(\Sigma_u^+ - \Sigma_g^+)$ and $\tilde{\nu}_1 + \tilde{\nu}_4^1 + \tilde{\nu}_5^1(\Sigma_u^+ - \Sigma_g^+)^2$ lie very close together ($\sim 13 \text{ cm}^{-1}$), and have the same symmetry. In order that the observed positions of these two bands be consistent with the data from other observed bands, it is necessary to postulate a resonance interaction between $\tilde{\nu}_3$ and $\tilde{\nu}_1 + \tilde{\nu}_4^1 + \tilde{\nu}_5^1$. The Hamiltonian given by Shaffer and Nielsen, however, contains no terms which give nonzero off-diagonal matrix elements connecting the upper levels of $\tilde{\nu}_3$ and $\tilde{\nu}_1 + \tilde{\nu}_4^1 + \tilde{\nu}_5^1$. On the other hand, the term $hcq_1 q_3 (r_4 s_5 - r_5 s_4)$ does have such a matrix element, and does indeed remove the difficulty about the positions of the bands.

It is suggested that terms such as those mentioned herein as having been omitted from the $Y_2 X_2$ molecule potential function have also been omitted from potential functions of other types of molecules where there are degenerate vibrations of different species. It may be necessary to reconsider the data of such molecules in the light of such terms.

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¹ W. H. Shaffer and A. H. Nielsen, J. Chem. Phys. 9, 847 (1941).

² The notation here is the same as that in Shaffer and Nielsen.

Further Note on the Calculation of Bond Lengths of Carbon-Chlorine Bonds

TOSINOBU ANNO, *Department of Chemistry, College of General Education, Kyushu University, Fukuoka, Japan*

AND

AKIRA SADÔ, *Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka, Japan*

(Received April 2, 1956)

TAKING the C—Cl bond as an example, we have recently derived¹ an equation similar in form to that of Coulson² for the C—C bond showing that the bond length (r) can be calculated from bond order (p) and also for bonds other than the C—C bonds. However, in I it was implicitly assumed that p_{CCl} in the reference molecule remains constant even when the C—Cl internuclear distance changes from its equilibrium value. From Eqs. (1), (2), and (3) of I we obtain, by the method similar to that of Coulson and Longuet-Higgins,³ the following expression for the second

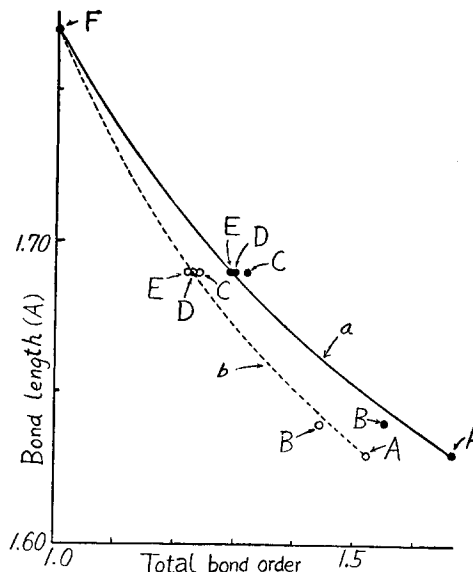


FIG. 1. Relation between bond order and bond length for C—Cl bonds. (a) Theoretical curve based on $\alpha_{\text{Cl}} = 4.68 \beta_{\text{CC benzene}}$ and $\beta_{\text{CCl}} = \beta_{\text{CC benzene}}$ ($\text{SCCl}/\text{SCC benzene}$). (See reference 1.) (b) Theoretical curve based on α_{Cl} and β_{CCl} derived from experimental data. (See text.) A—Chloroacetylene. B—Dichloroacetylene. C—1,3,5-Trichlorobenzene. D—*p*-Dichlorobenzene. E—*trans*-Dichloroethylene. F—Methyl chloride.

derivative of the total bond energy with respect to the internuclear distance:

$$\frac{\partial^2 V}{\partial x^2} = \sigma + p'(\kappa_a - \sigma) + \frac{1}{2} \frac{\pi}{p_a^2} \left\{ \frac{\sigma \kappa_a (s - d_a)}{\kappa_a p' + \sigma(1 - p')} \right\}^2, \quad (1)$$

where π is the self-polarizability of the C—Cl bond under consideration, the other notations being the same as in I. The right-hand side of (1) should become σ and κ_a for the C—Cl bond in methyl chloride and chloroacetylene, respectively. While this is the case for methyl chloride since $\pi = 0$, this is not the case for chloroacetylene, and (1) becomes

$$\frac{\partial^2 V}{\partial x^2} = \kappa_a + \frac{1}{2} \frac{\pi_a}{p_a^2} \{ \sigma (s - d_a) \}^2, \quad (2)$$

since $\pi_a \neq 0$ in this case, where π_a is the self-polarizability of the C—Cl bond in chloroacetylene. This unreasonableness results from the implicit assumption already mentioned. Equation (2) shows that κ_a should be considered as the force constant corresponding to the hypothetical change where p_{CCl} does not change, and may be obtained from the actual force constant inserted in the left-hand side of (2). From the α and β values used in I, π_a is calculated to be $0.8403/\beta_{\text{CC benzene}}$. From this and the necessary experimental values used in I, a theoretical curve *a* shown in Fig. 1 is obtained. Fortunately, this curve is practically identical with that presented in I.

Naturally, the calculated values of bond order depend on the assumed values of α 's and β 's. Recently, Bersohn⁴ concluded that $\beta_{\text{CCl}} \approx (1/3)\beta_{\text{CC}}$. In his argument, however, the value of α_{Cl} is assumed. We have deduced the best values of α_{Cl} and β_{CCl} from two experimental quantities of chlorinated hydrocarbons and found that these values are consistent with other experimental data. The results are shown in Table I. In calculating the shift of the absorption frequency of substituted benzene from that of benzene, an assumption analogous to Matsen's⁵ was made.

Bond orders calculated from these new values of parameters and experimental bond lengths are plotted in Fig. 1 (open circles). Curve *b* is the corresponding theoretical curve. It is seen that the theoretical curve *b* fits the empirical points as does curve *a*. Thus we see that, in the relative calculation of the bond length using