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-68.32 kcal,¹ and -208.14 kcal² for the heats of formation of CO₂(g), H₂O(l) and SiO₂(amor.) from standard elements, respectively, and are shown under -ΔH₂. The heats of formation in the gaseous state from monatomic gases, ΔE, were calculated using the values presented by Pauling for the heats of atomization of the constituent elements (except silicon). The value 89.2 kcal/g-atom was used for that of silicon.³ The latent heats of vaporization of these liquids were estimated from Trouton's rule. The value ΔE may be shown by the following expression:

\[ \Delta E = aE_{\text{Si-O}} + bE_{\text{C-O}} + cE_{\text{C-H}} + dE_{\text{Si-Si}}. \]

In this expression E represents the energy value of bond corresponding to each suffix and the factors a, b, c, and d the number of bonds in the molecules in question. As the energy terms of C-O and C-H bonds are well known from many studies, we can evaluate the Si-O bond energy. In the case of hexamethoxydimethylsilane Si-Si bond energy was considered as equal to the negative value of half of atomization heat of silicon. Si-O bond energy computed in this manner is shown in Table II, using the values proposed by Pauling for C-O and C-H bond energies.

In the past several values have been reported for Si-O bond energy, and of these the value obtained by Thompson is indicative of the considerable deviations in his results. We are not also satisfied with others.⁴ The Si-O bond energy derived here from four substances is in good agreement.

⁵ Thompson, J. Chem. Soc. 1933, 1908.
⁷ L. H. Baughan, Quart, Rev. 7, 103 (1953).

The Rule of Mutual Exclusion

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It is well known that in molecules possessing a center of inversion spectral lines corresponding to fundamental, overtone, and combination frequencies are mutually exclusive in Raman and infrared spectra, i.e., lines appearing in Raman effect are forbidden in infrared absorption and vice versa. The object of this note is to show that this rule is not universally true in crystals.

In molecules, the center of inversion is unique and it commutes with all other symmetry elements. The point group G of the molecule can be written as the direct product of two groups in the form \( G = G₁ \times G₂ \), where \( G₁ \) is the group of order 2 consisting only of the elements \( E \) and \( i \). Each irreducible representation of \( G \) can be designated by \( \rho \) or \( \sigma \) according to its trace of the identity element is positive or negative. Further every eigenfunction can be described as symmetric or antisymmetric with respect to \( \rho \). Modes of vibration which are symmetric with respect to \( \rho \) are permitted only in Raman and infrared spectra, and modes which are antisymmetric with respect to \( \rho \) are permitted only in infrared spectra.

In the case of crystals, the center of inversion is not unique. Instead, we have an infinity of centers of inversion and they do not necessarily commute with the other symmetry elements. The modes of vibration can no longer be designated symmetric or antisymmetric with respect to the centers of inversion, nor even with respect to one center of inversion. However, all permitted fundamentals in crystals correspond to modes in which equivalent atoms in neighboring unit cells move in phase.¹ Such modes can be described symmetric or antisymmetric with respect to any one \( \iota \) (and therefore with all \( \iota \)) and the rule of mutual exclusion is still valid. However, the following example shows that the rule breaks down in general.

The finite space group \( O₃ \) obtained by taking twice the Bravais primitive translations as equivalent to the identity element is of order 8X8. This group has twenty irreducible representations, 4 one-dimensional, 2 two-dimensional, 4 three-dimensional, 4 six-dimensional, 4 four-dimensional, and 2 eight-dimensional. The one-, two-, and three-dimensional representations correspond to the irreducible representations of the isomorphic point group \( O₃ \).

We give below the characters of the four three-dimensional and the four six-dimensional representations of our extended group. The first row refers to the order of the conjugate class. Typical symmetry elements in the first six conjugate classes are \( E, C₃, C₅, a, S₄, \) and \( i \). Modes coming under \( F₃ \) are Raman active (infrared inactive) while those coming under \( F₄ \) are infrared active (Raman inactive). Modes coming under all other representations are forbidden in both Raman and infrared absorption. The symmetry species of the combination modes of oscillations coming under \( H₁ \) and \( H₂ \) are given by the relation

\[ H₁ \times H₂ = F₁ + F₂ + F₃ + H₁ + H₂. \]

This shows that the corresponding combination line is permitted in both spectra. Diamond is a specific case coming under the space group \( O₃ \). (See p. 157, Theory of Groups and its Application to Physical Problems by S. Bhagavantam and T. Venkatarayudu, 1951). Fuller details on the combination and overtone lines in this context will be published separately.

The author's thanks are due Professor D. M. Dennison and Professor G. B. B. M. Sutherland for their interest in this work.

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Force Constants of the Hydrides of the Second and Third Periods

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SYMBOLS: \( k \)—force constant; \( n \)—number of valence electrons of the element; \( Z \)—atomic number; \( A, B, a, \alpha, \beta \)—constants.

Recently Mitra⁴ has shown that \( k₅ \) is linear with \( n \) for the hydrides of the 2nd and 3rd periods. It was shown by King⁵ and Shelton⁶ on semitheoretical grounds that \( \log k₅ \) should be linear with \( \log Z \).

\[ \log k₅ = A \log Z + B \]  

Now for each period

\[ Z = a + n \]  

\[ k₅ = B(a+n) \]  

\[ k₅^{1/4} = a + Bn \]

i.e., some power of \( k \) should be additive.

When Eq. (1) is tested for the 2nd group hydrides "A" comes out nearly 1.9, so the linearity of \( k₅ \) is justified in this case. But for the 3rd group hydrides, "A" is nearly 4. Hence \( k₅ \) should give

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better linearity, which is tested in Table I. The equation is

\[ \alpha = 15.30 + 1.68 \times 10^{-4} \]

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\[ \text{Table I.} \]

<table>
<thead>
<tr>
<th>n</th>
<th>Molecule</th>
<th>( k_1 \times 10^{-4} ) (obs)</th>
<th>( k_1 \times 10^{-3} ) (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaH</td>
<td>7.801</td>
<td>16.68</td>
</tr>
<tr>
<td>2</td>
<td>MgH</td>
<td>12.75</td>
<td>18.88</td>
</tr>
<tr>
<td>3</td>
<td>AlH</td>
<td>16.20</td>
<td>20.06</td>
</tr>
<tr>
<td>4</td>
<td>SiH</td>
<td>24.79</td>
<td>22.32</td>
</tr>
<tr>
<td>5</td>
<td>PH</td>
<td>32.57</td>
<td>23.89</td>
</tr>
<tr>
<td>6</td>
<td>SH</td>
<td>\ldots</td>
<td>25.38</td>
</tr>
<tr>
<td>7</td>
<td>CH</td>
<td>51.57</td>
<td>26.80</td>
</tr>
</tbody>
</table>

\[ \text{At each junction point it is assumed that (i) the wave functions are continuous and (ii) the algebraic sum of the first derivative of the wave functions is zero. From these we get the two following relations,} \]

\[ \sin 3\omega = 0 \]

and

\[ \cos(n-3)\omega = 3 \cos(n+3)\omega, \]

graphical solutions of which give the values of \( \omega \) and hence \( E \), the various energy states. (\( n \) in the above equation represents the number of bonds in the linear part starting from the terminal nitrogen atom to the junction point in the phenyl ring.) We then assume that each carbon atom in the conjugated system contributes one \( \pi \) electron each, while two nitrogen atoms together contribute 3. Electrons are distributed from the lowest filled level to the lowest vacant level. The results of such calculations are summarized in Table I. It is evident that the agreement is more than what can be expected and there is no need for making any empirical assumption as to the box dimension.

In the case of diphenyl polyenes the origin of the coordinate in the linear part is taken at the midpoint of the straight chain and relation obtained for \( \omega \) are

\[ \sin(3\omega) = 0 \]

and

\[ \cos(n2-3)\omega = 3 \cos(n2+3)\omega. \]

Owing to symmetry of the molecule energy levels are doubly degenerate. The results are summarized in Table II. Since

\[ \text{Table II.} \]

<table>
<thead>
<tr>
<th>( n )</th>
<th>Transition from the state</th>
<th>( \lambda ) (calculated)</th>
<th>( \lambda ) (experimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>9\ldots10</td>
<td>3660</td>
<td>3770</td>
</tr>
<tr>
<td>4</td>
<td>10\ldots11</td>
<td>4200</td>
<td>4040</td>
</tr>
<tr>
<td>5</td>
<td>11\ldots12</td>
<td>4300</td>
<td>4240</td>
</tr>
</tbody>
</table>

The origin of the coordinate of each wave function is taken at the point marked with a big dot and the coordinate \( x \) is expressed in units of C-C bond distance (1) taken as 1.39 A. The energy states are given by

\[ E = \frac{\hbar^2 \omega^2}{8\pi^2 m^*} \]

\[ \text{FIG. 1. Segments and wave function of cyanine molecule.} \]