

−68.32 kcal,<sup>4</sup> and −208.14 kcal<sup>5</sup> for the heats of formation of CO<sub>2</sub>(g), H<sub>2</sub>O(l) and SiO<sub>2</sub>(amorph.) from standard elements, respectively, and are shown under  $-\Delta H_f^\circ$ . The heats of formation in the gaseous state from monoatomic gases,  $\Delta E$ , were calculated using the values presented by Pauling<sup>6</sup> for the heats of atomization of the constituent elements (except silicon). The value 89.2 kcal/g-atom was used for that of silicon.<sup>7</sup> The latent heats of vaporization of these liquids were estimated from Trouton's rule. The value  $\Delta E$  may be shown by the following expression:

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

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 hexamethoxydisilane 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<sup>6</sup> 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<sup>5</sup> is indicative of the considerable deviations in his results. We are not also satisfied with others.<sup>6,8</sup> The Si—O bond energy derived here from four substances is in good agreement.

<sup>1</sup> Tanaka, Takahashi, Ōkawara, and Watase, *J. Chem. Phys.* **19**, 1330 (1951).

<sup>2</sup> R. Ōkawara and T. Tanaka, *Bull. Chem. Soc. Japan* **27**, 120 (1954).

<sup>3</sup> Calculated from the result of Prosen and Rossini, *J. Research Natl. Bur. Standards* **33**, 439 (1944).

<sup>4</sup> Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, *J. Research Natl. Bur. Standards* **34**, 143 (1945).

<sup>5</sup> R. Thompson, *J. Chem. Soc.* **1953**, 1908.

<sup>6</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940).

<sup>7</sup> L. H. Baughan, *Quart. Rev.* **7**, 103 (1953).

<sup>8</sup> K. S. Pitzer, *J. Am. Chem. Soc.* **70**, 2140 (1948); H. Gilman and G. E. Dunn, *Chem. Revs.* **52**, 77 (1953).

## The Rule of Mutual Exclusion\*

T. VENKATARAYUDU

*The Harrison M. Randall Laboratory of Physics,  
University of Michigan, Ann Arbor, Michigan*

(Received April 19, 1954)

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  $G = G_1 \times G_2$  where  $G_2$  is the group of order 2 consisting only of the elements  $E$  and  $i$ . Each irreducible representation of  $G$  can be designated  $g$  (gerade) or  $u$  (un-gerade) according as the trace of  $i$  in the representation is positive or negative. Further every eigenfunction can be described as symmetric or antisymmetric with respect to  $i$ . Modes of vibration which are symmetric with respect to  $i$  are permitted only in Raman effect and modes which are antisymmetric with respect to  $i$  are permitted only in infrared spectrum.

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.<sup>1</sup> Such modes can be described symmetric or antisymmetric with respect to any one  $i$  (and therefore with all  $i$ ) 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  $O_h$ <sup>7</sup> obtained by taking twice the Bravais primitive translations as equivalent to the identity element is of order  $48 \times 8$ . 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  $O_h$ . 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  $E$ ,  $C_3$ ,  $C_2$ ,  $\sigma$ ,  $S_4$ , and  $i$ . Modes coming under  $F_2$  are Raman active (infrared

	1	32	12	12	48	4	32	24	24	48	12	6	24	32	12	12	4	32	12	1
$F_1$	3	0	-1	-1	1	3	0	-1	-1	1	-1	3	-1	0	-1	-1	3	0	-1	3
$F_2$	3	0	-1	-1	1	3	0	-1	-1	1	-1	3	-1	0	-1	-1	3	0	-1	3
$F_3$	3	0	-1	-1	1	-3	0	1	1	-1	1	3	-1	0	-1	-1	-3	0	1	3
$F_4$	3	0	-1	-1	1	-3	0	1	-1	1	-1	3	-1	0	-1	-1	-3	0	-1	3
$H_1$	6	0	2	2	0	0	0	0	0	0	0	-2	-2	0	2	-2	0	0	0	6
$H_2$	6	0	-2	-2	0	0	0	0	0	0	0	2	2	0	0	0	2	0	0	-6
$H_3$	6	0	2	-2	0	0	0	0	0	0	0	-2	2	0	-2	-2	0	0	0	6
$H_4$	6	0	-2	-2	0	0	0	0	0	0	0	2	-2	0	0	0	2	0	0	-6

in-active) while those coming under  $F_4$  are infrared active (Raman in-active). 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  $H_1$  and  $H_2$  are given by the relation

$$H_1 \times H_2 = F_1 + F_2 + F_3 + F_4 + H_1 + H_2 + H_3 + H_4.$$

This shows that the corresponding combination line is permitted in both spectra. Diamond is a specific case coming under the space group  $O_h$ <sup>7</sup>. (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.

\* This work was sponsored by the U. S. Army Signal Corps under Contract DA-36-039 SC-5581.

<sup>1</sup> S. Bhagavantam and T. Venkatarayudu, *Proc. Indian Acad. Sci.* **9A**, 224 (1939).

## Force Constants of the Hydrides of the Second and Third Periods

S. S. MITRA AND Y. P. VARSHNI

*Department of Physics, Allahabad University, Allahabad, India*

(Received April 19, 1954)

**S**YMBOLS:  $k_e$ —force constant;  $n$ —number of valence electrons of the element;  $Z$ —atomic number;  $A$ ,  $B$ ,  $a$ ,  $\alpha$ ,  $\beta$ —constants.

Recently Mitra<sup>1</sup> has shown that  $k_e^{\frac{1}{3}}$  is linear with  $n$  for the hydrides of the 2nd and 3rd periods.

It was shown by King<sup>2</sup> and Sheline<sup>3</sup> on semitheoretical grounds that  $\log k_e$  should be linear with  $\log Z$ .

$$\log k_e = A \log Z + \log B \quad (1)$$

or

$$k_e = BZ^A.$$

Now for each period

$$Z = a + n$$

hence

$$k_e = B(a + n)^A$$

or

$$k_e^{1/A} = \alpha + \beta n \quad (2)$$

i.e., some power of  $k_e$  should be additive.

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

TABLE I.

<i>n</i>	Molecule	$k_e \times 10^{-4}$ (obs)	$k_e^{\frac{1}{2}}$ (obs)	$k_e^{\frac{1}{2}}$ (calc)
1	NaH	7.818	16.72	16.98
2	MgH	12.75	18.88	18.66
3	AlH	16.20	20.06	20.34
4	SiH	24.79	22.32	22.02
5	PH	32.57	23.89	23.70
6	SH	...	...	25.38
7	ClH	51.57	26.80	27.06

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

$$k_e^{\frac{1}{2}} = 15.30 + 1.68n.$$

The value of the force constant of SH is predicted to be  $41.5 \times 10^4$  dynes/cm.

The authors are thankful to Dr. K. Majumdar for his guidance. One of them (YPV) expresses his thanks to the Council of Scientific and Industrial Research (India) for the financial assistance.

<sup>1</sup> S. S. Mitra, J. Chem. Phys. (to be published 1954).

<sup>2</sup> G. W. King, J. Chem. Phys. 6, 378 (1938).

<sup>3</sup> R. K. Shelton, J. Chem. Phys. 18, 927 (1950).

## Free Electron Network Model for Cyanines and Diphenyl Polyenes

SADHAN BASU

Indian Association for the Cultivation of Science, Calcutta 32, India

(Received April 12, 1954)

SOME valuable results have been obtained for the absorption spectra of conjugated organic dye molecules by Kuhn,<sup>1</sup> Bayliss,<sup>2</sup> and others by adopting a free electron gas model for these compounds. In addition to this assumption, further empirical assumptions were made while applying this theory to cyanines and diphenyl polyenes. For example, Kuhn<sup>1</sup> assumed that the phenyl group at the end of the conjugated chain of the cyanine molecule increases the path of the electron by 2/3 the length of the linear part, while Bayliss proposed that introduction of a phenyl group at the end of a polyene chain is equivalent to the introduction of another double bond in the chain. Although with these assumptions the agreement between the calculated and experimental frequencies of absorption was good, there is no theoretical justification for such assumptions. In recent years, the free electron model has been extended with encouraging results by various workers,<sup>3,4</sup> replacing the one-dimensional box approximation by a free electron network structure and applying continuity and conservation conditions at the junction of conjugated segments of the molecule under consideration. Especially interesting are the results obtained by Nakajima<sup>5</sup> using this model for styrene homologs, polyphenyls, nonalternate hydrocarbons, and pyridine. This model, when used for cyanines and diphenyl polyenes, also gave close agreement with experimental absorption values as reported in the present note.

For this purpose the cyanine molecule is divided into segments as shown in Fig. 1. The free electron wave function for the  $\pi$  electron in each segment is then expressed in the form

$$u(x) = a \cos \omega x + b \sin \omega x.$$

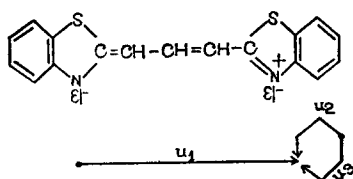
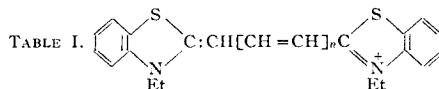


FIG. 1. Segments and wave function of cyanine molecule.

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 1.39A. The energy states are given by

$$E = \frac{\hbar^2 \omega^2}{8\pi^2 m^2}.$$



<i>n</i>	Transition from the state	$\lambda$ (calculated)	$\lambda$ (experimental)
1	7 → 8	5698	5550
2	8 → 9	6700	6500
3	9 → 10	7751	7600
4	10 → 11	8793	8700

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 energy state upwards, two on each state. Center of gravity of the absorption band corresponds to the transition from the highest 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.

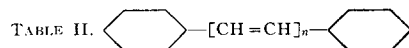
In the case of diphenyl polyenes the origin of the coordinate in the linear part is taken at the midpoint of the straight chain and relation obtained for  $\omega$  are

$$\sin(3\omega) = 0$$

and

$$\cos(n/2-3)\omega = 3 \cos(n/2+3)\omega.$$

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



<i>n</i>	Transition from the state	$\lambda$ (calculated)	$\lambda$ (experimental)
3	9 → 10	3660	3770
4	10 → 11	4200	4040
5	11 → 12	4300	4240

graphical evaluation of  $\omega$  was not very accurate it is expected that better agreement will be obtained by more accurate computation of  $\omega$  (detailed calculations will be published elsewhere).

<sup>1</sup> H. Kuhn, J. Chem. Phys. 16, 840 (1948).

<sup>2</sup> N. S. Bayliss, Quart. Revs. Chem. Soc. 6, 319 (1952).

<sup>3</sup> K. Ruedenberg and C. W. Scherr, J. Chem. Phys. 21, 1565 (1953).

<sup>4</sup> Y. Oshika, Busseiron Kenkyu 29, 16 (1950).

<sup>5</sup> T. Nakajima, Sci. Repts. Research Insts. Tôhoku Univ. 5, 98 (1953).