October, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(10), 2745—2750 (1975)

The Franck-Condon Factor of a Polyatomic Molecule. Its Method and Application to Acetylene and Dideuteroacetylene

Isao Kanesaka and Kiyoyasu Kawai
Faculty of Literature and Science, Toyama University, Gofuku, Toyama 930

(Received December 24, 1974)

An advanced method for the calculation of the Franck-Condon factor is reported. It is realized on the assumption of the neglect of the zero-point motions except for the three normal coordinates whose vectors are three-dimensionally orthogonal to each other. The overlap integral is given by the Cartesian displacement coordinate system in order to consider precisely the molecular structures of the ground and excited states. This coordinate system does not cause any conflicts with the above assumption. Thus, the overlap integral is defined every nucleus with one- to three-dimensional formulae to satisfy sufficiently the Franck principle, which has been considered precisely only in the case of the diatomic molecule. The method is applied to acetylene and dideuteroacetylene with very good results. The intensity factors obtained are discussed, along with the effects of the force constants and anharmonicity.

There has generally been found a wide variation in the intensity of each band in the progression of the electronic spectra of a polyatomic molecule, whose structure of the excited state changes greatly from that of the ground state. It has been found, in a progression for the $\tilde{A}\leftarrow\tilde{X}$ band of acetylene,[1] that the relative intensities vary from 1 for $v=1$ up to 285 for $v=5$. In this case, in the molecular structure of the excited state the angle of CCH is 120.2° and the distances of the H–C and C=C bonds are 1.08 and 1.383 Å respectively. Thus, it is suitable for the study of the Franck-Condon principle of a polyatomic molecule.

Ingold and King[1] have calculated the Franck-Condon factor of the progression of acetylene by the method established by Craig,[2] assuming the CH groups to be compound atoms. However, they could not explain the observed intensity distribution. In their treatment, the internal coordinate of the excited state is related one-dimensionally to that of the ground state in spite of the bent-linear transition. This is probably the reason for their failure. Smith and Warsop[3] have also calculated the Franck-Condon factor of the progression of acetylene by the method of Ansbacher.[4] However, they too could not explain the observed spectra. Their treatment of the overlap integral is based on this equation:

$$R(v,0) = \int \phi_0''(d-Q')\phi_v'(Q')\mathrm{d}Q' \tag{1}$$

where Q' is the normal coordinate of the excited state, d represents the separation of the origin of the two corresponding coordinates, and ϕ_0'' and ϕ_v' are the vibrational wave functions of the ground and excited states respectively. That is, the relation:

$$Q'' = d - Q' \tag{2}$$

is assumed. The approximation of Eq. (2) is very low,[5] and, furthermore, d has not been defined clearly by the molecular structures of the ground and excited states, but estimated from the accordance of the observed with the calculated relative intensities. Though it is easy to make the observed relative intensities accord with those calculated, the value of d obtained is deficient in reliability because of its low approximation.

However, it is easily found that Eq. (1) can be applied to the diatomic molecule as it is. That is, Eq. (1) is precise if the direction of the normal coordinate of the excited state coincides with that of the ground state. In this case, the difference in d in Eq. (1) or in a frequency parameter does not cause any difficulties. On the other hand, in a polyatomic molecule a normal coordinate of the ground state does not generally coincide with that of the excited state. Therefore, Eq. (1) does not fulfill the Franck principle. That is, the value of $\phi_0''(d-Q')\phi_v'(Q')$ in Eq. (1) is correct only at a point of intersection of the two coordinates and is estimated largely at the other points. Thus, more than one-dimensional formulae is needed to estimate the correct value of the latter points. In our treatment, the vertical transition is considered sufficiently.

Method

In a polyatomic molecule, the Franck-Condon factor is generally given by:

$$R_{\mathrm{v}'\mathrm{v}''} = \int \phi_{\mathrm{v}}'\phi_{\mathrm{v}}''\mathrm{d}\tau_{\mathrm{v}} \tag{3}$$

where the total wave function is given by:

$$\phi_{\mathrm{v}} = \phi_1(Q_1)\phi_2(Q_2)\cdots\phi_{3N-6}(Q_{3N-6}) \tag{4}$$

where the wave function $\phi_i(Q_i)$ is given by:

$$\phi_i(Q_i) = N_{v_i}\exp\{-(\alpha_i/2)Q_i^2\}H_{v_i}(\sqrt{\alpha_i}Q_i) \tag{5}$$

where N_v is a normalization constant, $\alpha_i=4\pi^2\nu_i/h$, and $H_v(\sqrt{\alpha_i}Q_i)$ is a Hermitte polynominal of the vth degree. We will here consider the means of Eq. (4) by following the discussion of Herzberg.[6]

If only one normal vibration is excited, the total eigen-function is given by:

$$\phi_{\mathrm{v}} = NH_{v_1}(\sqrt{\alpha_1}Q_1)\exp\{-(\alpha_1/2)Q_1^2-(\alpha_2/2)Q_2^2 -(\alpha_3/2)Q_3^2\cdots\} \tag{6}$$

If we neglect the zero-point motion of all the other normal vibrations, we have $\phi_{\mathrm{v}}=\phi_1(Q_1)$. In this case, as found from the equation:

$$\mathbf{X} = \mathbf{L}\mathbf{Q} \tag{7}$$

where $\mathbf{X}$ is a Cartesian displacement coordinate vector, and $\mathbf{Q}$ a normal coordinate vector, the displacement components of all the nuclei are proportional to Q_1. Then, the wave function conjugated with X_N is given by:

$$\psi(X_N) = \psi(Q_1) \tag{8}$$

However, actually we can not neglect the zero-point motion of the other vibration. In this case, Eq. (6) does not simplify to $\psi_1(Q_1)$ and Eq. (7) does, in general, not lead to such a simple expression for the $\mathbf{Q}$.

Departing from the discussion of Herzberg, if we use Eq. (7) as an approximation, we find that we may use $\psi_i(Q_i)$ instead of Eq. (4) as a wave function of the excited state. On the other hand, for the ground state, if the jth normal vibration is considered, we have $\psi_j(Q_j)$. If the kth normal vibration is considered, we have $\psi_k(Q_k)$, and so on. This shows, thus, that Eq. (3) can be expressed by:

$$R(v, 0) = \sum_j \int \psi_{0j}''(Q_j'')\psi_v'(Q_i')\mathrm{d}Q_i' \tag{9}$$

or

$$R(v, 0) = \sum_j \int \psi_{0j}''(d-Q_i')\psi_v'(Q_i')\mathrm{d}Q_i' \tag{10}$$

Eq. (10) is essentially equal to Eq. (1). That is, the zero-point motions different from ψ_0'' are also neglected or averaged in Eq. (1).

If we use the Cartesian displacement coordinate of each nucleus related linearly with a normal coordinate, d in Eq. (10) is defined clearly as the distance between the equilibrium positions of the nuclei of the ground and excited states. Thus, we transform Eq. (10) into the formula defined by the Cartesian displacement coordinate.

We use the $\psi(X_N)$ of Eq. (8) to resolve Eq. (10). However, $\psi_i(X_N)$ is not normalized on all Cartesian displacement coordinates of the ith normal coordinate as it is. That is shown by the consideration that the $\int\psi_i^*(X_N)\psi_i(X_N)\mathrm{d}X_N$ of a light atom such as hydrogen is larger than that of a heavy atom such as carbon. According to the reciprocal, l_N, of the **L** matrix element, a normal coordinate is expressed by:

$$Q_i = \sum_N^{Mi} l_N X_N \tag{11}$$

From the property of a normal coordinate in our approximation, there are these relations:

$$Q_i = l_1X_1 = l_2X_2 = \cdots = l_{M_i}X_{M_i} \tag{12}$$

That is, it is found that the above normalization can be settled by multiplying $\int\psi_i^*(X_N)\psi_i(X_N)\mathrm{d}X_N$ by l_N/M_i. Then, $\sqrt{|l_N|/M_i}\psi_i(X_N)$ is reasonable as the function of Eq. (9) or (10) and for the dimension of the vibrational wave function as well.

From Eq. (11) the overlap integral is given by the summation of $R_N(v,0)$ on all the coordinates. $R_A(v,0)$ is defined for every atom, and these one- to three-dimensional formulae are given by:

$$R_A(v, 0)_\mathrm{x} = \sum_i \int \sqrt{|l_{i\mathrm{x}}''|/M_i''}\psi_{0i}''(d_\mathrm{x}-X') \times \sqrt{|l_\mathrm{x}'|M'}\psi_v'(X')\mathrm{d}X' \tag{13}$$

$$R_A(v, 0)_\mathrm{xy} = 2\sqrt{M_i''M'}R_A(v, 0)_\mathrm{x}R_A(v, 0)_\mathrm{y} \tag{14}$$

$$R_A(v, 0)_\mathrm{xyz} = 3M_i''M'R_A(v, 0)_\mathrm{x}R_A(v, 0)_\mathrm{y}R_A(v, 0)_\mathrm{z} \tag{15}$$

where the summation is carried out for all the normal coordinates of the ground state in the case of the absorption spectra. Generally, the vibrational modes expressed by the Cartesian coordinate system are not independent of each other. However, it is easily found that Eq. (12) is realized in our approximation, as has been discussed above.

In our approximation, the $\psi_i(X)$ of the ith normal coordinate would be different from zero only along the line of the Cartesian displacement coordinate. Actually, $\psi_i(X)$ is not zero outside the line, but decreases in the direction perpendicular to this line. Therefore, it is found that Eq. (13) is a very low approximation in a case such as a bent-linear transition. That is, a factor should be multiplied to Eq. (13) to satisfy the Franck principle. In our treatment, $R_A(v,0)_\mathrm{y}$ is the factor for $R_A(v,0)_\mathrm{x}$. Thus though Eq. (14) is a two-dimensional formula, this means the one-dimensional overlap integral and Eq. (15) has also the same mean as Eq. (14). That is, though the zero-point motions of the same axis as $R_A(v,0)_\mathrm{x}$ are neglected in Eq. (7), those of the other axes are considered sufficiently.

By using Eqs. (13)—(15), the overlap integral of Eq. (10) is given by:

$$R(v, 0) = \sum_A R_A(v, 0) \tag{16}$$

where the sign of each term of $R_A(v,0)$ is easily determined by the displacement vector of each nucleus of the excited state, because ψ'' considered is always positive. In the case of the bent-linear transition, it is clear that the potential of the one axis, y, of the excited state is the double minimum and is symmetrical about the other, x. Then, the overlap integral of the axis becomes either double or zero. It is also possible to replace the integral for y in Eq. (14) with z. Then, Eq. (16) is rewritten by:

$$R_\mathrm{L}(v, 0) = 4R(v, 0) \tag{17}$$

The Cartesian displacement coordinate vector is related to the normal coordinate vector by Eq. (7) in every symmetry species. Then, the values of $\psi_v'(X_N)$ of the excited state are calculated by Eq. (8), and those of $\psi_{0i}''(d-X_N)$ of the ground state by the expression:

$$\psi_{0i}''(d-X_N) = \psi_{0i}''(Q_i'') \tag{18}$$

where Q_i'' is given by:

$$Q_i'' = (d-L_N'Q')/L_{N_i}'' \tag{19}$$

where L_N is the **L** matrix element. The calculation of such an integral as Eq. (13) is carried out by the numerical calculation of $\psi_{0i}''(d-X)\psi_v'(X)$ at various values of X. Thus, the $R(v,0)$ of Eq. (16) or (17) is calculated; the square of $R(v,0)$ or $R_L(v,0)$ gives the intensity factor.

Application

Acetylene. We applied our method to the progression (C progression) of the bending vibration (1049 cm^{-1}) of the first-excited state, $^1\mathrm{A}_\mathrm{u}$, of acetylene.

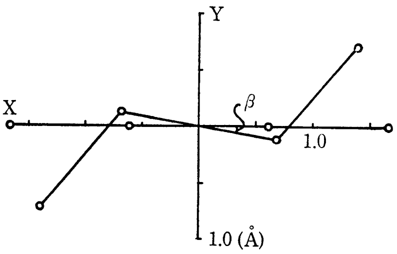

Fig. 1. The molecular structures of the ground and excited states of acetylene.

The absorption consists of a large number of very weak absorption bands, extending from 2400 to 2100 Å.[1,7] It has been determined, by an analysis of both the vibrational and rotational structures, that, in the excited state, acetylene is bent, taking the C_{2h} symmetry. The molecular structure of this excited state is shown in Fig. 1, along with that of the ground state, in which the bond lengths of the H–C and C≡C bonds are 1.064 and 1.201 Å[8] respectively. In our treatment, the principal axes of the ground and excited states should coincide as shown in Fig. 1. Thus, it is found that the relative equilibrium positions of the isomer differ considerably in the same Cartesian coordinate system, though their molecular structures are, of course, identical; we will describe dideuteroacetylene later. The intensities, expressed as the oscillator-strength, of the C progression have been measured from C_1 to C_5[1], where C_v represents the v–0 transition. They are shown in Table 1. All the fundamental frequencies of the A_g species of the excited state have been observed[1,7] at 1049, 1380, and 3000 cm^{-1}; they are assigned to the CCH bending, C=C, and C–H stretching vibrations respectively.

TABLE 1. THE OBSERVED OSCILLATOR-STRENGTHS (f_v) AND THE RELATIVE INTENSITIES OF C PROGRESSION OF ACETYLENE

Band	C_1	C_2	C_3	C_4	C_5
$10^5 f_v$	0.0042	0.036	0.145	0.51	1.2
Relative intensities	1	8.57	34.5	121	285

The normal coordinate analysis was carried out by the computer program reported by Shimanouchi,[9] using the electronic computer, FACOM-45S, of Toyama University. The $\mathbf{L_S}$ matrix obtained is expressed by:

$$\mathbf{S} = \mathbf{L_S Q} \tag{20}$$

where **S** is the symmetry coordinate vector. From the $\mathbf{L_s}$ matrix, the **L** matrix is obtained by this expression:

$$\mathbf{L} = \mathbf{M^{-1} B_S G L_S} \tag{21}$$

where the $\mathbf{M}^{-1}$ matrix consists of the reciprocal of the mass of the atom and where $\mathbf{B_S}$ and **G** are Wilson's $\mathbf{B_S}$ and **G** matrixes.[10] The **L** matrix (Set I) of Q_3' of the excited state is given in Table 2. The calculated frequencies agree completely with the observed ones. The force constants (Set I) are given in Table 3, where the H··C repulsive force constant was fixed in the least-squares adjustment. The fundamental frequencies of the ground state were quoted from a reference.[6] The **L** matrix of the ground state is also given in Table 2. The calculated frequencies agree with the observed ones. The force constants are also given in Table 3, where the interaction term between the CCH bending coordinates was taken into consideration. The calculation of Eq. (13) or Eq. (14) was carried out using the same computer mentioned above. In the summation of Eq. (14), there are two normal coordinates for y, with frequencies of 611.8(Π_g) and 729.1(Π_u) cm^{-1}, and three for x, with frequencies of 1973.8(Σ_g^+), 3287.0(Σ_u^+) and 3373.7(Σ_g^+) cm^{-1}.

It is interesting to compare the overlap integrals

TABLE 2. THE **L** MATRIX OF THE EXCITED AND GROUND STATES OF ACETYLENE[a)]

		Excited(A_g)		
		Set I	Set II	
X_H	=	0.525	0.515	Q_3'
Y_H		0.283	0.261	
X_C		0.0715	0.0914	
Y_C		−0.0812	−0.0730	
		Ground (Σ_g^+)		
X_H	=	0.639	0.302	Q_1
X_C		−0.0873	0.185	Q_2
		Ground (Σ_u^+)		
X_H	=	0.679		Q_3
X_C		−0.0566		
		Ground (Π_g)		
Y_H	=	−0.609		Q_4
Y_C		0.128		
		Ground (Π_u)		
Y_H	=	−0.679		Q_5
Y_C		0.0566		

a) Given only for two atoms

TABLE 3. THE FORCE CONSTANTS OF THE EXCITED AND GROUND STATES OF ACETYLENE

	Excited		Ground
	Set I	Set II	
K(C-H)	4.861	4.902	5.888
K(C=C)[a)]	6.348	6.223	15.660
H(HCC)	0.377	0.424	0.188
F(H···C)[b)]	0.0905	0.0	—
I(HCC, HCC)	—	—	−0.0686

a) Triple bond for ground state. b) Fixed force constant (mdyn/Å).

TABLE 4. THE OVERLAP INTEGRALS FOR y OF ACETYLENE[a)]

v	$Q_4(\Pi_g)$		$Q_5(\Pi_u)$	
	$H/10^{-4}$	$C/10^{-2}$	$H/10^{-3}$	$C/10^{-6}$
0	0.0552	0.0484	0.0083	0.0007
1	0.121	0.107	0.0175	0.0048
2	0.217	0.187	0.0306	0.0230
3	0.350	0.293	0.0483	0.0886
4	0.529	0.422	0.0712	0.293
5	0.758	0.578	0.101	0.864

a) Twice as much as Eq. (13).

of two normal coordinates for y, because only one of them has been considered. The results of Eq. (13) for hydrogen and carbon atoms are given in Table 4, where Eq. (16) is applied. The largest value of $R_A(v,0)$ is the $R_C(v,0)$ of the carbon atom of Q_4. The $R_H(v,0)$ of the hydrogen atom of Q_4 is nearly equal to that of Q_5, and both are smaller than the $R_C(v,0)$ of Q_4. The $R_C(v, 0)$ of Q_5 is negligible. It should be noticed that their large discrepancies result from the differences in the **L** matrix elements given in Table 2.

The overlap integrals for x are given in Table 5, where the results of Q_3 are omitted because they are similar to those of Q_1. In this case, the $R_H(v, 0)$ values of Q_1 and Q_2 are much larger than those in Table 4. This results mainly from the small value of d_x, 0.287 Å. The $R_C(v, 0)$ of the carbon atom of Q_2 is quite large.

From the above results, we estimated the intensity factor in two manners: (I) using only one term of Eq. (14), and (II) using all the terms of Eq. (14). Though we could not always expect a very large term in Eq. (14), it is found in acetylene that ${}^{Q_2}R_C(v,0)\cdot{}^{Q_4}R_C(v,0)$ (Manner I) is much larger than the other terms. The intensity factors obtained are given in Table 6, where Eq. (17) is applied. The calculated relative intensities to C_1 are also given in Table 6. The accordances with the observed values are sufficiently satisfactory.[1)]

TABLE 5. THE OVERLAP INTEGRALS FOR x OF ACETYLENE

v	$Q_1(\Sigma_g^+)$		$Q_2(\Sigma_g^+)$	
	$H/10^{-1}$	$C/10^{-3}$	$H/10^{-1}$	$C/10^{-1}$
0	0.0704	0.0003	0.0285	0.0216
1	0.209	0.0019	0.104	0.0422
2	0.415	0.0080	0.258	0.0666
3	0.645	0.0269	0.486	0.0937
4	0.818	0.0783	0.734	0.123
5	0.854	0.203	0.900	0.153

The oscillator-strength of the whole electronic transition is given by this relation:

$$f = f_v / R_L(v, 0)^2 \tag{22}$$

where f_v is the observed oscillator-strength of the vth band. Then, the value of f obtained is 0.51 from $v=5$. This value is as large as that of an ordinary allowed electronic dipole transition.

Dideuteroacetylene. With dideuteroacetylene, in the transition to the ^1A_u state the spectra or the vibrational structures are generally similar to those of acetylene.[1,7)] That is, the C progression forms the main milestones of the spectra, with an interval of about 800 cm^{-1} between successive bands. However, the frequency intervals are so small that there is more overlapping of bands, and the band intensity is lower. Since the intensity of the C progression has not been measured, we calculate it only to compare the intensity factor of dideuteroacetylene with that of acetylene.

In this case, the equilibrium positions of the atoms of the excited state are obtained by taking $\beta=16°40'$ in Fig. 1. The fundamental frequencies of the A_g species have been reported to be at 844, 1310, and 2215 cm^{-1}. However, C_0 and C_1 have not been observed because of the low intensity, and we assumed 864 cm^{-1} as the CCD bending vibration. The normal coordinate analysis was carried out in the same manner as for acetylene. The calculated frequencies completely accord with the observed ones. The **L** matrix is given in Table 7, and the force constants in Table 8. The fundamental frequencies of the ground state are quoted from a reference.[6)] A good accordance of the observed frequencies with those calculated was obtained. The **L** matrix and the force constants are also given in Tables 7 and 8 respectively.

In the summation of Eq. (14), there are two normal coordinates for y, with frequencies at 505(Π_g) and 539.1(Π_u) cm^{-1}, and three for x, with frequencies at 2700.5(Σ_g^+), 2427.0(Σ_u^+) and 1762.4(Σ_g^+) cm^{-1}. In this instance, there are two cases of a large contribution to the overlap integral for y, while the other two

TABLE 6. THE INTENSITY FACTORS AND THE RELATIVE INTENSITIES OF ACETYLENE

v	Intensity factors/10^{-5}			Relative intensities		
	Manner I		Manner II	Manner I		Manner II
	Set I	Set II		Set I	Set II	
0	0.00022	0.00040	0.00027	0.053	0.049	0.049
1	0.00417	0.0081	0.0055	1	1	1
2	0.0321	0.0635	0.0458	7.70	7.85	8.36
3	0.155	0.304	0.234	37.1	37.6	42.7
4	0.550	1.02	0.850	132	126	155
5	1.59	2.75	2.37	382	340	433

Table 7. The **L** matrix of the excited and ground states of dideuteroacetylene[a)]

Excited (A_g)
$\begin{vmatrix} X_D \\ Y_D \\ X_C \\ Y_C \end{vmatrix} = \begin{vmatrix} 0.361 \\ -0.183 \\ 0.0750 \\ 0.0935 \end{vmatrix} Q_3'$
Ground (Σ_g^+)
$\begin{vmatrix} X_D \\ X_C \end{vmatrix} = \begin{vmatrix} 0.342 & 0.364 \\ -0.149 & 0.140 \end{vmatrix} \begin{vmatrix} Q_1 \\ Q_2 \end{vmatrix}$
Ground (Σ_u^+)
$\begin{vmatrix} X_D \\ X_C \end{vmatrix} = \begin{vmatrix} 0.463 \\ -0.0772 \end{vmatrix} Q_3$
Ground (Π_g)
$\begin{vmatrix} Y_D \\ Y_C \end{vmatrix} = \begin{vmatrix} -0.363 \\ 0.168 \end{vmatrix} Q_4$
Ground (Π_u)
$\begin{vmatrix} Y_D \\ Y_C \end{vmatrix} = \begin{vmatrix} -0.463 \\ 0.0772 \end{vmatrix} Q_5$

a) Given only for two atoms.

Table 8. The force constants of the excited and ground states of dideuteroacetylene

	Excited	Ground
K(C–D)	4.825	5.965
K(C=C)[a)]	5.817	15.826
H(DCC)	0.423	0.179
F(D···C)[b)]	0.0905	—
I(DCC, DCC)	—	−0.0815

a) Triple bond for ground state. b) Fixed force constant (mdyn/Å).

are negligibly small. The large ones are the $R_C(v, 0)$ of Q_4 and the $R_D(v, 0)$ of the deuterium atom of Q_5. They are given in Table 9, where Eq. (16) is applied. As for x of Eq. (14), all the overlap integrals are of the same order; only the values of the carbon and deuterium atoms of Q_2 are given in Table 9. They are fully considered in the calculation of the intensity factor, which is given in Table 10, where Eq. (17) is applied. The intensities relative to C_2 are also given in Table 10. The intensity factors of dideuteroacetylene are to some extent larger than those of acetylene. Since the observed band intensity of dideuteroacetylene is lower than that of acetylene, it is considered that the oscillator-strength of dideuteroacetylene is smaller than that of acetylene.

Table 9. The overlap integral of dideuteroacetylene

v	$Q_5(\Pi_u)$[a)] $D/10^{-3}$	$Q_4\Pi(_g)$[a)] $C/10^{-3}$	$Q_2(\Sigma_g^+)$	
			$D/10^{-4}$	$C/10^{-1}$
0	0.0129	0.0433	0.0062	0.0686
1	0.0242	0.101	0.0341	0.155
2	0.0392	0.186	0.110	0.260
3	0.0583	0.306	0.242	0.364
4	0.0817	0.467	0.403	0.454
5	0.111	0.670	0.520	0.529

a) Twice as much as Eq. (13).

Table 10. The intensity factors and the relative intensities of dideuteroacetylene

v	Intensity factors/10^{-5}	Relative intensities
0	0.00012	0.0030
1	0.00378	0.092
2	0.0412	1
3	0.241	5.85
4	0.940	22.8
5	2.74	66.6

Discussion

The above results would seem to justify our method. As has been seen in the above discussion, it may be said that in Eq. (14) the wave function of the excited state is defined by the two-dimensional formula. This naturally causes overlaps with the corresponding wave functions of the ground state. A one-dimensional model of the Franck-Condon integral, that is, an explanation of Eq. (13), is given in Fig. 2, where the

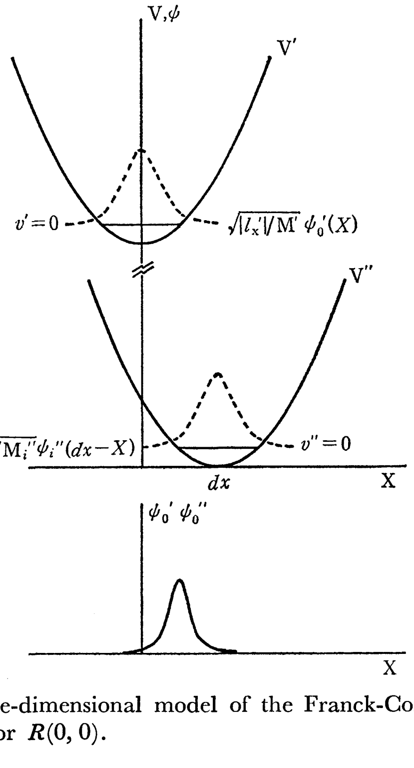

Fig. 2. One-dimensional model of the Franck-Condon integral for $R(0, 0)$.

$\psi_0''\psi_0'$ for $R(0,0)$ is also shown. The potential V' for y is similarly considered, though the V' for y is double minimum function, as has been described above. Actually V' and V'' are not generally on the same plane, as is shown in Fig. 2. That is, in the equilibrium position V' is on the plane separated by d_y perpendicular to the plane in Fig. 2. However, since the vertical transition in the Franck sense is the fundamental principle, V' and V'' should be on the same plane. In our treatment, the restriction is filled up by the overlap for y. The inverse consideration is realized. On the other hand, in Eq. (10) the above vertical transition could not be estimated precisely as it is.

The force constants of the ground state of acetylene agree satisfactorily with those of dideuteroacetylene. These values agree also with those given by Herzberg,[6] where the interaction term of the C–H with the C≡C bond is taken into consideration, *viz.*, I(C–H, C≡C) = −0.037 mdyn/Å in acetylene. The remaining differences are mainly due to the neglect of anharmonicity. The force constants of the excited state of acetylene are, to some extent, different from those of dideuteroacetylene. These differences may be caused mainly by using the same repulsive force constant in the isomer. Therefore, it is proper to use the other set of force constants to discuss the effect of force constants on the overlap integral; we do this for acetylene.

The new set (Set II) of the force constants of the excited state of acetylene is given in Table 3, where the repulsive force constant is assumed to be zero. The **L** matrix (Set II) of Q_3' is also given in Table 2. The intensity factors obtained by Manner I and the relative intensities are also given in Table 6. The intensity factors in Set II are, to some extent, larger than those in Set I, and the relative intensities are nearer to the observed ones. Thus, it is found that the small difference in the force constants does not have as much effect on the overlap integral.

Anharmonicity should be considered in the calculation of the overlap integral.[11] In a vibrational wave function of Morse oscillator, it is characteristic that there is asymmetry on the origin. This results in the differences of (1) the probability on both sides of the origin, and then (2) the distance from the origin at the same probability. To estimate the effect of (2) from the wave function of the harmonic oscillator, we assume this expression:

$$\alpha_v = 4\pi^2\nu_v/h \tag{23}$$

where ν_v is the difference between the observed frequencies of the $v+1$ and vth bands.

The normal coordinate vector of Q_3' is shown in Fig. 3 by the broad solid arrow. It is generally considered that the nucleus in this phase responds to a smaller potential than in the inverse-phase. Therefore, in our assumption, the ν_v of the narrow solid arrow of the carbon atom decreases with an increase in v, and that of the broken arrow increases. In the case of the increase we assumed a regular increase of 15 cm^{-1}. The results obtained using Manner I are given in Table 11. The intensity factors and the relative intensities are barely larger than those of Set I in Table 6. From Fig. 3, we can expect this to be a compensation for the increase and decrease in the overlap integrals of each coordinate. On the other hand, if the potential is the inverse of the above, results very similar to Set I in Table 6 are obtained; that is, complete compensations are found in this case. As a result, even if the precise wave function were used, a large change could not be expected in acetylene.

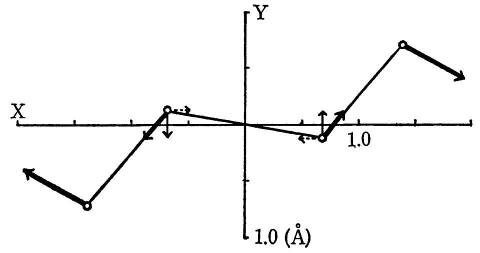

Fig. 3. The normal coordinate vector of Q_3' of the excited state of acetyleue. The vector for carbon atom is trebled.

Table 11. The intensity factors and the relative intensities involving the contribution of anharmonicity in acetylene

v	Intensity factors/10^{-5}	Relative intensities
0	0.00022	0.052
1	0.00424	1
2	0.0338	7.97
3	0.175	41.2
4	0.635	150
5	1.90	449

We wish to thank Dr. Y. Yasuda of the Faculty of Literature and Science of Toyama University for his valuable discussion of method.

References

1) C. K. Ingold and G. W. King, *J. Chem. Soc.*, **1953**, 2725.
2) D. P. Craig, *ibid.*, **1950**, 2146.
3) W. L. Smith and P. A. Warsop, *Trans. Faraday Soc.*, **64**, 1165 (1968).
4) F. Ansbacher, *Z. Naturforsch.*, **14a**, 889 (1959).
5) F. Duschinsky, *Acta Physicochim.*, **7**, 551 (1937).
6) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton (1945).
7) C. K. Ingold and G. W. King, *J. Chem. Soc.*, **1953**, 2745.
8) B. D. Saksena, *J. Chem. Phys.*, **20**, 95 (1952).
9) T. Shimanouchi, "Computer Program for Normal Coordinate Treatment of Polyatomic Molecule," Tokyo University Press (1968).
10) E. B. Wilson, J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York (1955).
11) T. Y. Chang and M. Karplus, *J. Chem. Phys.*, **52**, 783 (1970).