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Geometrical Structures of Excited States of Conjugated Molecules. II. The Calculated Vibronic Intensity Distributions in the Absorption Spectra of Naphthalene

Yuichi FUJIMURA, Masamune ONDA, and Takeshi NAKAJIMA

Department of Chemistry, Tohoku University, Sendai 980

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The normal coordinates and the vibrational frequencies in the first excited singlet ($^1B_{2u}$), the second excited singlet ($^1B_{1u}$), and the first excited triplet ($^3B_{1u}$) states of naphthalene, whose geometries were calculated by a semi-empirical method, are evaluated by assuming a simplified valence force field. The relation between the normal coordinates of two different electronic states is expressed on the basis of the Franck-Condon principle. The mixing among the excited-state normal coordinates, expressed in terms of the ground-state normal coordinates, is neglected in the present treatment. By using the simple relation between the normal coordinates of two different electronic states, the vibronic intensity distributions in the absorption spectra ($^1B_{2u}\leftarrow{}^1A_g$, ^1L_b, $^1B_{1u}\leftarrow{}^1A_g$, ^1L_a, and $^3B_{1u}\leftarrow{}^1A_g$, ^3L_a) have been calculated. The vibronic intensity distribution of the $^1B_{2u}\leftarrow{}^1A_g$ transition has been calculated, taking into consideration the intensity of the interpenetrating sets of the vibronic band groups on the basis of the Herzberg-Teller perturbation theory.

In the previous paper,[1] we proposed a computational method for determining the molecular symmetries and C–C bond distances in the electronically-excited states of conjugated molecules on the basis of the semiempirical SCF LCAO MO theory, and examined the geometrical structures of the lower excited states of benzene, naphthalene, azulene, and heptalene.

Many phenomena in the excited states of molecules, such as photochemical reactions or intramolecular nonradiative transitions, depend primarily on the geometrical structures of the excited states which are expressed by the multidimensional potential energy surfaces. For example, the large geometrical changes brought about by electronic excitation may lead to predissociation in small molecules,[2] or to photoisomerization[3–9] or to electrocyclic reactions,[10,11] in large

1) Y. Fujimura, H. Yamaguchi, and T. Nakajima, This Bulletin, **45**, 384 (1972).

2) G. Herzberg, "Molecular Spectra and Molecular Structure, Vol. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand Company Inc., Princeton, New Jersey (1966), p. 429.

3) G. N. Lewis, T. T. Magel, and D. Lipkin, *J. Amer. Chem. Soc.*, **62**, 2973 (1940).

4) D. Schulte-Frohlinde, H. Blume, and H. Güsten, *J. Phys. Chem.*, **66**, 2486 (1962).

5) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshow, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

6) W. M. Gelbart and S. A. Rice, *J. Chem. Phys.*, **50**, 4775 (1969).

7) E. E. van Tamlen and S. P. Pappas, *J. Amer. Chem. Soc.*, **85**, 3297 (1963).

8) A. W. Burgsthlen and P. L. Chien, *ibid.*, **86**, 2940 (1964).

9) D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, **1966**, 593.

10) R. B. Woodword and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

11) R. Hoffmann and R. B. Woodword, *ibid.*, **87**, 2046, 4388 (1965).

aromatic molecules, all of which may be interpreted by the strong coupling scheme. On the other hand, small geometrical changes in large aromatic molecules lead to nonradiative transitions, such as internal conversions or intersystem crossings, which may be interpreted by the weak coupling scheme.[12-18]

Another interesting manifestation of the geometrical changes on excitation is the appearance of the vibronic intensity distribution in the electronic absorption and emission spectra. As is well known from the Franck-Condon principle, the vibronic intensity distribution depends on the relative displacements of the potential energy surfaces of the two electronic states in the equilibrium positions. The geometrical structures of the excited state of interest can be estimated from the vibronic intensity measurement, provided the ground-state geometrical structure has been established. By analyzing the vibronic intensity distribution in the 2600 Å transition of benzene, Craig[19] has suggested that all the C–C bonds in the $^1B_{2u}$ state are longer by 0.037 Å than those in the ground state. Coon *et al.*[20] have also determined the excited-state molecular geometries of SO_2 and ClO_2 by using the same procedure. Similarly, Anno and Sadô[21] have applied the Franck-Condon principle to the analysis of the 4500 Å absorption system of *p*-benzoquinone. Hunt *et al.*[22] have given a conventional method for calculating the vibronic intensity distribution in aromatic hydrocarbons. Their calculation is based on the assumption that only one vibrational mode or set of degenerate modes contributes to the vibrational progressions. Miller and Murrell[23] have calculated the vibronic intensity distribution in the L_a bands of polyacenes, and have attempted to explain why a vibrational progression of about 1400 cm^{-1} appears in these bands. They have performed the normal coordinate analysis on the assumption that all the rings of polyacenes are hexagonal in the ground state and that the frequencies and the normal modes in the ground and the excited states are identical. Diner and Malrieu[24] have tried to reproduce the vibrational structures in the first UV band of linear polyenes, using the method proposed by Hunt *et al.*[22]

It is our purpose in this paper to examine theoretically the vibronic intensity distribution in the absorption spectrum ($^1B_{2u}\leftarrow{}^1A_g$, ^1L_b) of naphthalene, which is complicated by the occurrence of false origins, and the vibronic intensity distributions in the absorption spectra of the next singlet transition ($^1B_{1u}\leftarrow{}^1A_g$, ^1L_a) and of the lowest triplet transition ($^3B_{1u}\leftarrow{}^1A_g$, ^3L_a).

The following section will describe the relation between the normal coordinates of two different electronic states. In Section 3, a conventional method for determining molecular force fields will be described by using a simplified valence-force-field. The Badger relation[25] is used to obtain the C–C stretching force constant from the corresponding bond distance. The results of the normal coordinate analysis of the ground and excited states are also given in this section. In Section 4, the vibronic intensity distributions in the various absorption spectra of naphthalene are evaluated.

The Relation between the Normal Coordinates of Two Different Electronic States

Let us describe a method for the transformation of the normal coordinates of an electronic state, subjected to interaction with an electromagnetic field, into those of the resultant electronic state. First, let us consider a system in the absorption process. The progression-forming modes of large aromatic molecules are generally totally symmetric in so far as vibronic couplings such as the Jahn-Teller coupling or the pseudo-Jahn-Teller coupling may be neglected. It is recognized that molecular geometries in the lower electronic states of naphthalene belong to the D_{2h} symmetry. In the present calculations, the totally symmetric modes will be restricted to the C–C skeletal stretching modes. These modes are thought to have the strongest effects on the vibronic intensity distribution. Naphthalene has four skeletal stretching normal modes belonging to the A_g irreducible representation of the D_{2h} point group.

The internal symmetry coordinates for the totally-symmetric skeletal stretching modes of naphthalene in the ground state may be specified as follows:

$$S_1 = \frac{1}{2}\sum_{j=1}^{4}\Delta r_j, \qquad S_2 = \frac{1}{2}\sum_{j=5}^{8}\Delta r_j,$$
$$S_3 = \frac{1}{\sqrt{2}}\sum_{j=9}^{10}\Delta r_j, \text{ and } S_4 = \Delta r_{11} \tag{1}$$

where $\Delta r_j = r_j - r_j^0$, and where r_j^0 and r_j are the C–C bond distance at the vibrational equilibrium point and the corresponding instantaneous bond distance respectively. For the excited states also, the same relationships as above hold. (For the r_j^0 values, see Table 1.) By equating the instantaneous bond distances of the ground and excited electronic states, we obtain:

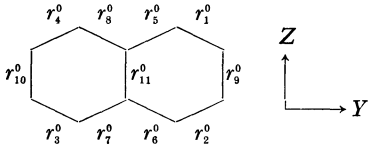
$$S' = S + D, \tag{2}$$

where the primed quantity refers to the excited states. The i-th component of the column matrix, D, is expressed in the form of $a_i\sum_j(r_j^0 - r_j^{0\prime})$, where a_i is a normalization constant for the i-th internal symmetry coordinate. The internal symmetry coordinates are

12) R. Willams and G. J. Goldsmith, *J. Chem. Phys.*, **39**, 2008 (1963).
13) G. B. Kistiakowsky and C. S. Parmenter, *ibid.*, **42**, 2942 (1965).
14) R. J. Watts and S. J. Strickler, *ibid.*, **44**, 2423 (1966).
15) E. M. Anderson and G. B. Kistiakowsky, *ibid.*, **48**, 4787 (1968).
16) J. Jortner and R. S. Berry, *ibid.*, **48**, 2757 (1968).
17) M. Bixon and J. Jortner, *ibid.*, **50**, 3284 (1969).
18) R. Englman and J. Jortner, *Mol. Phys.*, **18**, 145 (1970).
19) D. P. Craig, *J. Chem. Soc.*, **1950**, 2146.
20) J. B. Coon, R. E. DeWames, and C. M. Loyd, *J. Mol. Spectry.*, **8**, 285 (1962).
21) T. Anno and A. Sadô, *J. Chem. Phys.*, **32**, 1611 (1960).
22) G. R. Hunt, E. F. McCoy, and I. G. Ross, *Australian J. Chem.*, **18**, 591 (1962).
23) K. Miller and J. N. Murrell, *Theoret. Chim. Acta* (Berl.), **3**, 231 (1965).
24) S. Diner and J. P. Malrieu, *ibid.*, **7**, 15 (1967).
25) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934).

TABLE 1. C–C BOND DISTANCES (IN Å) IN NAPHTHALENE

Bonds	Electronic states			
	^1A_g [a]	$^1B_{2u}$ [b]	$^1B_{1u}$ [b]	$^3B_{1u}$ [c]
r_1^0	1.364	1.399	1.427	1.422
r_5^0	1.421	1.421	1.417	1.424
r_9^0	1.415	1.430	1.382	1.393
r_{11}^0	1.418	1.457	1.427	1.419



a) D. W. J. Cruickahank, and R. A. Sparks, *Proc. Roy. Soc., Ser. A*, **258**, 270 (1960).
b) Data taken from Ref. 1.
c) M. Onda, Thesis, Univ. of Tohoku, Sendai (1971).

connected with the normal coordinates, Q, by the transformation matrix, L_s:

$$S = L_s Q \tag{3}$$

and

$$S' = L_s' Q'. \tag{3'}$$

From Eqs. (2), (3), and (3'), the normal coordinates of the excited states are expressed in terms of those of the ground state in the form of:

$$Q' = C_a Q + \Delta Q, \tag{4}$$

$$C_a = (L_s')^{-1} L_s, \tag{5}$$

and

$$\Delta Q = (L_s')^{-1} D, \tag{6}$$

where the subscript, a, refers to the ground state. For the emission process, the following formula can be obtained:

$$Q = C_e Q' - \Delta Q', \tag{7}$$

with:

$$C_e = (L_s)^{-1} L_s', \tag{8}$$

and:

$$\Delta Q' = (L_s)^{-1} D, \tag{9}$$

where the subscript, e, refers to the emitting state.

We have thus obtained the formulas indicating the relation between the normal coordinates of two different electronic states. The off-diagonal matrix elements of the C_a and C_e matrices are related to the magnitudes of the mixing among the normal coordinates of the two relevant electronic states (the Duschinsky effect).[26] In the following section, we will show that the diagonal parts of the C_a matrix in Eq. (4) make the dominant contribution to the transformation of the normal coordinates of the electronic states, and that the Duschinsky effect can be neglected for the totally symmetric skeletal stretching modes in naphthalene. Consequently, Eq. (4) may be safely expressed as follows:

$$Q' = Q + \Delta Q. \tag{10}$$

Determination of the Molecular Force Fields

The molecular force field assumed is of a valence-force type consisting of the C–C stretching force constants, all the interaction constants being neglected. In order to obtain the C–C stretching force constants, k, the following relation is used:

$$k = A(r^0 - B)^{-3} \tag{11}$$

where k is given in millidynes per Å, A and B are the constants to be determined so as to reproduce the observed frequencies. The above relation between the equilibrium bond distances and the corresponding force constants has been proposed by Badger.[25] The relation is applicable not only for the force fields in the ground state, but also for those in excited states, with the proper choice of constants.

TABLE 2. CALCULATED FREQUENCIES AND THE TRANSFORMATION MATRIX IN THE GROUND STATE OF NAPHTHALENE

	Q_1	Q_2	Q_3	Q_4
Calcd (cm^{-1})	784	1032	1400	1545
Obsd[a]	762	1025	1380	1579
S_1	0.09333	0.16182	−0.21210	0.29459
S_2	0.18579	−0.08149	−0.19265	−0.29731
S_3	0.06778	0.25882	0.24496	−0.18730
S_4	0.14779	−0.13561	0.27487	0.22557

a) D. E. Freeman and I. G. Ross, *Spectrochim. Acta*, **16**, 1393 (1960).

The best values of A and B obtained by the variational procedure for the molecular force fields in the ground state of naphthalene are 2.4 millidyne Å^2 and 0.64 Å respectively. The results of the normal coordinate analysis for the ground-state naphthalene obtained by using Eq. (11) are given in Table 2. The fairly good agreement between the calculated and the observed frequencies supports the validity of the molecular force fields determined by the above procedure.

TABLE 3. CALCULATED FREQUENCIES AND THE TRANSFORMATION MATRIX IN THE $^1B_{2u}$ STATE OF NAPHTHALENE

	Q_1	Q_2	Q_3	Q_4
Calcd (cm^{-1})	757	993	1342	1495
Obsd[a]	702	987	1390	1435
S_1	0.09417	0.17379	−0.20016	0.29586
S_2	0.16647	−0.05821	−0.20789	−0.30389
S_3	0.06433	0.24507	0.25863	−0.18863
S_4	0.17148	−0.15571	0.26017	0.21290

a) Ref. 27.

TABLE 4. CALCULATED FREQUENCIES AND TRANSFORMATION MATRIX IN THE $^1B_{1u}$ STATE OF NAPHTHALENE

	Q_1	Q_2	Q_3	Q_4
Calcd (cm^{-1})	770	1024	1401	1513
Obsd[a]	710	995	1390	1520
S_1	0.11901	0.22766	−0.18282	0.25933
S_2	0.17044	−0.07946	−0.19191	−0.30737
S_3	0.05489	0.18317	0.29812	−0.20305
S_4	0.15177	−0.16472	0.23914	0.24354

a) Ref. 35.

26) F. Duschinsky, *Acta Physiochim. U. R. S. S.*,**7**, 551 (1937).

Table 5. Calculated frequencies and the matrix elements of the L_s matrix in the $^3B_{1u}$ state of naphthalene

	Q_1	Q_2	Q_3	Q_4
Calcd (cm^{-1})	766	1020	1394	1510
Obsd[a]	712	1024	1343	1562
S_1	0.11267	0.21829	−0.21333	0.24661
S_2	0.17651	−0.08444	−0.16541	−0.31784
S_3	0.05628	0.19928	0.30275	−0.17924
S_4	0.14650	−0.15098	0.22883	0.26466

a) Ref. 38.

In order to obtain the molecular force fields in the excited states, Eq. (11) with the constants, A and B, determined for the ground-state molecular force fields will be used. The results of the normal coordinate analysis for the $^1B_{2u}$, $^1B_{1u}$, and $^3B_{1u}$ excited states are shown in Tables 3, 4, and 5 respectively.

The Vibronic Intensity Distributions in Electronic Spectra

According to the Franck-Condon principle, the vibronic intensity distribution accompanied by a pure electronic transition is obtained by evaluating the square of the overlap integral between the vibrational wave functions for the relevant electronic states. If the geometrical changes on excitation are relatively small, and if the magnitudes of the off-diagonal matrix elements in the C_a or C_e matrix may be neglected, the vibrational wave function for each electronic state can be expressed in terms of the product of the harmonic-oscillator wave functions. The vibronic intensity distribution of the r-th mode relative to the 0—0 intensity in the electronic spectra is given as follows:

$$I_{I-J}(Q_r) = \frac{S^2_{I-J}(Q_r)}{S^2_{0-0}(Q_r)} \tag{12}$$

where $S_{I-J}(Q_r)$ is the overlap integral between the I and J quantum harmonic oscillators belonging to the normal coordinate, Q_r. The total vibronic intensity distribution relative to the 0—0 intensity is given by the product of the relative vibronic intensity distributions over the possible normal modes.

Because of the small energy separation between the lowest ($^1B_{2u}$) and the second ($^1B_{1u}$) singly-excited states of naphthalene, these two electronic states are strongly subjected to vibronic perturbation from each other, and the shifts of the point of origin, which correspond to the frequencies of b_{3g} vibrations (438 and 911 cm^{-1}), are observed in the absorption spectrum ($^1B_{2u}\leftarrow{}^1A_g$).[27] (see Fig. 1) The vibronic intensity in the absorption spectrum, where the vibronic bands are subjected to vibronic perturbation by a nontotally symmetric mode, Q_p, can be expressed by using the Herzberg-Teller perturbation theory.[28] The perturbed vibronic intensity distribution of the totally symmetric mode, Q_r, relative to the 0—0 vibronic transition of the pure electronic transition is approximately given as follows:

$$I_{I-J}(Q_r) = C(Q_p)\frac{S^2_{I-J}(Q_r)}{S^2_{0-0}(Q_r)} \tag{13}$$

where $C(Q_p)$ is the square of the ratio of the transition moment induced by a unit displacement along the p-th nontotally symmetric normal coordinate to the zeroth-order transition moment. Equation (13) has been derived on the assumption that the two excited states are subjected to vibronic perturbation by the inducing mode, Q_p, the frequency of which is the same in both ground and excited states, and on the assumption that the electronic wavefunction corresponding to the lowest excited state is expanded about the nuclear configuration in the ground state at the vibrational equilibrium to the first order of Q_p in the perturbation theory. $C(Q_p)$ will be evaluated empirically in the present calculation. The analysis of the vibronic intensity distribution in the spectra ($^1B_{2u}\leftarrow{}^1A_g$) of naphthalene vapor shows that the vibronic-band intensity of the false origin at 0+438 cm^{-1} (vs)[29] is five or ten times stronger than that of the 0—0 group (m),[29] and that the intensity of the false origin at 0+911 cm^{-1} (ms)[29] is somewhat stronger than that of the 0—0 group.[28] From the above experimental facts, for the 438 and 911 cm^{-1} inducing modes of b_{3g} the values of $C(Q_p)$ were taken to be 6.0 and 2.0 respectively.

The overlap integrals, $S_{I-J}(Q_r)$, were evaluated by using the formula derived in the previous paper.[30]

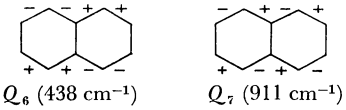


Fig. 1. b_{3g} modes inducing the vibronic perturbation between the $^1B_{2u}$ and $^1B_{1u}$ states. Quantities in parentheses indicate frequencies in the $^1B_{2u}$ state.

Discussion

The mixing among the excited-state normal coordinates expressed in terms of the ground-state ones was neglected in the calculation. This is sufficiently supported by the small off-diagonal matrix elements in the transformation matrixes C_a, *e.g.* for $^1B_{2u}\leftarrow{}^1A_g$ (see Table 6). Consequently, the Duschinsky effect can not be expected for the a_g skeletal stretching modes of naphthalene. On the other hand, for the nontotally

Table 6. The C_a matrix elements for the absorption spectrum ($^1B_{2u}\rightarrow{}^1A_g$) of naphthalene

	Q_1	Q_2	Q_3	Q_4
Q'_1	0.99684	−0.01834	0.03975	0.04397
Q'_2	0.02392	0.99659	−0.07259	−0.01761
Q'_3	−0.03969	0.07338	0.99700	0.01009
Q'_4	−0.04273	0.01701	−0.01240	0.99890

27) D. P. Craig, J. M. Hollas, M. F. Redies, and S. C. Wait, Jr., *Phil. Trans. Roy. Soc.*, **A253**, 543 (1961).

28) G. Herzberg and E. Teller, *Z. Physik. Chem.* (Leipzig), **B21**, 410 (1933).

29) The symbols in parentheses denote the qualitative measure of the band intensity in the absorption spectra observed by Craig *et al.*[27] The measures are as follows: vs–very strong, ms–medium strong, and m–medium.

30) N. Shimakura, Y. Fujimura, and T. Nakajima, This Bulletin, **45**, 695 (1972).

symmetric modes, which induce the vibronic coupling between the first and the second singlet electronic states, the Duschinsky effect must be operative.[31] The neglect of the mixing among the excited-state normal coordinates will be valid in the calculation of the vibronic intensity distribution of the large aromatic molecules, such as polyacenes, with small relative displacements in the points of origin of the normal coordinates. However, in calculating the vibronic intensity distribution of azulene, which retains the C_{2v} molecular symmetry in the first singlet excited state,[1,32] we cannot neglect the mixing among the normal coordinates in the a_g vibrational modes, because there are substantial geometrical changes, especially a shortening of the central bond in the first singlet excited state compared with that in the ground state. In fact, from the analysis of the 7000 Å absorption spectra of azulene vapor, Hunt and Ross[32] concluded that the upper-state vibrational frequencies are difficult to correlate with those of the ground state. The Duschinsky effect for the totally symmetric modes will also have to be explicitly taken into account in calculating the vibronic intensity in the absorption spectra ($S_1 \leftarrow S_0$) of heptalene, which is observed to suffer drastic changes in molecular symmetry on excitation; heptalene has C_{2h} and D_{2h} symmetries in the ground and the first excited states respectively.[1,33,34] The effect of the mixing among normal coordinates will be reflected in the appearance of the combination bands in the vibronic spectra.

The calculated vibronic intensity distributions in the absorption spectra will now be compared with the observed ones.

The analysis of the absorption spectrum ($^1B_{2u} \leftarrow {}^1A_g$) of naphthalene vapor indicates that the vibrational structures consist of three main interpenetrating sets of band groups which originate at the pure electronic origin and at false origins, 0+438 cm^{-1} and 0+911 cm^{-1}; it indicates further that the progression-forming modes are those with frequencies of 702, 987, and 1435 cm^{-1} with two quantum intervals, while for the 987 and 1435 cm^{-1} modes the one-quantum addition gives a band weaker than the fundamental.[27] On the other hand, for the 702 cm^{-1} mode, the one-quantum addition gives a band much weaker than the fundamental. The vibronic intensity distribution calculated for the absorption spectrum, $^1B_{2u} \leftarrow {}^1A_g$ is shown in Fig. 2. The progression-forming modes calculated are mainly those with frequencies of 757, 993, and 1495 cm^{-1}. For these modes, progressions with two-quantum intervals, in addition to the fundamentals, are thought to appear with significant intensities. It can be recognized that the vibronic intensity distribution calculated is in fairly good agreement with the observed one. However, a slight discrepancy remains between them: for the mode belonging to the lowest vibrational frequency in the calculation, the over-tone band intensity is somewhat stronger than the observed one. This indicates that the relative displacement along its mode on excitation has been slightly overestimated in calculating the geometrical structures in the $^1B_{2u}$ state.

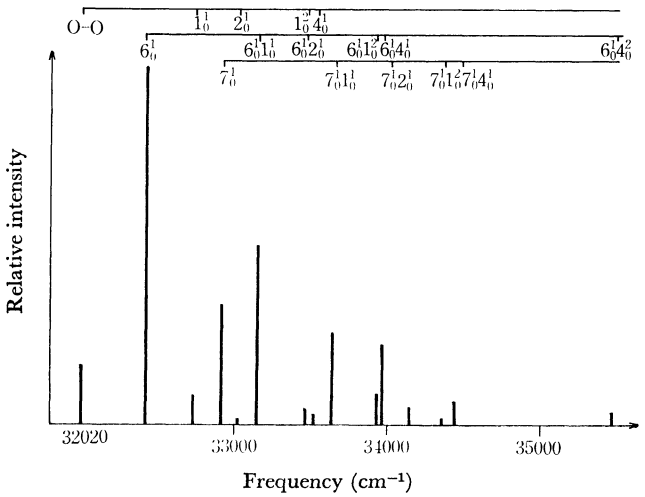


Fig. 2. Calculated vibronic intensity distribution in the absorption spectrum ($^1B_{2u} \leftarrow {}^1A_g$) of naphthalene. The numbers give the normal modes which are involved in the transition. Superscripts and subscripts give the number of vibrational quanta excited in the upper and lower states, respectively.

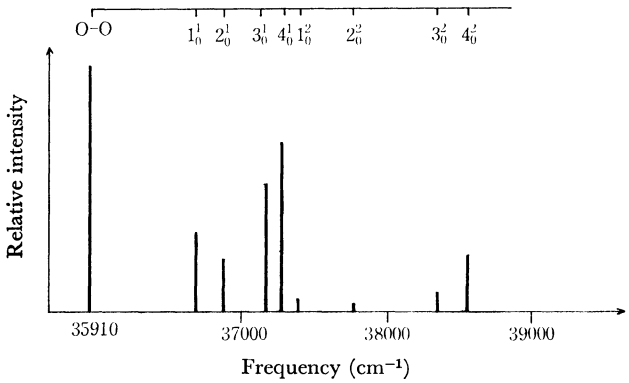


Fig. 3. Calculated vibronic intensity distribution in the absorption spectrum ($^1B_{1u} \leftarrow {}^1A_g$) of naphthalene.

The calculated vibronic intensity distribution in the absorption spectrum of the second singlet transition ($^1B_{1u} \leftarrow {}^1A_g$, ^1L_a) is shown in Fig. 3. The vibronic bands originating from the Herzberg-Teller vibronic coupling are neglected. The vapor absorption spectrum of naphthalene at 2900~2500 Å indicates that the 0—0 band is located at 35910 cm^{-1} and that the strong bands can be explained as resulting from two vibrations, with the 1390 and 485 cm^{-1} bands assigned to the totally symmetric skeletal stretching and bending vibrations respectively.[35] Miller and Murrell[23] have calculated the normal coordinate displacements between the second singlet, $^1B_{1u}$, and the ground states of naphthalene. There is a considerable difference in the vibronic intensity distribution of the absorption spectrum ($^1B_{1u} \leftarrow {}^1A_g$) between their results and ours. Their results indicate that the displacements with higher

31) G. J. Small, *J. Chem. Phys.*, **54**, 3300 (1971).
32) G. R. Hunt and I. G. Ross, *J. Mol. Spectry.*, **9**, 50 (1962).
33) H. J. Dauben, Jr. and D. J. Bertelli, *J. Amer. Chem. Soc.*, **83**, 4659 (1961).
34) T. Nakajima and A. Toyota, *Chem. Phys. Lett.*, **3**, 272 (1969).
35) H. Sponer and C. D. Cooper, *J. Chem. Phys.*, **23**, 646 (1955).

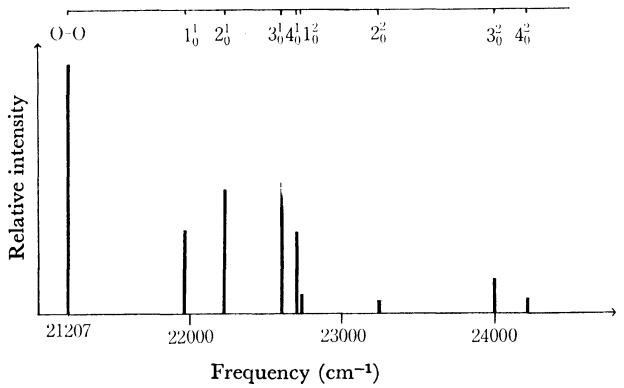


Fig. 4. Calculated vibronic intensity distribution in the absorption spectrum ($^3B_{1u}\leftarrow{}^1A_g$) of naphthalene.

frequencies are larger, and that the main intense bands of the spectrum correspond to the frequencies around 1500 and 1400 cm^{-1}. In our treatment, the changes of the C–C skelton on excitation are nearly equally distributed into the totally symmetric normal coordinates considered. These differences can be in part ascribed to the choice of the geometrical structures of the ground state of naphthalene.

Experimental studies of the $^3B_{1u}\leftarrow{}^1A_g$ absorption spectrum on naphthalene have been reported by many authors.[36–38] Castro and Robinson[38] have obtained the high-resolution $^3B_{1u}\leftarrow{}^1A_g$ absorption spectrum of crystalline naphthalene at 4.2 K. The absorption spectrum reported by them consists of the strong a_g modes (498 and 1343 cm^{-1}) primarily polarized normal to the molecular plane and, further, weak antisymmetric fundamentals that behave as false origins for the strong progression-forming modes. The most intense of the antisymmetric modes exhibits an intensity 15 times weaker than the 0—0 band. On the basis of the above experimental evidence, the vibronic spectrum of the lowest triplet transition is calculated, neglecting the bands originating from the false origins (Fig. 4). The calculated largest displacement of the C–C stretching normal coordinates between the lowest triplet and the ground states is that with the frequency of 1393 cm^{-1}. The band of the 1393 cm^{-1} mode with three-quantum intervals appears with a significant intensity. This is in agreement with the observed result. On the other hand, the other normal coordinate diplacements calculated indicate a more uniform distribution in the a_g normal coordinates of the C–C stretching modes than in the observed ones.

The lack of agreement between the calculated and observed $^3B_{1u}\leftarrow{}^1A_g$ spectra mainly originates from the neglect of the contribution of the in-plane C–C–C deformation on excitation.

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