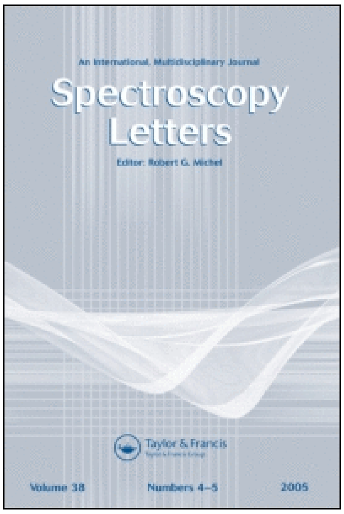

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VIBRONIC STRUCTURES OF THE GROUND AND EXCITED SINGLET ELECTRONIC STATES OF DIMETHYLNAPHTHALENES COOLED IN A SUPERSONIC JET

Key Words: Supersonic jet, naphthalenes, fluorescence, vibrations, model calculations.

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ABSTRACT

Fluorescence excitation and dispersed fluorescence spectra of jet-cooled naphthalene and 2,6-, 2,7-dimethylnaphthalenes have been measured. The frequencies of optical active vibrations in the ground and first excited singlet states have been determined. The new technique for calculation of planar vibration frequencies of polycyclic benzenoid hydrocarbons in the excited electronic states has been developed. The vibration frequencies in the ground and first excited singlet states of these molecules were calculated using the developed technique and the Ohno's model. The interpretation of vibronic spectral lines based on the comparison of the calculated and experimental data was made. The calculation rms errors for the vibration frequencies in the ground electronic states of the investigated molecules do not exceed 20 cm^{-1} and are approximately 1.5 times higher for excited states without additional adjustment of parameters for individual molecules.

INTRODUCTION

One of the main problems of complex molecules spectroscopy is a high accuracy determination of 0-0 transition frequencies and optical active vibration frequencies in the ground and excited electronic states. This is of essential importance for the structure investigation and the identification of organic compounds. The most reliable, undistorted by the environment, narrow-line spectra of these molecules are obtained in a supersonic jet. The frequency measurements in the jet may be accurate to better than 1 cm^{-1}. However, for decoding experimental narrow-line spectra of the new and little-studied compounds it is necessary to predict their spectra. There is a significant difference between the accuracy of calculation of complex aromatic molecules spectra (tens cm^{-1} for the vibrations and $\approx 10^3$ cm^{-1} for electronic transitions) and the accuracy of their registration. So it is necessary to develop new calculation techniques based on the reliable experimental data.

The aim of the study is to obtain the fluorescence excitation and dispersed fluorescence spectra of jet-cooled dimethylnaphthalenes, to determine the optical active vibration frequencies in the ground and first excited electronic states and to compare the experimental data with our theoretical predictions. The naphthalene-like molecules were chosen due to their high symmetry and rather simple structure to make calculations easier.

EXPERIMENTAL

The supersonic jet apparatus was described in detail in [1]. Molecular beam of cooled molecules was formed by the heated pulse valve with the nozzle diameter of 0.3 mm. 2 atm back pressure helium was employed as carrier gas. The initial vapor temperatures were 70°C, 80°C and 100°C for naphthalene, 2,6-dimethylnaphthalene (2,6-DMN) and 2,7-dimethylnaphthalene (2,7-DMN), respectively. Cooled molecules were excited by the second harmonic of tuned pulsed dye laser at 10 mm downstream from the orifice. The radiation frequency of the dye laser output was measured by means of laser wavelength meter with the accuracy of 0.5 cm^{-1}. Dispersed fluorescence spectra were measured using a scanned monochromator calibrated by iron spectrum. The accuracy of the frequency determination was about 1 cm^{-1} in the excited state and about 10 cm^{-1} in the ground state.

CALCULATION TECHNIQUE

The calculation of frequencies was made in approximation of valent forces. The harmonic force field for naphthalene and its methyl substituted fragments in the ground electronic state was obtained using MO/8 model [2]. To calculate the force fields in excited electronic states we developed a method, based on the Ohno's model with the same parametrization. In more detail this method will be described below. The harmonic force constants of ethane with anharmonic corrections, calculated in [3], were used for methyl groups.

Let us briefly consider the basic features of the Ohno's model [2]. The model is based on decomposition of potential function of a molecule on σ- and π-electronic parts:

$$V = E_\pi + E_\sigma \tag{1}$$

and using the Hückel method for π- electronic subsystem:

$$E_\pi = 2\sum_i P_i \beta_i \,, \tag{2}$$

where P_i and β_i are π- electronic orders and resonant integrals of the corresponding CC bonds. In such approximation and assumption of equality of the resonant integrals as well as their first and second derivatives on stretching coordinate of CC bond, three-parametrical expression is obtained for the CC stretching force constants:

$$F_{ij}(CC - CC) = f_1\delta_{ij} + f_2 P_i \delta_{ij} + f_3 \Pi_{ij} \,, \tag{3}$$

where f - parameters, and Π_{ij} - bond-bond polarizability:

$$\Pi_{ij} = (\partial P_i / \partial \beta_j) \,. \tag{4}$$

The model MO/8 contains 5 additional parameters describing E_σ. For our calculations we used the standard set MO/8ST. All 8 parameters of this set were obtained by Ohno by means of averaging of the individually optimized parameters for the five benzenoids. This set allows one to reproduce frequencies of planar vibrations for other benzenoids with the accuracy about 20 cm^{-1} without additional adjustment.

The simple Hückel method, used by Ohno, is suitable for calculation of the P_i and Π_{ij} in the ground electronic states. In this method molecular orbitals (MO) ϕ_k are linear combinations of atomic orbitals χ_a,

$$\phi_k = \sum_a C_{ka} \chi_a . \tag{5}$$

In this case, the bond order for the CC bond i connecting two carbon atoms a and b, is expressed in terms of the orbital coefficients C_{ka},

$$P_i = 2 \sum_k^{occ} C_{ka} C_{kb} , \tag{6}$$

where the summation for k should be taken for all double occupied MO. The bond-bond polarizability Π_{ij} is obtained from the following formula:

$$\Pi_{ij} = 2 \sum_k^{occ} \sum_l^{un} \frac{V_{kl}^{ab} V_{kl}^{cd}}{E_k - E_l} , \tag{7}$$

where the second summation for l should be taken for all unoccupied orbitals. The bond indices i and j refer to atomic pairs a-b and c-d, respectively. E_k is the orbital energy and V_{kl}^{ab} is symmetrized combination of the orbital coefficients:

$$V_{kl}^{ab} = C_{ka} C_{lb} + C_{kb} C_{la} , \tag{8}$$

Our method of calculation of vibration frequencies in excited electronic states consists in using expressions for P_i and Π_{ij} corresponding to electronic state under consideration. We use the same parameters as in MO/8ST.

Now let us introduce few definitions. The wave function describing the basic electronic state is represented as one Slater determinant (we designate it Φ). From this determinant the above mentioned simple expressions (6-8) were derived.

The wave functions describing excited electronic states are in general linear combinations of several determinants which are obtained from determinant Φ by replacement of spin-orbitals occupied in the ground electronic state with virtual spin-orbitals. We use only single excited configurations expressed in terms of determinants Φ_{o}^{u} which are obtained from Φ by replacement spin-orbital *o* with spin-orbital *u*. We specify spin-orbitals using numbers of ÌÎ, unbarred for spin α and barred for spin β. In these designations a single excited singlet configuration looks like

$$^{1}\Psi_{o\rightarrow u}=\frac{1}{\sqrt{2}}(\Phi_{o}^{u}+\Phi_{\bar{o}}^{\bar{u}}). \qquad (9)$$

We take into account that numbers of MO with higher orbital energy are greater than numbers of MO with lower orbital energy and let *o* be the number of the highest occupied MO in the ground electronic state, and *u* - the lowest virtual one (u=o+1). Using configurations with the maximum contribution to wave functions of the excited electronic states we can get the following expressions for the wave functions of two lowest excited electronic states of naphthalene:

$$\Psi_{S_1}=\frac{1}{\sqrt{2}}(\Psi_{o\rightarrow u+1}-\Psi_{o-1\rightarrow u}), \qquad (10)$$

$$\Psi_{S_2}=\Psi_{o\rightarrow u}. \qquad (11)$$

To obtain expressions similar to (6, 7) for these wave functions, we first write out expressions, which we have for the one-determinant wave function.

$$P_i(\Phi_{o}^{u})=\sum_{k}^{occ}C_{ka}C_{kb}+\sum_{\bar{k}}^{\overline{occ}}C_{\bar{k}a}C_{\bar{k}b}, \qquad (12)$$

here the summation for *k* should be taken for the occupied spin-orbitals with spin α in an excited electronic state, and for $\bar{k}$ - for the occupied spin-orbitals with spin β, $C_{\bar{k}a}=C_{ka}$. Similarly,

$$\Pi_{ij}(\Phi_{o}^{u})=\sum_{k}^{occ}\sum_{l}^{un}\frac{V_{kl}^{ab}V_{kl}^{cd}}{E_k-E_l}+\sum_{\bar{k}}^{\overline{occ}}\sum_{\bar{l}}^{\overline{un}}\frac{V_{\bar{k}\bar{l}}^{ab}V_{\bar{k}\bar{l}}^{cd}}{E_{\bar{k}}-E_{\bar{l}}}, \qquad (13)$$

here the summation for *l* should be taken for the unoccupied spin-orbitals with spin

α in an excited electronic state, and for $\bar{l}$ - for the unoccupied spin-orbitals with spin β, $V_{\bar{k}\bar{l}}^{ab} = V_{kl}^{ab}$, $E_{\bar{k}} = E_k$. Then for wave functions (10, 11) we obtain:

$$P_i(S_1) = \frac{1}{4}\left[P_i(\Phi_o^{u+1}) + P_i(\Phi_{\bar{o}}^{\overline{u+1}}) + P_i(\Phi_{o-1}^{u}) + P_i(\Phi_{\overline{o-1}}^{\bar{u}})\right], \tag{14}$$

$$P_i(S_2) = \frac{1}{2}\left[P_i(\Phi_o^{u}) + P_i(\Phi_{\bar{o}}^{\bar{u}})\right], \tag{15}$$

$$\Pi_{ij}(S_1) = \frac{1}{4}\left[\Pi_{ij}(\Phi_o^{u+1}) + \Pi_{ij}(\Phi_{\bar{o}}^{\overline{u+1}}) + \Pi_{ij}(\Phi_{o-1}^{u}) + \Pi_{ij}(\Phi_{\overline{o-1}}^{\bar{u}})\right], \tag{16}$$

$$\Pi_{ij}(S_2) = \frac{1}{2}\left[\Pi_{ij}(\Phi_o^{u}) + \Pi_{ij}(\Phi_{\bar{o}}^{\bar{u}})\right]. \tag{17}$$

The cross members in the formulas (14-17) are absent, because they are equal to zero for determinants, which differ by two or more spin-orbitals.

MOLECULAR MODELS

The following molecular models were chosen for calculation of planar vibrations of the investigated hydrocarbons.

The geometrical structure of naphthalene is assumed the same as in [2] for calculation of planar vibrations of polycyclic benzenoid hydrocarbons: CC distance = 1.397 Å and CH distance = 1.084 Å, and all the valence angles are equal to 120°. The symmetry group of the molecule is D_{2h}.

Molecular models of dimethylnaphthalenes are obtained by replacing of the appropriate hydrogen atoms in naphthalene molecule with methyl fragments of the ethane molecule. The geometry of the attached methyl groups is the same as in the work of Gribov et al. [4], namely: CC distance = 1.543 Å, CH distance = 1.093 Å, and all valence angles are tetrahedral.

In [5] it is pointed out that more stable conformer in 2-methylnaphthalene is the *e-s* conformer, in which one of CH bonds of the methyl group is in the plane of the naphthalene fragment and has a maximum projection on the short axis of the molecule. For this reason we have assumed the same orientation of the methyl fragments in dimethylnaphthalenes. In this case molecular models of 2,6- and 2,7-

dimethylnaphthalenes have C_{2h} and C_{2v} symmetry groups, respectively. The calculations were carried out also for other orientation of methyl fragments. The results will be discussed below.

The ground electronic state S_0 of naphthalene has A_g symmetry, state S_1 - B_{3u}, and state S_2 - B_{2u} symmetry. In a supersonic jet condition transitions take place mainly from vibrationally unexcited state, having A_g symmetry. These transitions are allowed only to A_g vibration states of S_1 (B_{3u}) electronic state. Transitions to B_{1g} vibration states are also allowed due to vibronic coupling with the S_2 (B_{2u}) state, and are more intense then those to A_g because the electronic transition $S_0 \rightarrow S_1$ is alternantly forbidden. As already pointed out, the geometrical configurations of 2,6- and 2,7-dimethylnaphthalenes have C_{2h} and C_{2v} symmetry, respectively. When the symmetry is reduced from D_{2h} to these groups the representations will be transformed as shown by arrows in Fig. 1.

We will assume, that the electronic states of 2,6- and 2,7-dimethylnaphthalenes are in the same sequence, as for naphthalene. Then for 2,6-DMN the sequence of the electronic states will be S_0 (A_g), S_1 (B_u) and S_2 (B_u), and for 2,7-DMN - S_0 (A_1), S_1 (B_1) and S_2 (A_1). Therefore transitions from a zero vibration state will be allowed for excitation of only totally symmetric vibrations for 2,6-DMN, and vibrations of A_1 and B_1 symmetry for 2,7-DMN. It should result in the sparsing of 2,6-DMN spectrum as compared to 2,7-DMN, where additional lines will be present; corresponding transitions are forbidden both for naphthalene and for 2,6-DMN. This theoretical prediction is in good agreement with the experimental spectra (see Figs. 2-4).

RESULTS AND DISCUSSION

Excitation and dispersed fluorescence spectra of jet-cooled naphthalene and dimethylnaphthalenes are shown in Figs. 2-4. The frequencies are measured from the 0-0 transitions, located at 32027, 31290 and 31536 cm^{-1} for naphthalene, 2,6-DMN and 2,7-DMN, respectively. As was expected, introduction of methyl substituents to naphthalene molecule and breaking the alternant symmetry lead to

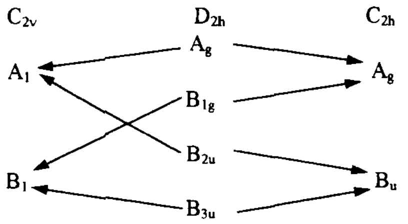

FIG. 1. Transformation of representations at symmetry reducing.

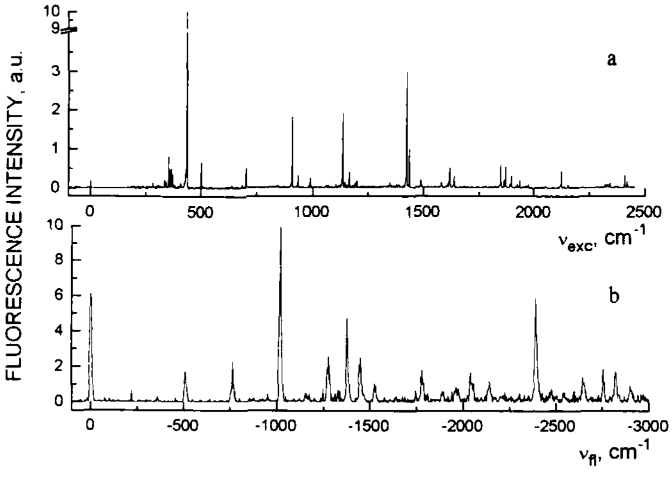

FIG. 2. Spectra of jet-cooled naphthalene: (a) fluorescence excitation, (b) dispersed fluorescence under excitation at the 0-0 +435 cm^{-1} transition.

higher 0-0 transition intensity in substituted naphthalenes. In addition all transitions in 2,6-DMN are more intense than in 2,7-DMN, it is clear seen in Figs. 3a and 4a: the excitation spectrum of 2,6-DMN has better signal to noise ratio.

We use the nomenclature for the designation of vibrational modes that is similar to those used by Stockburger [6] for naphthalene. Normal modes of certain symmetry are labelled beginning from "1" for the highest frequency vibrations. In contrast to totally symmetric vibrations the mode numbers of nontotally symmetric

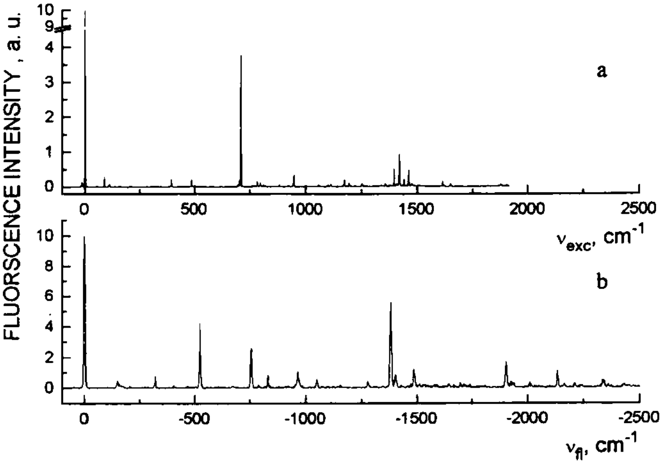

FIG. 3. Spectra of jet-cooled 2,6-dimethylnaphthalene: (a) fluorescence excitation, (b) dispersed fluorescence under excitation at the 0-0 transition.

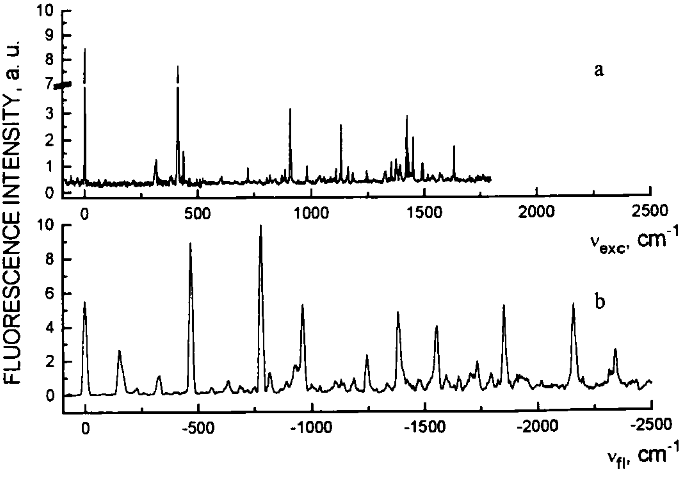

FIG. 4. Spectra of jet-cooled 2,7-dimethylnaphthalene: (a) fluorescence excitation, (b) dispersed fluorescence under excitation at the 0-0 transition.

vibrations, namely B_{1g} for naphthalene, B_u and B_1 for 2,6-DMN and 2,7-DMN respectively are barred.

Let us compare our experimental and calculated frequencies of fundamental vibrations of naphthalene with the literature values. The corresponding data are presented in Table 1. On the whole our measured fundamental mode frequencies differ very little from those found in the literature. The frequency of 1381 cm^{-1} of $\bar{4}^1$ mode is close to 1376 cm^{-1} determined in [7] by means of analysis of combination lines, because the spectral line corresponding to excitation of this mode was not observed due to its low intensity. The rms deviation of the calculated frequencies from experimental data is equal to 15 cm^{-1} for the ground electronic state and 36 cm^{-1} for the excited one. For example, the rms of frequencies obtained in recent work [8] by means of QCFF/PI technique equals to 32 cm^{-1} and 55 cm^{-1}, respectively. The remarkable difference between the experimental and calculated frequencies of $\bar{8}^1$ mode can be easily explained. It is necessary to take into account that the large intensity of the corresponding line indicates a strong vibrational interaction with S_2 state. Our calculations give for $\bar{8}^1$ mode in the S_2 state the value 414 cm^{-1} therefore such essential shift is possible. It was pointed out earlier in [9] that the large shift of $\bar{8}$ frequency in S_1 state with respect to S_0 may be caused by vibronic interaction with S_2 state. Our calculations give the additional confirmation of this assumption.

We offer our own version of assignment based on comparison of our data with those of other authors, their versions of assignment being taken into account too. Table 2 presents all lines of fluorescence excitation spectrum having intensities higher than 1 % with respect to the intensity of $\bar{8}^1_0$ transition. In addition to the assignment known from various literature sources we suggest a new assignment of combination lines 1863, 1890, 2322, and 2332 cm^{-1} (see Table 2). The lines shifted to the red 5, 9, 56, and 72 cm^{-1} from intense lines corresponding to nontotally symmetric vibrations are hot lines. We interpreted them following [11].

TABLE 1

Fundamental Vibration Frequencies of Naphthalene in Ground S_0 and Excited S_1 Electronic States

Mode number	S_0				S_1			
	calc	calc [8]	obs	obs [10]	calc	calc [8]	obs	obs [7]
3	1572	1590	1578	1578	1522	1552	1495	1495
4	1439	1467	1452	1460	1420	1446	1435	1432
5	1392	1336	1380	1380	1381	1397	1391	1388
6	1181	1156	1161	1163	1177	1153	1148	1143
7	1026	1005		1020	972	1015	988	984
8	754	802	766	757	711	763	703	700
9	493	516	505	505	491	515	501	501
$\bar{3}$	1626	1633		1624	1628	1631	1617	1617*
$\bar{4}$	1458	1481		1458	1419	1450	1381	1376
$\bar{5}$	1261	1296	1244	1240	1251	1281	1198	1196
$\bar{6}$	1129	1125		1158	1103	1106	1168	1166
$\bar{7}$	914	991	938	939	907	978	909	910
$\bar{8}$	515	548	511	508	515	541	435	435

* Ref. [11]

Let us consider now the dispersed fluorescence spectrum of naphthalene. The electronic S_1-S_0 transition of naphthalene is forbidden due to the alternant symmetry, therefore 0-0 transition has low intensity. We were not able to measure the dispersed fluorescence spectrum of the jet-cooled naphthalene with a good signal to noise ratio under excitation at the 0-0 transition, so the spectrum was measured under excitation to the $\bar{8}^1$ state at the frequency of 435 cm^{-1} above 0-0 transition. This spectrum is presented in Fig. 2b. Our version of assignment in combination with some data from [8] is shown in Table 3. It is interesting to note that in this case the main part of the excitable vibronic states in the ground

TABLE 2

Frequencies and Assignment of Lines in Fluorescence Excitation Spectrum of Naphthalene

Separation from 0_0^0 (cm^{-1})	Relat. Intens	Assignment	Literature data	Separation from 0_0^0 (cm^{-1})	Relat. Intens	Assignment	Literature data
0	4	0_0^0		936	3	$\overline{8}_0^1 9_0^1$	935[b]
281	1	$4(B_{1u})_0^1 4(A_u)_0^1$	284[a]	988	3	7_0^1	989[a]
336	1	$\overline{8}_0^1 4(B_{3g})_1^1$	337[a]	1105	1		
342	1	$\overline{8}_0^1 3(B_{3g})_1^1$	343[a]	1136	19	$\overline{8}_0^1 8_0^1$	1135[b]
355	8			1143	1		
363	5	$\overline{8}_1^2$	365[a]	1148	1	6_0^1	1150[c]
370	3	$\overline{8}_0^1 3(B_{2g})_1^1$	372[a]	1168	4	$\overline{6}_0^1$	1166[b]
379	1	$\overline{8}_0^1 4(A_u)_1^1$	381[a]	1192	1		
408	1			1198	2	$\overline{5}_0^1$	1196[b]
426	2	$\overline{8}_0^1 4(B_{1u})_1^1$		1351	2	$\overline{8}_1^2 7_0^1$	
430	5	$\overline{8}_0^1 8(B_{2u})_1^1$	431[a]	1381	1	$\overline{4}_0^1$	
435	100	$\overline{8}_0^1$	435[b]	1391	1	5_0^1	1389[c]
501	7	9_0^1	501[b]	1414	1	$\overline{8}_0^1 7_0^1 4(B_{1u})_1^1$	
637	1	$3(B_{2g})_0^2$	639[a]	1418	2	$\overline{8}_0^1 7_0^1 8(B_{2u})_1^1$	
685	1	$\overline{8}_0^1 4(A_u)_0^2$	686[a]	1423	30	$\overline{8}_0^1 7_0^1$	1422[b]
703	6	8_0^1	700[b]	1435	10	4_0^1	1432[b]
845	1	$\overline{7}_0^1 3(B_{2g})_1^1$		1488	2	$9_0^1 7_0^1$	1485[b]
872	1	$\overline{8}_0^2$	874[a]	1495	1	3_0^1	1495[b]
909	19	$\overline{7}_0^1$	910[b]	1583	2	$\overline{8}_0^1 6_0^1$	1579[b]

TABLE 2 (cont.)

Separation from 0_0^0 (cm^{-1})	Relat. Intens	Assignment	Literature data	Separation from 0_0^0 (cm^{-1})	Relat. Intens	Assignment	Literature data
1617	5	$\bar{3}_0^1$	1617^c	1976	1	7_0^2	1977^d
1637	3	$\bar{8}_0^1 8_0^1 9_0^1$	1634^b	2125	5	$\bar{8}_0^1 8_0^1 7_0^1$	2122^b
1847	7	$8_0^1 6_0^1$	1851^c	2155	1	$\bar{6}_0^1 7_0^1$	2153^b
1863	2	$\bar{6}_0^1 8_0^1$		2322	1	$\bar{3}_0^1 8_0^1$	
1870	6	$\bar{8}_0^1 4_0^1$	1868^b	2332	1	$\bar{8}_0^1 \bar{7}_0^1 7_0^1$	
1890	1	$9_0^1 5_0^1$		2343	1	$\bar{7}_0^1 4_0^1$	2342^b
1896	3	$\bar{7}_0^1 7_0^1$	1894^b	2410	3	$\bar{8}_0^1 7_0^2$	2410^b
1924	1	$\bar{8}_0^1 9_0^1 7_0^1$	1921^b	2421	2	$7_0^1 4_0^1$	2421^b
1936	2	$9_0^1 4_0^1$	1933^b				

a, b, c and d designate references [11,7,12,13] where corresponding lines were observed and assignment coincides with our own one.

electronic state have total symmetry, the exception is $\bar{5}_1$, $\bar{8}_1$ modes and those in which the last mode is excited together with totally symmetric modes: $\bar{8}_1 8_1$, $\bar{8}_1 5_1$, $\bar{8}_1 4_1$, $\bar{8}_1 8_1 5_1$.

The data presented show that the technique developed allows one to calculate the vibration frequencies in excited electronic states of naphthalene with the sufficient accuracy for interpretation of naphthalene spectra. Further extension of our method allows us to calculate frequencies of planar vibrations of methylnaphthalenes. Such calculations were used for interpretation of fluorescence excitation and dispersed fluorescence spectra of 2,6- and 2,7-dimethylnaphthalenes.

Experimental and calculated values of vibration frequencies of 2,6-DMN are presented in Table 4. It is worth noting that the spectra are well interpreted with assumption of excitation of totally symmetric normal vibrations only. The rms

TABLE 3

Line Positions in Fluorescence Spectrum under Excitation to $\overline{8}^1$

Separation from 0^0_0 (cm^{-1})	Relat, Intens	Assignment	Predicted values[a]	Separation from 0^0_0 (cm^{-1})	Relat, Intens	Assignment	Predicted values[a]
0	62	$\overline{8}^1_0$		-1745	7	$\overline{8}^1_1\overline{5}^0_1$	-1755
-511	17	$\overline{8}^1_1$	*	-1780	18	$\overline{8}^1_2 8^0_1$	*
-766	24	$\overline{8}^1_0 8^0_1$	*	-1890	6	$\overline{8}^1_1 5^0_1$	-1891
-1020	100	$\overline{8}^1_2$	*	-1963	9	$\overline{8}^1_1 4^0_1$	*
-1161	6	$\overline{8}^1_0 6^0_1$		-2044	17	$\overline{8}^1_1 8^0_2$	*
-1244	8	$\overline{8}^1_0\overline{5}^0_1$		-2142	12	$\overline{8}^1_0 8^0_1 5^0_1$	-2146
-1275	26	$\overline{8}^1_1 8^0_1$	*	-2398	60	$\overline{8}^1_2 5^0_1$	*
-1330	7			-2476	8	$\overline{8}^1_2 4^0_1$	-2474
-1380	48	$\overline{8}^1_0 5^0_1$	*	-2651	14	$\overline{8}^1_1 8^0_1 5^0_1$	-2657
-1449	25	$\overline{8}^1_1\overline{7}^0_1$	*	-2757	19	$\overline{8}^1_0 5^0_2$	-2760
-1526	10	$\overline{8}^1_2 9^0_1$	-1527	-2824	18	$\overline{8}^1_0 5^0_1 4^0_1$	-2832
-1578	3	$\overline{8}^1_0 3^0_1$		-2903	10	$\overline{8}^1_0 4^0_2$	-2904

[a] Predicted band positions were computed using mode frequencies obtained in our experiment and listed in Table 1.
*assignment taken from [8].

deviation of the calculated frequencies of fundamental modes from experimental values equals 23 cm^{-1} for the ground electronic state and 16 cm^{-1} for excited one.

Table 5 is the supplement to Table 4 and summarizes some intense combination transitions including 12^0_1.

The 2,7-DMN spectra are more complex. For their interpretation it is necessary to include nontotally symmetric (B_1) vibrations and to analyze fluorescence excitation and dispersed fluorescence spectra together. Our

TABLE 4

Vibrational Frequencies of 2,6-dimethylnaphthalene in Ground and Excited Electronic States

S_0				S_1			
observed	relat. intens.	calculated	assignment	observed	relat. intens.	calculated	assignment
0	100		0^0_0	0	100		0^0_0
148	5			89	3		
156	3						
319	8	264	22^0_1			263	22^1_0
		384	21^0_1	394	2	382	21^1_0
524	42	508	20^0_1	485	2	508	20^1_0
				703	1		
755	26	736	19^0_1	707	26	710	19^1_0
830	8	794	18^0_1	782	1	769	18^1_0
				796	1		21^2_0
963	11	963	17^0_1	946	2	933	17^1_0
		986	16^0_1			981	16^1_0
1050	6		20^0_2				
		1143	15^0_1			1113	15^1_0
		1196	14^0_1	1171	2	1192	14^1_0
				1193	1		$20^1_0 19^1_0$
1277	4	1274	13^0_1	1252	1	1274	13^1_0
1381	56	1385	12^0_1	1357	1	1344	12^1_0
		1386	11^0_1			1385	11^1_0
1403	8	1400	10^0_1	1398	5	1394	10^1_0
1485	12	1473	9^0_1	1442	2	1457	9^1_0
		1504	8^0_1	1460	5	1476	8^1_0
1510	2		19^0_2	1422	10		19^2_0
		1576	7^0_1			1534	7^1_0
1643	3	1643	6^0_1	1616	2	1641	6^1_0

TABLE 5

Vibrational Frequencies of 2,6-dimethylnaphthalene in Ground Electronic States

observed	relat. intens.	predicted	assignment	observed	relat. intens.	predicted	assignment
1695	4	1700	$22^{0}_{1}12^{0}_{1}$	2210	3	2211	$18^{0}_{1}12^{0}_{1}$
1715	2			2242	2		
1903	17	1905	$20^{0}_{1}12^{0}_{1}$	2339	5	2344	$17^{0}_{1}12^{0}_{1}$
1929	4			2360	2		
2010	4			2428	2		
2131	11	2136	$19^{0}_{1}12^{0}_{1}$	2445	1		
2162	3			2657	2	2658	$13^{0}_{1}12^{0}_{1}$

assignment version is presented in Table 6. The rms deviation of the calculated frequencies of fundamental modes from experimental values is equal to 20 cm $^{-1}$ for the ground electronic state and 24 cm $^{-1}$ for the excited one. Because of vibronic interaction with S_2 state the spectral lines corresponding to excitation of nontotally symmetric vibrations are more intense in general.

Table 7 is the supplement to Table 6 and summarizes some combination frequencies in the ground electronic state.

The results of interpretation of 2,6-DMN and 2,7-DMN spectra show that our calculation technique is quite suitable for the analysis of spectra of methyl substituted benzenoids. As was believed the 2,6-DMN spectra contain appreciably less lines than those of 2,7-DMN. For these molecules the difference in optical activity of vibrations is explained by their different symmetry.

With the opposite orientation of methyl fragments when the CH bonds have the maximal projection on the long molecular axis these molecules have the same type of symmetry. We made calculations of vibration frequencies for such structural configurations too. The frequencies obtained completely coincide with the previous values. This is explained by the fact that our force constants matrix does not depend on the methyl fragments orientation. On the other hand the

TABLE 6

Vibrational Frequencies of 2,7-dimethylnaphthalene in Ground and Excited Electronic States

S_0				S_1			
observed	relat. intens.	calculated	assignment	observed	relat. intens.	calculated	assignment
0	55		0^0_0	0	100		0^0_0
153	27						
227	4	189	22^0_1			188	22^1_0
322	11						
329	12	272	$\overline{21}^0_1$	315	17	271	$\overline{21}^1_0$
		396	21^0_1	380	9	394	21^1_0
467	90	444	$\overline{20}^0_1$	411	90	441	$\overline{20}^1_0$
		448	20^0_1	436	18	444	20^1_0
559	4		$22^0_1+\overline{21}^0_1$				
634	8	628	$\overline{19}^0_1$	605	7	628	$\overline{19}^1_0$
		635	19^0_1			629	19^1_0
683	6						
693	4		$22^0_1+\overline{20}^0_1$				
747	5	758	18^0_1			717	18^1_0
778	100	743	$\overline{18}^0_1$	721	10	709	$\overline{18}^1_0$
816	13						
891	8		$22^0_1+\overline{21}^0_2$				
929	18		$\overline{20}^0_2$	819	6		$\overline{20}^2_0$
				872	7		20^2_0
		943	17^0_1	887	9	891	17^1_0
960	53	953	$\overline{17}^0_1$	909	37	898	$\overline{17}^1_0$
998	6	981	$\overline{16}^0_1$	980	10	973	$\overline{16}^1_0$
1035	5		$22^0_1+\overline{18}^0_1$				
		1001	16^0_1			972	16^1_0

(continued)

TABLE 6 (cont.)

S_0				S_1			
observed	relat. intens.	calculated	assignment	observed	relat. intens.	calculated	assignment
1103	8		$\overline{21}{}_1^0+\overline{18}{}_1^0$	1039	6		$\overline{21}{}_0^1+\overline{18}{}_0^1$
		1135	15_1^0			1072	15_0^1
1130	9	1135	$\overline{15}{}_1^0$	1110	10	1106	$\overline{15}{}_0^1$
1141	7	1158	$\overline{14}{}_1^0$	1163	10	1142	$\overline{14}{}_0^1$
1187	10	1188	14_1^0	1132	26	1126	14_0^1
1242	23	1221	$\overline{13}{}_1^0$	1184	7	1213	$\overline{13}{}_0^1$
		1268	13_1^0			1237	13_0^1
1284	4	1272	$\overline{12}{}_1^0$	1244	8	1279	$\overline{12}{}_0^1$
1332	7	1322	12_1^0	1324	8	1310	12_0^1
		1360	$\overline{11}{}_1^0$	1328	8	1314	$\overline{11}{}_0^1$
1383	49	1385	$\overline{10}{}_1^0$	1393	11	1385	$\overline{10}{}_0^1$
		1385	11_1^0	1353	12	1351	11_0^1
		1393	10_1^0	1374	13	1385	10_0^1
1421	9	1421	$\overline{9}{}_1^0$	1431	16	1434	$\overline{9}{}_0^1$
1472	9	1458	9_1^0	1423	30	1391	9_0^1
1480	8	1479	$\overline{8}{}_1^0$	1452	21	1450	$\overline{8}{}_0^1$
		1476	8_1^0			1457	8_0^1
1514	7	1538	$\overline{7}{}_1^0$	1492	11	1482	$\overline{7}{}_0^1$
				1537	6		$\overline{20}{}_0^1 14_0^1$
1551	40		$\overline{18}{}_2^0$				
1594	11	1575	7_1^0	1514	7	1474	7_0^1
1629	5	1636	6_1^0	1569	8	1534	6_0^1
1649	11	1643	$\overline{6}{}_1^0$	1632	19	1639	$\overline{6}{}_0^1$

TABLE 7

Vibrational Frequencies of 2,7-dimethylnaphthalene in Ground Electronic State

observed	relat. intens.	predicted	assignment	observed	relat. intens.	predicted	assignment
1656	8			2016	7	2023	$\overline{20}^0_1+\overline{18}^0_2$
1690	8			2070	5		
1704	12	1709	$\overline{20}^0_1+\overline{13}^0_1$	2105	5		
1716	12			2158	53	2161	$\overline{18}^0_1+\overline{10}^0_1$
1734	19	1738	$\overline{18}^0_1+\overline{17}^0_1$	2198	9	2202	$\overline{17}^0_1+\overline{13}^0_1$
1777	7			2232	4		
1794	12			2257	5		
1823	8	1821	$22^0_1+7^0_1$	2316	13	2317	$\overline{20}^0_2+\overline{10}^0_1$
1851	52	1850	$\overline{20}^0_1+\overline{10}^0_1$	2326	13	2334	$\overline{18}^0_3$
1875	8	1876	$22^0_1+\overline{6}^0_1$	2343	26	2343	$\overline{17}^0_1+\overline{10}^0_1$
1906	11			2414	7		
1918	11	1920	$\overline{17}^0_2$	2432	7		
1928	10			2487	7	2484	$\overline{13}^0_2$
1958	8			2511	8		

methyl fragments have high symmetry hence there is no kinematic distortion of vibration frequencies. Other orientations of the methyl groups were not examined because the minimum of potential energy is reached only if one of the CH bonds of the methyl fragment lies in the plane of the molecule [5] whereas additional configurations satisfying this condition have lower symmetry. With lower symmetry the spectrum would contain more spectral lines and cannot be interpreted in the framework of our model.

It is to be noted that the high intensity of 2,6-DMN spectra with respect to those of 2,7-DMN is also related to the molecular symmetry. In our opinion this fact can be explained by a more effective vibronic interaction of S_1 and S_2

electronic states in 2,6-DMN with respect to 2,7-DMN, because these states have identical symmetry in 2,6-DMN and different in 2,7-DMN.

CONCLUSION

The technique developed by us for calculation of planar vibrations in excited electronic states of benzenoid hydrocarbons provides the accuracy of about 20-30 cm^{-1}. The accuracy is sufficient in most cases for interpretation of fine-structured vibration spectra of jet-cooled aromatic molecules. A large discrepancy between the calculated and experimental values in some cases is explained by intense vibronic interaction with the high lying electronic state, which is not taken into account in the model. The extension of this technique by means of the fragment method allows one to simulate the planar vibrations of benzenoid hydrocarbons with substituents. The calculations and theoretical analysis gave the possibility to explain the peculiarities of spectra of naphthalene and 2,6- and 2,7-dimethylnaphthalenes, in particular the sparsing of 2,6-DMN spectra.

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