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Phonon Structures of Optical Absorption Bands of Radicals Produced by Irradiation in Naphthalene Single Crystals

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The electronic spectra of impurities in molecular crystals are usually characterized by the presence of phonon sidebands.[1-5] For a forbidden transition, the coupling with phonons may enhance the transition probability and cause phonon sidebands, which may become more intense with increasing temperature.[6] For an allowed transition, sideband structures are the manifestation of the coupling between electrons and local phonons.[3] If the lattice distortion around the impurity is small, the sidebands display the density of lattice phonon states. In this case the relative intensity of the sidebands to the zero-phonon line is a measure of the strength of the electronic coupling of the impurity to the surrounding molecules. If the lattice distortion is large, coupling to the local phonon modes would affect the sideband structures. Studies of electron-phonon coupling have provided important information on the impurity state in the crystal.

Recent studies on irradiation effects in naphthalene[7] have identified radicals which show sharp optical absorption bands. Among them the hydronaphthyl radical ($\dot{H}_2\text{-}C_{10}H_7$, abbreviated as HNR, hereafter) is of particular interest, since it has been studied in detail with EPR technique and is one of the primary products of irradiation at low temperatures. The radical has a 0-0 vibronic transition at 539 nm.[8] Another radical which has a 0-0 vibronic transition at 712 nm is produced after prolonged room-temperature annealing of the specimen irradiated at liquid nitrogen temperature. This radical is concluded to be a secondary product of radiation and suggested to be the hydrobinaphthyl radical ($\dot{H}_2\text{-}C_{10}H_7\text{-}C_{10}H_7$, abbreviated as HBNR, hereafter).

On the HNR, detailed Pariser-Parr-Pople calculation has been made by Hanazaki[9], and it is known that the 539 nm transition of isolated HNR is partially allowed with an oscillator strength of about 10^{-3}. The electronic states are described as a linear combination of $2p\pi$ carbon orbitals and a pseudo-π orbital formed by two $1s$ hydrogen orbitals which lie perpendicular to the molecular plane.[10] Since the electronic state of the HNR has become relatively clear, it is of interest to study the coupling between the radical and the surrounding molecules.

The purpose of the present paper is to describe the phonon sidebands of the 539 nm band of HNR and the 712 nm band of HBNR. The phonon sidebands of both transitions are compared with the state density of the lattice phonons obtained from the sideband structures of ${}^3B_{1u}\to{}^1A_g$ phosphorescence,[5] Raman spectra[11] and theoretical calculation.[12]

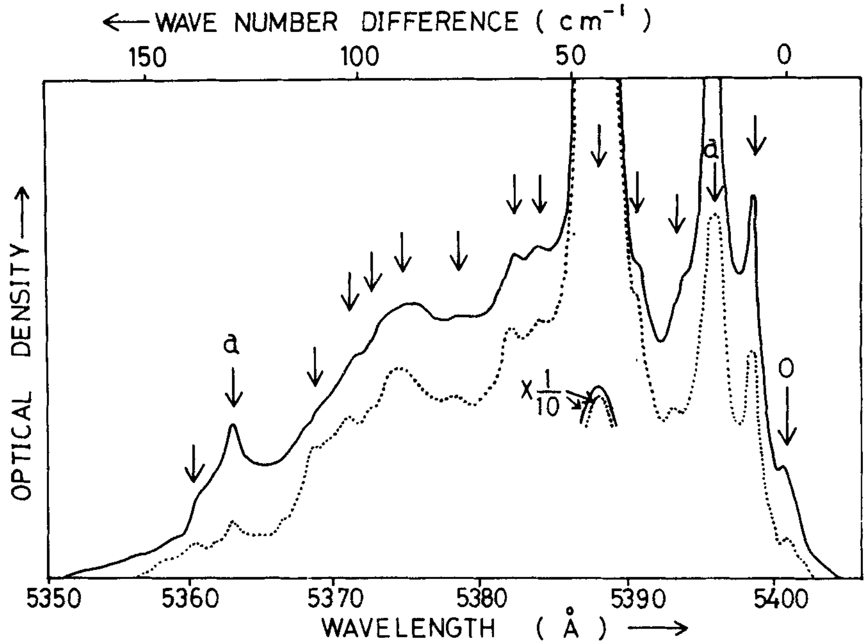

FIGURE 1 Phonon sidebands of the 539 nm absorption band of the hydronaphtyl radical created by irradiation at liquid nitrogen temperature, measured at about 10K using photographic spectrometry. The solid and dotted lines are spectra obtained with *a*- and *b*-polarized light, respectively, incident parallel to the *c*'-axis. The spectra with a scale of 1/10 was obtained with a specimen containing smaller concentration of hydronaphthyl radical. The line designated by 0 (18515 cm^{-1}) is assigned as the zero-phonon line and those designated by *a* are *a*-polarized.

Naphthalene single crystals were grown with the Bridgeman-method from scintillation grade naphthalene powder after zone-refining 100 times. The specimens were cooled to 77K in a cryostat and were irradiated with 2 MeV electrons from a Van de Graaff accelerator for 25 minutes or with 50 kV X-rays from an X-ray tube operated at 40 mA, for 40 hours. Absorption spectra of the specimen were taken in the cryostat with Shimadzu monochromater GE-100 (1 m; dispersion 16.6 Å/mm), with slit width of 30 μm and photographed on spectroscopic plates (Fuji) for visible region and on infrared film (Sakura) for infrared region. A 150 W xenon lamp was used as a light source. The optical density of the photographic film was measured with a microphotometer. The overall resolution of the optical system was 1.0 Å.

The optical absorption of specimens irradiated at liquid nitrogen temperature was measured at about 10K. The structures of the 539 nm absorption band for *a*- and *b*-polarized light are shown in Figure 1. A very strong line is observed at 18560 cm^{-1} (539 nm). This band has nearly the same intensity for *a*- and *b*-po-

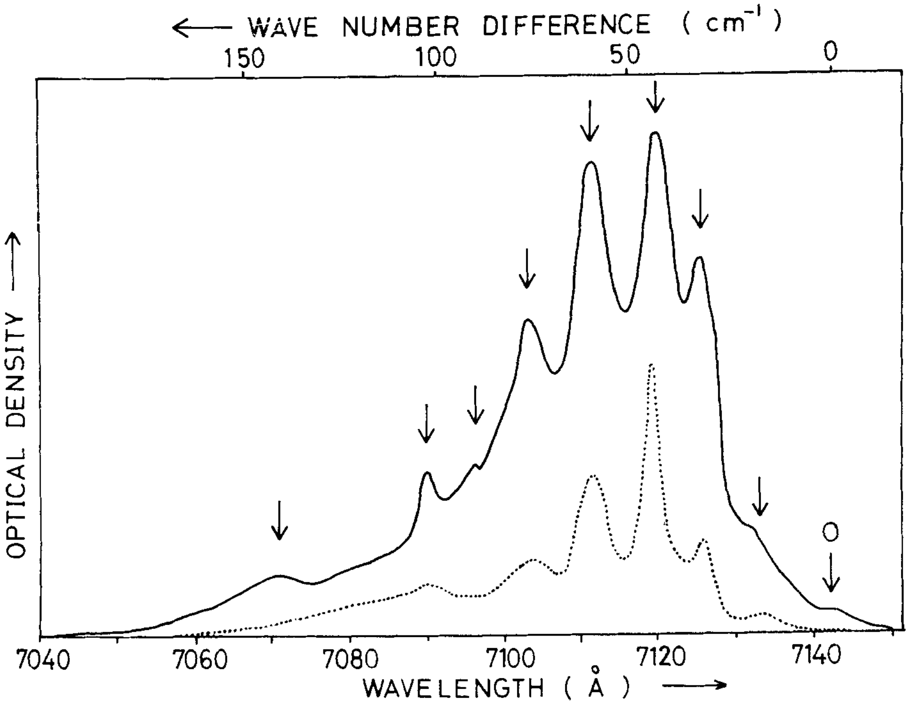

FIGURE 2 Phonon sidebands of the 712 nm absorption band created by irradiation at room temperature, measured at about 10K using photographic spectrometry. The solid and dotted lines are spectra obtained with *a*- and *b*-polarized light, respectively, incident parallel to the *c*'-axis. The line designated by 0 (14001 cm^{-1}) is assigned as the zero-phonon line.

larized light. Besides this line, 15 other less intense lines can be resolved. Two of these lines designated by *a* in Fig. 1 are strongly *a*-polarized and others are nearly isotropic. Similar optical absorption measurements of specimens irradiated at room temperature were made to obtain the structures of the 712 nm absorption band, the result being shown in Fig. 2. Nine lines, all of which are *a*-polarized, are resolved. The temperature dependence of the area under the absorption curves for both 539 nm and 712 nm bands was measured and it was shown that total intensities of both bands are independent of temperature between 10K and 300K within the accuracy of 5%.

In order to compare the structures of the radical absorption bands with phonon structures, the difference between the transition energy of each peak and that of the peak at the lowest energy, 18515 cm^{-1} (5400.9 Å) for HNR and at 14001 cm^{-1} (7142.3 Å) for HBNR, was obtained. Table I lists the results and also the phonon structures derived from $^3B_{1u}\rightarrow{}^1A_g$ phosphorescence spectrum[5] of $C_{10}D_8$ and Raman spectrum.[11] The peak positions of the phonon structures in $C_{10}D_8$ may slightly smaller than in $C_{10}H_8$. The difference may be small enough for low frequency phonons, but for 96 cm^{-1} and 128 cm^{-1} phonons this fact was taken into account in comparing with the peak positions in the sidebands of the radical transitions. Peak positions observed in the radical absorption bands generally agree with the phonon structures derived from other experiments. This result indicates that the zero-phonon transitions are at 18515 cm^{-1} for HNR and at 14001 cm^{-1} for HBNR and that the broad bands with structures at the high energy side of them are phonon sidebands.

The zero-phonon line of the 539 nm bands, is nearly isotropic† and much smaller than the sidebands, and it occupies less than 1% of the total intensity. The line coupled with the 45 cm^{-1} phonon mode is the strongest and nearly isotropic. Since the total intensity of the 539 nm band has no temperature dependence, it is concluded that the 45 cm^{-1} phonon peak, which occupies 60% of the total absorption, is nearly independent of temperature. It follows that the Franck-Condon factor[5] for the 45 cm^{-1} phonon peak is much larger than those for other phonon modes. It appears that the 45 cm^{-1} phonon mode, which has been assigned as an antisymmetric rotational mode around the vertical axis of the molecular plane,[11] modifies most strongly the energy of the excited state of HNR.[5]

There are ten lines with the same polarization as the zero-phonon line. The extent of contribution of each mode may depend on the value of the phonon Franck-Condon factors. The *a*-polarized lines at 17 cm^{-1} and 130 cm^{-1} are considered to arise from assisted transitions, the transitions made partially allowed due to the coupling with the phonon modes which produce the odd potential

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† Apparently the a-polarized absorption is stronger than b-polarized, but this difference is ascribed to the overlap of the tail of the 17 cm^{-1} line.

along the long axis. The lines at 17, 26, 94 and 130 cm^{-1}, which are not observed in phosphorescence spectra, may be caused by the transitions to the electronic states coupled with the localized phonons around HNR.

In the phonon structures of the 539 nm band, the absorption at 45 cm^{-1} is the strongest and is accompanied with a broad region with several singularities described above and with a broad hump around 90 cm^{-1}. This tendency is similar to the shape of the calculated phonon density-of-states in naphthalene single crystal,[12] and also to the sidebands of the $^3B_{1u} \rightarrow {}^1A_g$ transition.[5] Although the strong absorption lines at 17 and 26 cm^{-1} are ascribed to the local mode coupling, the fact that the phonon sidebands of the HNR transition represent the phonon structures above 40 cm^{-1} may indicate that the HNR molecule does not distort the crystal lattice so severely. This conclusion is consistent with the assignment[7] that the 539 nm band originates from the HNR.

Concerning to the 712 nm band, it is seen from Table I that the phonon structures of this band can be mostly ascribed to coupling with crystal phonons.

TABLE I

Naphthalene phonon peaks derived from the radical absorption, phosphorescence and Raman scattering[a] (cm^{-1}).

539 nm absorption band	712 nm absorption band	phosphorescence of $C_{10}H_8$ in $C_{10}D_8$ [b]	Raman
9 ± 1	11 ± 2 (a)	8 ± 1	
17 ± 1 (a)			
26 ± 2			
33 ± 2	30 ± 1 (a)	29 ± 3	
45 ± 1	42 ± 1 (a)	47 ± 1	
56 ± 2	59 ± 1 (a)	56 ± 1	56
65 ± 2		64 ± 2	69
	74 ± 1 (a)	70 ± 2	
77 ± 3		78 ± 1	81
87 ± 3	91 ± 2 (a)	89 ± 1	88
94 ± 3			
102 ± 2	102 ± 1 (a)	96 ± 2	
109 ± 2		111 ± 3	120
130 ± 1 (a)			
139 ± 2		128 ± 1	141
	145 ± 3 (a)		

[a] a in parentheses designates that the transition dipole is oriented to the *a* axis. Wave numbers not followed by parentheses show isotropic absorption lines.

[b] R. Kopelman, F.W. Ochs, P.N. Prasad, reference (5). The phonon frequencies in this column are in $C_{10}D_8$ and not in $C_{10}H_8$. To make comparison with the first and second columns, 96 cm^{-1} and 128 cm^{-1} phonons in $C_{10}D_8$ are assigned to correspond to the 102 cm^{-1} and 139 cm^{-1} phonons in $C_{10}H_8$, respectively.

[c] M. Suzuki, T. Yokoyama and M. Itoh, reference (11).

All eight absorption lines in the sidebands are *a*-polarized; having the same polarization as the zero-phonon line. It follows that the phonon assisted transition is not observed in this case and therefore intensities of the lines may represent the magnitude of the phonon Franck-Condon factor. The line at 145 cm^{-1} may originate from the localized mode around an HBNR.

Both the 539 nm and 712 nm bands have small zero-phonon lines, indicating that the electronic states of the radicals are strongly coupled to the lattice. The remarkable difference between the sidebands of the HNR and HBNR transitions is that the singularities at 64, 78, 111 and 128 cm^{-1}, which appear in the phosphorescence sidebands, are not observed for HBNR. Instead of that, the localized modes at 145 cm^{-1} are observed to couple with the HBNR transitions. Although the peak positions of the lines in the sidebands below 59 cm^{-1} agree with the phonon frequencies, each peak in this region is pronounced much more than the corresponding peak in the sidebands of the phosphorescence. Thus it is concluded that the sideband structures of the HBNR transition have more localized character than that of the HNR transition. It is to be noted that all phonon peaks observed in Raman spectra appear in the phonon structures of the 539 nm band but mostly absent in those of the 712 nm band. It appears that the optical phonon mode is particularly distorted by the presence of HBNR. This conclusion is consistent with the assignment[7] that the 712 nm band is caused by the HBNR.

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