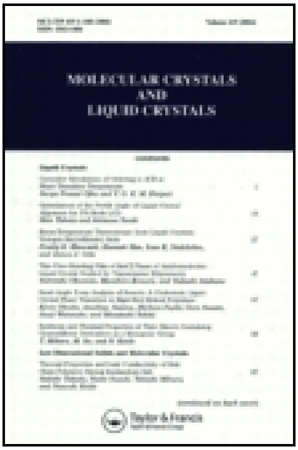

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Vibronic Transitions in Radicals in Irradiated Naphthalene Single Crystals

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Recently it has been made clear that cyclohexadienyl-type radicals are created by irradiation of simple aromatic hydrocarbons, such as benzene,(1) naphthalene(2) and anthracene.(3) Optical absorption band associated with the cyclohexadienyl and hydronaphthyl radicals (the latter is referred as HNR) have been identified and the vibronic structures associated with one of the transitions in the former have been analyzed.(1) The purpose of this note is to present the vibronic structures for the α-HNR and for the other radicals which have not been identified. It is suggested that one is associated with β-HNR and the other is the radical with a hydrogen added to binaphthyl (Fig. 1).

Specimens were obtained from a single crystal block grown by the Bridgeman method. The raw material had been purified by the conventional chemical method and passed through the molten zone 50 times. The specimen was irradiated with 2 MeV electrons generated from a Van de Graaff accelerator. The measuring techniques were described elsewhere.(2)

The naphthalene single crystal irradiated at liquid nitrogen temperature (LNT) has optical absorption bands at 2.307 and 1.962 eV, both of which have vibronic structures. When the specimen is annealed at room temperature, new bands at 1.747 eV accompanied with a vibronic structure appear. The vibronic structures are summarized in Tables 1, 2 and 3. Column 3 in each table shows the orientations of the absorption spectrum, determined by dichroic measurements. The assignment of the vibrational mode was made from the result of Raman spectra(4) by considering that the coupling with a_g

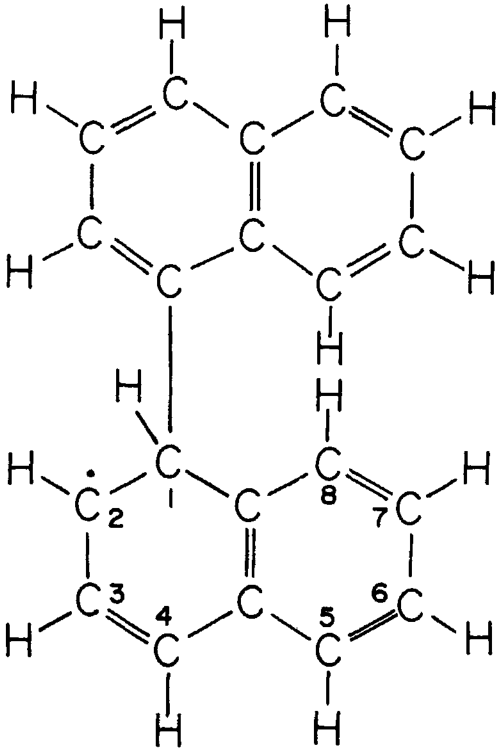

Figure 1. The radical with a hydrogen added to binaphthyl.

mode does not alter the dipole orientation. Since the agreement between the vibronic energy intervals and Raman energies is reasonable, it is concluded that all absorption bands arise from the molecular species whose main component is naphthalene. Since these species have transitions in the near infrared and all of them also have transitions with larger oscillator strength in the visible and ultraviolet region,(5) it is suggested that these species are radicals.

It has been shown already from a comparison of optical and EPR studies that the band at 2.307 eV is due to α-HNR.(2) The band at 1.962 eV is considered to be caused by β-HNR since it is produced by irradiation at LNT. The existence of β-HNR has been verified by an EPR study.(6) The 1.747 eV band grows with annealing at room temperature where the naphthyl radical disappears at a considerable rate. Thus, it is suggested that this band is created by the reaction

Table 1 Vibronic Structure Associated with 2.307 eV Band

Energy (eV)	Energy difference (eV)	Polarization	Assignment	Vibrational energy (eV)
2.307		isotropic		
2.366	0.059	*a*	$\nu_{10}(b_{1g})$	0.049
2.394	0.087	isotropic	$\nu_2(a_g)$	0.095
2.426	0.119	*a*	$\nu_{12}(b_{1g})$	0.118
2.441	0.134	*b*	$\nu_{19}(b_{3g})$	0.145
2.450	0.143	isotropic	$\nu_4(a_g)$	0.142
2.497	0.190	isotropic	$\nu_6(a_g)$	0.182
2.517	0.210	isotropic	$\nu_7(a_g)$	0.195

Table 2 Vibronic Structure Associated with 1.962 eV Band

Energy (eV)	Energy difference (eV)	Polarization	Assignment	Vibrational energy (eV)
1.962		*b*		
2.022	0.060	*b*	$\nu_1(a_g)$	0.063
2.050	0.088	*a*	$\nu_{11}(b_{1g})$	0.090
2.103	0.151	*a*	$\nu_1 + \nu_{11}$	0.153
2.134	0.182	*b*	$\nu_6(a_g)$	0.182
2.156	0.204	*b*	$\nu_7(a_g)$	0.195
2.164	0.212	*b*	$2\nu_1 + \nu_{11}$	0.216
2.222	0.270	*a*	—	
2.250	0.298	*a*	—	

Table 3 Vibronic Structure Associated with 1.747 eV Band

Energy (eV)	Energy difference (eV)	Polarization	Assignment	Vibrational energy (eV)
1.747		*a*		
1.811	0.064	*a*	$\nu_1(a_g)$	0.063
1.844	0.097	*a*	$\nu_2(a_g)$	0.095
1.871	0.124	*a*	$\nu_3(a_g)$	0.126
1.912	0.165	*a*	$\nu_5(a_g)$	0.171
1.936	0.189	*a*	$\nu_6(a_g)$	0.182
1.948	0.201	*a*	$\nu_7(a_g)$	0.195

of the naphthyl radical with the neighboring naphthalene molecule. The tentative model of the radical for this band is that with a hydrogen added to binaphthyl (Fig. 1). Details of this work including the other optical transitions will be published elsewhere.†

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† The present study was carried to higher radiation doses than the earlier one and new bands at 1.962 eV and 1.747 eV bands were found. It was shown that the 1.962 eV and the 3.25 eV band and the 1.747 eV and the 2.95 and 2.78 eV bands arise from the same species. Thus the suggestion by T. Okubo *et al.*(2) that the species for both the 3.25 eV band and for the 2.95 and 2.78 eV bands are binaphthyls appears incorrect.

REFERENCES

1. Shida, H. and Hanazaki, I., *Bull. Chem. Soc. Japan* **43,** 646 (1970).
2. Okubo, T., Itoh, N. and Suita, T., *J. Phys. Soc. Japan* **24,** 1179 (1968); *Mol. Cryst. and Liq. Cryst.* **6,** 227 (1969).
3. Harrah, L. A. and Hughes, R. C., *Mol. Cryst.* **5,** 141 (1968).
4. Hanson, D. M. and Gee, A. R., *J. Chem. Phys.* **51,** 5052 (1969).
5. Itoh, N., Chong, T. and Okubo, T., to be published in the Proceedings of the IVth International Congress of Radiation Research.
6. Itoh, N. and Okubo, T., to be published.