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$T_1 \leftarrow S_0$ EXCITATION SPECTRUM OF 1,4-DICHLORONAPHTHALENE

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A well-resolved $T_1 \leftarrow S_0$ excitation spectrum of 1,4-dichloronaphthalene has been obtained at 4.2 K. The frequency of one of the out-of-plane vibrations is found to be markedly reduced in the triplet state. This is discussed in terms of vibronic coupling in the triplet manifold.

1,4-Dichloronaphthalene (DCN) in the triplet state has been studied from the viewpoints of the dynamics of energy states in disordered systems,1) exciton trapping2) and the position dependent heavy atom effect.3) The $T_1 \leftarrow S_0$ absorption spectrum of DCN crystal at 2 K reported by Prasad's group1) was rather affected by noise and the vibronic structure was not clear. In this letter we report the well-resolved $T_1 \leftarrow S_0$ excitation spectrum of DCN and discuss the frequency reduction of an a_2 out-of-plane vibration in terms of vibronic coupling in the triplet manifold in connection to ODMR (optically detected magnetic resonance) results on DCN in biphenyl.

DCN was synthesized by the Sandmeyer reaction from 1-amino-4-chloronaphthalene (Aldrich Chemical Co.). After multiple recrystallization from ethanol and chromatographic isolation on a silica gel column, the compound was further purified by sublimation and zone-refining. DCN crystal was grown in a Bridgman furnace. The relative orientation of the crystal axes to the excitation and detection beams was not determined.

The $T_1 \leftarrow S_0$ excitation spectrum of DCN was obtained at 4.2 K by monitoring total emission from x-traps. An Ushio UXL 1000DO 1 kW Xenon lamp coupled with a

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Jobin-Yvon HR-1000 monochromator was used as an excitation light source. The slit width was set at 30 μm. The emission was detected by a photomultiplier tube (EMI-9789QB) after being passed through a band-path filter combination (Toshiba V-52 + Corning 4-96). The set-up for ODMR experiments was described elsewhere.4)

In order to investigate the radiative properties of the $T_1 \leftrightarrow S_0$ transitions in DCN, the sublevel kinetic constants were determined for the mixed crystal with biphenyl. The results are summarized in Fig. 1. The three total decay rate constants (k_z, k_y, and k_x) are similar to those found in a durene host.2) In accordance with the assignment of the orbital symmetry of B_2 (B_{1u} of naphthalene),2,5,6) the T_z sublevel is most radiative for the 0-0 transition at 20066 cm^{-1}. For the strongest vibronic band at 0-327 cm^{-1} in the phosphorescence spectrum, the radiative transition probability of T_z relative to that of T_x is about twice as large as the relative probability for the 0-0 transition (see the right columns in Fig. 1). This vibrational mode is attributed to one of the a_2 out-of-plane vibrations, most likely a C-Cl wagging mode, based on the radiative activity of the T_z sublevel and the analogy with the assignment for 1-chloronaphthalene.6)

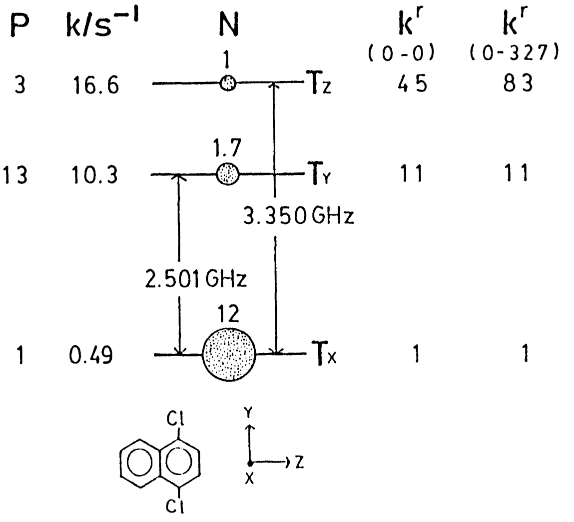

Fig. 1. The zero-field splitting and the kinetic rate constants of DCN in biphenyl. P:pumping rate, k:total decay rate, N:population, k^r:relative radiative decay rate.

The $T_1 \leftarrow S_0$ excitation spectrum of the DCN single crystal at 4.2 K is shown in Fig. 2. The $T \leftarrow S$ absorption origin is at 20243.0 cm^{-1}, which is different from the 0,0 position (20257 cm^{-1}) reported by Prasad's group. The reason for this discrepancy is not clear at present, but we have determined the position very carefully. According to x-ray diffraction measurements7) the molecular stacks in the DCN crystal are parallel to the crystal b axis. The very sharp origin band suggests one-dimensional character of excitons similarly to the case of 1,4-dibromonaphthalene.8)

The prominent feature of the excitation spectrum is the appearance of the long and nearly harmonic progression of the 263 cm^{-1} vibration built on the 0,0 band and the a_1 bands at 0 + 515, 0 + 1320 and 0 + 1569 cm^{-1}. The progression on the 0,0 band can be seen up to the seventh member and that on the a_1 bands up to the second or third member. The 0 + 263 cm^{-1} band is correlated to the 0 + 250 cm^{-1} (b_{2g}) band in the $T_1 \leftarrow S_0$ spectrum of DBN9) and corresponds to the a_2 vibrational band at 0-327 cm^{-1} in the $T_1 \leftarrow S_0$ spectrum in biphenyl. The a_2 out-of-plane vibration of DCN shows the remarkable reduction in the frequency in the lowest triplet state. The feature of the reduction is summarized in Table 1 in comparison with that of the skeletal vibration for DCN, 1-bromo-4-chloronaphthalene (BCN) and DBN. The frequency reduction of the a_2 vibration in the triplet state relative to the ground state amounts to 20 per cent, whereas the reduction of other vibrational frequencies is only $2 \sim 3$ per cent. This frequency change and the long progression up to the seventh member in the excitation spectrum suggest that the lowest triplet state couples strongly with $^3B_1(\pi,\sigma^*)$ states through the a_2 vibration and that the potential curve for the a_2 mode in the triplet state is greatly different from that in the ground state. This inference is consistent with the large value of k_z^r/k_y^r observed for the vibronic band in the phosphorescence spectrum.

Dzvonik et al.10) have proposed that the predissociation in 1-iodonaphthalene occurs on intersystem crossing from the $^1(\pi,\pi^*)$ state to the repulsive $^3(\pi,\sigma^*)$

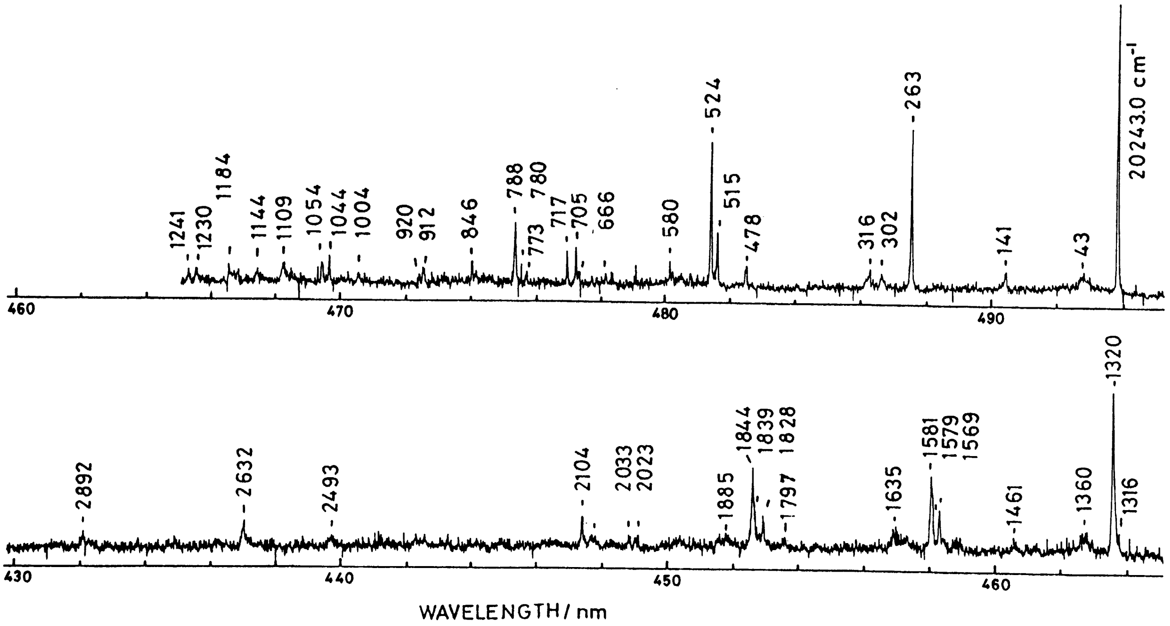

Fig. 2. The $T_1 \leftarrow S_0$ excitation spectrum of DCN single crystal at 4.2 K. The spectrum is not corrected for the intensity distribution of the exciting light source.

state. As shown by them, this $^3(\pi,\sigma^*)$ state of bromonaphthalene is not located below the lowest $^1(\pi,\pi^*)$ state, but it could not be far from the low lying singlet and triplet states. The σ^* molecular orbital is rather localized at halogen atom(s). The corresponding $^1(\pi,\sigma^*)$ states are observed at 59000, 50000 and 38500 cm^{-1} in CH_3Cl, CH_3Br and CH_3I, respectively, as their lowest excited singlet states.[11] A similar situation is expected in DCN, BCN and DBN. It is therefore quite probable that there occurs strong vibronic coupling between the lowest $^3(\pi,\pi^*)$ state and the $^3(\pi,\sigma^*)$ state. This coupling makes the potential surface of the $^3(\pi,\pi^*)$ state outspread along the vibrational coordinate concerned, resulting in the frequency reduction of this vibration in the $^3(\pi,\pi^*)$ state.

Table 1. Comparison of the vibrational frequencies in the ground state with those in the lowest triplet state.

Compound	C-X out-of-plane vibration			Skeletal vibration		
	S_0 ν''/cm^{-1}	T_1 ν'/cm^{-1}	Ratio ν'/ν''	S_0 ν''/cm^{-1}	T_1 ν'/cm^{-1}	Ratio ν'/ν''
1,4-dichloronaphthalene	332	263	0.79	1366	1320	0.97
1-bromo-4-chloronaphthalene[a)]	319	256	0.80	1367	1323	0.97
1,4-dibromonaphthalene[b)]	314	250	0.80	1350	1317	0.98

a) Unpublished results. b) From Ref. 9.

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