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Reassignment of the $n \rightarrow \pi^*$ Transitions of Phthalazine*

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We have measured the dipole-moment changes for excitation to different vibronic levels of the near ultraviolet, 4200 Å, absorption bands of phthalazine (2,3-diazanaphthalene). The value of $|\Delta\mu|$ is found to be 3.05 ± 0.10 D (for $E_c = 0.54 E_{eff}$) for all vibronic transitions including bands associated with the so-called second $n\pi^*$ state. Armed with this new information we have revised the previous analysis and show that the main bands belong to just one $n\pi^*$ state (1A_2) and not to two $n\pi^*$ states as previously asserted. The analysis leads us to some new ideas on nonradiative processes in azines, especially 1,2-diazines.

INTRODUCTION

Exhaustive studies of the spectra of the diaza derivatives of naphthalene¹ have failed to reveal the presence of more than one $n \rightarrow \pi^*$ transition in all cases except for phthalazine (2,3-diazanaphthalene). A study of the absorption spectrum of mixed crystals of phthalazine in naphthalene at 4.2°K and of neat phthalazine crystals, revealed a vibronic pattern that was interpreted by Hochstrasser and Marzocco² as two nearby 1A_2 , $n\pi^*$ electronic states separated by 1657 cm⁻¹.

It is extremely important to expose the various $n\pi^*$ states of polyazines for in this way one can begin to understand the interactions between nonbonding electrons. It was therefore important to search for new methods of confirming the phthalazine assignments that were previously based on polarization, vibrational analysis, and isotopic shifts. Accordingly we have made precise Stark effect measurements in the phthalazine $n\pi^*$ region, and in this paper we use these and other results to demonstrate that the main bands in the phthalazine 4200-Å system represent only one $n\pi^*$ (1A_2) state. In addition we have obtained the dipole moment for this state, and the revised analysis has revealed new features of the upper state that may influence radiationless transitions in azines.

THE PHTHALAZINE 4200-Å SYSTEM²

In a naphthalene host at 4.2°K the spectrum starts at 23 577 cm⁻¹ with an extremely weak band that is thought to be the electronic origin of an A_2 state induced by the crystal field.² The long-axis polarized spectrum is strongest and the principal a_2 false origins are at 0+529 cm⁻¹ and 0+549 cm⁻¹. The short-axis polarized spectrum mainly originates on b_1 levels at 0+298 cm⁻¹ and 0+448 cm⁻¹. The very strong band at 0+2199 cm⁻¹ is long-axis polarized and this band was previously interpreted² as a 529-cm⁻¹ vibronic origin corresponding to a second A_2 state at 0+1670 cm⁻¹. The interval 1670 cm⁻¹ was not considered likely to be an upper state a_1 mode since it increased to 1685 cm⁻¹ on deuteration, whereas there were no high-frequency modes in the ground state that did other than decrease significantly on deuteration. The alternative assignment for

0+2199 cm⁻¹ as 529(a_2)+1670(a_1) will be shown below to be the more likely one. The long-axis polarized spectrum and some of the important assignments, are shown in Fig. 1.

EXPERIMENTAL

Phthalazine (Aldrich Chemical Company) was extensively zone refined, and 0.1% solid solutions with naphthalene were grown from the melt. At this concentration the 0+529-cm⁻¹ and 0+2199-cm⁻¹ transitions had linewidths of 3 and 6 cm⁻¹, respectively, at 4.2°K.

The Stark measurements were performed on a Jarrell-Ash Czerny-Turner Fastie spectrograph used in the 14th and 15th order for the lower- and higher-energy lines studied. The dispersion in these orders is about 30 cm⁻¹ per cm with a resolution of ~ 0.05 cm⁻¹.

STARK EFFECT STUDIES

A pseudo-Stark splitting of vibronic transitions of the guest molecules arises when an electric field is applied across the host molecular crystal.³ If the orientation of the guest molecule is known relative to the host principal axes then one single electric field spectrum suffices to determine the change in dipole moment on excitation. For the case of phthalazine in naphthalene we assume perfect alignment of host and guest molecule principal axes, and our experiments are done with the field down the c' axis of naphthalene which is quite near to the long axis. The vibronic lines are split by $2E_{eff}|\Delta\mu \cdot \hat{c}'|$ where E_{eff} is the effective Stark field and $\Delta\mu$ the change in dipole moment. For E_{eff} we have assumed a Lorentz approximation which yields⁴ $E_{eff} = 1.85E_c$ where E_c is the applied field along c' .

Figure 2 shows the absorption spectrum of the 0+529-cm⁻¹ and 0+2199-cm⁻¹ transitions in an electric field of 81.5 kV/cm along c' . Both lines are split by 13.6 cm⁻¹. The experimental data for different fields are shown in Fig. 3: Not only is the linearity of the effect verified but it is clear that the Stark effects for 0+529 cm⁻¹ and 0+2199 cm⁻¹ are the same within experimental error. From these data we find $|\Delta\mu| = 3.06 \pm 0.10$ D for 0+529 cm⁻¹ and 3.04 ± 0.10 D for

FIG. 1. The c' -polarized absorption spectrum of phthalazine in naphthalene at 4.2°K is shown with the progression $0+529$ (a_2), $0+529+1670$, and $0+529+3298$ cm^{-1} marked on the figure. The top of the diagram represents zero plate blackening so the higher-energy lines are more intense than they appear on the densitometer tracing shown.

$0+2201$ cm^{-1} . Actually we can say that the two values do not differ by more than 1%, and this *comparison* does not depend on internal field nor on orientational considerations.

Because there is a large (1782-cm^{-1}) blue shift of the crystal spectrum² vs the mixed crystal spectrum, we conclude that the dipole moment is decreased on excitation to the $^1A_2(n\pi^*)$ state. This is in accord with expectations based on an $n \rightarrow \pi^*$ promotion scheme for the transition.

ASSIGNMENTS

The $0+2199\text{-cm}^{-1}$ transition is now assigned as $0+529(a_2)+1670(a_1)$: We consider it most unlikely that two $n\pi^*$ electronic states could have such similar dipole moments as we have found. In addition we have

found strong (broader) bands in the 1670-cm^{-1} overtone region (see Fig. 1). For example in the b -polarized spectrum, there is a very strong broad band at $0+922+1670+1659 \pm 3$ cm^{-1} : the 1659-cm^{-1} interval definitely increases to 1669 cm^{-1} on deuteration. This observation removes any compelling reason to consider the vibronic structure as being due to two electronic states. The intervals 1657 cm^{-1} (crystal), 1670 cm^{-1} (mixed crystal), and 1685 cm^{-1} (d_4 mixed crystal) are now assigned to a totally symmetric vibration.

An interesting new feature that emerges is that the spectrum must consist of a strong progression of the 1670-cm^{-1} mode. That is why the spectrum has the unusual appearance already remarked upon by Mason⁵; unusual because the Franck-Condon maximum is so far removed from the origins. It appears as if the maximum intensity lies beyond two quanta of the 1670-cm^{-1}

FIG. 2. The Stark spectra of $0+529$ cm^{-1} (upper curve) and $0+529+1670$ cm^{-1} (lower curve) in a field of 81.5 kV/cm. Both spectra were photographed in the same sample with identically the same applied field.

FIG. 3. Stark splittings for $0+529\text{ cm}^{-1}$ (solid dots) and $0+529+1670\text{ cm}^{-1}$ (open circles) as a function of applied field. Both sets of measurements are for the same crystal at identical field settings.

mode, and in addition the vibronically inducing mode 529 cm^{-1} contributes to the gap between the zero-zero band and the intensity maximum. We do not find that the frequency of the first overtone of 1670 cm^{-1} is constant for different origins, but deuteration always causes an increase of the interval.

CHARACTERISTICS OF THE 1670-cm^{-1} (a_1) MODE

The lowest energy $n \rightarrow \pi^*$ transition is expected to arise from a $n_{-}\pi^*$ configuration.^{2,5} Since the promoted electron comes from n_{-} which is antibonding across the N-N bond, we could even expect a shortening of the N-N bond on excitation due to this effect. We suggest that the 1670-cm^{-1} mode represents essentially an N-N stretch in the excited state, and that this is the reason for the unusually small deuteration shifts. It is not clear why deuteration increases the intervals, although Innes, Tincher, and Pearson⁶ have suggested that Fermi resonances among the a_1 modes could cause such an effect. We are unable at this time to single out one ground-state mode with which the 1670-cm^{-1} vibration must correlate.

RADIATIONLESS TRANSITIONS IN 2,3-DIAZINES

Now that we have established that the lowest state of phthalazine is $^1A_2(n\pi^*)$ and that there are no nearby states such as those proposed earlier, the unusual nature of the absorption spectrum gives a clue to the radiative properties of 2,3-diazines. Both pyridazine⁷ and phthalazine² fail to show luminescence under normal condi-

tions of excitation and detection: Probably the lifetimes of their potentially fluorescent states are at most 10^{-4} times the natural lifetimes, with the same inequality applying to phosphorescence lifetimes. If indeed the N-N distance is significantly changed on excitation—such that there is a large Franck-Condon factor for transitions involving quanta of the N-N mode—then this mode will become an ideal accepting mode for nonradiative processes into the ground state. A large Franck-Condon factor for a high-frequency mode is what is needed to give an effective radiationless transition. This feature renders phthalazine and pyridazine different from other diazines and from aromatics, and it may be the source of their puzzling nonluminescent behavior.

CONCLUSIONS

Recent calculations of the σ orbitals of naphthalene⁸ have shown that the highest filled σ orbitals are of b_{3g} and a_g type: Because of the nodal patterns for these σ orbitals, it is expected¹ that the $n_{-}(b_2)$ lone pair orbital will become considerably more delocalized than $n_{+}(a_1)$. Accordingly it would be anticipated that the charge distributions for transitions involving n_{-} and n_{+} electrons would be significantly different. The Stark effect method used here, perhaps with electric field modulation refinements, would be an effective way of locating and distinguishing different $n\pi^*$ states in other systems. With sharper bands than phthalazine presents, it should be readily possible to make comparative measurements of $|\Delta\mu|$ for different vibronic levels to an accuracy of 0.5%, that is to 0.005 D for a dipole moment change of 1 D. In the present work we have shown that the difference in dipole-moment change for two vibronic states is less than 0.03 D and the linewidths were 3 and 6 cm^{-1} which are large for mixed crystal spectra at low temperatures.

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