COMMENTS

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On the Lowest Triplet State of the Pyridazine Crystal

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Synopsis. The lowest singlet-triplet transition recently observed at 440 nm by Yamamoto, Takemura, and Baba for pyridazine in EPA is shown to correlate with the 410 nm transition observed by Hochstrasser and Marzzacco. This correlation is contrary to that of Yamamoto *et al.*

In a recent article in this journal, Yamamoto, Takemura, and Baba[1] reported on the singlet-triplet absorption of pyridazine measured by means of sensitized-phosphorescence excitation in EPA rigid-glass solution at 77 K. They observed weak broad intensity in the 370—440 nm spectral region and assigned it to two singlet-triplet absorption transitions. The main basis for the two transition assignment is that there are two absorption regions, a weaker one at 440—410 nm and a stronger one at 410—370 nm. These authors correlate the long wavelength system with the 445 nm singlet-triplet absorption observed by Innes *et al.*[2] for pyridazine vapor and the short wavelength system to the 410 nm singlet-triplet absorption observed by Hochstrasser and Marzzacco[3] in the pyridazine neat crystal. This assignment of the 410 nm crystal absorption to the $S_0 \rightarrow T_2$ transition is contrary to Hochstrasser and Marzzacco's analysis and would imply that they missed the observation of a lower energy singlet-triplet system, $S_0 \rightarrow T_1$. In correlating their spectral data for pyradazine in EPA with spectral data of pyridazine in two different phases, Yamamoto, Takemura, and Baba do not take into account the large blue shifts in the $n \rightarrow \pi^*$ transitions upon going from the vapor to the solid phase of pyridazine. In the pyridazine vapor, the origin of the $S_0 \rightarrow S_1$ ($^1B_1(n\pi^*)$) transition lies at 26649 cm^{-1} [2] whereas it is found at 28351 cm^{-1} in the crystal.[3,4] This huge blue shift of 1702 cm^{-1} may be due in part to the large dipole moment change accompanying the transition. The origin of the triplet system observed by Innes *et al.*[2] appears at 22487 cm^{-1} in the vapor and that in the crystal appears at 24251 cm^{-1}.[3] The similarity of this 1764 cm^{-1} shift observed in the triplet system to the 1702 cm^{-1} shift in the singlet system is strong evidence that the 440 nm vapor and the 410 nm crystal absorptions are both due to the same singlet-triplet transition namely $S_0 \rightarrow T_1$. This transition correlates with the 440 nm absorption observed by Yamamoto *et al.* In the phosphorescence excitation of pyridazine in EPA. It should also be noted that the singlet-triplet gap is about 4000 cm^{-1} in all three environments consistent with the lowest triplet being of the same character as the lowest singlet excited state namely $B_1(n\pi^*)$.

These comments are in no way meant to refute the suggestion of Yamamoto *et al.* that a second singlet-triplet transition occurs at 410 nm for pyridazine in EPA. Since transitions to other than the lowest excited state of a given multiplicity are often very broad,[5] such a transition would not have been observed under the high resolution spectrographs used by Innes *et al.* for the vapor work or by Hochstrasser and Marzzacco for the low temperature crystal work.

References

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5) R. M. Hochstrasser and C. Marzzacco, *J. Chem. Phys.* **49**, 971 (1968).