Phosphorescence of Crystalline Pyrazine: Emission due to Crystal Defects

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Phosphorescence of crystalline pyrazine at 4°K is considerably more complex when compared with the solution spectrum. The onset of the phosphorescence spectrum of a vacuum sublimed pyrazine crystal, which is shown in Fig. 1a, consists of several dozen bands. In this communication we present experimental evidences which reveal that all of these bands are due to pyrazine at some crystalline defects; this observation is in contrast to the interpretation given recently by Moomaw and El-Sayed.[1] The present paper also aims to point out the importance of the sample preparation in the measurements of crystal emission.

Of the bands shown in Fig. 1a we focus our attention to the highest energy weak band, labeled A, and to the relatively intense and sharp bands, B,C···, and G. All of these bands constitute progressions of 606, 759, 953, 1012 and 1254 cm^{-1}. In view of the agreement of these values with the observed Raman frequencies[2] it is certain that all of the above-mentioned bands are due to pyrazine, and not to some chemical impurities.

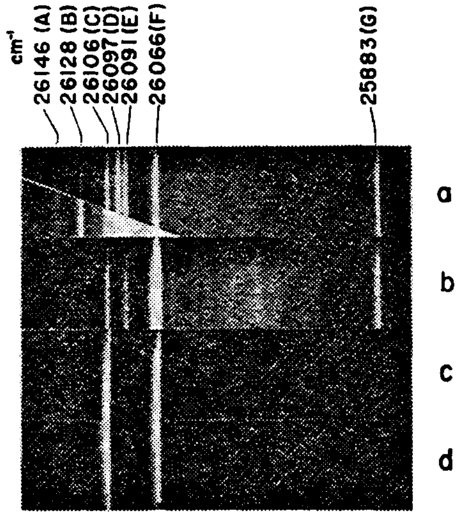

Fig. 1. Phosphorescence spectrum of crystalline pyrazine at 4°K. Spectrum for vacuum sublimed sample, shown in a), changes by successive continuation of zone-melting as shown in b), c) and d).

The vacuum sublimed sample, for which the phosphorescence shown in Fig. 1a is obtained, is subject to zone-melting. Phosphorescence spectra observed at various stages of zone-melting are shown in Fig. 1b, c and d. As is clear from Fig. 1 in the earlier stage of zone-melting bands B and D are weakened. By further continuation of zone-melting bands E and G also are weakened, and finally, only bands C and F remain intense. These observations lead us to conclude that those bands which disappear by the zone-melting process, which is nothing but a repetition of slow crystallization, are due to pyrazine at some crystal defects. The nature of the remaining bands C and F, which are 40 and 80 cm^{-1} apart, respectively, from the highest-energy band A, remains unsolved. However, since no ground state phonons of these frequencies exist, we believe that these bands are also due to crystal defects, which are very difficult to remove.

Moomaw and El-Sayed[1] interpreted the bands shown in Fig. 1a to be due to the coupling with the ground state phonon. They state that bands E and F are[3] due to two strongly coupled phonons of 57 and 86 cm^{-1}. Disagreeing with these authors, we emphasize, in the first place, that the former band is to disappear by zone-melting process, and secondly, that for the latter band the energy separation of 80 cm^{-1} (which is accurate to within 1 cm^{-1}) from band A is greatly different from the observed Raman frequency of 86 cm^{-1} (which is accurate to within 2 cm^{-1}) at 4°K and can, is no way, be correlated with the phonon.[4]

In further support of the above conclusion, phosphorescence lifetimes are obtained for bands E and F, separately, and the results are 19 and 22 msec, respectively. Such different decay behavior alone can unambiguously verify the fact that the emitting states are different for these bands.

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[1] W. R. Moomaw and M. A. El-Sayed, *J. Chem. Phys.*, **47**, 2193 (1967); **48**, 2502 (1968).

[2] M. Ito and T. Shigeoka, *ibid.*, **44**, 1001 (1966).

[3] Wave numbers given by Moomaw and El-Sayed[1] are different from ours by about 10 cm^{-1}. This difference is probaly caused by the two factors: a) These authors *apparently* did not convert to the wave numbers *in vacuo*. b) The errors of the wave numbers given by these authors[1] amount to 3 cm^{-1}.

[4] It is probably the large wave number errors (as much as 3 cm^{-1}) inherent to the work of Moomaw and El-Sayed[1] which have led these authors to the interpretation different from ours.