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The Near Ultraviolet Absorption Spectrum of Quinoxaline Vapor

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We have measured the n–π^* absorption spectrum of quinoxaline vapor from 20 to 200°C with absorption cells of 40 and 120 cm in length, using a Shimadzu GE-340 grating spectrograph (dispersion in the second order=1.3 Å/mm) and a Jarrell Ash 3.4 m grating spectrograph (dispersion in the second order=2.4 Å/mm).

It has been found in this spectrum,*[2] just as had previously been found in the spectrum of pyrazine vapor,[1,2] that the bands consist of two systems, one broad-band system originating at 26016.7 cm^{-1} and with a prominent progression of 525.3 cm^{-1}, and one sharp-band system with a 524.7 cm^{-1} progression with strong false origins at 27496.2 and 27670.1 cm^{-1}. Each band of the sharp system has a clear-cut head on the shorter-wavelength side and degrades toward the longer wavelengths.

Contrary to the case of the pyrazine spectrum, however, we can assign the broad system as an allowed $^1A_1$–$^1B_1$ transition with the 0–0 band at 26016.7 cm^{-1} and the sharp system as a vibronic transition induced by "intensity borrowing" from the $^1A_1$–$^1A_1$ transition, on the basis of the following considerations:

(1) The broad system exhibits a spectral-band feature characteristic of the vibrational structures for an allowed electronic transition, while the sharp system is characteristic of those for a vibronically-induced transition.

(2) In the n–π^* absorption bands of pyrazine,[1,2] the sharp bands have been observed to belong to the parallel bands of a near-oblate symmetric top (the asymmetric parameter, $\kappa \approx +0.7$) and assigned as an allowed electronic transition, while the broad bands, which can be regarded as the perpendicular bands, have been assigned as a vibronic transition. On the other hand, the quinoxaline molecule can be regarded as a near-prolate symmetric top (approximately, $\kappa \approx -0.7$). As is well known,[3] the parallel bands of a prolate symmetric top have nearly the same rotational structures as have of an oblate symmetric top. Therefore, it is natural to suppose that the sharp bands of the quinoxaline spectrum correspond to the parallel bands, (in-plane polarized perpendicular to the N–N axis of the molecule) and the broad bands, to the perpendicular bands, (polarized normal to the molecular plane).

It can not be determined with certainty, however, whether the sharp bands are the "forbidden"[4] bands in the allowed $^1A_1$–$^1B_1$ transition or the electronically-forbidden bands ($^1A_1$–$^1A_2$ transition, a component of the n–π^* splitting), since no hot bands corresponding to the strong false origins at 27496.2 and 27670.1 cm^{-1} appeared at all.*[3]

If we can regard the two vibrational frequencies, 525.3 and 524.7 cm^{-1}, observed in the broad and sharp system respectively as belonging to one electronic transition, we might assign the sharp bands to the "forbidden" bands in the allowed $^1A_1$–$^1B_1$ transition with the 0–0 band at 26016.7 cm^{-1}. The strong false origins at 27496.2 and 27670.1 cm^{-1} may also be then assigned to 0+1479 and 0+1653 cm^{-1} respectively. It seems, however, that the 1653 cm^{-1} is too high to be a fundamental frequency of the n–π^* state. However, this frequency is unlikely to be a combination.

Although several points remain uncertain, the proposed assignment seems most probable in the light of present knowledge. The vibrational analysis will be reported in detail elsewhere.

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*[2] A part of the photograph of the vapor spectrum has already been presented in Ref. 5.

1) M. Ito, R. Shimada, T. Kuraishi and W. Mizushima, *J. Chem. Phys.*, **26**, 1508 (1957).

2) K. K. Innes, J. D. Simmons and S. G. Tilford, *J. Mol. Spectry.*, **11**, 257 (1963); K. K. Innes and J. E. Parkin, *ibid.*, **21**, 66 (1966).

3) A. C. Allen and P. C. Cross, "Molecular Vibrotor," John Wiley and Sons Inc., New York (1963).

4) A. C. Albrecht, *J. Chem. Phys.*, **33**, 156 (1960); *ibid.*, **33**, 169 (1960).

*[3] Previously,[5] three of us (Y.H., Y.A. and H.A.) stated explicitly that the sharp bands of the quinoxaline spectrum are the "forbidden" bands. However, it would be better to state that the assignment is tentative, not conclusive.

5) Y. Hasegawa, Y. Amako and H. Azumi, This Bulletin, **41**, 2608 (1968).