The Near Ultraviolet Absorption of Pyridine Vapor

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THE near ultraviolet absorption spectrum of pyridine vapor has been studied in detail by Henri and Angenot.[1] These authors measured some 250 bands, made a careful study of the pressure and temperature dependence of the spectrum, and proposed an analysis which comprised most of the stronger bands. Their five series formulas contain five different ground state frequencies and one upper state frequency. Closer inspection of the analysis reveals that some of the given intensities seem rather high for the Boltzmann factors which can be computed from the interpretation of the bands. This observation and some irregularities in the intensity distribution within the series made a reinvestigation desirable. It was carried out in collaboration with Dr. Hildegard Stücklen. To work out the new analysis, it proved necessary to secure our own plates and to make measurements from them.

Since the work of Henri and Angenot, who made use of Raman measurements by Kohlrausch[2] in their analysis, new material on Raman spectra[3] and infra-red spectra[4] has been published. The vibrational spectrum of pyridine was discussed recently by Kline and Turkevich[5] on the basis of previous and the new measurements.

The ultraviolet absorption spectrum was photographed in the first order (dispersion 5.54A per mm) of a 3-m grating spectrograph (Eagle Mounting) with a hydrogen discharge lamp of the ordinary type as light source. During exposures the pyridine was kept in a side arm at temperatures varying from $-60°C$ to $+32°C$ covering pressures from a few hundredths to 30 mm.

The spectrum shows a marked difference from that of benzene: the group character of the benzene spectrum has disappeared, and the bands have a line-like appearance instead of the pronounced degradation to the red of the benzene bands. The electronic transition connected with the absorption is allowed and represents an $A_1 - B_1$ transition corresponding to the symmetry C_{2v} of the pyridine molecule. The direction of the transition moment is in the molecular plane perpendicular to the CN axis.

According to the new analysis the 0,0 band is located at 34769 cm^{-1}. Henri and Angenot had taken the band 35762 cm^{-1} as origin of the system. Progressions involving the excitation of totally symmetrical carbon vibrations appear with only medium intensity while they represent the strongest bands in benzene and benzene derivative spectra. Frequency values of 995 and 968 cm^{-1} in the upper state are correlated with the ground state frequencies 1031 and 992 known from Raman spectra and appearing also in ultraviolet absorption.

The most characteristic feature of the pyridine spectrum, noticed and stressed by all observers, is a progression with separations of 542 cm^{-1}. It is the strongest in the spectrum. The 542 frequency (in the excited state) is interpreted as the symmetrical component α_1 which results for symmetry C_{2v} from the splitting of the degenerate 606 benzene vibration of type ϵ_g^+. Its value in the ground state is given by the Raman line 604 cm^{-1} while we find 601 cm^{-1} from the absorption spectrum. The 542 progression occurs in all combinations with the 995 progression as would be expected from symmetric vibrations appearing strongly. Besides these combinations involving vibrations in the upper state only, there are also present bands in which one or both vibrations are excited in the ground state.

The other component β_1 produced by the splitting of the 606 benzene vibration in pyridine should have a value close to 604. There has been observed another fairly strong Raman line in

[1] V. Henri and P. Angenot, J. de Chim. Phys. **33**, 641 (1936). See their previous references.

[2] K. W. F. Kohlrausch, Zeits. f. physik. Chemie **B30**, 305 (1935).

[3] E. Herz, L. Kahovec and K. W. F. Kohlrausch, Zeits. f. physik. Chemie **B53**, 124 (1943).

[4] J. Turkevich and P. C. Stevenson, J. Chem. Phys. **11**, 328 (1943).

[5] Ch. K. Kline and J. Turkevich, J. Chem. Phys. **12**, 300 (1944). See this paper for detailed references on Raman and infra-red work.

this region of frequency value 652 cm^{-1}. However, both the 604 and 652 lines are depolarized,[3] and hence cannot represent the α_1 and β_1 component of the 606 vibration. It has been suggested,[3, 5] therefore, to consider the 604 as unresolved containing both components α_1 and β_1. The Raman frequency of 652 cm^{-1} was assigned[3, 5] to an out-of-plane vibration, a CH vibration by the Kohlrausch group, and a ring vibration by Kline and Turkevich. Both interpretations present certain difficulties in view of the fact that the vibration appears excited in the ground state in ultraviolet absorption.

Of particular interest is the occurrence of hydrogen vibrations since it proved very difficult to locate H-vibrations unambiguously in the spectra of benzene derivatives previously studied. An examination of pyridine plates taken at high pressures reveals at once on the long wavelength side of the 0,0 band the presence of many bands whose frequencies coincide with Raman lines and infra-red bands, and which cannot be explained as ring vibrations or combinations of such. Prominent separations towards longer waves from the 0,0 band are in cm^{-1}: 345, 395, 464, 487, 519, 601, 651, 766, 864, 890, 945, 992, 1031, 1063, 1202, 1218. Weaker bands appear at separations of 676 and 712. The separations 601, 652, 992, 1031 have been mentioned before. The difference 487 is explained as superposition of 542 upon[6] -1031, the 579 as $-1063+542$, the 676 as $-1218+542$, the 345 as $-890+542$ and the 1202 coincides with $2\times(-601)$. The differences 1218, 1063, 945, 890, 712 agree with frequencies observed in the Raman and infra-red spectrum. Assignments of these frequencies to modes of vibration have been offered by Kohlrausch and co-workers, and by Kline and Turkevich. Both groups consider them as hydrogen vibrations, but disagree in the individual interpretations. Investigation whether these interpretations are compatible with the

observations in the ultraviolet absorption spectrum leads to some interesting conclusions.

Except for the very weak band at 712, all four bands are of similar intensity in ultraviolet absorption. The corresponding vibrations appear also in other bands in conjunction with the symmetric ring vibrations 542, 968 and 995 in the upper state. Especially the 890 frequency occurs in numerous superpositions and combinations with these ring vibrations. We take this as proof that none of the four frequencies can be correlated with a vibration of type β_2 because this would mean a forbidden transition.

The 945 vibration, when combined with the 542 progression, shows peculiar deviations which might be ascribed to anharmonicity effects. The intensity distribution in this combined progression is somewhat unusual so that it seems possible that some bands in it are really the result of a superposition of more than one transition. It would be interesting in this connection to investigate again[7] the absorption of α-picoline (2-methyl-pyridine) which is the most likely impurity.[5]

The $\epsilon_u{}^+$ benzene ring vibration of 406 cm^{-1} splits in pyridine into the components β_2 374 and α_2 404 cm^{-1}. From the ultraviolet absorption spectrum, it was found[8] that the benzene vibration dropped by 160 cm^{-1} in the excited electronic state. Assuming a similar behavior in pyridine, tentative assignments have been made for several bands.

The line-like appearance of the bands may be discussed under the assumption that the moments of inertia are very nearly the same in both the lower and upper states and that the bands represent an intense and narrow Q branch with the P and R branches falling off rapidly in intensity on both sides.

The detailed paper will be published later in association with Dr. Hildegard Stücklen.

[6] The minus sign is used for bands with longer wavelengths than the 0,0 band thus indicating vibrational excitation in the ground state.

[7] Henri and Angenot mention in their paper that they have also photographed the α-picoline spectrum, but it seems that their results have not been published. Earlier publication by E. Herrmann, Zeits. f. wiss. Phot. 18, 253 (1919).

[8] H. Sponer, G. Nordheim, L. A. Sklar, and E. Teller, J. Chem. Phys. 7, 207 (1939).