

## The N—H Harmonic Bands of Pyrrole at $\lambda 9900$ , and the Structure of the Pyrrole Molecule

LLOYD R. ZUMWALT AND RICHARD M. BADGER

*Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California*

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IN their study of the infra-red absorption of organic substances in carbon tetrachloride solution Wulf and Liddel<sup>1</sup> found that the strong second harmonic N—H band of pyrrole is accompanied by a weak satellite which lies approximately  $50\text{ cm}^{-1}$  to the long wave side and has roughly one-twentieth the intensity of the main band. The main band has been attributed by Pauling<sup>2</sup> to a planar pyrrole molecule and the weak satellite to a second molecular species in which the imino hydrogen lies out of the plane of the other atoms.

In a study of pyrrole vapor in the third harmonic region M. Freyman<sup>3</sup> found three components in the N—H absorption; a strong band at  $\lambda 9818$ , a much weaker one at  $\lambda 9890$ , and a very faint band at  $\lambda 9961$ , respectively. These Freyman attributed to three molecular species.

Since this explanation did not appear very plausible it has seemed worth while to make further studies of the third harmonic region. Consequently the N—H absorption of pyrrole vapor has been photographed both with low and high dispersion and at two temperatures ( $150^\circ$  and  $250^\circ\text{C}$ ). In the low dispersion studies it was observed that with rise in temperature the  $\lambda 9890$  and  $\lambda 9961$  bands show moderate and large increases in intensity, respectively, relative to the  $\lambda 9818$  band. From this fact it is clear that while the main band presumably arises from absorption from the ground level the two subsidiary maxima must involve absorption from two *different* excited states. That these states do not, however, correspond to different geometrical configurations of the molecule but merely to vibrational excitation is shown by the high dispersion studies.

It was not possible to photograph the faint  $\lambda 9961$  band under high dispersion but the other

two bands showed very characteristic envelopes which were apparently identical except for the difference in intensity. As shown in the figure they consist of *P* and *R* branches and narrow *Q* branches which are not very strong but have in both cases the same intensity relative to the rest of the band. Since the intensity of the *Q* branch will be very sensitive to the direction of change of electric moment in the N—H vibration,<sup>4</sup> and consequently to the orientation of the N—H bond it seems quite certain that the two bands just mentioned originate in one and the same molecular species. Consequently it is reasonable to ascribe the  $\lambda 9890$  band to a transition in which some low frequency vibration is excited in both lower and upper levels. The equality of spacings between the bands and the intensity ratios indicates that the  $\lambda 9961$  component is the third member of the sequence.

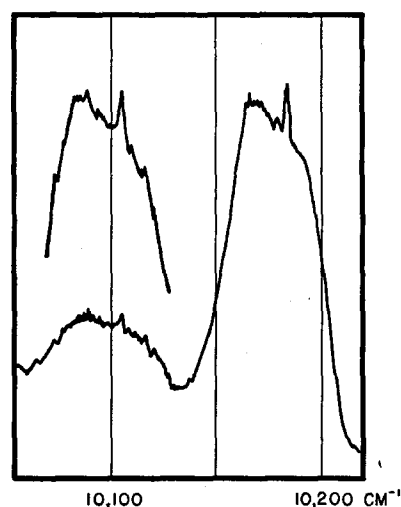


FIG. 1. Microphotometer curve of the third harmonic N—H bands in pyrrole vapor taken under high dispersion at  $250^\circ\text{C}$ . The upper curve at the left shows the second member of the band sequence recorded with increased microphotometer sensitivity for better comparison with the main band.

<sup>1</sup> Wulf and Liddel, *J. Am. Chem. Soc.* **57**, 1464 (1935).

<sup>2</sup> L. Pauling, *J. Am. Chem. Soc.* **53**, 94 (1936).

<sup>3</sup> M. Freyman, *Comptes rendus* **205**, 852 (1937); *Ann. de Chemie* **11**, 11 (1939).

<sup>4</sup> For a discussion of band envelopes of unsymmetrical molecules see: R. M. Badger and L. R. Zumwalt, *J. Chem. Phys.* **6**, 711 (1938).

Such sequences, with two or more members of appreciable intensity, are of general occurrence in molecules with low frequency vibrations though in most cases the separation between members is too small for them to be detected in incompletely resolved bands. The fact that in pyrrole one such sequence has been resolved implies an unusually large interaction between the N-H valence

vibration and some other mode of motion of low frequency. The intensity ratios and also the temperature effect indicate that the second vibration has a frequency in the neighborhood of  $650\text{ cm}^{-1}$ . The large interaction with the N-H valence vibration suggests that it involves some bending motion of the N-H bond with respect to the rest of the molecule.

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## LETTERS TO THE EDITOR

*This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must*

*reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.*

### Erratum and Addendum: Vibration Spectra and Molecular Structure. VII. Further Infra-Red Studies on the Vapors of Some Carboxylic Acids

(J. Chem. Phys. 7, 460 (1939))

In a publication with the above title we reported a spectroscopic determination of the heat of association of propionic acid-*d* and remarked erroneously that our calculation of the heat of association was independent of the absorption constant. This remark would be true if the quantity  $P_D/P$ , which occurs in the formula

$$K_p = \frac{(1 - P_D/P)^2 P}{P_D/P},$$

is maintained at a constant value by adjusting the temperature and pressure. In this case a knowledge of the true absorption constant would be unnecessary. In the determination reported  $P_D/P$  was not always kept constant and therefore a value of the absorption constant has to be assumed. If the absorption constant assumed for these calculations differs from the true value by more than about 17 percent, the curve for  $\log_{10} K_p$  vs.  $1/T$  deviates from a straight line by a measurable amount. However, if the

absorption constant differs by less than about 17 percent, the only effect noticeable above the scattering of points due to experimental error would be a change of slope of the straight line by about 5 percent.

Since the data we have obtained for propionic acid-*d* seem to fit a straight line, it would seem that the value of the absorption constant we have assumed for propionic acid-*d* cannot differ from the true value by more than about 17 percent. It now becomes necessary to change the probable error in the heat of association of propionic acid-*d* by about 350 calories per mole per bond because of a possible error in the absorption constant. In the case of acetic acid-*d* the absorption constant was calculated with the aid of MacDougall's data and since our results gave a straight line consistent with that of MacDougall we feel that no revision is necessary.

It is a pleasure to thank Professor E. Teller for an interesting discussion.

R. C. HERMAN  
R. HOFSTADTER

Palmer Physical Laboratory,  
Princeton University,  
Princeton, New Jersey,  
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