

First Overtone NH Band Splitting and Intramolecular NH...X Hydrogen Bonds

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(Z. Naturforschg. **18 a**, 1239 [1963]; eingegangen am 13. August 1963)

Although the first overtone NH stretching bands (sym. and asym.) in o-, m-, and p-substituted anilines might be expected to be qualitatively similar to the corresponding fundamental bands, it is well established that the symmetric ν_{02} band is split into an observable doublet in aromatic amines where intramolecular NH...X hydrogen bonding to o-substituents is possible¹⁻⁶. No band splitting is observed in the high-resolution ν_{01} spectra, even when a strong proton accepting o-substituent is present, e. g. X = o-COOC₂H₅. The ν_{02} symmetric band is not doubled when a small hydrocarbon group, e. g. methyl, is present in the o-position. No apparent doubling of the ν_{02} asymmetric band has been reported to date.

Examination of the doublet separation (Δ) and the absorbance ratio (α = low frequency component/high frequency component) for twenty compounds in dilute CCl₄ solution shows that the two quantities are related. A plot of Δ vs. α is asymptotic to both axes. The classification of the overtone NH spectra into a number of types^{5,6} thus appears to be rather artificial. Arrangement of the data in order of increasing Δ (including the published frequencies for eleven additional compounds) indicates that Δ increases and α decreases fairly smoothly as the strength of the intramolecular NH...X hydrogen bond increases (from $\Delta = 33$ cm⁻¹, $\alpha = 9.3$ in o-aminodiphenyl to $\Delta = 254$ cm⁻¹, $\alpha = 0.2$ in o-aminoacetophenone), bearing in mind the rigid geometrical restrictions of the systems involved. As the NH...X interaction commences the intensity switches dramatically from the low frequency component into the high frequency component, with only a slight increase in the doublet separation. After the high frequency component predominates a further increase in

the strength of the NH...X interaction alters the absorbance ratio little, but increases the doublet separation markedly.

For most o-substituted anilines the high and low frequency symmetric ν_{02} components respectively lie above and below the general frequency correlation with HAMMETT σ and TAFT σ^* substituent constants established previously⁷. The doublet is concentration and temperature independent over the range 0–60 °C in CCl₄ solution.

The absence of a doublet ν_{01} symmetric band and the systematic variation of Δ and α provide strong support for a double-minimum potential function for the stretching motion of the hydrogen bonded proton, with the secondary minimum lying in the vicinity of the $v=2$ vibrational level, and separated from the main minimum by a small potential barrier⁸. As expected for such a system, deuteration of o-nitroaniline decreases Δ but does not affect α .

The failure to observe splitting of the asymmetric ν_{02} band can be attributed to the relative insensitivity of the asymmetric mode to such interaction effects, as the calculations of WOLFF and STASCHEWSKI show⁹.

For the secondary amines N-methyl-o-nitroaniline, o-nitrodiphenylamine, and methyl N-methyl anthranilate, where a single sharp and very intense fundamental NH stretching band exists at a frequency below that found in the corresponding p-compound (indicative of NH...X hydrogen bonding), a split weak ν_{02} band is observed, as expected.

The details of this work and a more complete discussion of the concept of a double-minimum potential for intramolecular hydrogen bonds will be published shortly. These systems may lead to more refined calculations on the nature of the potential function for hydrogen bonded protons, since the A–H...B distance and the A–H...B angle are known. The lack of knowledge of the AB distance in intermolecular hydrogen bonds is a major obstacle in such calculations.

The author thanks the National Research Council of Canada for financial assistance.

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Verantwortlich für den Inhalt: A. KLEMM

Gesamtherstellung: Konrad Triltsch, Würzburg



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