Notes

Laser Raman Spectra of Light & Heavy Dithiopropionic Acids in the Solution Phase

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Raman spectroscopic studies on dithiopropionic acid in the SH stretching region reveal that it exists mainly as an open chain dimer in the solution phase and as a cyclic dimer in the liquid phase.

Recently, we have reported the laser Raman spectra of light and heavy dithioacetic acids in the solution phase. In order to supplement our results we are reporting in this note, the laser Raman spectra of light and heavy dithiopropionic acids in dichloromethane in the SX (X = H or D) stretching region. The sample of dithiopropionic acid was prepared by the method reported in the literature and the liquid with b.p. 48°/17 mm was used in the present investigations. The deuterated dithiopropionic acid was prepared by the direct exchange of acid with heavy water. Deuteration was of the order of 85%.

The Raman spectra of 40% (w/v) solutions of C₂H₆CSSH and C₂H₆CSSD in CH₂Cl₂ in the SX stretching region were recorded on a Cary 82 spectrophotometer, using 6471 Å line of Kr laser.

The solution spectrum of C₂H₆CSSH shows two clearly resolved bands at 2570 and 2553 cm⁻¹ which may be due to Fermi resonance or free and H-bonded SH group. The doublet structure of the band is may be due to Fermi resonance or free and H-bonded CH₂CSSH and CH₂COSH. Thus we can conclude that the doublet in the SH stretching region is not due to the accidental degeneracy but because of the existence of an open chain oligomer (I) of dithiopropionic acid in the solution phase as observed for dithioacetic acid.

The presence of only one band at 2498 cm⁻¹ in the spectrum of pure dithiopropionic acid like that in the spectrum of dithioacetic acid could perhaps best be explained as due to the existence of dithiopropionic acid mainly in the cyclic dimeric (II) form. The band corresponding to the 2498 cm⁻¹ band in C₂H₆CSSH is observed at 2990 cm⁻¹ in CH₃COOH.

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References

Hydrogen Bonding Effect on In-plane Bending Motions

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The 80-D of phenol-OD is found to undergo large frequency shift to higher energy on formation of hydrogen bond with strong bases. The increase of 80-D is, however, much less than the decrease of v0-D for hydrogen bonding with same base.

The main vibrational modes of a hydrogen bonded system X—H .... Y are stretching (v), in-plane bending (b) and out-of-plane bending (t). Of these three modes, the most extensively studied band is the vX-H which is shifted to lower frequency on hydrogen bonding. The explanation for the decrease in vX-H hence the lowering of the force constant kₓ for the parallel displacement of the proton is well known. If V be the electrostatic potential of the proton in a hydrogen bonding system, then from Poisson's equation we have

\[ V = -4\pi \rho(H) \]

where \( \rho(H) \) is the total electron density at the position of the proton. This equation was also arrived at for a hydrogen bonding system by Srebrenik et al., employing the Hellmann-Feynman theorem.

One may write now

\[ k_{\perp} + 2k_{\perp} = 4\pi(\rho(H)) \]

where \( k_{\perp} \) is the force constant for the displacement of the proton perpendicular to the bond. For spherical electron distributions on X and Y the two perpendicular frequencies form a degenerate pair with identical force constants. But in real molecules the electron distributions are not spherically sym-