

ANALYSIS OF THE SYMMETRIC AND ANTI-SYMMETRIC N-H STRETCHING
MODES OF N-PROPYLAMINE IN BINARY MIXTURES WITH METHANOL:
A CONCENTRATION DEPENDENT RAMAN STUDY AND *AB-INITIO*
CALCULATIONS

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Keywords: *hydrogen bonding, binary mixture, n-propylamine, methanol, ab-initio calculations*

Abstract: A polarization-resolved Raman spectroscopic analysis of neat n-propylamine and a series of binary mixtures with methanol is presented. The observed spectral changes for the symmetric and anti-symmetric N-H stretching modes are assigned to hydrogen bonding and compared with *ab-initio* calculations on various hydrogen-bonded complexes of n-propylamine and methanol.

The analysis of wavenumber shifts and vibrational line profiles in neat liquids and binary mixtures by Raman spectroscopy allows detailed studies of both inter- and intra-molecular interactions and molecular motions [1]. The wavenumber position of a Raman band, which relates essentially to the corresponding force constant, is influenced by molecular structure and electron density distribution. The Raman linewidth, however, contains information on dynamic aspects in molecular liquids and solids, for instance on vibrational relaxation (dephasing) and reorientational motions [2-3]. The possibility to separate out these effects by performing polarized Raman measurements is an obvious advantage over IR spectroscopy. The precise determination of the depolarization ratio by measurements of the parallel, $I_{||}$, and perpendicular, $I_{\perp}$, components of the Raman scattered radiation, respectively, helps in ascertaining the symmetry of the vibration. For totally symmetric vibrations, the corresponding depolarization ratio is zero; deviations from zero observed upon solvent addition are attributed to intermolecular interactions. Polarization-resolved measurements also enable the determination of the isotropic part of the Raman scattered, which provides useful information on vibrational dephasing.

Raman spectra of neat n-propylamine (C_3H_9N) and its binary mixtures with methanol (CH_3OH) were acquired with the scanning multichannel detection technique (SMT). The $I_{||}$ and $I_{\perp}$ components of the Raman scattered radiation for n-propylamine mole fractions ranging from 0.1 to 0.9 were recorded in intervals of 0.1. The isotropic Raman spectra for neat n-propylamine and a 1:1 mixture with methanol are shown in Figure 1. The deconvolution of the asymmetric band shape observed for neat n-propylamine yields two peaks at $\sim 3326\text{ cm}^{-1}$ and $\sim 3303\text{ cm}^{-1}$, which are assigned to the anti-symmetric and symmetric N-H stretching vibration, respectively. Upon dilution with methanol, these two bands exhibit significant changes in relative intensities, wavenumber positions and linewidths. The observed shift towards lower wavenumbers for both bands is assigned to hydrogen bond formation. The experimental results are compared with *ab-initio* calculations performed both earlier by others [4] as well as by us. Structures of various hydrogen bonded complexes calculated at the MP2 level are presented and correlated with the observed spectral changes.

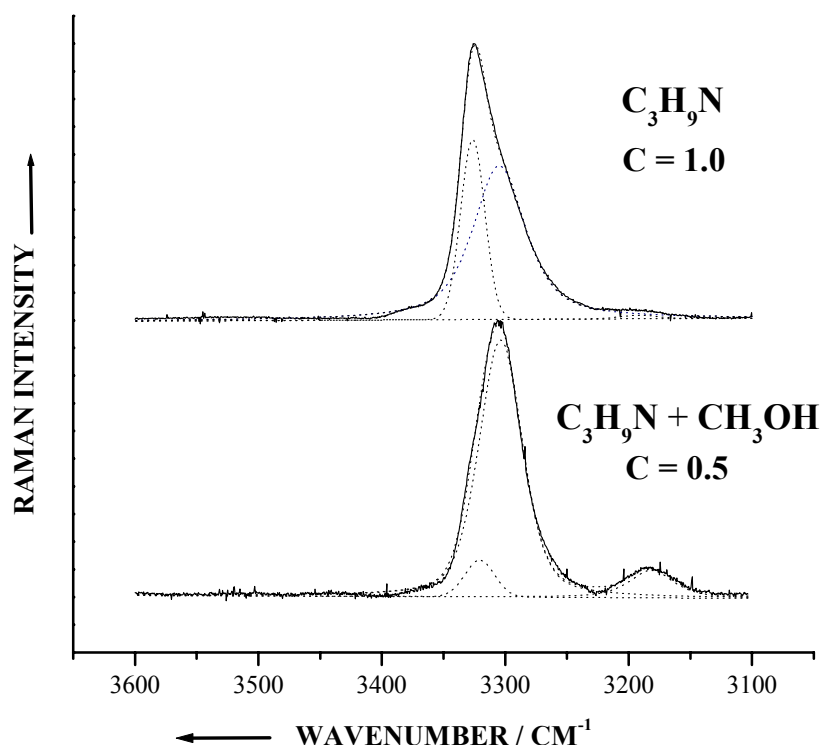


Fig. 1. Isotropic part of the Raman spectra of neat n-propylamine and a 1:1 mixture of n-propylamine and methanol in the wavenumber range 3600-3100 cm^{-1} . The two bands at $\sim 3326 \text{ cm}^{-1}$ and $\sim 3303 \text{ cm}^{-1}$ observed for neat n-propylamine are assigned to the anti-symmetric and symmetric N-H stretching mode, respectively. Both bands exhibit significant changes in relative intensities, wavenumber positions and linewidths upon dilution with methanol.

Acknowledgments:

The authors thankfully acknowledge the support received through DST-DAAD Exchange Program. BPA expresses his thankfulness to the AvH-Stiftung for a support through 'Wiederaufnahme'.

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