Raman Spectroscopic Study on the Two Distinct Solvated Structures of *p*-Nitroaniline in Acetonitrile

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Structure of the two distinct forms of p-nitroaniline (pNA) associated with solvent acetonitrile (AN) has been elucidated by a curve fitting analysis of the observed Raman spectra of pNA in AN/CCl_4 mixed solvents.

In a recent paper[1] we showed from a Singular Value Decomposition (SVD) analysis of UV-VIS absorption spectra of pNA in AN/CCl_4 mixed solvents that the bathochromic shifts observed in these solutions are actually due to the presence of different solvated structures of pNA. Three distinct species were identified; the 1:0 (free) species, the 1:1 species (one AN is associated with pNA), and 1:2 species (two AN associated with pNA). In order to obtain structural information of these solvated species, we have measured the Raman spectra of pNA in AN/CCl_4 mixed solvents. From a curve fitting analysis we now show that the initial association of pNA to AN is through the amino group and the further association takes place through the nitro group.

Previous Raman spectral studies[2,3] have shown some interesting spectral features of pNA in solution. There exists a doublet in the 1350-1300 cm^{-1} region, whose relative intensity depends markedly on the solvent polarity. This doublet has been assigned to the symmetric NO_2 stretch vibrations of associated and non-associated nitro group[4] of pNA. However, the nature of the association has not been known.

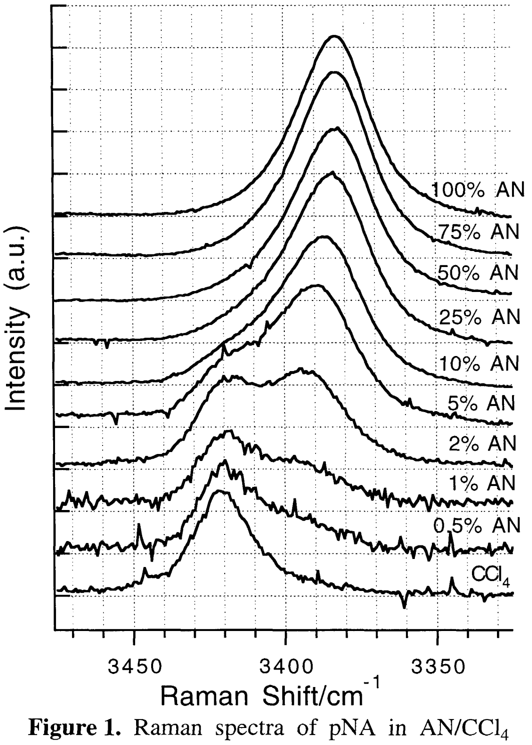

Figure 1. Raman spectra of pNA in AN/CCl_4 (NH_2 symmetric stretch region).

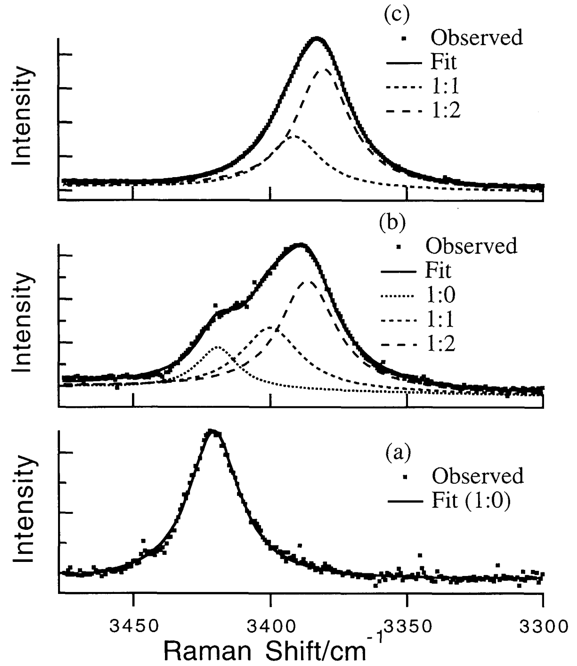

Figure 2. Raman spectra of pNA in AN/CCl_4 (NH_2 symmetric stretch region) : curve fitting results for solutions containing 0% (a), 5% (b) and 100% (c) of AN.

The Raman measurements were carried out with the 514.5 nm line from an Ar$^+$laser. The Raman scattered light was analyzed by a triple polychromator (Jobin-Yvon T64000) equipped with an intensified photodiode array (Princeton Instruments IRY 1024G/RB), or by a single monochromator (Instruments SA, HR320) and a CCD detector (Princeton Instruments LN/CCD-1024 TKB).

The Raman Spectra of pNA in AN/CCl_4 mixed solvents in the amino (NH) stretching region are shown in Figure 1. The Raman spectrum of pNA in CCl_4 exhibits a band at 3421 cm^{-1} arising from the free N-H symmetric stretch vibration. Whereas the Raman spectrum in AN shows a strong band around 3384 cm^{-1} (later we show that it actually contains two Raman bands). The results of the multi-Lorentzian curve fitting results in the NH region are shown in Figure 2. The following AN concentration-dependent behavior of the pNA/AN association is already known from the SVD analysis of the UV-VIS absorption spectra. In CCl_4 (0 % AN), only the 1:0 species exists; in the very small AN concentration range (<< 1%), the 1:0 and 1:1

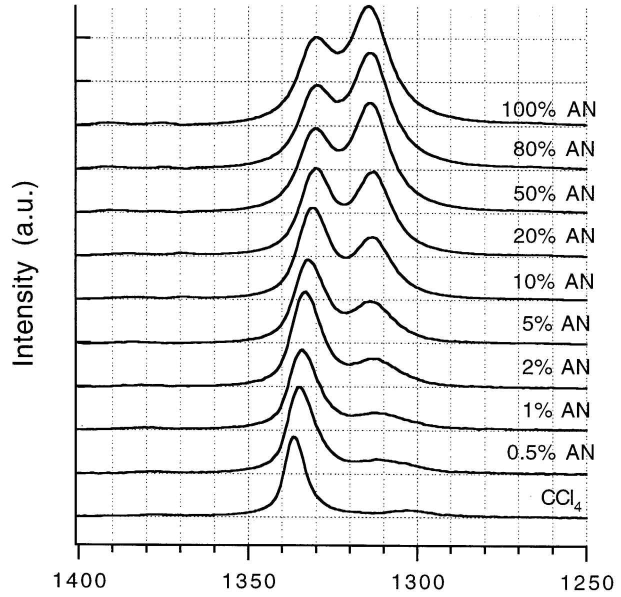

Figure 3. Raman spectra of pNA in AN/CCl_4 (NO_2 symmetric stretch region).

species coexist; in the intermediate concentration range around 5 %, all the three species exist; in the higher concentration range near 100 %, only the 1:1 and 1:2 species exist. In accordance with this concentration dependence, the Raman band(s) in the NH stretch region can be well fitted with a single Lorentzian for 0 % AN (Figure 2a), with three Lorentzians for 5 % AN (Figure 2b), and with two Lorentzians for 100 % AN (Figure 2c). The NH stretching frequencies obtained from the resolved spectra are 3420 cm^{-1} for the 1:0 species at 0 % AN, 3390 cm^{-1} for the 1:1 species at 100 % AN, and 3380 cm^{-1} for the 1:2 species at 100 % AN. Apart from these stepwise changes (30 and 10 cm^{-1}) among different solvated structures, there is also a small and gradual frequency shifts (less than 4 cm^{-1}) within each species, which is most probably due to the local dielectric-field effect. The stepwise decrease of the NH stretching frequency is consistent with the increased intramolecular charge transfer in pNA with AN association. The frequency shift (30 cm^{-1}) on going from the 1:0 to 1:1 species is much larger than that (10 cm^{-1}) on going from 1:1 to 1:2. This fact suggests that the association of AN in the 1:1 species takes place at the amino part of the pNA molecule rather than the nitro part.

Similar Raman spectral analysis has been carried out for the NO_2 symmetric stretch region. Figure 3 shows the Raman spectra of pNA in AN/CCl_4 in the NO_2 stretch region. The results of the curve fitting analysis in this region are given in Figure 4. The band at 1336 cm^{-1} in pure CCl_4 (0 % AN, Figure 4a) corresponds to the 1:0 species. The origin of the band at 1303 cm^{-1} is not clear at present. Three resolved bands in Figure 4b correspond to the three species, 1:0, 1:1 and 1:2 coexisting at 5% AN

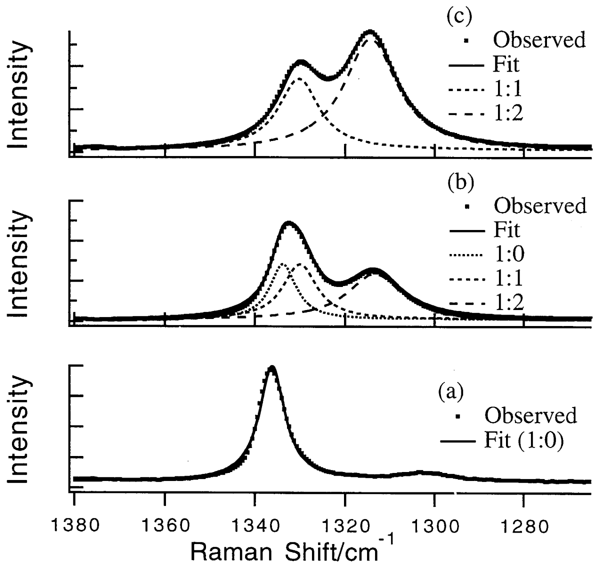

Figure 4. Raman spectra of pNA in AN/CCl_4 (the NO_2 symmetric stretch region) : curve fitting results for solutions containing 0% (Pure CCl_4) (a), 5% (b) and 100% (c) of AN.

concentration. At 100% AN (Figure 4c), the observed spectrum is well described by two lorentzians (1:1 and 1:2). All these results are consistent with the observation in the NH region. The frequency shift of about 6 cm^{-1} on going from 1:0 to 1:1 is much smaller than the shift of 15 cm^{-1} on going from 1:1 to 1:2, which is the reverse of the magnitude of frequency shifts observed in the NH region. This fact indicates that the second association is through the nitro group. The observed frequencies of 1:1 and 1:2 associated forms are again very consitent with the increased intramolecular charge transfer in pNA with AN association.

To conclude, it was shown through Raman spectral analysis of pNA in AN/CCl_4 that the association of AN with pNA first occurs at the amino part for the 1:1 species and the second association takes place at the nitro part in the 1:2 species. It seems that the initial association of NH group of pNA with AN results in increased charge transfer and this facilitates further association of pNA with AN through the NO_2 group.

References and Notes

1 K. Mohanalingam and H. Hamaguchi, *Chem. Lett.*, **1997**, 157.

2 M. Harrand, *Compt. Rend. Acad. Sci.*, **280B**, 271 (1975).

3 E. D. Schmid, M. Moschallski and W. L. Peticolas, *J. Phys. Chem.*, **90**, 2340 (1986).

4 G. Reck, F. Marlow, J. Kornatowski, W. Hill and J. Caro, *J. Phys. Chem.*, **100**, 1698 (1996).

5 K. Mohanalingam and H. Hamaguchi, Abstract of the Symposium on Molecular Structure and Molecular Spectroscopy (Bunshikozo Sogo Toronkai), 4P2b44, October 9, 1996 at Fukuoka.