The Aggregation of Acetonitrile Molecules in the Pure Liquid State and in Solutions with Proton Donor Solvents

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Liquid acetonitrile molecules are dimeric aggregated, and this aggregation is connected not only with interaction of molecular charges, but as showed the calculations (Gaussian 98W in Hartry-Hock approximation with basic set of gaussians RHF 6-31G (d,p), but also with formation of two intermolecular hydrogen bonds between one hydrogen atom of CH_3 group of molecule and nitrogen π - electrons of neigboring molecule. The calculations show that at such aggregation C≡N band in Raman spectra must slightly shift towards less frequencies. The asymmetry of C≡N band at low frequency side, on our opinion, is connected namely with this circumstance: the low frequency band of aggregates is not resolved, but overlapping on monomer band (2254 cm^{-1}) manes it asymmetric. In acetonitrile solutions with formic and acetic acids, according calculation, it is also possible the aggregation by formation closed dimers, and in its formation the hydrogen atom of acetonitrile CH_3 group participates also. However, observed on experiments in Raman spectra the high frequency shift of C≡N band in above indicated solvents, as well as in solution with isopropyl alcohol testify about formation of R_1-O-H….NC_2H_3 chain dimers with rapprochement of molecules towards of the acetonitrile molecule stretching (σ-bond). According to calculations at such rapprochement o molecules and H-bond formation the C≡N frequency must slightly grow.