

Acetonitrile–water hydrogen-bonded interaction: Matrix-isolation infrared and *ab initio* computation



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HIGHLIGHTS

- Experimental evidence for the formation of linear 1:1 CH₃CN–H₂O.
- Computation showed two minima a linear and cyclic complex.
- Computations were also carried out for 1:2 and 2:1 complexes of CH₃CN and H₂O.
- AIM and NBO analyses were carried out for the complexes A and B.

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ABSTRACT

The 1:1 hydrogen-bonded complex of acetonitrile (CH₃CN) and water (H₂O) was trapped in Ar and N₂ matrices and studied using infrared technique. *Ab initio* computations showed two types of complexes formed between CH₃CN and H₂O, a linear complex A with a C≡N...H interaction between nitrogen of CH₃CN and hydrogen of H₂O and a cyclic complex B, in which the interactions are between the hydrogen of CH₃CN with oxygen of H₂O and hydrogen of H₂O with π cloud of –C≡N of CH₃CN. Vibrational wavenumber calculations revealed that both the complexes A and B were minima on the potential energy surface. Interaction energies computed at B3LYP/6-311++G(d,p) showed that linear complex A is more stable than cyclic complex B. Computations identified a blue shift of ~ 11.5 cm^{−1} and a red shift of ~ 6.5 cm^{−1} in the CN stretching mode for the complexes A and B, respectively. Experimentally, we observed a blue shift of ~ 15.0 and ~ 8.3 cm^{−1} in N₂ and Ar matrices, respectively, in the CN stretching mode of CH₃CN, which supports the formation of complex A. The Onsager Self Consistent Reaction Field (SCRF) model was used to explain the influence of matrices on the complexes A and B. To understand the nature of the interactions, Atoms in Molecules (AIM) and Natural Bond Orbital (NBO) analyses were carried out for the complexes A and B.

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Introduction

Acetonitrile (CH₃CN) is a simple organic nitrile detected in the gas phase in interstellar clouds [1]. CH₃CN has a unique property such as high relative permittivity ($\epsilon_r = 37.5$) and hence possess remarkable miscibility with range of ionic and polar solvents [2], which makes CH₃CN as a solvent of choice for variety of organic synthesis. CH₃CN is also used as a mobile phase in HPLC and LC–MS. CH₃CN has been extensively used in synthetic organic chemistry.

Freedman and Nixon investigated the infrared spectra of CH₃CN in solid argon matrix [3]. Later, Kim and Kim re-investigated the vibrational spectra of CH₃CN using Fourier transform infrared

spectra and made precise assignments of monomers, dimers and higher multimers of CH₃CN [4]. Givan and Loewenschuss studied the Raman spectrum of CH₃CN using matrix isolation spectroscopy [5]. Several groups have studied the H-bonded interaction of CH₃CN with a variety of electron acceptors [6–20].

Recently, we have reported the hydrogen-bonded interaction of CH₃CN with C₂H₂ in an Ar and N₂ matrices and found evidences for the formation of 1:1, 1:2 and 2:1 C₂H₂–CH₃CN complexes [21].

Interaction of CH₃CN with H₂O was studied extensively by many theoretical groups. Doo-sik Ahm and Sungyul Lee computationally studied the σ - and π -type hydrogen-bonded complexes of acetonitrile–water clusters. They found at MP2/6-31+G(d,p) level of theory the π -type complex to be slightly lower in ZPE corrected energy by 0.11 kcal/mol, while the σ -type complex is lower in energy by 0.09 kcal/mol at MP2/aug-cc-pVDZ level of theory [22]. Ajay chaudhari and Shyi-Long Lee using DFT/6-31+G(d) level of

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theory studied the interaction of CH_3CN with one, two, and three water molecules. For the 1:1 $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ complex, it was found that the cyclic structure is less stable than open structure [23].

Canuto et al. performed *ab initio* computations on the $\text{CH}_3\text{CN} \cdots \text{H}_2\text{O}$ complex to obtain the structure, vibrational frequencies, Rayleigh and Raman activities including light scattering depolarization and binding energies. All the theoretical models showed shortening of the CN distance, leading to a blue shift of around $\sim 15 \text{ cm}^{-1}$ in the CN stretching mode. In the Raman spectrum, the depolarization due to the intense CN stretching vibration was increased by 20% after the hydrogen bond formation. Further, there was a large red shift of 75 cm^{-1} in the OH mode of water, which leads to intensification of the Raman scattering activity [24].

Bako et al. [25] investigated the structure of $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ mixture using *ab initio* computations, molecular dynamics and X-ray diffraction techniques. Computations showed two types of complexes; (a) H-bonded complex between the nitrogen of CH_3CN and hydrogen of H_2O and (b) CH_3CN and H_2O molecules are in side-by-side anti dipole arrangement. Both the complexes were minima on the potential energy surface, which have nearly the same interaction energy. They also confirmed the formation of microheterogeneity in the $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ system.

Tabata et al. [26] studied the liquid structure of $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ using X-ray diffraction and Infrared technique. They observed due

to the dipole–dipole interaction between water and $\text{CH}_3\text{CN}-\text{H}_2\text{O}$, CH_3CN completely miscible with water at all concentration ratios. Furthermore, they found that $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ and water clusters coexist, as microheterogeneity occurs in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ mixtures.

Chaban studied the interaction of three nitrile molecules, cyanide ($\text{H}_2\text{N}-\text{C}\equiv\text{N}$), CH_3CN and aminoacetonitrile ($\text{H}_2\text{N}-\text{CH}_2-\text{C}\equiv\text{N}$) with water molecules using second order Moller–Plesset perturbation theory with triple- ξ basis sets. For the $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ system, *ab initio* computations identified two equilibrium geometries. The lowest energy complex was the one where the hydrogen of water molecule is bound to the $\text{C}\equiv\text{N}$ end of the nitrile molecule through hydrogen bond and the second complex has two weak hydrogen bonds between CH_3CN and H_2O [27].

Allamandola et al. studied 16 nitriles and related compounds in Ar and H_2O matrices. The strong $\text{C}\equiv\text{N}$ stretching vibrations of these compounds were probed using vibrational spectroscopy in matrices. They have compared the IR spectra in the $\text{C}\equiv\text{N}$ stretching region of 19 nitriles in Ar and H_2O matrices. They observed two major bands for the CH_3CN molecule in the CN stretching region at 2258.3 cm^{-1} and 2293.0 cm^{-1} in Ar matrix. The low frequency band is assigned to the $\text{C}\equiv\text{N}$ stretching vibration and the high frequency band is due to the combination band produced by the strong vibrational modes at 1376 and 917 cm^{-1} . In contrast, the CH_3CN spectrum in ice matrices is broad and the frequencies were

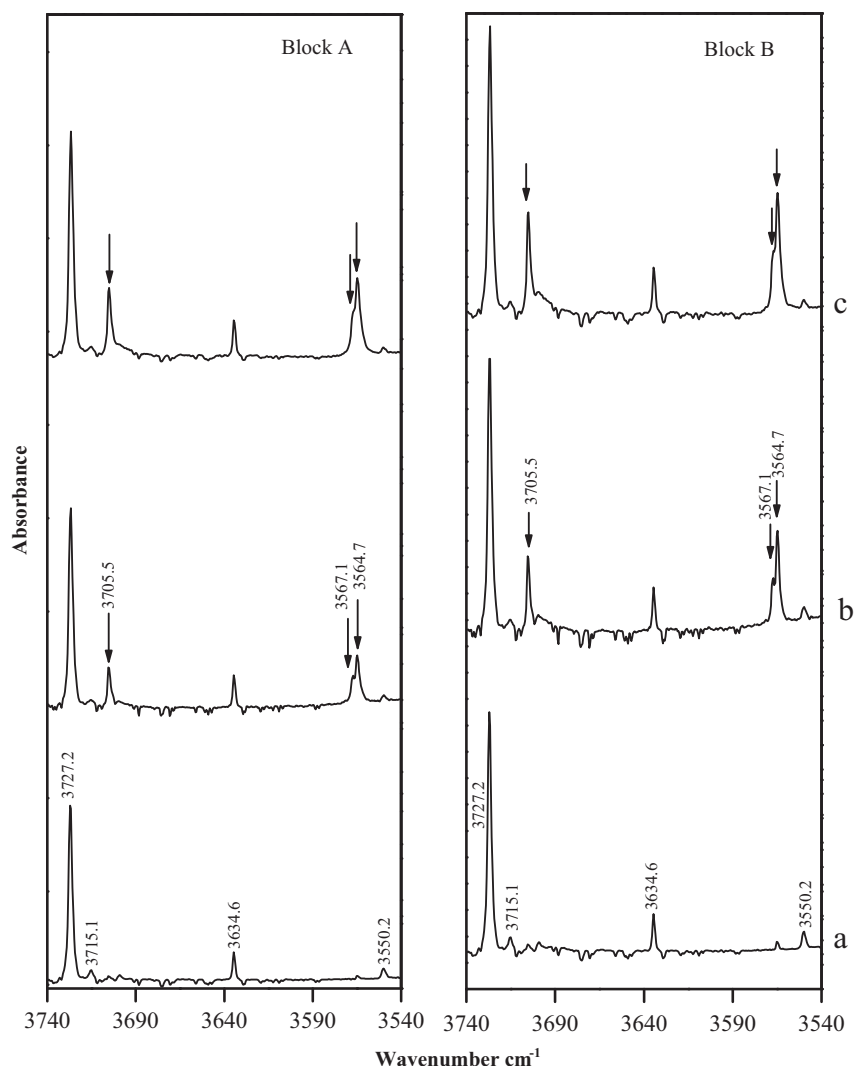


Fig. 1. Spectra of $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ complexes in N_2 matrix in the region $3740-3540 \text{ cm}^{-1}$. Block A shows the as-deposited spectra and block B shows the 30 K annealed spectra. Matrix isolation infrared spectra of various concentrations of $\text{CH}_3\text{CN}/\text{H}_2\text{O}/\text{N}_2$; (a) 0/1/1000; (b) 1/1/1000; (c) 2/1/1000.

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