



# Hydrogen-bonded complexes of acetylene and acetonitrile: A matrix isolation infrared and computational study



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## HIGHLIGHTS

- Experimental evidence for the formation of 1:1 CH<sub>2</sub>...N complex of C<sub>2</sub>H<sub>2</sub>—CH<sub>3</sub>CN.
- The experimental and calculated vibrational wavenumbers agreed well with each other
- Higher 1:2 C<sub>2</sub>H<sub>2</sub>—(CH<sub>3</sub>CN)<sub>2</sub> and 2:1 (C<sub>2</sub>H<sub>2</sub>)<sub>2</sub>—CH<sub>3</sub>CN complexes were also observed.
- The nature of interaction in the complexes was characterized by AIM and NBO analysis.

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## ABSTRACT

Hydrogen-bonded complexes of acetylene (C<sub>2</sub>H<sub>2</sub>) and acetonitrile (CH<sub>3</sub>CN) have been investigated using matrix isolation infrared spectroscopy and *ab initio* computations. The complexes were trapped in both solid argon and N<sub>2</sub> matrices. The structure of the complexes and the energies were computed at the B3LYP and MP2 levels of theory using a 6-311++G(d,p) basis set and also at B3LYP/aug-cc-pVDZ level. Our computations indicated one minimum corresponding to the 1:1 C<sub>2</sub>H<sub>2</sub>—CH<sub>3</sub>CN complex, with C—H...N interaction, where C<sub>2</sub>H<sub>2</sub> is the proton donor. Experimentally, we observed the 1:1 C<sub>2</sub>H<sub>2</sub>—CH<sub>3</sub>CN complex in Ar and N<sub>2</sub> matrices, which was evidenced by the shifts in the vibrational wavenumbers of the modes involving the C<sub>2</sub>H<sub>2</sub> and CH<sub>3</sub>CN sub-molecules. Computations were also performed to study the higher complexes of C<sub>2</sub>H<sub>2</sub> and CH<sub>3</sub>CN. One minimum was found for the 1:2 C<sub>2</sub>H<sub>2</sub>—CH<sub>3</sub>CN complex and two minima for the 2:1 C<sub>2</sub>H<sub>2</sub>—CH<sub>3</sub>CN complexes, at all levels of theory. Experimentally we observed features corresponding to the 1:2 C<sub>2</sub>H<sub>2</sub>—CH<sub>3</sub>CN complexes in an Ar and N<sub>2</sub> matrices. The computed vibrational wavenumbers of C<sub>2</sub>H<sub>2</sub>—CH<sub>3</sub>CN complexes at B3LYP/6-311++G(d,p) level correlate well with the experimental wavenumbers. Atoms in Molecules (AIM) analysis was performed to understand the nature of interaction in the complexes. Natural Bond Orbital (NBO) analysis was performed to understand the effect of charge-transfer hyperconjugative interactions towards the stability of different C<sub>2</sub>H<sub>2</sub>—CH<sub>3</sub>CN complexes.

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## Introduction

Studies of hydrogen-bonded complexes, both experimental and theoretical, are of considerable interest [1–14]. The conventional hydrogen bond (H-Bond) where an X—H bond interacts with Y is represented by X—H...Y. Here X is an electronegative atom and Y with its electrons is a hydrogen bond acceptor and the formation of the H-Bond results in a red-shift of the X—H stretching frequency. There are a number of experimental and theoretical studies on this subject. During the last fifteen years there has been an emphasis on the study of weak hydrogen bonds involving C—H...O,

C—H...π, O—H...π and C—H...N interactions, as these serve as a driving force for many molecular phenomena and processes in chemistry, biology and material science [15]. Our interest in these weak hydrogen-bonded systems led early studies on hydrogen bonded complexes formed by CHF<sub>3</sub>, CHCl<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>H<sub>5</sub>N with C<sub>2</sub>H<sub>2</sub> using matrix isolation infrared spectroscopy in an Ar matrix [16–19].

We have earlier found the experimental evidences for the 1:1 n-σ complex of C<sub>2</sub>H<sub>2</sub> and Pyridine (C<sub>6</sub>H<sub>5</sub>N) in an Ar matrix. The complex is stabilized by C—H...N, where the H-bonded interaction is between the hydrogen of C<sub>2</sub>H<sub>2</sub> and the lone pair of electrons on the nitrogen. *Ab initio* computations at the HF and B3LYP levels of theory using a 6-311++G(d,p) basis set were performed on the C<sub>2</sub>H<sub>2</sub>—NC<sub>6</sub>H<sub>5</sub> complex supported the experimental observations [19].

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Acetonitrile, CH<sub>3</sub>CN has a unique properties such as high dielectric constant and remarkable miscibility with range of ionic and polar solvents [20] which makes CH<sub>3</sub>CN as a solvent of choice for variety of organic synthesis. CH<sub>3</sub>CN is also used as a mobile phase in HPLC and LC–MS. CH<sub>3</sub>CN has been extensively used in synthetic organic chemistry and enormous literature on this area has been reported. Earlier, Freedman and Nixon investigated the infrared spectra of CH<sub>3</sub>CN in solid argon matrix [21]. Later, Kim and Kim re-investigated the vibrational spectra of CH<sub>3</sub>CN using Fourier transform infrared spectra and made precise assignments of monomers, dimers and higher multimers of CH<sub>3</sub>CN [22]. Givan and Loewenschuss studied the Raman spectrum of CH<sub>3</sub>CN using matrix isolation spectroscopy [23]. Coussan et al. studied the CH<sub>3</sub>OH–CH<sub>3</sub>CN complexes trapped in Ar and N<sub>2</sub> matrices. On photolysis, they observed both hydrogen-bonded homo and hetero aggregates of methanol in these matrices. Further, these aggregates are better formed in an Ar than in N<sub>2</sub> matrix [24]. Kryachko and Nguyen theoretically studied the hydrogen-bonded complexes of phenol and CH<sub>3</sub>CN [25]. The computational results were correlated well with the experiments [26–29]. From the computations they predicted phenol and CH<sub>3</sub>CN forms 1:1  $\sigma$  and  $\pi$ -type complexes, where the former is more stable than the later. The  $\pi$ -type structure becomes more stable when one more acetonitrile molecule interacts with 1:1 phenol-acetonitrile complex. Phillips et al. studied the vibrational spectra of CH<sub>3</sub>CN–BF<sub>3</sub> complexes in solid argon [30]. Later, Shimizu et al. studied the matrix effects on the vibrational spectra of the CH<sub>3</sub>CN–BF<sub>3</sub> complex in solid matrices of Ar, N<sub>2</sub>, and Xe [31].

Doo-sik Ahm and Sungyul Lee computationally studied the  $\sigma$ - and  $\pi$ -type hydrogen-bonded complexes of acetonitrile–water clusters. They found at MP2/6-31+G(d,p) level of theory the  $\pi$ -type complex is slightly lower in ZPE corrected energy by 0.11 kcal/mol, while the  $\sigma$ -type complex is of lower energy by 0.09 kcal/mol when MP2/aug-cc-pVDZ level of theory is employed [32].

Mixtures of CH<sub>3</sub>CN and water are popular solvents and has been studied extensively both experimentally and theoretically [33–38]. Rutkowski et al. studied the formation of 1:1 complexes between acetylene and trimethylamine in liquefied krypton solvent. They observed red shift in the C–H region and blue shift in the CN stretching region in the complex. The experimental wavenumbers were correlated with MP2/6-311++G(2d,2p) level of theory [39]. Domagala and Gabrowski performed *ab initio* computations on the hydrogen-bonded complexes between hydrogen cyanide (HCN)·HF and acetylene (C<sub>2</sub>H<sub>2</sub>)·HF using B3LYP and MP2 levels of theory with 6-311++G(d,p) basis set. They found that  $\pi$ -electrons of acetylene act as a proton accepting centers and the C<sub>2</sub>H<sub>2</sub>·HF complex forms a T-shaped structure whereas in the HCN·HF complex, the nitrogen atom in the hydrogen cyanide molecule acts as the proton acceptor center but not  $\pi$ -electrons [40]. Ault et al. reported photochemical reaction of CH<sub>3</sub>CN with CrCl<sub>2</sub>O<sub>2</sub> and OVCl<sub>3</sub> and the product was trapped in an Ar matrix. The formation of 1:1 complex was identified using UV/Vis spectroscopy. When the matrix was irradiated with light of  $\lambda > 300$  nm, new features in the infrared spectra was observed and assigned for ONCCH<sub>3</sub> complexes of CH<sub>3</sub>CN n-oxide with CrCl<sub>2</sub>O and VCl<sub>3</sub>, respectively. Identification of these species was supported by extensive isotopic labeling (<sup>2</sup>H and <sup>15</sup>N), as well as by B3LYP/6-311++G(d,2p) density functional calculations [41]. Suzuki et al. studied the 1:1 hydrogen-bonded complexes of acetonitrile with BF<sub>3</sub> in Ar, N<sub>2</sub> and Xe matrices. The experimental observed shift agreed well the calculation performed at B3LYP/6-311++G(d,p) level of theory [42]. Samet et al. studied the C–H···N hydrogen-bonded complexes of penta-chlorocyclopropane (PCCP) with the bases acetonitrile, ammonia, monomethyl amine and dimethyl amine isolated in argon matrices at 10 K. Both IR spectroscopy and DFT computations supported the formation of 1:1 complexes between PCCP with different bases

which was evidenced from the shift in the vibrational modes of PCCP and base sub-molecule [43].

Allamandola et al. studied 16 nitriles and related compounds in Ar and H<sub>2</sub>O matrices. The strong C≡N stretching vibrations of these compounds are probed using vibrational spectroscopy in matrices. The absorption band of these nitriles in Ar and H<sub>2</sub>O matrices are then used to facilitate the search for these features observed by Infrared Space Observatory (ISO) [44]. Several groups studied the C–H···N interactions both by experimental and theoretical methods [45–48]. Recently, Zins and Krim studied the formation of 1:1 complex between Acetonitrile (CH<sub>3</sub>CN) and formic acid (HCOOH) in neon matrix. The formation of the 1:1 complex is evidenced in the modes corresponding to the formic acid and acetonitrile sub-molecules. *Ab initio* computations performed at MP2/6-31++G(d,p) and MP2/aug-cc-pVTZ level of theories gave one minima for the 1:1 and 2:1 complex and two minima for the 1:2 complex. Experimentally, they also observed 2:1 and 1:2 CH<sub>3</sub>CN–HCOOH complexes in Ne matrix. Further, they have photolysed the Ne matrix using VUV photons. The photochemical reaction induces the formation cyanomethanoic acid [49].

To best of our knowledge there is no matrix isolation infrared studies on the C<sub>2</sub>H<sub>2</sub> with CH<sub>3</sub>CN system. CH<sub>3</sub>CN has two electron rich sites, lone pairs on nitrogen and C≡N triple bond, which can form either a  $\sigma$ - or  $\pi$ -type hydrogen bond or both. Acetylene (C<sub>2</sub>H<sub>2</sub>) acts as a proton donor as the hydrogen attached to the 'sp' carbon atom is sufficiently acidic. Alternatively, C<sub>2</sub>H<sub>2</sub> can also play the role of a proton acceptor through its  $\pi$ -cloud. It is interesting to study the interaction between the C<sub>2</sub>H<sub>2</sub> and CH<sub>3</sub>CN and to see the competing ability of CH<sub>3</sub>CN and C<sub>2</sub>H<sub>2</sub> as proton donors and acceptors. The present work is carried out with an aim to explore the possibility of forming 1:1 complexes between C<sub>2</sub>H<sub>2</sub> and CH<sub>3</sub>CN in Ar and N<sub>2</sub> matrices and to correlate with the computational results. We also explored the formation of higher C<sub>2</sub>H<sub>2</sub>–CH<sub>3</sub>CN complexes both computationally and experimentally.

## Experimental and computational methods

Matrix isolation experiments were performed using a RDK-408D2 (Sumitomo Heavy Industries Ltd.) closed cycle helium compressor cooled cryostat. The cryostat was housed in a vacuum chamber where the base pressure was  $< 1 \times 10^{-6}$  mbar. C<sub>2</sub>H<sub>2</sub> (Commercial Grade, Asiatic Oxygen Limited, India) and CH<sub>3</sub>CN (Merck, HPLC grade 99.8%) were used as such, without further purification. Ar and N<sub>2</sub> (IOLAR Grade 2) is used as matrix gases, in which C<sub>2</sub>H<sub>2</sub> were pre-mixed to obtain the desired matrix-to-sample ratios. The C<sub>2</sub>H<sub>2</sub>/matrix gas mixture and CH<sub>3</sub>CN was then deposited using double jet nozzle onto a KBr substrate maintained at 12 K. We used typical matrix-to-sample ratios ranging from 1000:0.1 to 1000:0.2 for C<sub>2</sub>H<sub>2</sub> and 1000:1 to 1000:2.5 for CH<sub>3</sub>CN. The matrix was then deposited at a typical rate of  $\sim 3$  mmol/h and a deposition typically lasted for about 60 min.

Infrared spectra of the matrix isolated samples were recorded in the range 4000–400 cm<sup>-1</sup>, using a BOMEM MB 100 FTIR spectrometer, operated at a resolution of 1 cm<sup>-1</sup>. The matrix was then slowly warmed to 35 K for Ar and 30 K for N<sub>2</sub> which was maintained at this temperature for about 15 min and then re-cooled to 12 K. Spectra of the annealed matrix were again recorded.

Theoretical calculations were performed for the C<sub>2</sub>H<sub>2</sub>–CH<sub>3</sub>CN complexes using GAUSSIAN 94W suite of programs package running on a Pentium 4 machine with 3.0 GHz processor [50]. Geometries of the precursor molecules were first optimized at B3LYP and MP2 levels of theory using 6-311++G(d,p) basis set and also at the B3LYP level using aug-cc-pVDZ basis set. Starting from the optimized monomer geometries, the geometry of the 1:1 complexes was then optimized without imposing any constraints. Calculations

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