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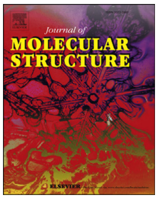

Does a hydrogen bonded complex with dual contacts show synergism? A matrix isolation infrared and *ab-initio* study of propargyl alcohol–water complex

Jyoti Saini, K.S. Viswanathan*

Department of Chemical Sciences, Indian Institute of Science Education and Research, Mohali 140306, India

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When hydrogen bonded complexes are formed with more than one contact, the question arises if these multiple contacts operate synergistically. Propargyl alcohol-H_2O complex presents a good case study to address this question, which is discussed in this work. Complexes of propargyl alcohol (PA) and H_2O were studied experimentally using matrix isolation infrared spectroscopy, which was supported by quantum chemical computations performed at the M06-2X and MP2 level of theories, using 6-311++G (d,p) and aug-cc-pVDZ basis sets. A 1:1 PA-H_2O complex was identified in the experiments and corroborated by our computations, where the PA was in the gauche conformation. This complex, which was a global minimum, showed dual interactions, one of which was an n-σ interaction between the O–H group of PA and the O of H_2O, while the second was a $H\cdots\pi$ contact between the O–H group of H_2O and the π system of PA. We explored if the two interactions in the 1:1 complex exhibited synergism. We finally argue that the two interactions showed antagonism rather than synergism. Our computations indicated three other local minima for the 1:1 complexes; though these local minima were not identified in our experiments. Atoms-in-molecules and energy decomposition analysis executed through LMO-EDA were also performed to understand the nature of intermolecular interactions in the PA-H_2O complexes. We have also revisited the problem of conformations of PA, with a view to understanding the reasons for gauche conformational preferences in PA.

1. Introduction

Propargyl alcohol (PA) has been considered as a possible candidate molecule for detection in interstellar medium and has therefore been a subject of intense study [1]. It has also been popular as a probe for the study of both gas phase ion chemistry and surface chemistry on dust grains [1]. The isomer of PA, propenal, has been identified in the interstellar region [2], which therefore renders this molecule of astrochemical interest. Interestingly, the energy difference between the gauche+ and gauche- conformers of PA in the submillimetre region allows for a sensitive detection of this molecule in various interstellar sources [1].

The molecule also has interesting implications in combustion chemistry, as two propargyl radicals combine to yield benzene, which eventually can provide a route for the production of polycyclic aromatic hydrocarbons (PAHs) [3,4]. Tranter et al. using shock-tube experiments studied the kinetics of the reaction [5].

$$C_3H_3 + C_3H_3 \rightarrow C_6H_6 \rightarrow PAH \rightarrow soot$$

The conformations of PA arise from the internal rotation of the C–OH group in PA, which results in two conformations: the gauche (g-PA) and the trans (t-PA) form [6]. Calculations at the CCSD(T)-F12/VDZ-F12 level of theory [7] indicated the g-PA to be the lower energy conformer, with the higher energy trans structure (t-PA) being about 6.7 kJ/mol above g-PA. Hirota proposed that the intramolecular hydrogen bond between the –OH group and π electrons, was the reason for the g-PA being the ground state conformer [8]. Subsequent atoms-in-molecules (AIMs) investigations did not support this explanation [9], as it was shown that there did not exist any bond critical point between the two functional groups mentioned above.

There have been previous experimental microwave [6,10] and infrared (IR) studies on PA [11]. The microwave spectrum of PA has

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* Corresponding author.
E-mail address: vish@iisermohali.ac.in (K.S. Viswanathan).

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confirmed the occurrence of only the g-PA [6,7]. Similarly, for propargyl thiol (C_3H_4S) [12-15] and propargyl selenol (C_3H_4Se) [16], only the g-PA conformer has been observed.

We have studied PA in an effort to understand its conformational preferences using matrix isolation infrared spectroscopy and *ab initio* computations. No study exists on this molecule using matrix isolation spectroscopy, a technique ideally suited for the study of conformations [17,18]. *Ab initio* computations were performed to obtain the structures of the conformers and their vibrational features. Natural bond orbital (NBO) analysis was also performed.

Complexes of PA also pose interesting questions, given that the molecule presents a number of sites for weak non-covalent interactions. Arunan and group have reported the pure rotational spectra of Ar···PA complex [6], which was the first study on any weakly bound complex of PA. In this work, we have explored the 1:1 hydrogen bonded complexes of PA-H_2O, using matrix isolation infrared spectroscopy and *ab initio* computations. Atoms-in-molecules (AIMs) and LMOEDA analysis were done to study the nature of bonding in complex.

2. Experimental details

Matrix isolation experiments were performed using a Sumitomo closed cycle helium compressor-cooled cryostat (HC-4E1) to attain a temperature of 12 K. The experimental details have been described elsewhere [17-21].

Specifically in this experiment, N_2 (Sigma Gases and Services 99%) and Ar (Sigma Gases and Services 99%) were used as matrix gases. PA (Sigma Aldrich 99%) and H_2O (Millipore) was used without further purification and subjected to several freeze-pump-thaw-cycles before use. The sample-matrix gas mixture was prepared at the desired ratio using standard manometric procedures as described in the references mentioned above.

Once the sample and matrix gas were deposited at 12 K, the spectra of the matrix isolated species were recorded using a Bruker Tensor 27 FTIR spectrometer, operating at a resolution of 0.5 cm^{-1}. After recording the spectrum, the matrix was warmed to ~30 K (for N_2 matrix) and ~35 K (for Ar matrix), maintained at this temperature for about 30 minutes using a heater-temperature controller unit and recooled to ~12 K. The spectrum of the annealed matrix was again recorded.

3. Computational details

The Gaussian-09 suite of programs [22] was used to compute the optimized geometries of PA. All computations were performed at M06-2X and MP2 level of theory, using 6-311++G(d,p) and aug-cc-pVDZ basis sets. In the study of the PA-H_2O complexes, the geometries of the monomers were first optimized. Using the optimized monomer geometries, the geometries of PA-H_2O complexes were obtained. Vibrational frequency calculations were performed on the optimized structures of the monomers and the complexes, to confirm that the computed geometries did correspond to minima on the potential surface. The vibrational frequency calculations were used to assign the vibrational features observed in the experiments. The computed vibrational frequencies for different complexes were scaled on a mode-by-mode basis, by comparing the computed frequencies of the *monomeric* species, PA and water, with the observed experimental frequencies, in a given matrix, bringing them in agreement with experimental vibrational frequencies. The scaling factors thus derived from the spectra of the monomers, were then used in the analysis of the spectra of the complexes. The matrix perturb the modes in diverse spectral regions differently; and thus for these systematic differences, we have used a varying mode-by-mode scaling [23,24].

The MP2 level frequencies matched very closely with our experimental frequencies, and hence we have used the frequencies computed at the MP2/aug-cc-pVDZ level to compare with our experiments.

The energies of the complexes and the monomers were used to arrive at the interaction energies of the complexes. These interaction energies were corrected separately for BSSE (basis set superposition error), using Boys and Bernardi's counterpoise method [25] and ZPE (Zero point energies). AIM2000 [26] was used to perform analysis on the charge density topology. This method proves to be very useful in identifying and characterizing hydrogen bonding interaction in PA-H_2O complexes.

We will first present our results on PA and its conformers, and then discuss our results on the PA-H_2O hydrogen bonded complexes.

4. Results – PA conformers

Even though the study of conformers of PA has been reported in the literature, we have revisited this problem in an effort to understand the reasons for the conformational preferences in PA. Experiments were performed using both Ar and N_2 matrices, and the results in the two are comparable. We discuss only the results of our experiments using N_2 matrix since the spectral features in the N_2 matrix were sharper than that obtained in the Ar matrix.

4.1. Experimental

Fig. 1 shows the infrared spectra of PA in N_2 matrix, over the spectral region 3750-2850 cm^{-1} corresponding to the O–H stretch, ≡C–H stretch and symmetric CH_2 stretch, 1420-1370 cm^{-1} corresponding to the (CH_2 wag + O–H bend), 1060-1020 cm^{-1} corresponding to the C–O stretch in PA and 690-620 cm^{-1} where the bending modes of PA occur, as shown in Table 1.

As discussed in an earlier section, scaling factors mentioned as a footnote in Table 1 were calculated so as to bring to agreement, the experimental and computed wavenumber of vibrational modes of the gauche conformer of PA. For example, the factor 0.9548 for the region of the O–H stretch was obtained by dividing the experimental feature at 3641.9 cm^{-1} of PA with the computed feature at 3814.4 cm^{-1} corresponding to the O–H stretch in PA. Similarly, the C–O stretch and ≡C–H bend ⊥ to C–C–O plane were respectively used to obtain the scaling factors 0.9852 and 1.139 for the relevant regions of the spectra.

Table 1 gives the optimized structures and assignment of the vibrational modes of conformers of PA observed in our experiments. Strong features of PA are observed at 3641.9, 3311.0, 2926.1/2881.2, 1040.8, 669.4 and 644.0 cm^{-1}.

4.2. Computational

Computations performed at M06-2X and MP2 levels of theory, using 6-311++G(d,p) and aug-cc-pVDZ basis sets indicated the *gauche* conformer of PA (g-PA) to be the ground state conformer. At all the above levels of theory, the gauche conformer optimized to two equivalent minima, corresponding to the CCOH dihedral angles of nearly ±50°. The trans conformer, with the CCOH dihedral angle of 180°, optimized to a minimum at all the levels of computation mentioned above, except at the MP2/6-311++G(d,p) where this structure was indicated to be a saddle point. This saddle point connected two degenerate local minima with CCOH dihedral angles of ±163°, which are therefore referred to as near-trans structures, as indicated in Table 2. The energy barrier for the interconversion of these two equivalent near-trans MP2/6-311++G(d,p) structures