J. Phys. Chem. A **2005,** *109,* 9499−9506

Observation of the π···H Hydrogen-Bonded Ternary Complex, $(C_2H_4)_2H_2O$, Using Matrix Isolation Infrared Spectroscopy

Matthew G. K. Thompson,[†,‡] Errol G. Lewars,[‡] and J. Mark Parnis*[,†,‡]

Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6, and Department of Chemistry, Trent University, Peterborough, Ontario, Canada, K9J 7B8

Received: June 27, 2005; In Final Form: August 22, 2005

FTIR absorption spectra of water-containing ethene:Ar matrices, with compositions of ethene up to 1:10 ethene:Ar, have been recorded. Systematically increasing the concentration of ethene reveals features in the spectra consistent with the known 1:1 ethene:water complex, which subsequently disappear on further increase in ethene concentration. At high concentrations of ethene, new features are observed at 3669 and 3585 cm^{-1}, which are red-shifted with respect to matrix-isolated ν_3 and ν_1 O−H stretching modes of water and the 1:1 ethene:water complex. These shifts are consistent with a π···H interaction of a 2:1 ethene:water complex of the form (C_2H_4···H−O−H···C_2H_4). The analogous $(C_2D_4)_2H_2O$ complex shows little shifting from positions associated with $(C_2H_4)_2H_2O$, while the $(C_2H_4)_2D_2O$ isotopomer shows large shifts to 2722.3 and 2617.2 cm^{-1}, having identical $\nu_3(H_2O)/\nu_3(D_2O)$ and $\nu_1(H_2O)/\nu_1(D_2O)$ values when compared with monomeric water isotopomers. Features at 3626.1 and 2666.2 cm^{-1} are also observed and are attributed to $(C_2H_4)_2HDO$. DFT calculations at the B3LYP/6-311+G(d,p) level for each isotopomer are presented, and the predicted vibrational frequencies are directly compared with experimental values. The interaction energy for the formation of the 2:1 ethene:water complex from the 1:1 ethene:water complex is also presented.

Introduction

The chemistry of the water molecule is quite diverse, owing to the relatively high electron density of the O atom and the high polarity of the O−H bonds in the molecule. The combination of these two factors makes water a molecule which can act as a hydrogen bond donor, hydrogen bond acceptor, or sometimes both with appropriate complementary molecules. Thus, understanding the intermolecular interactions of water with other molecules is of critical importance in appreciating fully the chemistry of water.

The interaction of water with hydrocarbons containing π electrons is of particular interest. The nature of such systems serves as an important prototype for understanding similar molecular interactions in biological systems, wherein both water and π systems are simultaneously abundant. Since the infrared spectra of water and the water dimer in inert gas matrices are well-known,[1−5] complexes of these water species with other molecules can be studied by observing changes in corresponding infrared spectra. Specifically, the positions of the ν_1 and ν_3 O−H stretching bands in the infrared spectrum of water are sensitive to complexation with additional molecules, and shifts from the fundamental absorption position of these bands have been used as a means of observing hydrogen-bonded complexes of water both as a hydrogen bond donor,[3−11] and as a hydrogen bond acceptor through lone pairs on the oxygen atom.[6,7,9] When water acts as a hydrogen bond donor, the positions of the ν_1 band red shifts significantly (50−200 cm^{-1}) and similarly the ν_3 band red shifts less significantly (~25 cm^{-1}), while the ν_2 band shifts to blue (10−30 cm^{-1}). In each case, the magnitude of the shift varies with the strength of hydrogen bonding interaction. In contrast, as a hydrogen bond acceptor (or lone pair donor), there is still a trend corresponding to the strength of the interaction with the complex partner; however, the shifts of the positions of the vibrational modes of water are much less significant (~1−15 cm^{-1}), and, depending on the specific case, either blue or red shifts can be observed.[7]

Complexes involving water acting as a hydrogen bond donor to the π-bond of various different unsaturated hydrocarbons have been observed by infrared spectroscopy in inert gas matrices on several occasions.[7−9,12−14] The simplest water complex with an unsaturated hydrocarbon is that of water with ethene, a system which has been explored numerous times computationally,[15−19] and experimentally.[7,12,20,21] Engdahl and Nelander reported the first infrared spectrum of the complex in an argon matrix and estimated both its structure and binding energy.[7] For the interaction of water with unsaturated hydrocarbons, the general trend is for water to align the polar O−H bond toward the center of the C═C bond. Cooperative effects contribute to the lengthening and polarization of the O−H bonds involved in water, as well as the C═C bond of the hydrocarbon, with additional contributions and considerations for substituents bonded on the C═C bond. The impact of π···H complexation of water and an unsaturated hydrocarbon is 2-fold: First, the oxygen atom in the water molecule is slightly more susceptible to further hydrogen bonding, and second the uncomplexed H atom is slightly less acidic, both when compared to the corresponding atom in a "free" water monomer. All studies which involve complexation of the water molecule, beyond the first complexation, have examined further hydrogen bonding with the oxygen atom as an acceptor, and thus there are many studies involving the water dimer with unsaturated hydrocarbons.[7,17,22] There is also at least one example of a water monomer in a ternary complex, under conditions of matrix

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* To whom correspondence should be addressed. E-mail: mthompso@trentu.ca, elewars@trentu.ca, mparnis@trentu.ca.

[†] Queen's University.

[‡] Trent University.

10.1021/jp053495t CCC: $30.25

isolation, which involves combinations of water, ethene, and hydrogen chloride.[9] However, there have been no studies exploring the further interaction of the uncomplexed H atom in a binary water−hydrocarbon complex, and this work is the first example of the observation of such a complex. Specifically, we present infrared and computational evidence for the formation of the complex $(C_2H_4)_2H_2O$, where the π cloud of each of the two ethene molecules interacts with an O−H bond of water. Furthermore, we propose a stepwise reaction scheme in which the formation of the 2:1 ethene:water complex is formed by the combination of the 1:1 ethene:water complex with ethene.

Experimental and Computational Details

Unless otherwise specified, matrices formed in this work employed argon (99.995%, Matheson) as the matrix support gas. Matrices were deposited on a KBr spectroscopic window (4000−400 cm^{-1} infrared transparency) with the temperature of the window maintained at approximately 16K or lower during deposition. Temperature was controlled using a closed-cycle helium refrigeration unit (APD Displex), in all experiments. Base pressures in the experimental region varied between 10^{-6} and 10^{-8} Torr. Unless otherwise specified, matrices were formed over 1.5 h deposition times with deposition gas flow rates of 0.5 standard cubic centimeters per minute (sccm), or approximately 1.2 mmol total gas deposited per hour. All spectra were collected over the region 4000−400 cm^{-1} using a BOMEM Michelson MB-102 Fourier transform infrared (FTIR) absorption spectrometer which was modified to house the matrix isolation apparatus. Gas mixtures were prepared on the basis of partial pressures using standard techniques. Reagents used include ethene, C_2H_4 (C.P grade, Matheson), which contained trace water as an impurity. In some experiments, this ethene was used only after freeze-drying the ethene using a copper coil cooled in a methanol-slush bath held well below the freezing point of water. The dried C.P. ethene had water levels similar to those present when we employed U.H.P. ethene (99.99%, Sigma Aldrich). To confirm the presence of water in our identified spectra, additional water was added to some experiments as noted in the text. For isotopic experiments we used perdeuterioethene (99.9% atom D, C/D/N Isotopes, Quebec, Canada) and also D_2O (99.5% atom D, Sigma/Aldrich) without further purification.

Density functional theory calculations were performed in order to identify the molecules observed in our matrices. We employed the B3LYP method[23,24] using Gaussian 98.[25] Each calculation was performed using the 6-311+G(d,p) basis set, ensuring tighter convergence requirements due to the use of diffuse (+) functions on the atoms. While it is not possible to know that a global minimum has been obtained in all cases, several input geometries were used to explore this system thoroughly. The structures reported below are those of lowest energy obtained by optimization of the input structures. For all optimized calculations, vibrational analysis of the resultant frequencies was used to ensure final reported structures are minima and not saddle points. Where reported, energies of each species have been corrected for zero-point energy and also corrected for basis set superposition error (BSSE) using the counterpoise method of Boys and Bernardi.[26]

From the line spectra and relative intensity data generated by the Gaussian 98 program, the representations of the IR spectra were generated using the SWizard program, revision 4.1,[27] using the Lorentzian model. The half-bandwidths, $\Delta_{1/2,I}$, were taken to be equal to 15 cm^{-1}.

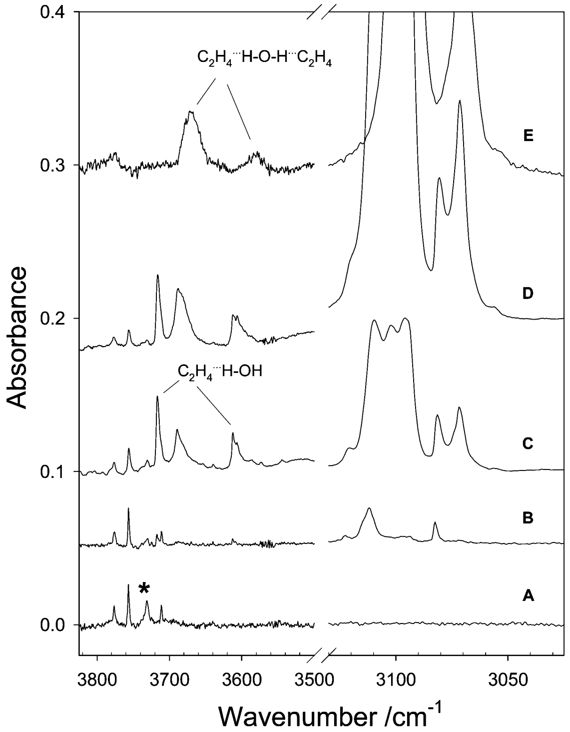

Figure 1. FTIR absorption spectra in the O−H and C−H stretching regions for argon matrices containing: (A) H_2O:Ar, 1:1000, (3 h deposit) (B) ethene:Ar, 1:1000, (C) ethene:Ar, 1:100, (D) ethene:Ar, 1:50 and (E) ethene:Ar, 1:10. The peak marked with an asterisk (*) denotes the absorption associated with nonrotating matrix-isolated water. This feature is used as the reference feature for determining complexation shifts.

Experimental Results

Concentration Variation Experiments. Portions of the Fourier transform infrared (FTIR) spectrum in the C−H and O−H stretching region are given in Figure 1, for argon matrices containing various concentrations of ethene (C_2H_4) and water. The bottom spectrum (labeled A) is the infrared absorption spectrum of water (H_2O) in argon with no ethene present, for which the four lines at 3776.4, 3756.6, 3731.3, and 3711.1 cm^{-1} are the only major absorptions in the O−H stretching region. Of these four bands, the band at 3731.1 cm^{-1} (labeled with *) corresponds to the nonrotating matrix-isolated water monomer,[1,2] while the remaining three correspond to known rovibrational lines associated with the lowest states of a rotating water molecule.[2] The spectrum labeled B is that of an argon matrix containing ethene at a concentration of 1:1000 ethene:Ar. Major lines occur in this spectrum in three separate groups: Group I: 3776.1, 3756.5, 3730, 3711.0, Group II**:** 3111.2, 3082.5, 2995.9, 1888.5, 1440.4, 947.5, and Group III: 3717.3, 3612.7, 959.3 cm^{-1} (959.3 cm^{-1} not shown in figure). Group I appears as in spectrum A, at known wavenumber values attributed to water molecules isolated in argon.[2] The features of Group II correspond to the major absorptions of ethene in an argon matrix.[28,29] Finally, Group III have also been previously observed by Engdahl and Nelander and correspond to a 1:1 ethene-water $\pi\cdots H$ complex.[7] In Figure 1, spectrum C is that of an argon matrix containing ethene at a concentration of 1:100 ethene:Ar. All of the previously mentioned vibrational mode absorptions, characteristic of ethene in Ar, grow in accordance with the 10-fold ethene concentration increase. Features corresponding to higher-order ethene species (ethene dimer, trimer, etc.) also appear in this spectrum.[29] Additionally, it is obvious in these spectra that the amount of background water increases with increasing ethene concentration, suggesting the original ethene source (C.P. grade ethene) contained water as an impurity. Nevertheless, the group of features corresponding to the 1:1 ethene:water complex, observed at 3716.6, and 3612.4 along with the blue-shifted shoulder on the ν_7 mode of ethene at 960.3 cm^{-1}, are again present with increased intensity. Another set of features are observed in the spectrum at 3689.2 (broad) and 1904.5 and have been tentatively assigned previously by Engdahl and Nelander as $C_2H_4(H_2O)_2$.[7] For the spectrum labeled D, the concentration of ethene in argon is 1:50. At this concentration there is an almost complete absence of nonrotating matrix-isolated water, although the 1:1 ethene:water complex is present. Additionally, small growth is observed as shoulders, shifting to the red, on the features near 3680 and 3600 cm^{-1}. Finally, in the spectrum labeled E, the ethene concentration is further increased in the argon matrix to a ratio of 1:10 ethene:Ar. The absorptions of uncomplexed matrix-isolated water, and of the 1:1 ethene water complex are totally absent from this spectrum. Two broad features, present as shoulders in 1:50 spectra, now appear strongly in the O−H stretching region at 3669.8 (s), and 3585.4 (m) cm^{-1}. As described in further detail in the discussion below and with the support of theoretical results presented in the following section, we assign these two modes as the respective ν_3 and ν_1 stretching modes of a water molecule hydrogen-bonded through the two O−H bonds to the π-clouds of two different ethene molecules, (i.e. $(C_2H_4)_2H_2O$) or $C_2H_4\cdots H-O-H\cdots C_2H_4$). Note, for convenience of reference, we have preserved the nomenclature of the ν_3 (asymmetric O−H) and ν_1 (symmetric O−H) stretches of a water monomer, as our discussion (below) shows that the water molecule in this complex behaves similarly to the water monomer.

Since we note that the water in most samples was present as a contaminant from the original precursors, we have also formed matrices of argon containing ethene (ethene:Ar 1:10) in which the concentration of water has been augmented by direct inclusion of H_2O, or depleted by freezing out H_2O as ice. In these control experiments, increasing the relative water concentration increases the strength of the absorptions at 3669.8 and 3585.4 cm^{-1}, and correspondingly decreasing the water present in the sample has the effect of diminishing those same features, implicating water directly in this species.

Isotopic Substitution Experiments. Figure 2 shows portions of the O−H and C−H/O−D stretching regions of the infrared spectrum of argon matrices containing isotopomers of water and ethene. The bottom spectrum is that of C_2H_4:Ar containing H_2O, which has been described above. The middle spectrum is that of an analogous water containing matrix formed with perdeuterioethene C_2D_4:Ar in a ratio of 1:10. In this spectrum, features appear with similar broad structure and relative intensity profiles at 3664.2 and 3578.0 cm^{-1}, shifted only slightly from the matrix formed with C_2H_4/H_2O. The topmost spectrum is that of an argon matrix containing C_2H_4 (1:10 C_2H_4:Ar) in which D_2O has been included. Since H_2O is present as a background species, the equilibrium for H/D exchange of D_2O/H_2O ensures that this sample must also contain some HDO which cannot be avoided under our experimental setup. In this spectrum, four new features appear in the O−H and O−D stretching regions at 3626.1, 2722.3, 2666.2, and 2617.2 cm^{-1}. On the bases of hydrogen/deuterium exchange, relative intensity profiles and density functional theory calculations (as discussed below), we have assigned these four bands to the two isotopomers of the ethene:water 2:1 hydrogen-bonded complex. The absorptions at 3626.1 and 2666.2 are assigned, respectively, as the O−H stretch (ν_{O-H}) and the O−D stretch (ν_{O-D}) of an HDO molecule hydrogen bonded to two different ethene molecules (i.e. $C_2H_4\cdots H-O-D\cdots C_2H_4$). Similarly, the bands at 2722.3 and 2617.2 cm^{-1} are assigned to the ν_3 and ν_1 bands of D_2O that is hydrogen bonded through its O−D bonds to the π-clouds of two different ethene molecules. (i.e. $C_2H_4\cdots D-O-D\cdots C_2H_4$).

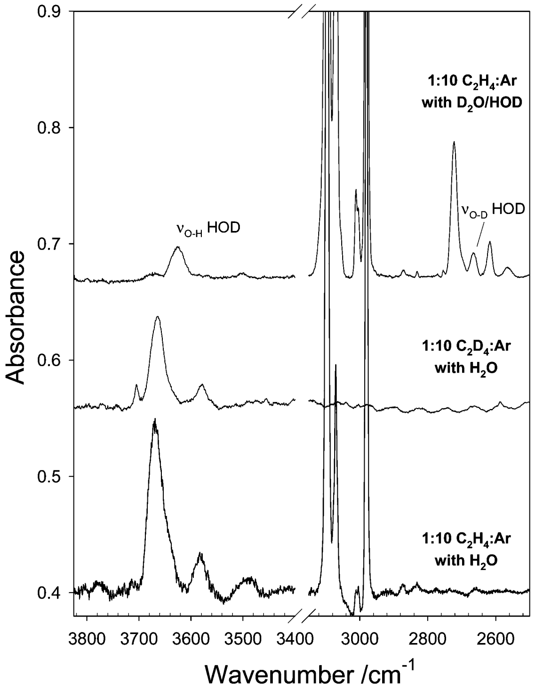

Figure 2. FTIR absorption spectra in the O−H and C−H/O−D stretching regions for argon matrices prepared containing isotopomers of ethene and water. The labeled features ν_{O-H} and ν_{O-D} represent the stretching of an HDO molecule in the 2:1 ethene:water complex.

Thermal Annealing Experiments. The earlier work of Engdahl and Nelander shows that a complex $C_2H_4\cdots H_2O$, called the 1:1 ethene:water complex, appears in matrices when ethene and water are cocondensed at cryogenic temperatures.[7] Our observation of the 2:1 ethene:water under high concentration of ethene, along with the absence of the observation of the 1:1 complex, suggests that the 2:1 complex is formed in a stepwise fashion. Figure 3 shows portions of the infrared spectra in the O−H stretching region for argon matrices containing ethene, at a concentration of 1:50 (ethene:Ar) both before and after annealing to 30K. On deposition, features consistent with both the 1:1 and 2:1 ethene:water complexes appear, with the 1:1 ethene:water complex being dominant. Annealing of the matrix to 28K for 20 min allows the species isolated in argon to slowly diffuse, and the resultant spectrum shows an increase in intensity of the two majors modes associated with the 2:1 ethene:water complex, with a corresponding diminiution of the 1:1 complex. These changes are most clearly seen in the difference spectrum given in Figure 3. Further annealing or irradiation of the matrix gives rise to no observable changes.

Computational Results

Calculations on the structure of the 2:1 ethene water complex were performed using the B3LYP method[23,24,25] with the 6-311+G(d,p) basis set. Of the structures obtained, the optimized structure having the lowest energy is shown in Figure 4. As can be seen from the structure, each of the O−H bonds of the water molecule is hydrogen bonded to the π-cloud of an ethene molecule, thereby producing a structure of the form $(\eta^2\text{-}C_2H_4)\cdots H-O-H\cdots(\eta^2\text{-}C_2H_4)$. In the remainder of the text, this

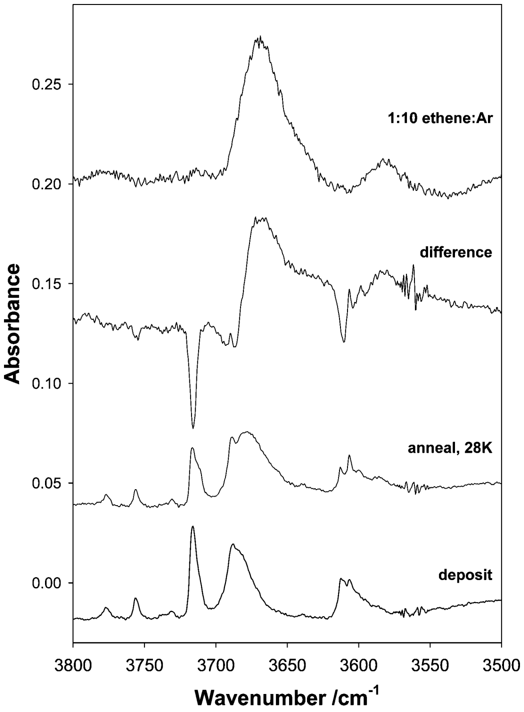

Figure 3. FTIR absorption spectra in the O−H stretching region for argon matrices containing 1:50 ethene:Ar before and after annealing to 28 K. The difference spectrum shows that the features attributed to 1:1 ethene:water complex diminish, with the increase in features attributed to the 2:1 ethene:water complex (shown in the top spectrum). The topmost spectrum is a deposition of 1:10 ethene:Ar, for comparison.

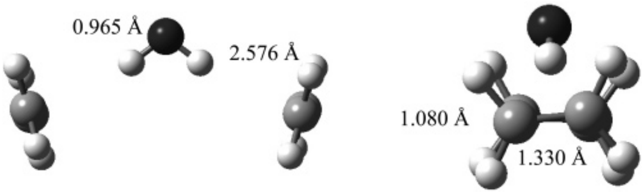

Figure 4. Optimized geometry of the $(C_2H_4)_2H_2O$ complex. The angle of the HOH bond in water is 105.3°, in this complex. The symmetry of the molecule is C_1, but is only very slightly distorted from C_{2v}. The local symmetry of each of the constituent molecules, however, is preserved.

structure shall be referred to as $(C_2H_4)_2H_2O$, for convenience. The bond lengths of the species in the complex are given in Figure 4, and in the complex the HOH bond angle of water is 105.3°. For comparison, the bond lengths in "free" ethene calculated with this method and basis set are: C−H 1.080 Å and C−C 1.320 Å and for "free" water the O−H bond is 0.962 Å and HOH angle 105.0°. For both for water and ethene, the local symmetry of the molecule in the complex is preserved; however, the minimum energy structure obtained has C_1 symmetry overall. It is likely that the true complex has C_{2v} symmetry, but the potential for rotation of ethene around the hydrogen bond is very shallow such that other lower symmetry configurations are virtually identical in energy. Since the differences in these complexes are slight, they would be qualitatively similar species spectroscopically in the infrared region. This last consideration may be the reason the infrared spectra obtained experimentally have such breadth associated with absorption, as the distribution of similar rotamers would be essentially statistical.

The unscaled vibrational wavenumber positions and relative infrared intensities of the 2:1 ethene:water complex, along with corresponding isotopomers and precursors, are presented in Tables 1 and 2. It is important to point out that the predicted normal modes of vibration for the ethene:water 2:1 complex show that the motion associated with water and ethene is essentially preserved after complexation. That is to say, for water modes, ethene motion is negligible upon vibration, and similarly, for ethene modes, water motion is negligible upon vibration. The effect of complexation is predicted to have a larger effect on the vibrational modes of water than on the vibrational modes associated with ethene. This effect can be seen by comparing the shifts of absorption position of the free molecules to the corresponding mode in the complexed molecules using Tables 1 and 2. A spectral representation of the calculated wavenumber positions and relative intensities for water and $(C_2H_4)_2H_2O$, in the O−H stretching region of the infrared spectrum are given with corresponding experimental infrared spectra in Figure 5. In these spectra, it can be seen that both the predicted shift in wavenumber position associated with complexation and the relative intensity of the infrared signal match quite well. Similar spectral representations of the calculated wavenumber positions and infrared intensities for complexation of the isotopes of water, HDO and D_2O, are given along with the corresponding experimental spectra as Figure 6.

Discussion

The results presented above suggest that we have infrared spectroscopic evidence for the $\pi\cdots H$ hydrogen-bonded ternary complex, $C_2H_4\cdots HOH\cdots C_2H_4$. Upon increasing the concentration of ethene in matrices comprised of pure argon (containing water) through to 1:100 (ethene:Ar), there is a progression from matrix-isolated water to the 1:1 ($\pi\cdots H$) $C_2H_4\cdots H{-}OH$ (absorptions at 3716.6, 3612.7 and 959.3 cm^{-1}) complex identified by Engdahl and Nelander.[7] In our work, further increases of ethene concentration (through 1:50 ethene:Ar to 1:10 ethene:Ar) show the features attributed to the 1:1 ethene:water complex progressing through a maximum, along with the appearance of two new broad features at 3669.8 and 3585.4 cm^{-1}. These new features, appearing with the increasing ethene concentration employed in this work, in combination with the disappearance of features attributed to the 1:1 ethene:water complex, suggest that the 1:1 ethene:H_2O species is consumed in the formation of a higher order ethene:water complex. Although the 1:1 ethene:water complex has sites which can either accept a lone pair, or donate electron density to a proton, the excess of the slightly basic ethene present would suggest further complexation at the remaining available O−H bond of the 1:1 ethene:water complex. Thus, features appearing concomitantly with the disappearance of the 1:1 complex would be expected to belong to a complex having the ratio ethene:water = 2:1, as are seen in Figure 3.

In further support of this assignment, we compare the water molecule in the 1:1 ethene:water complex to matrix-isolated water. The ν_3 band of H_2O shifts from 3731 to 3717 cm^{-1} ($\Delta\bar{\nu} = -14$ cm^{-1}), and the ν_1 mode of water at 3638 cm^{-1} shifts to 3612 cm^{-1} ($\Delta\bar{\nu}Z = -26$ cm^{-1}). The magnitude of these shifts suggests that the water molecule is acting as a proton donor in the observed complex.[7] The positions measured for the complex in our experiments represent red-shifts of 62 cm^{-1} for the ν_3 and 52.6 cm^{-1} for the ν_1 with respect to the free water. These shifts are further to the red than the 1:1 complex by 48 and 26 cm^{-1}, respectively, which suggests the water molecule in the 2:1 complex is acting as a proton donor through both O−H bonds. Given the excess of ethene present in the matrix at 1:10 ethene:Ar, it seems likely that the free proton in the 1:1 complex is coordinated with the π-cloud of a second ethene molecule, forming a complex of the form $(C_2H_4)_2H_2O$.

TABLE 1: Unscaled Vibrational Wavenumber Positions Calculated Using B3LYP/6-311+G(d,p) for $\pi\cdots$H Bonded Complex of Water with Ethene (C_2H_4) and Perdeuterioethene (C_2D_4)[a]

C_2H_4	$(C_2H_4)_2H_2O$	H_2O	$(C_2D_4)_2H_2O$	C_2D_4
	14.7		12.4	
	16.5		13.7	
	19.2		17.6	
	55 (0.02)		47.7 (0.01)	
	55.6		47.8 (0.01)	
	69.2		55.7 (0.02)	
	75.7 (0.04)		64.2	
	98		95.1	
	128.7		97.5	
	301.2 (0.32)		294.7 (0.34)	
	318.5 (0.36)		317.5 (0.36)	
	321.2		320.7	
	836.2		601.2	
835 (0.01)	836.3		601.3	600.2 (0.01)
	986.3		747 (0.39)	738.3 (1.0, *66.4*)
974.7 (1.0, *116.5*)	987 (0.64)		749.5 (0.03)	
	987.1 (0.04)		752.9	
977	990.1 (0.05)		753.1	749
	1064.3		814.3	
1057.9	1064.6		814.9	808.4
	1239.8		1001.2	
1238.1	1240.1		1001.5	1000.3
	1377.3		1010.1	
1377.6	1377.8		1010.3	1009.2
	1473.5 (0.01)		1091.6 (0.01)	
1471.9 (0.09)	1473.8 (0.05)		1091.8 (0.03)	1090.4 (0.09)
	1614.5 (0.05)	1603.1 (1.0, *67.1*)	1562.2	
	1679.4		1562.5	1567.2
1683.9	1679.8		1614.4 (0.07)	
	3123.6 (0.01)		2256.3 (0.01)	
3122.1 (0.15)	3124 (0.05)		2256.6 (0.02)	2255.1 (0.12)
	3137.2		2321.7	
3136.7	3137.3		2321.8	2322.4
	3197.3		2383.7	
3193.8	3197.4		2383.8	2380.9
	3224.9 (0.01)		2400.5 (0.01)	
3222.1 (0.21)	3225.1 (0.08)		2400.6 (0.04)	2398.8 (0.20)
	3766.5 (0.16)	3816.2 (0.15)	3766.5 (0.16)	
	3859 (1.0, *354.6*)	3921.4 (0.85)	3859 (1.0, *354.8*)	

[a] The numbers in parentheses represent the predicted relative infrared intensity of the mode, and where absent the predicted intensity is zero. For the most intense mode of each complex, the absolute intensity (/km mol^{-1}) is also provided in the parentheses as the italicized number.

Isotopic Substitution. For a more detailed identification of this species, isotopic substitution of both the water and ethene molecules was performed. In the matrix formed containing 1:10 C_2D_4:Ar with H_2O, the positions of the new complex barely shift with the change in ethene composition. This suggests that the water molecule is perturbed only by some weak interaction with the ethene molecule, consistent with the idea of an O−H bond hydrogen-bonded to the π-cloud of ethene. In the spectrum of 1:10 C_2H_4:Ar containing D_2O and HDO, the features present in Ar/C_2H_4 matrices containing H_2O are absent and are replaced by four new features at: 3626.1, 2722.3, 2666.2, and 2617.2 cm^{-1}. Of these features, the two at 2722.3 and 2617 cm^{-1} are both in the O−D stretching region and have the same relative intensity profile and breadth as the features observed at 3669.8 and 3585.4 cm^{-1} in Ar/C_2H_4 matrices containing H_2O. The ratio of the positions 3669/2722 and 3585/2617 are 1.348 and 1.370, respectively. For noncomplexed H_2O and D_2O in argon matrices, the corresponding ratio of the ν_3 band is $\nu_3(H_2O)/\nu_3(D_2O) = 3733/2770 = 1.348$ and for the ν_1 band, $\nu_1(H_2O)/\nu_1(D_2O) = 3638/2657 = 1.370$. Thus, owing to the striking agreement upon H/D substitution, it would appear that the features observed at 2722.3 and 2617.2 cm^{-1} are the analagous ν_3 and ν_1 modes of the $(C_2H_4)_2D_2O$ species.

The features observed at 3626.1 and 2666.2 in the Ar matrix formed containing C_2H_4/D_2O/HDO show similar intensities and are found respectively in the O−H and O−D stretching regions. The presence of these modes suggests HDO is present, the absorption positions of which are red-shifted from matrix-isolated HDO. Similar to the comparison above for H_2O and D_2O, we assign these features to the analagous complex $(C_2H_4)_2$-HDO. In HDO, the stretching vibrational modes associated with O−H and O−D motions are decoupled as a result of the difference in nuclear mass. Thus each O−H or O−D bond absorbs essentially as if it were an independent oscillator. It is worth noting that, if the motion of the nuclei in the analagous H_2O or D_2O cases were similarly decoupled, the respective positions for vibrational absorption would be approximately $(\nu_3 + \nu_1)/2$. For free HDO, the $\nu_{(O-H)}$ and $\nu_{(O-D)}$ absorptions occur at 3687.3 and 2709.5 cm^{-1}.[1,2] Decoupling free H_2O and D_2O in noncomplexed water gives H_2O: $(\nu_3+\nu_1)/2 = (3731+3638)/2 = 3684$ cm^{-1} and for D_2O: $(2770+2657)/2 = 2713$ cm^{-1}.[1,2] These values agree very well with the experimental positions observed for free HDO in an Ar matrix. If this approach is carried through for H_2O and D_2O in the observed complex, we compare $(\nu_3+\nu_1)/2$, for complexed H_2O (i.e. $(C_2H_4)_2H_2O$): $(3669.8+3585.4)/2 = 3627.6$ cm^{-1} and for complexed D_2O (i.e. $(C_2H_4)_2D_2O$): $(2722.3+2617.2)/2 = 2669.7$ cm^{-1} to the observed values for the tentative $(C_2H_4)_2$HDO (at 3626.1 and 2666.2). By this procedure, we see that in both cases the comparative modes agree to within three or fewer wavenumbers,

TABLE 2: Unscaled Vibrational Wavenumber Positions Calculated Using B3LYP/6-311+G(d,p) for $\pi\cdots$H Bonded Complex of the Major Isotopomers of Water with Ethene[a]

D_2O	$(C_2H_4)_2D_2O$	HOD	$(C_2H_4)_2HDO$
	14.6		14.6
	16.4		16.5
	18.9		19
	54.8 (0.03)		54.9 (0.04)
	55.2		55.4
	68.1		68.6
	72.6 (0.06)		74.3 (0.06)
	95.1		96.5
	128.1		128.4
	223.8 (0.23)		230.4 (0.16)
	229.5		254.2 (0.33)
	233.1 (0.3)		319.7 (0.29)
	836.2		836.2
	836.3		836.3
	986.1		986.2
	986.8		987 (0.8)
	987 (1.0, *224.5*)		987 (0.3)
	990.1		990.1 (0.08)
	1064.2		1064.2
	1064.6		1064.6
1173.3 (1.0, *35.6*)	1179.9 (0.06)		1239.8
	1239.8		1240.1
	1240.1		1377.3
	1377.3		1377.7
	1377.8	1405.2 (1.0, *59.3*)	1416.8 (0.13)
	1473.5 (0.02)		1473.5 (0.02)
	1473.8 (0.08)		1473.8 (0.08)
	1679.4		1679.4
	1679.8		1679.8
2750.9 (0.19)	2715.6 (0.15)	2810.4 (0.3)	2770.6 (0.46)
2873.9 (0.99)	2828.8 (0.88)		3123.6 (0.02)
	3123.6 (0.02)		3124 (0.07)
	3124 (0.07)		3137.2
	3137.2		3137.3
	3137.3		3197.3
	3197.3		3197.4
	3197.4		3224.9 (0.02)
	3224.9 (0.02)		3225.1 (0.12)
	3225.1 (0.12)	3870.9 (0.62)	3814.4 (1.0, *220.8*)

[a] The numbers in parentheses represent the predicted relative infrared intensity of the mode, and where absent the predicted intensity is zero. For the most intense mode of each complex, the absolute intensity (/km mol^{-1}) is also provided in the parentheses as the italicized number.

as was the case for free HDO. These calculations support each of the assignments for the molecules as water containing species which are perturbed, mostly likely through complexation, and given the relatively high concentration of ethene, it seems the most likely complexation partner. Thus, we confidently assign the absorption positions listed above to stretching modes of O−H and O−D bonds in water species of the form: $(C_2H_4)_2H_2O$, $(C_2H_4)_2D_2O$, and $(C_2H_4)_2HDO$.

Computational Support. To further confirm this assignment, we have performed calculations using B3LYP/6-311+G(d,p).[23−25] The lowest-energy optimized structure, verified through frequency analysis as a relative minimum, is represented in Figure 4. Each of the O−H bonds is hydrogen bonded to the π-cloud of an ethene molecule, an extension of the work presented by Engdahl and Nelander.[7] Calculations were performed on each of the free monomers, as well as the suspected complexes, to obtain the associated shifts in infrared vibrational wavenumber positions. As a summary, the wavenumber positions calculated for H_2O, C_2H_4, $(C_2H_4)_2H_2O$, and relevant isotopomers are given in Tables 1 and 2. In many cases, upon complexation there are new features in the range of 200−400 cm^{-1}, unfortunately, these features are below the 400 cm^{-1} cutoff of our experimental apparatus. Thus, we are unable to use these modes for identification in this work.

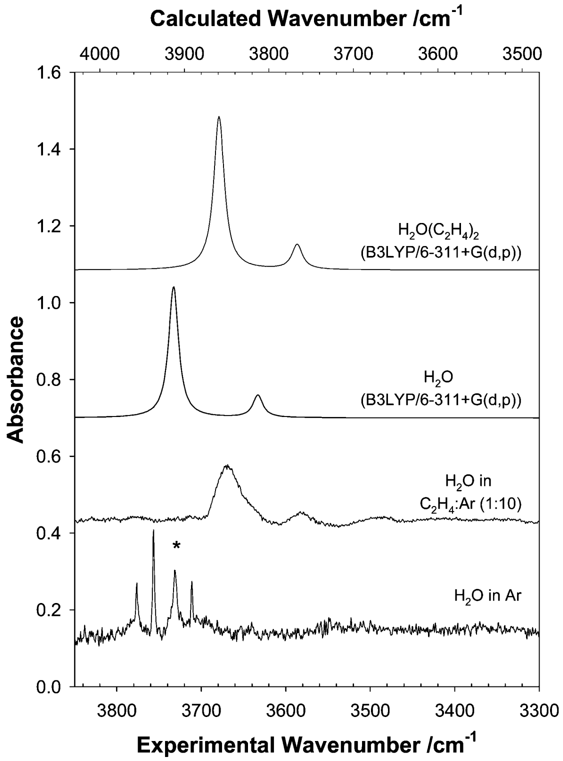

Figure 5. Comparison of experimental and unscaled predicted infrared spectra for H_2O and $(C_2H_4)_2H_2O$. The lower two spectra are experimental, and correspond to the bottom ordinate axis. Asterisk denotes the ν_3 O−H stretching mode of nonrotating water isolated in an argon matrix. The upper two spectra have been synthesized using B3LYP/6-311+G(d,p), broadened to simulate typical experimental bandwidths. The two ordinate axes have been chosen to align the O−H stretching wavenumber of H_2O, for clarity.

Comparing the data presented in Tables 1 and 2, the shift in wavenumber positions for modes that primarily involve the motion of ethene molecules is typically only 1−5 cm^{-1} from the position of the free ethene monomer. Since the concentration of ethene in our matrices is quite large, for cases where we observe the 2:1 complex, the broadening of the features associated with the ethene precursor is much too large to allow for observation of a 1−5 cm^{-1} shift. Thus, in our experiments, the only features observable for the 2:1 complex are those associated with water, as the O−H stretching region is free from interfering absorptions due to ethene. As well, the calculated shifts in wavenumber positions associated with water on complexation are comparatively large, on the order of 40−60 cm^{-1} (see Table 3). Specifically, for the ν_3 mode of water, the predicted (unscaled) red shift is 62.4 cm^{-1} and for the ν_1 band, the predicted (unscaled) red shift is 50 cm^{-1}. In our experiments, the measured shifts in wavenumber position of water modes is 62 cm^{-1} for the ν_3 and 52.6 cm^{-1} for the ν_1 bands upon complexation, compared from the experimental positions for uncomplexed water. It is also interesting to note that the position of the ν_2 mode is predicted to shift only 11 cm^{-1}; however, as a result of complexation this mode is predicted to change from the most intense mode observed, to the weakest of the three normal modes of water.

For D_2O, upon complexation, an analogous red shift is predicted by calculation for the two O−D stretching modes. For the ν_3 O−D stretching mode a shift of 45.1 cm^{-1}, and for the ν_1 O−D stretching mode, a shift of 35.3 cm^{-1} is predicted upon complexation to form $(C_2H_4)_2D_2O$. As with H_2O, the ν_2 mode of D_2O is predicted to shift only 6 cm^{-1}, and upon complexation this mode becomes a very weak absorber when

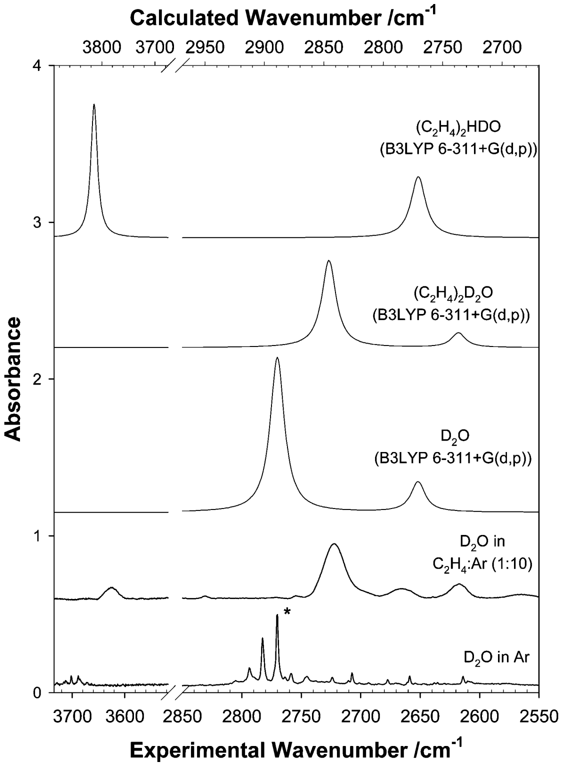

Figure 6. Comparison of experimental and unscaled predicted infrared spectra for D_2O and HDO and the corresponding complexes $(C_2H_4)_2D_2O$ and $(C_2H_4)_2HDO$. The lowest two spectra are experimental, and correspond to the bottom ordinate axis. Asterisk denotes the ν_3 O−D stretching mode of nonrotating D_2O isolated in argon. The top three spectra have been synthesized using B3LYP/6-311+G(d,p), broadened to simulate typical experimental bandwidths. The two ordinate axes have been chosen to align the O−D stretching wavenumber of D_2O, for clarity.

TABLE 3: Observed and Calculated Wavenumber Shifts of Stretching Vibrational Mode Absorptions Associated with Water in Isotopomers of $(C_2H_4)_2H_2O$

	$\Delta\nu_1$ (/cm^{-1})		$\Delta\nu_3$ (/cm^{-1})	
	expt	calcd	expt	calcd
$(C_2H_4)_2H_2O$	−53	−50.0	−62	−62.4
$(C_2H_4)_2D_2O$	−40	−35.3	−48	−45.1
$(C_2H_4)_2HDO$[a]	−43	−39.8	−61	−56.5
$C_2H_4H_2O$[b]	−26	−37.0	−14	−22.0

[a] For this molecule, ν_3 refers to ν_{O-H} and ν_1 refers to ν_{O-D}. [b] Shift values for $C_2H_4H_2O$ are also given for comparison. Data taken from ref 7.

considering relative intensities. Experimentally, the ν_3 and ν_1 modes of D_2O are observed to shift 48 and 40 cm^{-1}, respectively. Finally, for HDO complexed with two ethene molecules, there is a similar analogous shift predicted upon complexation. The shifts of the O−H and O−D wavenumber positions are predicted to be respectively 56.5 and 39.8 cm^{-1}, with the major absorptions predicted as the O−H and O−D stretches. Once again, the ν_2 mode is predicted to shift only 11 cm^{-1}, with significant reduction in relative intensity. For the O−H stretching mode, a shift of 61.2 cm^{-1} is observed for the O−H mode we associate with $(C_2H_4)_2HDO$, and a shift of 43.3 cm^{-1} is observed for the shift of the O−D mode of HDO. Figures 5 and 6 summarize the comparison between calculated infrared spectra and experimental infrared spectra for free H_2O (and its isotopomers) and the 2:1 ethene:H_2O complex. As the shifts upon complexation match very well for the predicted wavenumber positions, we feel confident in assigning these features to 2:1 ethene:water complexes of the form $(C_2H_4)_2H_2O$, $(C_2H_4)_2D_2O$, and $(C_2H_4)_2HDO$.

It is interesting to note that the shifts predicted by B3LYP/6-311+G(d,p) calculations for the 1:1 ethene:water complex in which the O−H bond of water is linearly bonded to the π cloud of ethene show significant deviation from the corresponding experimental shifts. In light of the excellent agreement obtained for all three of the isotopomers of the 2:1 ethene:water $\pi\cdots$H complex, this discrepancy is unexpected. These results suggest that the structure of the 1:1 complex in the matrix may deviate from the experimental gas-phase structure,[20,21] upon which our calculation of the 1:1 ethene:water complex shifts given in Table 3 are based.

Formation and Characteristics of the $(C_2H_4)_2H_2O$ Complex. Since the spectroscopy of the water molecule is otherwise preserved, the water molecule in the 2:1 complex appears as if it were an isolated water molecule, experiencing a weak "centrosymmetric" perturbation about each of the O−H bonds by the π-cloud of the olefin. If such a supposition were true, then, isotopic substitution of the C_2H_4 molecules in the complex for C_2D_4 should have little effect on the O−H stretching wavenumber positions associated with the observed complex. In fact, the calculated O−H wavenumber predictions for the analogous 2:1 C_2D_4: H_2O complex show only slight shifts associated with O−H stretching modes of water compared from those calculated for $(C_2H_4)_2H_2O$, similar to the very small shifts which can be observed experimentally in Figure 2. As with C_2H_4, comparing the C_2D_4 modes in $(C_2D_4)_2H_2O$ to those of "free" C_2D_4 shows almost no change in position, which further suggests that the H_2O molecule is only weakly interacting with the surrounding ethene molecules, in an interaction such as a $\pi\cdots$H hydrogen bond.

Finally, it is worthwhile recalling that the formation of the 2:1 complex appears upon increasing the concentration of ethene in argon, as described above. This behavior suggests that the 1:1 ethene complex behaves, as might be expected, as an intermediate species in the formation of $(C_2H_4)_2H_2O$. Using the optimized structures generated by the B3LYP calculations, it is possible to calculate the stepwise energetics associated with the formation of $(C_2H_4)_2H_2O$.

$$C_2H_4 + H_2O \rightarrow C_2H_4\cdots HOH \quad \Delta E = -8.8\ \text{kJ mol}^{-1}$$

$$C_2H_4\cdots HOH + C_2H_4 \rightarrow C_2H_4\cdots HOH\cdots C_2H_4 \quad \Delta E = -3.4\ \text{kJ mol}^{-1}$$

In both cases, these interaction energies have been corrected for zero point energy differences and have also been corrected for basis set superposition error (BSSE) using the counterpoise method of Boys and Bernardi.[26] As an estimation of the quality of these calculations for determining interaction energies of this type of complex, we have also calculated the counterpoise corrected interaction energy of the water dimer with the B3LYP method and the 6-311+G(d,p) basis set For the water dimer, we obtain an interaction energy for the reaction:

$$H_2O + H_2O \rightarrow HOH\cdots OH_2 \quad \Delta E = -14.8\ \text{kJ mol}^{-1}$$

In this case, the agreement of the theoretical prediction with the experimental value of −13.4 ± 2.1 kJ mol^{-1} for the water dimer[30] provides support for the use of this method and basis set to reliably estimate the interaction energies of the ethene−water π complexes. Furthermore, the interaction energy associated with the formation of the 1:1 ethene:water complex is calculated to be −8.8 kJ mol^{-1}, with the experimental estimate of this energy being −7.5 kJ mol^{-1}.[7] Thus, this method seems reliable in predicting the interaction energies associated with $\pi\cdots$H interactions. It is interesting to note that the second complexation reaction is less energetically favorable than the first. Mulliken population analysis of the 1:1 ethene:water complex shows a slight decrease in the partial positive charge on the free hydrogen atom of water with respect to free water, as would be expected intuitively. Such a decrease in the partial positive charge on the free hydrogen atom may provide an explanation for the weaker interaction predicted for the second complexation.

Notwithstanding this consideration, the formation of the 2:1 ethene:water complex would nevertheless appear to have favorable energetics, from a thermodynamic perspective. Thus, the association of ethene with the 1:1 complex should be expected to be a barrierless process. The favorable thermodynamics of this reaction suggest that it should be possible to form the 2:1 ethene:water complex from the 1:1 ethene:water complex under the low-temperature conditions of the matrix-isolation environment, via thermal annealing of the matrix. Indeed, thermal annealing of the matrix containing 1:50 ethene:Ar causes a reduction in the 1:1 complex, with a corresponding increase in the 2:1 complex as described above. This result demonstrates that the formation of the 2:1 complex is facile under our conditions.

Conclusion

The $(C_2H_4)_2H_2O$ ternary $\pi\cdots$H bonded complex is formed when water and ethene are cocondensed at high ethene concentration in argon matrices. The complex forms on deposition and following thermal annealing from the known 1:1 ethene:water binary complex. The ternary complex exhibits a nearly symmetrical geometry, with its principle perturbation being a weakening of the O−H bonds of water. IR spectral features associated with the O−H modes of the complex and their isotopic counterparts are observed and assigned.

Acknowledgment. The authors would like to acknowledge the support of NSERC through the Discovery Grant program. M.G.K.T. would like to acknowledge the scholarship support of NSERC through the PGS program.

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