Quantum Studies of Acetylene Adsorption on Ice Surface

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The interaction of acetylene with the surface of ice was investigated using two quantum ab initio methods. The adsorption energies were calculated with the periodic Hartree−Fock method. It was found that the acetylene molecule is hydrogen bonded to the surface and acts as a proton acceptor. The cluster Hartree−Fock method was applied in order to calculate the vibrational frequency shifts induced by this adsorption process. The theoretical values were compared to the experimental results and proved instrumental in explaining the observed spectra, whereas the dimer $H_2O-C_2H_2$ data (experimental and theoretical) failed in this interpretation. This paper includes a discussion on how to interpret the failure of the dimer model compared to the periodic model.

I. Introduction

The adsorption of acetylene on water ice is of great importance in the physical and chemical processes occurring in the interstellar medium (ISM). The ISM contains about 10% of the mass of our galaxy[1] and consists of gas (99%) as well as grain particles (1%). These grains hold a typical temperature of 10 K in molecular clouds[2] and are covered with an icy mantle. Atoms, radicals, and molecules from the gaseous phase are accreted on this mantle, and they are identified via IR spectroscopy. Acetylene has thus been observed among these accreted molecules. When C_2H_2 reacts with H, an active hydrocarbon chemistry is initiated, which can produce molecules such as polycyclic aromatic hydrocarbons (PAHs).[3] The ice substrate of the grain mantle certainly has a catalytic influence on these reactions. The short wavelength spectrometer on board the IR space observatory (ISO) detected C_2H_2 in dense clouds; it is supposed to be produced primarily in the gaseous phase and then accreted on icy grains.[4] PAHs are also produced by the cosmic ray particle interaction with methane, ethylene, and acetylene ices.[5]

Acetylene is also found in abundance in or on the ices of a number of comets such as Hyakutake[6] and Hale−Bopp[7] and several laboratory experiments have been conducted to reproduce the IR spectra and the reactivity of acetylene mixed with ice and various hydrocarbons.[8] These few examples emphasize the fundamental importance of acetylene reactivity on ice in the astrophysical domain. It is therefore fundamental to understand how acetylene interacts with ice and what are the consequences on its IR spectrum.

A few years ago, Devlin et al.[9] carried out an experiment on acetylene adsorption on amorphous ice at temperatures close to the temperature of icy interstellar grains. This experiment showed that the system water−acetylene is of particular interest because C_2H_2 may act both as proton donor through its acidic hydrogen and as proton acceptor through its π-electrons in the hydrogen bonds responsible for the stability of the system. Experimental and theoretical studies of the $H_2O-C_2H_2$ dimer indicate that the structure where the acetylene bonds as proton donor is more energetically stable. The binding energy is estimated at 2−3 kcal mol^{-1} by Nelander et al.[10] This value is close to the theoretical results of Pople et al.[11] between 2.1 and 3.2 kcal mol^{-1} for the acetylene proton donor and 1.2−1.9 kcal mol^{-1} for the acetylene proton acceptor complexes.

Devlin et al.[9] tried to exploit the dimer results to interpret their experiment of acetylene adsorption on an amorphous ice surface. Although the general trends deduced from the water−acetylene dimer have been established, there is a qualitative gap between the interaction with a single H_2O molecule and that with the ice surface. This discrepancy is ascribed to the cooperative contribution[12−15] of in-ice H-bond strings and many body effects[16] that reinforce the acetylene−surface stability.

This paper is devoted to the quantum study of acetylene adsorption on the perfect (0001) hexagonal ice surface considered as a periodic infinite 2D system. The adsorption energies and topologies were determined for the two hypotheses, i.e., acetylene acting as a proton donor or as a proton acceptor. The corresponding IR frequencies were then calculated and discussed.

II. Method of Calculation

Structures and Adsorption Energies. In an earlier paper,[17] we studied the adsorption of CO on amorphous ice surfaces using the periodic Hartree−Fock (PHF) method[18] and we were able to calculate very small adsorption energies that proved in very good agreement with our experimental values.

The same method was used in the present work; the solid substrate was represented as a slab of infinite 2D layers whose structure was optimized by Pisani et al.[19] using the same PHF method.

The optimized adsorption structures were calculated using the CRYSTAL98 computer program,[20] and the minimum was determined at the HF/6-31 g** level of approximation by successive quadratic interpolation techniques, as described elsewhere.[21] All the acetylene parameters were optimized, the surface remaining unchanged. At the stationary point, the total energy of each subsystem, ice + acetylene, ice, acetylene, was corrected by a posteriori estimation of the correlation energy based on the density functional theory. Several functionals

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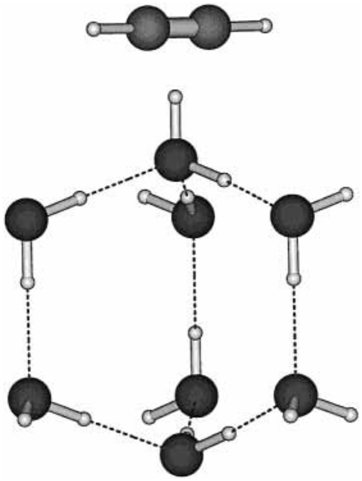

Figure 1. Adsorption on ice of acetylene acting as proton acceptor.

proposed in CRYSTAL98 were tested: various local spin density parametrizations[22−25] and some nonlocal and gradient-corrected functionals.[26,27] The adsorption energies were then calculated as follows:

$$\Delta E_A = E(\text{ice}) + E(C_2H_2) - E(\text{ice} + C_2H_2)$$

and corrected from the basis set superposition error (BSSE) using the usual full counterpoise method.[28]

Vibrational Frequencies. Since it is not very feasible to calculate the vibrational frequencies within the PHF method, these quantities were calculated with the usual molecular HF method. For this purpose, a cluster representative of the local symmetry of the system was extracted from the optimized periodic structure, and then the vibrational frequencies of these clusters were calculated using the GAMESS(US)[29] computer program. The large size of the cluster made it necessary to proceed only at the HF level of approximation. Only the acetylene stretching modes are discussed here: ν_1 the symmetric CH mode, ν_2 the CC mode, and ν_3 the antisymmetric CH mode.

The calculated frequencies were corrected by a unique scaling factor (0.9),[30] which is a rather standard value for stretching modes.[31] Because the discussion is restricted to frequency shifts only, this correction is not of fundamental importance since a uniform reduction by 10% of the calculated frequencies does not modify the sign of the shifts and does not alter significantly their absolute values. The quality of the ab initio prediction of vibrational transition dipole moments has often been discussed[32−34] in the literature. At the present level of approximation, and despite the often poor quality of the predictions in this domain, it is justified to compare the calculated IR intensities between very similar systems such as proton acceptor and proton donor acetylene adsorbed on the same substrate at least from a qualitative point of view since the variations were mainly imposed by symmetry constraints. More generally, the discussion in this paper will not develop on exact numerical values but rather on semiquantitative trends.

III. Results and Discussion

Proton Acceptor Acetylene. Figure 1 shows the stationary structure as determined from CRYSTAL98 calculation. For graphical convenience, only the cluster used to calculate the vibrational frequencies is displayed.

The uncorrelated RHF adsorption energy is 2.9 kcal mol^{-1}. The correction from the electronic correlation energy by various local spin density approximations leads to very similar values, about 4.0 kcal mol^{-1}(Table 1), similar to Devlin et al.'s[9] experimental value, 3.7 kcal mol^{-1}. It has been reported already that local density functionals provide good results for the calculation of chemisorption properties on ionic solids.[35,36] It appears that the nonlocal and gradient-corrected functionals seem to overrate the dispersion energy, but no general conclusion can be drawn from this isolated test (it is well-known[37] that the major contribution to the dispersion energy is due to the correlation functional). Nevertheless, the quantum adsorption energy of the proton acceptor acetylene ranges from 3.9 to 5.3 kcal mol^{-1}, this difference lies within the practical limits of error of the methods used here.

The acetylene molecule is slightly twisted, the HCCH torsion angle is 9.7°. This effect is certainly ascribable to the mismatch between the molecule and slab symmetries. The molecule has a C_2 axis perpendicular to the surface, whereas the ice surface has a C_3 local axis of symmetry along the same direction. The other structural parameters are little affected (Table 2): the CC bond length is very slightly longer than in the isolated molecule structure optimized using the same approximations. The molecular CC axis forms a 68.3° angle versus the plane of the H-bonded water molecule.

The distance between the CC axis and the ice dangling OH is $d = 2.241$ Å. This value is typical of a hydrogen bond that involves the dangling proton and the acetylene π electronic system. This value is also in good agreement with the Peterson et al.[38] microwave experiment, 2.229 Å, taking into account the specific perturbing effect of the surface.

The calculated vibrational frequencies corresponding to the acetylene stretching modes are all high-shifted, and the larger shift is calculated for the CC ν_2 mode (Table 3).

The most interesting result concerns the changes in IR intensities: in the gaseous phase, ν_1 and ν_2 are IR inactive. The surface electric field makes them active, ν_1 becomes very strong, and ν_2 remains nearly inactive.

The analogous calculation was performed on the H_2O cluster. The dangling OH frequency is calculated at 3874 cm^{-1} (uncorrected) for the H_2O cluster. In the complete $H_2O + C_2H_2$ system, the OH coordinate contributes to two transitions at 3766 and 3780 cm^{-1}. These values imply downshifts of respectively 108 and 94 cm^{-1} (97 and 84 cm^{-1} after frequency scaling), which is in remarkable agreement with the results of Devlin et al.,[9] a downshift of 95 cm^{-1} with respect to pure amorphous ice.

Proton Donor Acetylene. The stationary geometry displayed in Figure 2 corresponds to an RHF adsorption energy of −2.4 kcal mol^{-1} and a DFT correlated adsorption energy ranging from 3.1 (LSD) to 4.1 kcal mol^{-1} (LYP). Compared to the former case, this result establishes that the system ice + proton donor acetylene is less stable for all the methods used here (Table 1).

The molecule remains linear and perpendicular to the surface plane at a distance of 2.288 Å, thus reflecting a weaker H-bond than on the other adsorption site. This particular configuration induces a small dissymmetry between the two CH bonds, with the closest to the surface slightly longer (0.006 Å).

The ν_1 and ν_2 modes are high-shifted with respect to the isolated molecule, but to a smaller extent than earlier. Moreover, the H-bond induces a rather significant downshift (30 cm^{-1}) of the antisymmetric ν_3 mode.

The IR intensities are even more informative since the ν_1 mode again becomes weaker compared to the acceptor case.

TABLE 1: Total Energies (Hartree) and Adsorption Energies (kcal mol^{-1})

	proton acceptor acetylene		proton donor acetylene	
	total energy	adsorption energy	total energy	adsorption energy
RHF	−761.774459	2.9	−761.748663	2.4
Perdew−Zunger LSD	−768.854322	3.9	−768.829001	3.1
Vosko−Wilk−Nusair LSD	−768.898243	3.9	−768.872952	3.1
Von Barth−Hedin LSD	−770.826192	4.1	−770.800885	3.3
Perdew−Wang LSD	−768.868549	3.9	−768.843243	3.1
Perdew 91	−765.605129	5.0	−765.579341	3.8
Perdew−Wang GGA	−765.619714	5.0	−765.593957	3.9
Perdew−Burke−Ernzerhof	−765.366618	5.0	−765.340978	3.9
Lee−Yang−Parr	−765.473952	5.3	−765.444166	4.1

TABLE 2: Acetylene Optimized Structure

	isolated	proton acceptor	proton donor
C≡C (Å)	1.173	1.178	1.179
CH_1 (Å)	1.057	1.058	1.063[a]
CH_2 (Å)	1.057	1.059	1.057
H_1CC (deg)	180	178.2	180
H_2CC (deg)	180	178.3	180
d		2.241[b]	2.288[c]

[a] In this case H_1 is the proton close to the surface. [b] Distance from the dangling OH's proton to the CC axis. [c] Distance from H_1 the surface oxygen.

TABLE 3: Calculated Acetylene Vibrational Frequencies (cm^{-1})[a]

	ν_1		ν_2		ν_3	
	freq	Intensity	freq	Intensity	freq	Intensity
isolated	3322	0	1991	0	3226	2.223
adsorbed proton acceptor site	3339	5.918	2063	0.024	3231	2.402
adsorbed proton donor	3329	0.250	2053	0.239	3198	6.635

[a] ν_1 and ν_3 are the symmetric and antisymmetric CH stretching modes; ν_2 is the CC mode. All the calculated frequencies are corrected by a unique scaling factor (0.9), intensities in D Å^{-2} amu^{-1}.

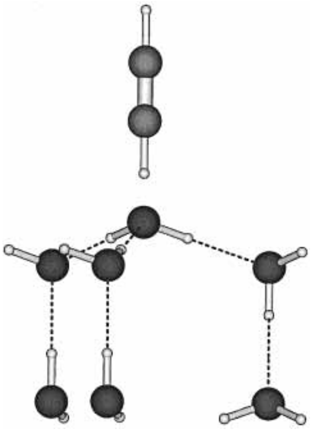

Figure 2. Adsorption on ice of acetylene acting as proton donor.

The trend is reversed on ν_3. It must also be noted that the ν_2 mode is 10 times more intense when C_2H_2 acts as the donor than when it is the acceptor. This point is further discussed in the next section.

IV. Discussion

Devlin et al.[9] estimated the acetylene adsorption energy on an amorphous ice surface to 3.7 kcal mol^{-1}. This value was compared to the binding energies in the dimer complex $H_2O-C_2H_2$ taken from Nelander et al.,[10] 2−3 kcal mol^{-1} from the matrix isolation study, and from theoretical values from Pople et al.,[11] between 2.1 and 3.2 kcal mol^{-1} for proton donor acetylene and from 1.2 to 1.9 kcal mol^{-1} for the proton acceptor complex. The latter result is in contradiction with Devlin's spectroscopic conclusion that the most energetic site should be an acceptor, which is clearly confirmed by the PHF calculation. In fact, according to the functional form selected for the correlation energy, the PHF adsorption energy ranges from 3.9 to 5.3 kcal mol^{-1} for the proton acceptor case and from 3.1 to 4.1 kcal mol^{-1} with a proton donor. The difference is about 1 kcal mol^{-1}, and the two structures are so close in energy that a moderate increase in temperature causes the acetylene to move from an acceptor to a donor site.

The discrepancy between the PHF and the dimer results is ascribable to two effects, themselves associated with cooperative effects within the ice substrate. First, the PHF calculation determines a total wave function that is periodic and delocalized in the whole system and more particularly on the ice surface. This delocalization obviously favors the combination of the acetylene π electronic system that is parallel to the surface in the acceptor form, whereas it is perpendicular to the surface in the other structure. The other reason is described in the literature as cooperativity of the hydrogen bonds. The strings of H-bonds developing inside the ice bulk and toward the surface provoke a reinforcement of the ice−acetylene H-bonding. In their theoretical work on *N*-methylacetamide, Karplus et al.[14] showed that cooperativity is responsible for the shortening of a specific H-bond by about 0.02−0.045 Å and an increase of the binding energy by about 0.3−0.9 kcal mol^{-1}. Our results are consistent with these results as discussed in the former paragraph concerning energies. The comparison with Pople's intermolecular distances, from 3.320 to 3.491 Å (2.241 and 2.288 Å in our work), further confirms our point.

Another point that should be discussed here concerns the ice surface structure. Devlin's surface is amorphous and rather disordered. Our study assumes a perfect ice surface whose geometric parameters are not relaxed during the calculations because such a reconstruction of the surface would not be justified if the supporting slab features only two bilayers and because a thicker slab would induce tremendous computational efforts. The good agreement between our results and Devlin et al.'s,[9] plus the fact that these authors see only two adsorption sites, tends to prove that acetylene is rather insensitive to the surface ordering, at any rate as far as energy and the IR spectra are concerned. We have already developed a very similar discussion in our paper on CO adsorption, and our conclusion was that the ice surface seems locally ordered over a long distance given to the molecule's dimensions, the consequence being that the periodic calculation is still reliable.

The most valuable features that can be deduced from the ab initio calculation on this system are relative to IR spectroscopy. Of course, it is well-known that the quantum calculated vibrational frequencies are systematically overestimated, but precisely because this error is systematic, the frequency shifts between two similar structures can be legitimately argued, at least from a semiquantitative point of view.

Dangling OH Mode. Considering the clusters that support this calculation, only the complex with proton acceptor acetylene is considered, in the other site this mode is assumed to be unaffected. This coordinate contributes to two frequencies in the adsorbed phase at 3766 and 3780 cm^{-1} (uncorrected), which corresponds to 3874 cm^{-1} for the unperturbed ice surface. The downshift is about 100 cm^{-1}, whereas Devlin observed a 95 cm^{-1} downshift for this signal. Obviously, this excessively perfect numerical matching must not be taken stricto senso. Nevertheless, this frequency shift has remained unexplained by the earlier theoretical calculations or by the experimental results for the water−acetylene dimer. This points out the limitations to any interpretation of an adsorption experiment based only on dimer behavior and demonstrates that the cluster HF calculation highlights the right behavior in magnitude and in direction.

Acetylene Stretching Modes. Devlin's discussion on the possibility for acetylene to be H-bonded to the surface under two reactive modes is based on the interpretation of the ν_2 and ν_3 stretching modes. Again, the calculation unequivocally confirms his analysis.

In the gaseous phase, the ν_2 mode is Raman active but dipole forbidden in IR spectroscopy. In the adsorbed phase, the Raman spectrum shows that this band is constituted as a doublet at 1957 and 1963 cm^{-1}, with the splitting then being 6 cm^{-1} (7 cm^{-1} unscaled). It can be seen in Table 3 that the theoretical splitting between proton acceptor and proton donor is 10 cm^{-1}. Moreover, the IR intensity corresponding to the first of these two forms is 10 times weaker than the other one, which is why a unique band is observed in Devlin's spectrum, the low-frequency one being associated with the proton donor acetylene in the calculation and in Devlin's conclusion.

The calculation on the dimer water−acetylene showed a 24 cm^{-1} splitting of the ν_3 mode, the proton donor form yielding the lower frequency. The splitting here calculated is 33 cm^{-1} (37 cm^{-1} without frequency scaling), which is still too small but closer to experiment, 40 cm^{-1}, and in the right direction.

V. Conclusion

This calculation and its comparison with experiments on acetylene adsorption on water ice demonstrates the limits of the applicability of dimer system results in interpreting reactivity and spectroscopy on ice surfaces. Only the combined periodic Hartree−Fock and large cluster calculation proved to correctly reproduce features such as the adsorption energy, the dangling OH frequency shift, and the splitting of the ν_2 and ν_3 bands of acetylene. The partial failure of the dimer model that predicts a proton donor structure in contradiction with expriments and with the present calculation is partly due to the cooperative effects of the hydrogen bonds. These effects are implicitly included in the periodic Hartree−Fock calculation and to some extent in the rather large cluster calculation since only a limited part of the H-bond chains is explicitly introduced. These cooperative effects act in favor of the proton acceptor form and account for the fact that acetylene interacts with the ice surface through a hydrogen bond between the ice dangling proton and the acetylene electronic π system.

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