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# Quantum study of the adsorption of small molecules on ice: The infrared frequency of the surface hydroxyl group and the vibrational stark effect

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A periodic Hartree–Fock quantum calculation has been developed for the adsorption of small nonpolar model systems ( $C_2H_2$ ,  $C_2H_4$ ,  $O_3$ ,  $CO$ ,  $N_2$ , and  $Ar$ ) on ice in order to determine the physical variables responsible for the large infrared frequency shifts of the surface hydroxyls. It is shown that the correlation between these shifts and the corresponding interaction energies is not quite convincing. On the contrary it appears that the frequency shifts are tightly correlated to the variation with adsorption of the local electric field along the OH bond thus demonstrating that the dangling hydroxyl frequency is largely governed by the vibrational stark effect. © 2001 American Institute of Physics. [DOI: 10.1063/1.1331106]

## I. INTRODUCTION

The study of the interaction of atoms and molecules with water ice surfaces received considerable attention during the last decade due to its importance for the atmospheric chemistry (Arctic and Antarctic polar ices,<sup>1</sup> stratospheric clouds,<sup>2</sup> Antarctic ozone hole<sup>3</sup>) and also in the area of astrochemistry (icy mantle of interstellar grain particles,<sup>4</sup> planetary ices, ices in the comet tails).<sup>5</sup>

In both these areas, infrared spectroscopy has proved to be a powerful tool of investigation. A typical example was given by the recent results of the short wavelength spectrometer (SWS) on board the infrared (IR) space observatory (ISO).<sup>6</sup> In these two areas also, the trace gases are adsorbed in very small quantities and often they are not directly detectable. Even in laboratory simulations, many among the adsorbed symmetric molecules are not visible through infrared spectroscopy or their signal is so weak that the adsorption process is detected only through the changes of the  $-OH$  (or  $-OD$ ) fundamental modes of the ice water molecules.

The infrared signal of ice in the domain of the OH stretching modes is made up of a very broad band corresponding to the in-bulk molecules (four-coordinated) and a signal at  $3696\text{ cm}^{-1}$  ( $-OH$ ) or  $2727\text{ cm}^{-1}$  ( $-OD$ ) associated by Devlin *et al.*<sup>7–9</sup> to three-coordinated water molecules. Another band at  $3720\text{ cm}^{-1}$  ( $-OH$ ) and  $2748\text{ cm}^{-1}$  ( $-OD$ ) is assigned to two-coordinated molecules but is not easily observed. These features are very weak in comparison with the signal arising from the bulk water–ice and are the signature of the dangling OHs in Devlin's terminology. The  $3696$  ( $2727$ )  $\text{cm}^{-1}$  signal is very much dependent on the interaction of the ice surface with other molecules; in this case it is always shifted towards the lower frequencies. The shift ranges from a few ( $Ar, N_2$ ) to a hundred wavenumbers

( $C_2H_2, C_2H_4, O_3$ ). Surprisingly these large shifts reflect rather small interaction energies: Up to a maximum value of  $20\text{ kJ mol}^{-1}$  in the case of acetylene. Energies in the same range of magnitude are observed in many other fields of chemical physics such as rare-gas matrices but they are associated to frequency shifts rarely exceeding a few wave numbers. Therefore, it is not easy to establish a straightforward correspondence between interaction energies and frequency shifts.

On the other hand, in many cases the interpretation of experiments is deduced from quantum calculations of restricted systems, dimers in most cases. The quantum models give complexation energies which are generally good estimates of the adsorption energies but they are of little help in explaining the shift of the OH fundamental mode. As an example, in our laboratory we did not manage to reproduce from the dimer  $O_3-H_2O$  the right order of magnitude for the OH frequency shift: All the quantum methods we used predicted a shift of  $-5$  to  $-10\text{ cm}^{-1}$  although the experimental shift is  $-62\text{ cm}^{-1}$ . Sadlej *et al.*<sup>10</sup> have also calculated the frequency shifts in the dimers. They have found that both experimental and calculated shifts have similar sign and order of magnitude, but the latter is smaller by a factor 2 to 3.

This paper has a dual purpose: For a selection of nonhydrophilic model systems ( $Ar, N_2, CO, O_3, C_2H_2$ , and  $C_2H_4$ ) we will first calculate the interaction energy  $\Delta E_{\text{Int}}$  and the harmonic frequency  $\omega_{OH1}$  of the dangling  $OH_1$  mode. Then using these results we shall attempt to elucidate the nature of the physical processes responsible for such large frequency shifts. These systems were chosen for the following reasons: (i) Experimental data are available, (ii) the molecules are small enough to allow rather extensive calculations, (iii) they are nonpolar, nonchemically reactive, and weak Lewis acids or bases. Therefore, it is expected that these kinds of molecule do not significantly alter the ice surface. It is all ready well known before any calculation that some of these systems will interact more with the dangling hydroxyl group,

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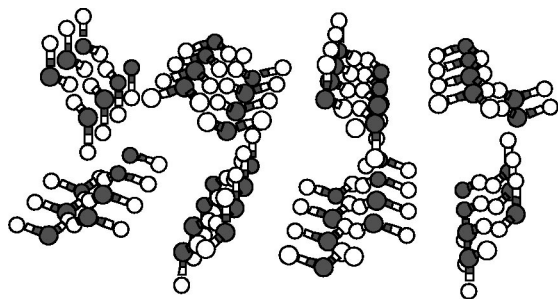


FIG. 1. Graphical representation of the two bilayers slab of water molecules used in this calculation. On the upper part of the figure, from the left to the right: The dangling OH, the dangling lone pair oxygens and the four-coordinated water molecules.

whereas the others will not; nevertheless,  $\omega_{\text{OH}_1}$  will be perturbed in both cases. In the rest of this paper the dangling hydroxyl group will always be referred to as  $\text{OH}_1$ .

## II. METHODS OF CALCULATION

### A. Geometries and vibrational frequencies

The periodic Hartree–Fock method<sup>11</sup> (PHF) already applied in our earlier papers<sup>12–14</sup> has proved to be very fruitful in studying the adsorption of small molecules on ice surfaces. Representing the surface as a two-dimensional (2D)-infinite slab, the PHF method very accurately reproduces the cooperative properties of the hydrogen bonds responsible for the solid cohesion. The corollary of this is that the model surface is perfectly symmetric and defectless although our IR experiments are conducted at very low temperature on porous ices. Nevertheless, our earlier studies have demonstrated that the model of perfect surface is transferable to porous ice at a good level of approximation precisely because the collective and cooperative effects of the hydrogen bonds persist and remain the fundamental aspect of the system even if ice is porous or “amorphous.”<sup>15,16</sup>

The PHF method is implemented in the CRYSTAL98<sup>17</sup> program package. As before we adopted the ice surface unit cell optimized by the Turin group.<sup>18</sup> The water molecules forming the ice surface (Fig. 1) are divided into three categories (i) the molecules bearing a dangling OH group perpendicular to the surface plane, (ii) the molecules whose lone pairs of electrons point outward, (iii) the four-coordinated water molecules whose hydroxyls point downward.<sup>19</sup>

In this context, the adsorbed system constitutes what we shall call an adlayer in the following of the paper: Each dangling hydroxyl group is associated to one adsorbed molecule, all of the ad molecules are then strictly equivalent. This definition does not correspond exactly to the physical definition of an adlayer in which the ad molecules would form a structure with its own symmetry, often different from that of the crystal.

The chosen atomic basis set is the standard extended Gaussian basis 6-31g(*d,p*). The incompleteness of the basis set induces a basis set superposition error (BSSE) which is corrected through the usual counterpoise method.<sup>20</sup> The electronic correlation energy is added to the PHF energy by a posteriori density functional (DFT) calculation using the

PHF density matrix in the GGA approximation of Perdew and Wang.<sup>21</sup> This method is adopted in lieu of a full Kohn–Sham DFT calculation because it is faster and overall because, as it is well known, HF errors on the frequencies are systematic,<sup>22</sup> as opposed to the case of DFT calculated frequencies.

The optimization procedure has already been detailed on several occasions, see for example, in our previous papers, in the present work it was also applied to the water molecule bearing the dangling OH.

The frequency calculation was performed for this molecule alone within some approximations. First of all, it should be noted that in an isolated water molecule, the two stretching modes  $\text{OH}_1$  and  $\text{OH}_2$  are combined into anti-symmetric and symmetric vibrations. On the contrary, for the surface water molecules, the  $\text{OH}_2$  mode (hydroxyl group pointing towards the in-bulk) is strongly coupled to the H-bond collective modes. The  $\text{OH}_1$  mode is completely decoupled from  $\text{OH}_2$ <sup>23</sup> and from the other bulk hydroxyls. It can be coupled only to its counterparts in the neighboring unit cells respectively at 4.401 and 7.920 Å in the Turin P-ice model. As a consequence, since we are only interested in  $\omega_{\text{OH}_1}$ , we can calculate the Wilson force field<sup>24</sup> for the dangling  $\text{H}_2\text{O}$  molecule in the potential arising from the rest of the crystal. The vibrational force field is calculated in the system of internal coordinates  $\{\Delta r_{\text{OH}_1}, \Delta r_{\text{OH}_2}, \Delta \alpha_{\text{H}_1\text{OH}_2}\}$  using a numerical evaluation of the potential derivative described elsewhere.<sup>25</sup> The harmonic frequency resulting from the diagonalization of the Wilson *F* matrix is then scaled by a standard and unique factor of 0.85.<sup>26</sup> This scaling process does not affect the direction nor the range of variation of the frequency shifts, its function is only to take into account the systematic error inherent to the Hartree–Fock method and also to introduce a certain amount of anharmonicity. The dangling OH frequencies thus calculated are 3695  $\text{cm}^{-1}$  ( $\text{OH}_1$ ) and 2691  $\text{cm}^{-1}$  ( $\text{OD}_1$ ); these values are to be compared against the experimental ones: 3696 and 2728  $\text{cm}^{-1}$  for the bare surfaces. The downside of this methodology is that the infrared intensities remain completely out of reach since there is no simple means to evaluate the partial dipole moment of a subsystem of a crystalline unit cell in CRYSTAL98.

### B. Electric properties

The CRYSTAL98 program allows calculating the electrostatic potential and the electric field strength in any point of the slab. The electric field  $\mathcal{F}$  is calculated at the center of mass of the adsorbed species above the ice surface. It induces in the adsorbate a dipole moment that can be expanded as<sup>27</sup>

$$\mu = \mu_0 + \alpha^T \mathcal{F} + \frac{1}{2} \beta^T \mathcal{F}^2 + \frac{1}{3!} \gamma^T \mathcal{F}^3 + \dots, \quad (1)$$

where

$\mu_0$  is the permanent dipole moment,  $\alpha^T$  is the linear polarizability,  $\beta^T$  is the first-order hyperpolarizability,  $\gamma^T$  is the second-order hyperpolarizability.

The induced dipole moments are calculated using this equation at the first order of approximation. The linear polarizability tensor  $\alpha^T$  is calculated by the TDHF method

TABLE I. Interaction energies ( $\Delta E_{\text{Int}}$ ), Mulliken populations on oxygen ( $q_{\text{O}}$ ), H-bonded proton ( $q_{\text{H2}}$ ), dangling OH bond length ( $d_{\text{OH1}}$ ), dangling proton Mulliken total charge ( $q_{\text{H1}}$ ) with the gain (positive sign) or loss (negative sign) respect to the bare surface in parenthesis, calculated scaled harmonic frequencies and shifts ( $\omega_{\text{OH1}}$  and  $\Delta\omega$ ), experimental frequency shifts ( $\Delta\nu$ ) for the dangling hydroxyl fundamental mode. The first line corresponds to the bare ice surface, the following lines correspond to the adsorption of the test molecules.

Adsorbed system	$\Delta E_{\text{Int}}$ (kJ mol <sup>-1</sup> )	$q_{\text{O}}$	$q_{\text{H2}}$	$d_{\text{OH1}}$	$q_{\text{H1}}$	$\omega_{\text{OH1}}$ cm <sup>-1</sup>	$\Delta\omega$ cm <sup>-1</sup> Calculated	$\Delta\nu$ cm <sup>-1</sup> Exp
bare H <sub>2</sub> O		8.723	0.591	0.9345	0.661	3692		
D <sub>2</sub> O						2691		
C <sub>2</sub> H <sub>2</sub> H <sub>2</sub> O	20.9	8.757	0.588	0.9418	0.746	3570	-122	-95 <sup>a</sup>
D <sub>2</sub> O					(+0.085)	2607	-84	-73 <sup>a</sup>
C <sub>2</sub> H <sub>4</sub> H <sub>2</sub> O	13.8	8.752	0.584	0.9411	0.741	3586	-106	-100 <sup>a</sup>
C <sub>2</sub> H <sub>4</sub> D <sub>2</sub> O					(+0.086)	2617	-74	-75 <sup>a</sup>
O <sub>3</sub> H <sub>2</sub> O	14.6	8.726	0.594	0.9342	0.657	3611	-81	-62 <sup>b</sup>
					(-0.004)			
CO H <sub>2</sub> O	11.7	8.763	0.586	0.9402	0.742	3620	-72	-58 <sup>c</sup> -60 <sup>d</sup>
CO D <sub>2</sub> O					(+0.081)	2639	-52	-44 <sup>d</sup> -36 <sup>d</sup>
N <sub>2</sub> H <sub>2</sub> O	3.3	8.739	0.582	0.9363	0.657	3675	-16	-22 <sup>e</sup> -16 <sup>f</sup>
N <sub>2</sub> D <sub>2</sub> O					(-0.004)	2678	-13	-19 <sup>d</sup> -16 <sup>d</sup>
Ar H <sub>2</sub> O	0.4	8.733	0.581	0.9357	0.664	3675	-17	-12 <sup>e</sup> -21 <sup>g</sup>
Ar D <sub>2</sub> O					(+0.003)	2676	-15	-12 <sup>g</sup>

<sup>a</sup>Reference 50.

<sup>b</sup>Reference 14.

<sup>c</sup>Reference 29.

<sup>d</sup>Reference 10.

<sup>e</sup>Reference 31.

<sup>f</sup>Reference 9.

<sup>g</sup>Reference 51.

implemented in the GAMESS(US) package,<sup>28</sup> using the same orbital basis set 6-31g(*d,p*), the admolecule having the same coordinates as adsorbed on the ice surface, this because the polarizability tensor components depend on the local cartesian axes.

In turn, the dipole moment  $\mu$  induced in each molecule adsorbed in a point  $\mathcal{P}$  above the surface generates an electric potential  $\mathcal{U}$  in each point  $\mathcal{O}$

$$\mathcal{U} = \frac{\mu \mathcal{P}\mathcal{O}}{\mathcal{P}\mathcal{O}^3}. \quad (2)$$

The electric field components in  $\mathcal{O}$  are deduced

$$\mathcal{F}_\alpha = -\frac{\partial \mathcal{U}}{\partial \alpha} \alpha = x, y, z. \quad (3)$$

### III. STRUCTURE OF THE ADSORBED ADLAYER AND VIBRATIONAL FREQUENCIES

All the systems described in this section, except Ar, have been or will be the subject of a separate paper, in this section only the major results are recalled and collected in Table I. The calculated interaction energies are not discussed again here, they are in general good agreement with the experimental ones, when available. Concerning the experimental methods developed in our laboratory, they are described in Refs. 14, 29, 30, and in a forthcoming paper.

#### A. Acetylene<sup>13,30</sup>

In the present work, only the model where the acetylene acts as proton acceptor is considered since it is expected to be the most perturbing structure for OH<sub>1</sub>. The molecular center-of-mass is located right above OH<sub>1</sub>.

The geometry of the dangling water molecule shows a noticeable lengthening of  $d_{\text{OH1}}$  due to the H-bond between H<sub>1</sub> and the acetylene  $\pi$  systems. This is reflected also by a transfer of the electronic density toward H<sub>1</sub> (0.085 electron), while H<sub>2</sub> remains unaffected. On the whole, the acetylene molecule undergoes a loss of 0.12 electron thus demonstrating its very weak Lewis base character.

The frequency shift [ $\Delta\omega_{\text{OH1}} = \omega_{\text{OH1}}(\text{ice} + \text{C}_2\text{H}_2) - \omega_{\text{OH1}}(\text{ice})$ ] is in good agreement in sign and magnitude with the experimental shifts. The point that the agreement between theory and experiment is similar for OH<sub>1</sub> and OD<sub>1</sub> is a good test for the validity of the force field since it is well known that a force field must be valid not only for the molecule itself but also for all its isotopic derivatives.

#### B. Ethylene<sup>31</sup>

Much like acetylene, ethylene is a proton acceptor but OH<sub>1</sub> interacts more directly with one of the two carbon atoms. C<sub>2</sub>H<sub>4</sub> does not act on ice as a proton donor, only one site of adsorption has been found.

The general trend is similar to C<sub>2</sub>H<sub>2</sub> but the H-bond is less energetic, as a consequence  $d_{\text{OH1}}$  is shorter.

The frequency shift is in remarkable agreement with the experimental ones for H<sub>2</sub>O as well as for D<sub>2</sub>O ices. The charge transfer from C<sub>2</sub>H<sub>4</sub> to the surface is of 0.10 electron, the ethylene basicity is even smaller than the acetylene one's.

#### C. Ozone<sup>14</sup>

Unlike the former systems, the ozone molecule is not adsorbed directly above OH<sub>1</sub>, but its central oxygen atom



lies above a four-coordinated water molecule. The stability of the system is provided by the electrostatic and van der Waals interactions and also by a very weak H-bond between one of the terminal ozone's oxygen and OH<sub>1</sub>.

The ice surface is very slightly perturbed by the ozone adlayer,  $d_{\text{OH1}}$  differs only by 0.0003 Å from its value on bare surface which is meaningless at the present level of calculation, the electron density on H<sub>1</sub> also is rather unaffected (−0.004 electron). However, the calculated shift is surprisingly large (−81 cm<sup>−1</sup>) in regards of these results, but in fairly good agreement with experiments (−62 cm<sup>−1</sup>).

#### D. Carbon monoxide<sup>12,31</sup>

The new optimization we performed for this work clearly confirms the major finding of the earlier paper,<sup>12</sup> i.e., carbon monoxide adsorbs preferentially above OH<sub>1</sub> through direct interaction with carbon, even if another less energetic adsorption site certainly exists.

CO being a typical model molecule for adsorption on all kinds of substrates including ice, a great amount of data has already been published, some of which are collected in Table I. The data differs according to experimental conditions. In our laboratory, a value of −58 cm<sup>−1</sup> was found on porous ice surface at a temperature of 60 K, showing there was good agreement with the quantum prevision. The charge transfer from CO to ice is 0.12 electron like in the case of acetylene.

#### E. Nitrogen<sup>31</sup>

Like ozone, the nitrogen molecule does not adsorb above OH<sub>1</sub>, it lies parallel to the surface plane above the four-coordinated water molecules, at equal distance from the dangling OH<sub>1</sub> and the dangling oxygen lone pairs. The interaction with ice is very weak and consequently the ice surface is unaltered.

The frequency shift is slightly underestimated but in good agreement with the experimental ones as determined in our Group, −22 cm<sup>−1</sup> at 60 K.

#### F. Argon

Ar adsorbs right above OH<sub>1</sub> but we did not look for an extra site elsewhere on the surface since this paper was only focusing on the  $\omega_{\text{OH1}}$  shift under adsorption.  $\Delta E_{\text{Int}}$  is near to zero after BSSE correction, but a real minimum was found in the potential energy surface as a function of the Ar altitude above the surface. Nevertheless, the interaction energy is far below the limit of confidence of the quantum method here carried out.

Despite this quasi zero adsorption energy, the calculated shift is in good agreement with experiment (−12 cm<sup>−1</sup> at 60 K, our Group experiment).

#### G. Discussion

Table I shows a good general agreement between (scaled) calculated and experimental frequency shifts. This good agreement is found for the various types of surface–adsorbate interaction: “strong” H-bond (C<sub>2</sub>H<sub>2</sub>), weak H-bond (C<sub>2</sub>H<sub>4</sub>), very weak H-bond (O<sub>3</sub>), van der Waals

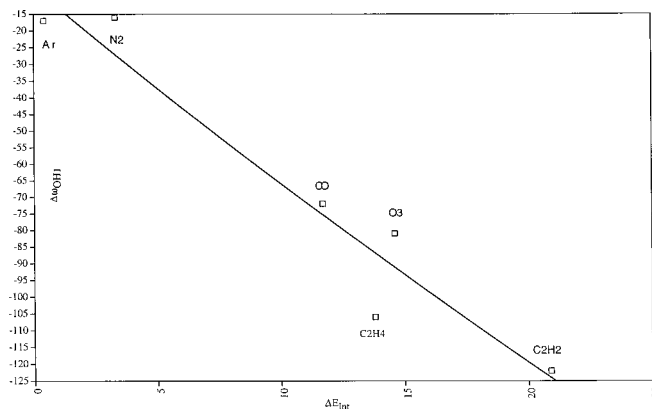


FIG. 2. Linear fitting of the calculated dangling OH harmonic frequency shifts (in cm<sup>−1</sup>) vs the calculated adsorption energy (in kJ mol<sup>−1</sup>).

forces (N<sub>2</sub>, Ar) and also for the subclass constituted by O<sub>3</sub> and N<sub>2</sub> that does not interact primarily with OH<sub>1</sub>. For most cases, H<sub>1</sub> is electron acceptor (about 0.08 electron) except in case of O<sub>3</sub> where it is electron donor (−0.004 electron) but the charge transfers are very small.

The adsorbate molecules are electron donors (C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, CO) or neutral (Ar, N<sub>2</sub>, O<sub>3</sub>). In any case, the water molecule always globally gains electronic charge from the adsorbate molecule or from its neighboring water molecules, but in a very small extend (0.102–0.119 electron). This underlines the very small effect of the chemical reactivity on the model molecules here investigated.

Furthermore, the ozone molecule provides a larger frequency shift although its interaction with OH<sub>1</sub> is very weak; the same for nitrogen which interaction is even smaller. This observation supports our assumption that for the chosen molecules, the chemical nature and also the acid/base character have little influence on the property under study. Obviously this would probably not be valid for more reactive systems.

At first sight, Fig. 2 exhibits a certain proportionality between the adsorbate–surface interaction energy and the frequency shift: the linear fitting is rather good. But, looking into the details and considering that these energies are theoretical ones, it can be seen for example that between acetylene and ethylene, an energy difference of 34% corresponds to a shift difference of 13%, although they both act as proton acceptors. Ozone molecule does not interact directly with OH<sub>1</sub> but its frequency shift and interaction energy are similar to those of ethylene.

The interaction of the OH<sub>1</sub> vibrator with the adlayer leads to weaken the associated chemical bond and then to make  $d_{\text{OH1}}$  longer. For the same reason the vibrator force constant is smaller and the vibrational frequency is red-shifted. Therefore, it certainly exists a relation between  $d_{\text{OH1}}$  and the interaction energy  $\Delta E_{\text{Int}}$ . As it can be seen in Fig. 3, a quadratic relation can be established but only subject to the imperative condition that the O<sub>3</sub> point be eliminated. For many aspects (frequency shift, hydroxyl bond length, Mulliken population and interaction energy), O<sub>3</sub> is very similar to N<sub>2</sub>. In particular, the quantum calculated moments of these two systems are comparable: O<sub>3</sub>, 16 D Å and N<sub>2</sub>, 10 D Å.

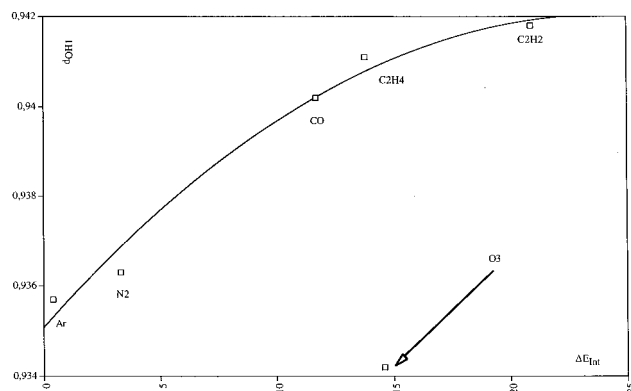


FIG. 3. Fitting of the calculated dangling OH bond lengths (in Å) vs the calculated adsorption energy (in  $\text{kJ mol}^{-1}$ ).

The conclusion that can be drawn from these considerations is that  $\Delta\omega_{\text{OH1}}$  does not depend on  $\Delta E_{\text{Int}}$  but  $\Delta\omega_{\text{OH1}}$  and  $\Delta E_{\text{Int}}$  and  $d_{\text{OH1}}$  presumably depend on a fourth physical variable. From this point of view, Holmes and Sodeau,<sup>32</sup> in their extensive experimental study on the halogenocarbons, have evidenced linear dependencies between  $\Delta\omega_{\text{OH1}}$  and the polarizability of the considered molecules, at least within homogeneous families:  $\text{CH}_3\text{X}$ ,  $\text{CH}_2\text{X}_2$ ,  $\text{CHX}_3$ ,  $\text{CX}_4$ .

For the systems covered in this work, there is no evidence of a simple relation (whether linear or not) between polarizability and  $\Delta\omega_{\text{OH1}}$ . The investigations will then be oriented towards the electric field that the polarizability of the adsystem is capable of inducing.

#### IV. ELECTRIC FIELDS IN ICE

##### A. Electric field above the bare ice surface

Table II shows the electric field strengths calculated using CRYSTAL98 at the center of mass of the adsorbed molecules (1 a.u. =  $5.1429 \cdot 10^{11} \text{ V m}^{-1}$ ). The induced dipole moments are also reported in the table. The  $z$  direction is along  $\text{OH}_1$ , positive fields are directed from O toward H. The calculated electric fields are very strong, they are of the same order of magnitude as those calculated by Toubin *et al.*<sup>33</sup> above a water monolayer adsorbed on  $\text{MgO}(100)$ . As a comparison, we also used CRYSTAL98 to calculate the electric field strength above the  $\text{O}^{2-}$  ion of the  $\text{MgO}(100)$  surface. At 4 Bohr (2.117 Å) this field is of  $17.4 \cdot 10^9 \text{ V m}^{-1}$ , and at 6 Bohr (3.175 Å)  $2.0 \cdot 10^9 \text{ V m}^{-1}$ . These two altitudes correspond approximately to those of  $\text{C}_2\text{H}_2$  and Ar above the ice surface. Comparing these values to those of Table II, it can be concluded that from an electrostatic point of view, the ice surface is nearly an ionic surface, just slightly less ionic than  $\text{MgO}$ .

The electric field exerted on the nitrogen molecule can be compared with Cohen de Lara *et al.* results.<sup>34</sup> These authors have studied the electric field encountered by this molecule when adsorbed in the NaA zeolite. Using the integrated IR intensity, they evaluated this field at  $4.7 \cdot 10^9 \text{ V m}^{-1}$ . A nonquantum theoretical model they developed concluded to  $4.5 \cdot 10^9 \text{ V m}^{-1}$ . Of course the coincidence of these values and that of Table II is purely fortuitous but it demonstrates that the fields calculated in the present work are in a credible

TABLE II. Components of the electric field exerted by the ice surface at the center of mass of the adsmolecule ( $F_x$ ,  $F_y$ , and  $F_z$ ), total electric field strength and induced dipole moment ( $\mu_{\text{Ind}}$ ).

Molecule	$F_x$ (a.u.)	$F_y$ (a.u.)	$F_z$ (a.u.)	Total field ( $\text{Vm}^{-1}$ )	$\mu_{\text{Ind}}$ (D)
$\text{C}_2\text{H}_2$	-0.0002	-0.0001	-0.0144	$7.4 \cdot 10^9$	0.39
$\text{C}_2\text{H}_4$	0.0104	-0.0031	-0.0080	$6.9 \cdot 10^9$	0.51
$\text{O}_3$	0.0096	0.0016	0.0051	$5.7 \cdot 10^9$	0.41
CO	-0.0001	-0.0001	-0.0075	$3.9 \cdot 10^9$	0.23
$\text{N}_2$	0.0079	-0.0003	0.0046	$4.7 \cdot 10^9$	0.25
Ar	-0.0001	-0.0000	-0.0043	$2.2 \cdot 10^9$	0.11

range of magnitude and also that the nitrogen molecule experiences the same electric field on the ice surface as on the ionic part of the zeolite. This last assumption is consistent with the comparison with the  $\text{MgO}$  surface.

The total field strengths encountered by the different adsorbed molecules vary continuously and approximately correspond to the order of the amplitude of the frequency shifts; the larger field is associated to the larger shift, and the smallest shift to the smaller field. Nevertheless, only the  $z$  component of the field influences the  $\omega_{\text{OH1}}$  frequency. From this point of view it should be noted that all the  $z$  components are negative except for ozone and nitrogen, again substantiating the idea that these two systems constitute a special subset of the ensemble.

The induced dipole moments are rather large and in proportion to the electric field strength. As an illustration the Ar atom gets a dipole moment equivalent to the permanent momentum of carbon monoxide.

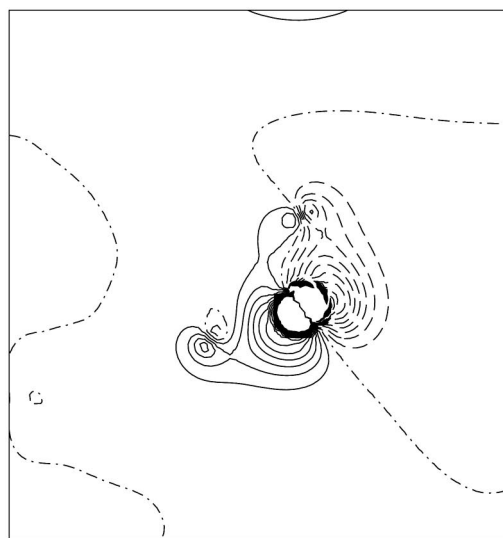
The field produced by the adlayer in turn causes the molecules constituting the ice surface to be polarized. This polarization is due to the change in the electronic distribution in the water molecules but also to the changes of geometry;<sup>35</sup> as a result the physical environment of  $\text{OH}_1$  is altered. Fig. 4(A) shows the electronic density of the  $\text{OH}_1$  water molecule with the argon adsorbed atop. Figure 4(B) shows the difference [ice+Ar] minus bare ice. There is a noticeable transfer of charge from the outer part of the molecule toward the inner part of the plane included between the two OH bonds. Globally, the atomic net charges thus remain quite unchanged as it can be observed on the Mulliken populations but the electric field along the  $\text{OH}_1$  direction is nevertheless perturbed. The same phenomenon occurs for all the other systems here considered, Ar just being the most demonstrative.

##### B. Electric field along the $\text{OH}_1$ direction

From the former section, it appears that the  $\text{OH}_1$  hydroxyl group is embedded in an electric field generated by the adsorbed adlayer: In our model the slab is covered by a layer of induced dipole moments all parallel to one another and their total field is the sum of each individual contribution. Considered separately, however, this electric field is certainly not very strong, the potential being in  $R^3$  vanishes very rapidly. The major perturbation of the system is more likely to arise from the ice surface polarization in the vicinity of  $\text{OH}_1$ .



(a)



(b)

FIG. 4. Electronic density of the dangling OH bearing water molecule (A) under Ar adsorption (B) difference with bare ice surface. In solid lines the gain in density with respect to the bare surface, in dotted line the loss in density. The contour map is computed for densities ranging from  $-0.5$  to  $+0.5$  electron with an interval of  $0.02$  electron between two successive contour lines.

As reported by Hermansson<sup>36</sup>  $\omega_{\text{OH1}}$  is only sensitive to the electric field along the OH bond, the effect of each of the perpendicular field components is negligible. We, therefore, calculated the total field by numerical differentiation of the PHF electrostatic potential along this bond, between  $\text{H}_1$  and O, and at a distance of  $0.5 \text{ \AA}$  from the oxygen atom, i.e., approximately at the middle point of the bond. On Table III are reported the total electric field strength  $F(0.5)$  calculated at this special point for the systems under consideration. Of course the field is very strong since the point is situated between two very close electric distributions, but if the reference is the bare surface (last line of Table III), the field variation  $\delta(0.5)$  is included within the same range of magnitude as the field above the surface.

Considering the  $\delta(0.5)$  values in Table III, it can be

TABLE III. Total electric field strength,  $F(0.5)$ , along the dangling OH bond, between O and H, at  $0.5 \text{ \AA}$  of O, the positive fields are directed from O to H.  $\delta(0.5)$  is the difference with respect to the bare ice surface (last line of the tableau). The calculated harmonic frequency shifts are from Table I.

Adsorbed system	$F(0.5)$ (a.u.)	$\delta(0.5)$ (a.u.)	$\Delta\omega_{\text{OH1}}$ ( $\text{cm}^{-1}$ )
C2H2	$-3.2900$	$-0.0324$	$-122$
C2H4	$-3.2872$	$-0.0297$	$-106$
O3	$-3.2468$	$0.0108$	$-81$
CO	$-3.2824$	$-0.0248$	$-72$
N2	$-3.2673$	$-0.0102$	$-16$
Ar	$-3.2648$	$-0.0072$	$-17$
H2O	$-3.2576$	$0$	$0$

noted that all of them are negative and the field is directed from  $\text{H}_1$  to O, except for ozone. The associated curve (Fig. 5, solid thick line) shows a neatly parabolic appearance although the curve fitting is done through a third order polynomial. This also remains true if the  $\text{O}_3$  point is discarded from the data set: the ozone point cannot be considered as an artifact but as a real physical point plainly belonging to the function  $\Delta\omega_{\text{OH1}}$  versus  $\delta(0.5)$ . In fact, this curve is typical of the vibrational Stark effect (VSE) of the hydroxyl group as described by Hermansson in a series of papers<sup>36</sup> where it is shown that if a homogeneous electric field  $\mathcal{F}$  is applied to the OH group ( $\text{OH}^-$  or  $\text{H}_2\text{O}$ ):

- The frequency shifts are always down-shifts, this is also observed experimentally,<sup>37,38</sup>
- the function  $\Delta\omega$  vs  $\mathcal{F}$  is approximately parabolic.

More precisely, the same author<sup>36</sup> gave the frequencies for an isolated water molecule calculated with the approximation double zeta plus polarization/second-order Møller–Plesset (DZP/MP2), i.e., a level of approximation similar to the present work and for an electric field of strengths ranging from  $-0.065$  to  $0.075$  a.u. The associated shifts (also scaled by a factor  $0.85$ ) are represented in Fig. 5 (broken line). The two curves (solid and dotted lines) are almost perfectly ho-

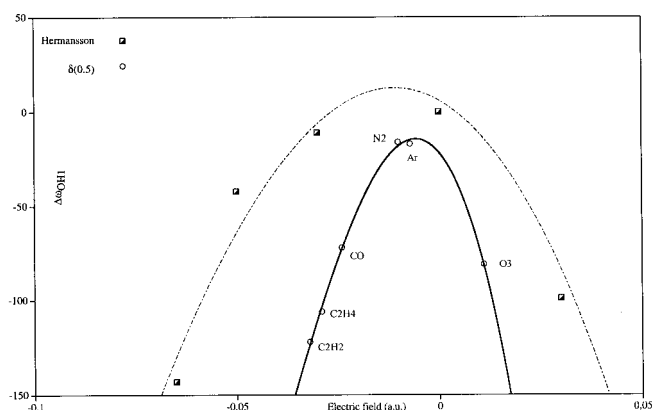


FIG. 5. Calculated dangling OH harmonic frequency shifts (in  $\text{cm}^{-1}$ ) vs the electric field component along the dangling OH bond. The solid thick line represents the present calculation, the electric field in  $\delta(0.5)$  the variation of the field strength calculated at  $0.5 \text{ \AA}$  of O. The dotted line illustrates Hermansson's calculation for a homogeneous electric field.

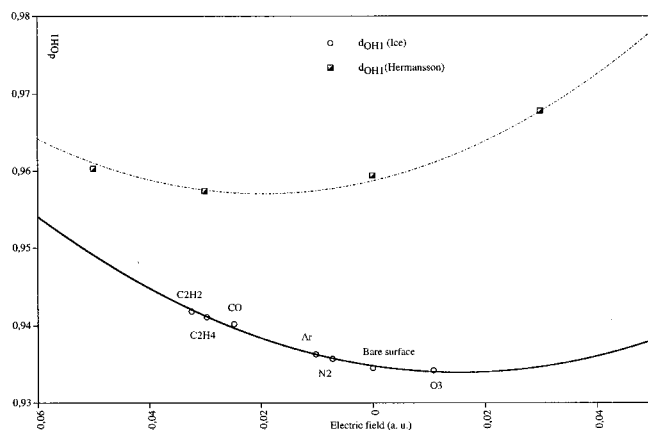


FIG. 6. Calculated dangling OH bond lengths (in Å) vs the electric field component along the dangling OH bond, same convention as in Fig. 5.

mothetic, the ratio can be evaluated to about 0.6. The Hermansson maximum is only more shifted toward the negative fields.

It is just as if every one of the  $\text{OH}_1$  water molecules were isolated in an effective electric field resulting from two components:

- A component belonging to the ice, i.e., the neighboring  $\text{H}_2\text{O}$  molecules on the surface and in the bulk. From Table III, this field is around  $-3.257$  a.u. and directed from  $\text{H}_1$  to O;
- a perturbing electric field resulting partly from the adsorbed layer and partly from the ice polarization thus retro-induced. This component ranges from  $-0.0324$  to  $+0.0108$  a.u. following the system under study.

This analysis is further substantiated by Fig. 6 representing the  $\text{OH}_1$  bond length as a function of the applied field strength. Again our results are displayed in a solid thick line and Hermansson's in a dotted line. The two representations are again almost homothetic. The two of them point to a minimum with a positive field for ice, negative for the isolated water molecule. The bond lengths are shorter in ice because of the cooperative effects of the hydrogen bonds.<sup>39,40</sup>

Compared with Fig. 3, the  $\text{O}_3$  point is now perfectly on the curve. Therefore, it would seem that what differentiates ozone from the other systems is that it generates a positive field on  $\text{OH}_1$  whereas the others generate a negative field.

## V. DISCUSSION AND CONCLUSION

A first analysis must be carried out on the selection of those variables representative of the problem under study: The large frequency shift of the dangling OH mode provoked by the adsorption of nonpolar, non reactive molecules.

From this point of view the comparison of Figs. 2 and 5 is very informative. The choice of the variable " $\Delta E_{\text{int}}$ " the adsorption energy, leads to a rather large dispersion of the data: Obviously the linear fitting is not credible. On the contrary if the chosen independent variable is the local variation

$\delta(0.5)$  of the electric field along  $\text{OH}_1$ , a parabolic law then emerges that exactly fits the calculated frequency shifts as displayed in Fig. 5.

Moreover, in Fig. 3 the  $\text{O}_3$  point appears as completely anomalous whereas in Fig. 6 it is normally situated on the parabola; its only specificity is that it induces a positive field component while the other systems induce negative fields. As explained in Sec. III, ozone does not adsorb directly above  $\text{OH}_1$  like the other molecules (except  $\text{N}_2$ ) but above a four-coordinated water molecule. Its induced dipole moment is nearly parallel to the  $\text{OH}_2$  bond and this explains why the field generated in  $\text{OH}_1$  is positive. Another consequence of this structure can be found in the Wilson  $F$  matrix and more precisely in the non diagonal element  $F_{12}$  between the  $\text{OH}_1$  and  $\text{OH}_2$  stretching modes. This constant is rigorously zero for  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{CO}$  adsorption: the two modes are exactly decoupled.  $F_{12}$  is nearly zero,  $-0.056$  and  $-0.039$   $\text{md } \text{\AA}^{-1} \text{rd}^{-1}$ , for  $\text{N}_2$  and  $\text{Ar}$  and its influence is negligible. For  $\text{O}_3$ ,  $F_{12}$  is large:  $0.730$   $\text{md } \text{\AA}^{-1} \text{rd}^{-1}$ .

Certainly a larger number of similar systems is needed to analyze exactly the physical meaning of this result. Nevertheless one explanation could be that in the case of ozone, the major component of the electric field along  $\text{OH}_1$  is due to the polarization of a water molecule relatively far from this vibrator. This polarization is transmitted to  $\text{OH}_2$  through the hydrogen bonds system and induces finally a stronger coupling between the two stretching modes and a large frequency shift. The conclusion is that the frequency shifts are all provoked by electric field variation but in case of  $\text{O}_3$  this variation is a consequence of the ice surface polarization whereas for the other systems the dangling OH bearing molecule is more directly involved.

In view of the well-known capabilities and limitations of the *ab initio* quantum calculations, the numerical results presented here are to be considered only at a semi quantitative level. Nevertheless, the very good accuracy of  $\Delta\omega_{\text{OH}_1}$  concerning argon, nitrogen and ethylene must be highlighted. On another hand, the discrepancy of the quantum results with respect to experiment is more significant for acetylene and ozone and to a lesser extent for carbon monoxide. Keeping in mind that in the definition of the adlayer adopted in the present paper all the molecules are equivalent and mutually parallel, there is only one adsorption site per unit crystalline cell. In fact, it has been well established, both experimentally and theoretically, that for example there are two nearly equivalent sites of adsorption for acetylene. Only one site has been found in our laboratory for ozone, but two infrared bands are assigned to carbon monoxide<sup>12,41</sup> and nitrogen<sup>42</sup> on amorphous ice. Therefore, the "real" adlayer is certainly constituted by differently oriented molecules. Nevertheless, adding a perturbing admolecule to the main site we have determined would require too much calculation and it must borne in mind that the adlayer that supports the present analysis is only an approximation and that the fields thus calculated can be perturbed by non equivalent molecules. However, this has little influence on the general analysis of the physical phenomenon.

The works published on the VSE in relation to the physics and chemistry of surfaces are rather scarce and they al-



ways deal with the spectra of the adsorbed moieties, never with the substrate.

Bagus *et al.*<sup>43</sup> devoted their analysis to CO and CN chemisorbed on Cu(100) electrodes. They aimed to differentiate the Stark effect on the vibrational frequencies from the physical and chemical effects. They concluded also that the shifts are chiefly due to the VSE but showed that the most important effect of the electric field is to change the equilibrium bond length  $r_e$ . This conclusion is not transferable to the ice surface:  $d_{\text{OH1}}$  varies only on its fourth digit under ozone adsorption, yet the shift is considerable. This emphasizes the importance of the water molecules' polarization in ice.

Bishop *et al.*<sup>35</sup> studied the VSE by a quantum method. They were interested in the effect of the physical environment (solvents and zeolites) on the molecular properties. In an application to CO<sup>35</sup> they showed that the frequency shift can be developed as

$$\Delta\omega = -1.81 \cdot 10^4 (\mathcal{F}_z^2) + 1.99 \cdot 10^3 (-\mathcal{F}_z). \quad (4)$$

This equation justifies the parabolic appearance of the two curves in Fig. 5. In Ref. 35 Bishop also discussed the nonlinear effects. The frequency dependent hyperpolarizability for instance modifies the electric field but also induces changes in the geometry and the electronic density. This type of effect is implicitly included in the PHF calculation and therefore in the results displayed in Table I, but the explicit calculation of hyperpolarizabilities is impossible to investigate in a system as complex as an ice slab.

Holmes *et al.*<sup>32</sup> tried to prove a relation between halomethane polarizabilities and OH frequency shifts on amorphous ice surfaces. A linear law was established within each set CXH<sub>3</sub>, CX<sub>2</sub>H<sub>2</sub>, CX<sub>3</sub>H, and CX<sub>4</sub>, but the law fails if the four sets are collected in one unique ensemble. In fact, the field generated by the adsorbed molecules depends not only on the polarizability but also on the adsorption site topology. The polarizability being a tensor, its nine components depend on the molecule orientation above the surface. Holmes *et al.* have little information on this orientation since they did not perform any structural calculation. They claimed that this sort of system interacts with ice through lone pair donation to the proton H<sub>1</sub>. It is, therefore, likely that within a homogeneous family the molecular orientations are all similar and then they generate a field roughly proportional to the polarizability tensor trace. But this cannot be generalized from a family to another and then the linearity disappears hopping from CXH<sub>3</sub> to CX<sub>2</sub>H<sub>2</sub> for example. According to the present analysis, the whole series should become homogeneous if the frequency shifts were related to the electric field arising from polarizabilities.

Andres *et al.*<sup>44</sup> reported *ab initio* harmonic frequencies for the water OH vibrator in external fields of strength ranging between 0 and 0.05 a.u. They found a frequency down shift in each case but they did not mention the nonlinearity of these shifts. In the present work, nonlinearity, expressed through a polynomial fit, is essential to explain the special behavior of ozone.

Liu and Dijkstra<sup>45</sup> investigated the changes in vibrational transition frequencies as effects of hydrogen bonding. They attributed them (i) to the mutual, linearly varying part of the electric interaction of the species in the complex and (ii) the intrinsic anharmonicity of the HF potential curve.

The papers most closely related to the present work are clearly those already mentioned by Hermansson. They deal with the OH<sup>-</sup> anion<sup>36</sup> or the water molecule<sup>36</sup> plunged in a homogeneous electric field. These studies confronted to the present one particularly through Figs. 5 and 6, back up our assertion that the ice surface water molecule bearing the dangling OH group can be represented as an isolated molecule immersed in an effective electric field generated by the rest of the solid. The vibrational spectra of this molecule is modified by a perturbing field, oriented negatively or positively with respect to the OH<sub>1</sub> direction. This field is generated by the induced dipole moments in the adsorbed molecules and by the polarized medium. Figure 5 is demonstrative enough of this representation. The important point is that this model is unique for all the nondipolar adsystems here considered and independent of the strength of the interaction potential. The bond length  $d_{\text{OH1}}$  is consistent with this representation (Fig. 6).

It is remarkable that the Lewis acidity (resp. basicity) of the test molecules is reflected through the electric field variation  $\delta(0.5)$ : A base which adsorbs above the dangling OH provides a negative value of  $\delta(0.5)$ ; on the contrary, an acid interacts preferentially with the oxygen part of the surface and generates a positive value of  $\delta(0.5)$ . These calculations reveal to a certain extent a link between the acid (resp. base) character and  $\delta(0.5)$ , whereas the chosen molecules are weak Lewis acid (resp. base). Nevertheless, the very small number of test molecules considered in this paper does not allow to conclude definitely on this interesting point.

Note that the only goal of our model is to contribute to the understanding of one of the physical phenomenon responsible for the large frequency shifts observed under adsorption. The numerical results can be criticized on two points:

- (1) It can seem totally artificial to isolate the vibration modes of one molecule from a solid such as ice. In fact, this approximation would not be possible for the other OH mode entangled into the H-bond network. OH<sub>1</sub> is not H-bonded and within each unit cell it can be considered with a good degree of accuracy as a local mode isolated from the other collective modes of the bulk. However, a certain amount of disorder is found in porous ices that support the comparison of present results with experiment. That is considering it is more than likely that the collective modes extend over more than a few molecules.<sup>46,47</sup>
- (2) The structure of the admonolayer is rather artificial since all the adsorption sites are strictly equivalent. It has not been determined whether the lateral interactions impose a different structure when the coverage extends and reaches completion. This could be noticeable for quadrupolar molecules such as N<sub>2</sub> or CO. This effect could

explain to some extent the discrepancy between experimental and theoretical shifts for acetylene.

Concerning ozone, however, this seems improbable in view of the spectroscopy experiment developed in our group and the anharmonic effects must also be taken into account. It is well known that they can be very important for H-bonded solids,<sup>48</sup> up to 20% of the total frequency shifts according to Silvi *et al.*,<sup>49</sup> but we do not have any tools to investigate them in the present case. Nevertheless, differences of up to 27 cm<sup>-1</sup>, the maximum in Table I, are very usual in *ab initio* calculation and cannot alter the major conclusions of this study.

The most important conclusion of this analysis is that it is clearly established that the electric field generated by the adsorbed species plays an important role in the adsorption processes on ice surfaces while it was shown that the VSE dramatically influences the vibrational frequencies.

The electric field variation must also perturb the chemical reactivity of the adsorbed systems. An electric field acts in an opposite fashion on nuclei and electrons. As a consequence the geometries of minima and transition states of the molecular systems are changed. Moreover, in electronic excited states, the excited electrons are located at a larger distance from the nuclei than in the ground state, then they are certainly more sensitive to the electric field. The result is that the chemical reactivity on ice must be reconsidered in detail and more particularly photoreactivity. As a consequence, in our forthcoming works, we plan to represent the perturbing electric field in the quantum calculations by an effective homogeneous field.

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