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A Study of the Interaction between Halomethanes and Water-Ice

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The infrared spectra of a series of twenty-three halogenocarbon compounds co-deposited onto water-ice held at 12 K have been investigated. Perturbations to the water (D_2O) sites which are not saturated in the absence of guests show distinct trends depending on the type and extent of halogen substitution in the occluded molecules. The data are quantified in terms of the IR spectral positions of the so-called “dangling bond” of water; interaction also leads to changes in the halogenocarbon compound IR spectra. It is clear from the results that the halomethanes interact through lone pair donation from a halogen atom to a deuterium atom of the water molecule. A high level of correlation is found between the shift in the dangling bond and both the charge density and the molecular polarizability *within each separate series* for compounds of the formula CF_nH_{4-n}, CCl_nH_{4-n}, and CBr_nH_{4-n} (where $n = 1-4$). It is demonstrated that profiles correlating either ionization potentials or molecular polarizabilities for Cl- and Br-containing halogenocarbons with dangling bond shift provide an accurate method for predicting the respective physicochemical parameters. When a combined polarizability/charge interaction parameter is plotted against the dangling bond shift a straight line, also with predictive capabilities, results.

Introduction

The interactions between molecules and ions with water-ice surfaces have attracted considerable experimental attention over the last 10 years because of their key influence on the chemistry associated with the Antarctic ozone “hole”.[1] Several studies have shown that the interfacial water-ice sites are sensitive to occluded molecules and that the type and extent of interaction can be monitored using infrared spectroscopy.[2−8] The interpretation of the results is based upon the measurement of the wavenumbers observed for the −OH (−OD) fundamental mode of surface water molecules.

Water is capable of forming four hydrogen bonds to other water molecules but in amorphous water-ice films, the coordination sites of H_2O (D_2O) molecules may not be fully saturated. Devlin and co-workers[2−3,9] have shown that these sites give rise to two bands in the IR spectra at 3720 (2748) and 3696 (2727) cm^{-1} corresponding to 2- and 3-coordinated water molecules, respectively. These features are very weak in comparison to the signal arising from the bulk water-ice and are trivially termed the “dangling bonds”.[2−10] They are observed to shift as a function of interaction with other molecules. For example, studies involving the adsorption of hydrogen and nitrogen have been carried out on amorphous ice. In both cases, shifts of 10 cm^{-1} to lower wavenumbers were observed for each adsorption site.

IR absorption frequencies of the guest can also be monitored. For example, the C−O stretch of carbon monoxide adsorbed on amorphous water-ice was found to split into a doublet at 2153 and 2137 cm^{-1}, which indicates that adsorption occurs at two sites. The position of the higher wavenumber band agrees with the value for CO complexes with HF, HCl, and HBr at low temperatures,[11] in which the carbon monoxide molecules act as proton acceptors.

The effects of adsorption for more complicated molecules have also been studied on water-ice surfaces. Horn et al.[7] observed that the dangling bond shift (again to lower wavenumbers) varies within the halogenocarbon series as follows: $CCl_2F_2 < CCl_3F < CCl_4$. They reported that the magnitudes of the measured shifts show a strong correlation with a number of physicochemical parameters including the molecular polarizability and the C−Cl bond dissociation energy. However, the limited range of compounds studied meant that they were unable to make any universal or quantitative conclusions.

When strong hydrogen bonds are formed with the surface water molecules, the dangling bonds disappear. This behavior is evident for propanone on ice when shifts in the C═O stretching modes are observed as a result of adsorption, but the weak surface water features are not observed because the shift is of such a magnitude that the vibrational band due to the bulk water system dominates the spectrum.[12,13]

From the above studies, it is clear that the surface water molecules can interact with guest molecules in two ways. One type of behavior is based on the −OH function acting as a proton donor, and the other is based on water functioning as a Lewis base. The hydrogen atom of water can interact with an electron dense center either when present in the guest as a highly electronegative atom, such as chlorine, or with its bonding electrons, as is the case with the hydrogen molecule.

The extent of the dangling bond shift depends on both the mode and strength of interaction where the change in the bond strength can be described by eq 1:

$$\Delta\nu = 1/2\pi c_o \frac{(k-k')}{\sqrt{\mu}} \tag{1}$$

where ($\Delta\nu$ is the shift in wavenumber of the dangling bond, c_o is the speed of light in a vacuum, k is the force constant of the OD bond, k' is the force constant of the OD bond in the complex, and μ is the reduced mass of D_2O.

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Therefore the shift in the dangling bond absorption to lower wavenumbers in these (and previous) studies implies that the bonding within the surface water molecules has been weakened by the interaction with the guest molecules. Furthermore, the guest molecules also undergo changes in their bonding structure, as is evident by shifts in their vibrational spectra. In the past researchers have used such measurements to predict parameters such as proton affinity from the IR spectra. The purpose of this report is to assess whether the spectral changes can also be used in a predictive sense to monitor molecular polarizability, ionization potential, and atomic charge, i.e., data which is otherwise difficult to directly measure. To this end the IR spectra of a series of twenty-three halogenocarbon compounds on water-ice has been investigated.

Experimental Section

Refrigeration was provided by a helium compressor (model HC-2D, (APD Cryogenics). The device consists of a single-stage, water-cooled, rotary compressor capable of cooling the two-stage DE202 expander (DE202, APD Cryogenics) down to 12 K. The temperature was monitored and controlled by a Lakeshore 330 model autotuning temperature controller, which has two independent silicon diode sensor inputs and a heating output of 25W.

The deposition cold window consisted of a 25 mm diameter, 2 mm thick polished cesium iodide window seated on indium gaskets to provide good thermal contact with the nickel-plated copper holder. This was housed inside a stainless steel vacuum shroud fitted with a removable extension sheath. The four ports of the rotatable sheath were fitted with a pulsing nozzle, a Spectrosil B window to allow photolysis with light of wavelengths greater than 200 nm, and two 38.5 mm diameter, 5 mm thick cesium iodide windows to allow infrared detection.

The cesium iodide window was arranged at a 45° angle to both the infrared beam and the deposition manifold. In this arrangement the absorption intensity was maximized and allowed the shroud to remain at a fixed position in the beam for both deposition and data collection. This arrangement results in more accurate subtraction of the experimental spectra from the background spectrum.

Infrared absorption spectra were recorded with a Digilab FTS-40 FTIR spectrometer using a liquid nitrogen cooled HgCdTe (MCT) detector. A He/Ne 633 nm laser serves as the internal infrared source. Typically single beam spectra were taken at 1 cm^{-1} resolution and boxcar apodized. Background spectra were computed from the coaddition of 1024 interferograms and the experimental spectra from 64 scans.

Matrix Preparation and Deposition. Gas handling, purification, and mixture preparation for the matrix experiments were carried out on a mercury-free Pyrex-glass vacuum line fitted with Young's greaseless Teflon stopcocks. The vacuum was maintained by a silicone oil diffusion pump backed by a two-stage rotary pump. This pumping arrangement was capable of attaining pressures of the order of 10^{-5} mbar as measured by Pirani and Penning gauges (Edwards). The pressures of the gases introduced into the vacuum line were monitored by two MKS Baratron capacitance manometers (1000 and 10 Torr). Cajon Ultra-Torr stainless steel connectors and Young's greaseless ball joints fitted with O-rings were used to make attachments to the gas line.

Two bulbs were used: a 2 dm^3 glass bulb for the D_2O and a 500 cm^3 bulb for the halogenocarbon. Typical pressures in each bulb were less than 13 mbar. The matrix bulbs were transferred to the cold-head pulsing manifold, and then the line was evacuated to 10^{-7} mbar by an Edwards Diffstak diffusion pump (model 100MLN2) backed by a two-stage rotary pump (Edwards E2M8). The pressures were monitored by Pirani and Penning gauges (Edwards).

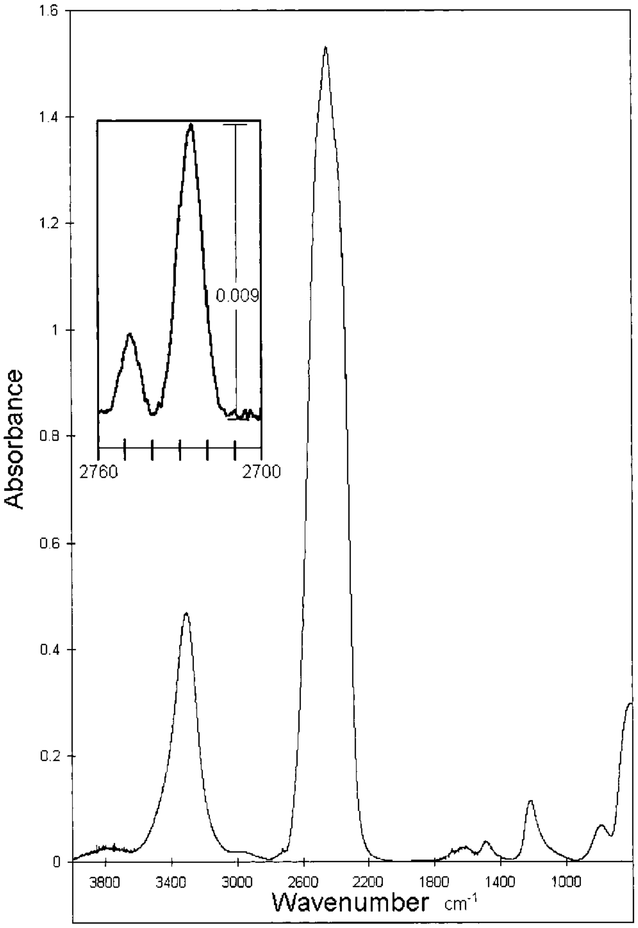

Figure 1. FTIR spectrum for D_2O measured at 12 K showing the "dangling bond" positions.

The gas mixtures were allowed to mix in the line attached to the deposition manifold for at least 15 min prior to deposition. The mixtures were then pulsed on manually by consecutively opening and closing two Young's taps on the manifold to produce water:halogenocarbon matrixes with a ratio of 1:5. The volume of each pulse was approximately 10 cm^3, and the pulsing rate was 2 min^{-1}. The thickness of the film is estimated by absorption intensity to be on the order of 500 monolayers. Spectra were initially recorded upon deposition at 12 K, then all films were warmed to 85 K and then recooled prior to remeasurement of IR spectra, which were measured before and after annealing; no shifts were observed other than for CF_4, as discussed below.

D_2O was used instead of H_2O in order to minimize the problems associated with gas-phase water vapor in the spectra.

Results

The IR spectrum associated with the deposition of deuterium oxide at 12 K was measured and is shown in Figure 1. The spectral characteristics are the same as those found by Devlin[1] and are therefore consistent with the production of an amorphous film rather than a more structured nanocrystal. The bulk −OD stretching band is observed as a broad absorption feature centered at 2473 cm^{-1}, and the associated ν_2 bending mode appears at 1212 cm^{-1}. In the spectrum shown in Figure 1,

TABLE 1: Measured "Dangling Bond" IR Shifts for the Halomethanes

compound	dangling bond position cm^{-1}	dangling bond shift cm^{-1}
CF_4	2718	10
CF_3H	2708	20
CF_2H_2	2694	34
CCl_4	2697	31
CCl_3H	2690	38
CCl_2H_2	2680	48
$CClH_3$	2663	65
CBr_4	2681	47
CBr_3H	2679	49
CBr_2H_2	2670	58
$CBrH_3$	2658	70
$CClF_3$	2717	11
$CBrF_3$	2714	14
CCl_2F_2	2708	20
CBr_2F_2	2699	29
CBr_3F	2691	37
$CFCl_3$	2701	27
$CBrCl_3$	2694	34
CF_2ClH	2703	25
CCl_2BrH	2686	42
$CClBr_2H$	2682	46
$CClBrH_2$	2673	55
CF_2ClBr	2706	22

absorption peaks associated with H_2O and HDO are also apparent. The bulk H_2O/HDO stretch appears at 3322 cm^{-1} and the respective ν_2 modes are observed at 1696 and 1482 cm^{-1}. Two weak bands, which are superimposed on the bulk −OD stretching feature, are observed at 2749 and 2728 cm^{-1}. These bands are due to vibrations of 2- and 3-coordinated dangling −OD bonds, respectively.

The assignment of the bands to such surface defects was confirmed by monitoring their behavior as a function of increasing surface coverage and temperature. These weak features grow less rapidly as further water is deposited and, as the film is annealed, the intensities of the two bands decrease. The 2749 cm^{-1} band disappears at temperatures between 60 and 80 K, and the three-coordinate band disappears when 160 K is reached. These latter changes coincide with a sharpening of the other absorption bands and the appearance of structure within the −OD stretching band.

When a series of haloalkane guests are introduced to the system, the two weak bands due to the dangling bonds of the unperturbed water-ice system are replaced by a single weak absorption peak that has shifted to a lower wavenumber. The positions of these new features are presented in Table 1. The spectra of the halogenocarbon compounds themselves are also modified: the carbon−halogen stretching modes shift to lower wavenumber from their gas-phase, counterpart values.

Discussion

The Interaction between the Water-Ice Surface and the Halogenocarbon Guests. The two absorption peaks observed, which are due to the unperturbed dangling bond of D_2O appear in water-ice at 2749 and 2728 cm^{-1}. The introduction of halogenocarbon guests to this surface result in the spectral perturbations which are summarized in Table 1. In each case only one band is observed and the values are given relative to the wavenumber for three-coordinated water at 2728 cm^{-1}, because computer simulations have shown that there are three times the number of 3-coordinated species than their 2-coordinated counterparts.[14] Furthermore, in the same report, it was shown that annealing of water-ice to 30−60 K leads to a structural rearrangement of the film where the 2-coordinate sites reorganize to form the more fully saturated sites.[14] In the present study the dangling bond at 2749 cm^{-1} disappears as the film is annealed to 80 K corresponding to a loss of 2-coordinate sites; the 2728 cm^{-1} band remains unchanged. The observation of only one dangling bond absorption band upon interaction of the adsorbates with the water-ice is consistent with a similar reorganization occurring in which the 2-coordinate sites disappear.

There are some very clear trends in the red-shift observed for the dangling bond, in particular along the individual brominated, chlorinated, and fluorinated methane series, i.e., CBr_4−CH_3Br, CCl_4−CH_3Cl, and CF_4−CF_2H_2. In each series the magnitude of the shift of the dangling bond increases as the halogen atoms are replaced by hydrogen atoms.

In studies of the hydrogen bonding between chlorinated methanes and the oxygen atom of liquid water dimers, Hobza and co-workers[15,16] found that the interaction energy increased in the order $CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$. It was predicted from their calculations that CH_3Cl and CH_2Cl_2 were "far from able" to perturb the hydrogen bonds in the water dimer and therefore may be expected to not complex. However, in the present low-temperature experiments, the wavenumber shifts associated with the water-ice dangling bonds for the compounds CCl_4, $CHCl_3$, CH_2Cl_2, and CH_3Cl (31, 38, 48, 65 cm^{-1}, respectively) were observed to *increase* as the number of halogen atoms was reduced. These results imply that the degree of interaction with the water-ice surface occurs in an order opposite to that predicted from the liquid-phase study. Such a contrast indicates that the dominant interaction on the surface of the water-ice films is not the same as that calculated for the bulk fluid system.

Hydrogen-bonding interactions in the bulk solid phase for the CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl series have also been investigated. In these low-temperature studies, the interactions between HF and CCl_4, $CHCl_3$, CH_2Cl_2, or CH_3Cl[17] in argon matrixes were analyzed using IR spectroscopy. In all cases the H−F infrared stretching frequency was observed to shift to lower wavenumbers upon interaction with the compounds and a variety of 1:1 complexes were revealed. Complexation was shown to occur with varying efficiency either through the H- or the F-atom of the diatomic. Thus the RCl−HF hydrogen-bonded complex predominated over its FH counterpart in the cases of CCl_4 and $CHCl_3$, but for CH_2Cl_2 the trend was reversed to give the "anti-hydrogen-bonded" complex as the major product. For the case of $CHCl_3$ a third 1:1 complex of the type, HF−$HCCl_3$ was also identified; however, later theoretical studies were unable to confirm its existence.[18]

The shifts (from the matrix HF Q-band at 3919 cm^{-1}) were determined and shown to follow the order $CCl_4 < CHCl_3 \ll CH_2Cl_2 \ll CH_3Cl$ for the hydrogen-bonded interactions. Proton affinities were calculated for the halogenocarbon compounds from the IR shift data and the following values were given: 130 (CCl_4), 133 ($CHCl_3$), 145 (CH_2Cl_2), 160 (CH_3Cl) kcal mol^{-1}. However, it should be noted that the treatment does not take the conformation of the complexes fully into account and therefore provides a better indication of proton affinity trend rather than exact value.

More recent ab initio calculations have determined the equilibrium structures of the 1:1 complexes. They also calculated that the order of stability for the most stable complexes on the MP2-level potential energy surfaces is as follows: $HF{:}CCl_4 < HF{:}CHCl_3 < HF{:}CH_2Cl_2 < HF{:}CH_3Cl$. This prediction parallels the order of the increasing electron density on the chlorine atom. However, the geometries of the complexes were determined to

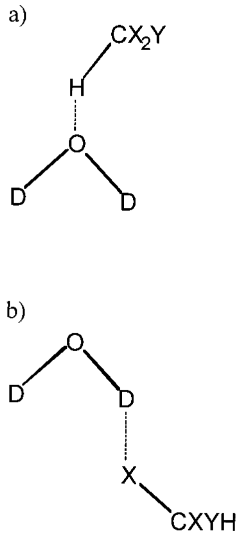

Figure 2. Schematic to visualize (a) anti-hydrogen bonding type interaction, (b) hydrogen bonding type interaction.

be highly diverse and so the H−F stretching frequency was found only to correlate with complex stability when the HF acted as a proton donor within a set of the same structural type.[19]

In view of the above studies, the magnitudes and trends of the shifts observed in the present water-ice experiments are consistent with the occurrence of hydrogen-bonded interactions between the surface water and the halogen atom of the guest, a theory which supports the suggestion by Devlin[2,14] that a water molecule in a three-coordinated surface site prefers to act as a proton donor. One possible schematic to help visualize this interaction (and the anti-hydrogen bond) is shown in Figure 2.

The controlling influences on the interaction are expected to be those normally associated with molecular species, although they could be modified by the heterogeneous nature of the system. A priori, the observed IR shifts should result from a direct Coulomb component (proportional to charge) along with a second factor due to an induced dipole interaction (proportional to polarizability). These features were therefore initially considered in an attempt to build a predictive method for physicochemical parameters such as atomic charge using IR shift data.

The Effect of Charge and Molecular Polarizability on the Interaction between the Halogenocarbons and Water-Ice. In a preliminary communication by Horn et al.,[7] shifts in the dangling bond IR frequency were shown to vary along the sequence CF_2Cl_2 < $CFCl_3$ < CCl_4 for deposition of the compounds on D_2O-ice. The observation was made for this limited data set that correlations between the magnitude of the dangling bond shifts and either the molecular polarizabilities or the C−Cl bond dissociation energies were apparent. However, no details were given in the report and therefore a quantitative treatment has been performed in this study for twenty-three pentatomic halogenocarbon compounds in order to gain a more detailed insight into the shift phenomenon.

Specifically, the strength of the interaction would be expected to be larger for compounds with a greater dipole−dipole attraction. Thus, a molecule with a greater negative charge on the halogen atom should form a stronger bond with the water-ice deuterium atom and subsequently exhibit a larger red-shift in the dangling bond.

Two factors affect the amount of charge localized on the halogen atom, which interacts with the surface water. The first is intramolecular and depends on the ability of the remainder of the halogenocarbon molecule (CY_3) to inductively donate or withdraw electrons in the C−halogen bond. The second is intermolecular and depends on the degree of electron cloud distortion (polarizability) experienced by the guest upon interaction with the surface.

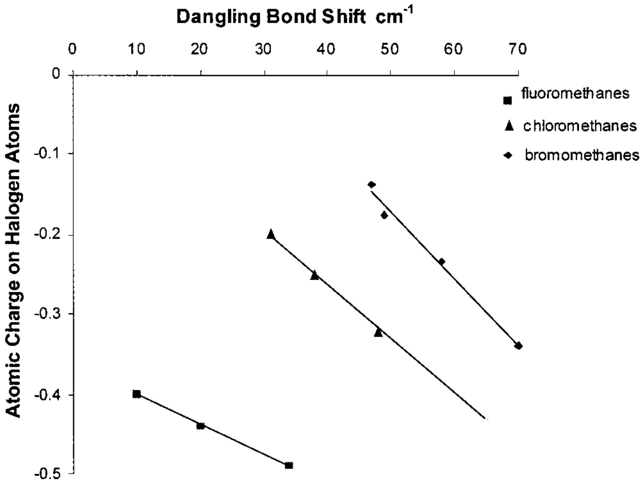

Figure 3. Graph of charge density[19,20] of the halomethanes against “dangling bond” IR shift.

As the number of hydrogen atoms in the molecule increases for each series of halogenocarbon, CF_nH_{4-n}, CCl_nH_{4-n}, and CBr_nH_{4-n} (where $n = 1-4$), the negative charge on the remaining halogen atoms has been shown to increase.[19,20] In the series CBr_nH_{4-n}, where $n = 1-4$, the bonding with the water-ice film in each case is through the bromine atom. The electron withdrawing effect of the CY_3 group, to which the bromine atom is bonded, affects the electron donating ability of the bromine atom. Therefore the sequential replacement of halogen in the CY_3 group by a hydrogen atom would make the CY_3 group less electron withdrawing. In the extreme case where all the halogens are replaced to form a CH_3 group, the electrons would be pushed toward the halogen.

The present experimental study shows that a simple inductive interpretation of the interaction is not sufficient when a water-ice surface is involved. Hence Figure 3 shows a plot of halomethane charge density against dangling bond shift. Although *within a series* (F, Cl, or Br) the predicted shift vs charge trend appears to be followed, an apparent contradiction arises for the overall picture. Thus, the fluorinated methanes have a greater negative charge compared to the chlorinated counterparts, which in turn are more negatively charged than the brominated compounds, but the observed IR shifts are found to follow an inverse order. Hence for the fluorine compound series, the electrons are held closest to the nucleus and are therefore less able to interact with the surface deuterium atom of the water-ice. In addition, the C−halogen bond strength increases in the order C−Br < C−Cl < C−F. This fact indicates that the electrons on the halogen are more localized in the bond with a C−F group compared to the C−Cl or C−Br cases and means that they are less available to directly interact with the surface deuterium atom. Such an effect is known to manifest in kinetics experiments: for example, the reaction between CF_3Cl and hydrogen atoms.[21,22] Here the results agree with predictions based on the difference in C−F and C−Cl bond strengths because the reaction produces CF_3 and HCl. The analogous reaction between CF_3Br and hydrogen atoms has been studied by Skinner and Ringrose[23] who observed formation of CF_3 and HBr rather than HF and CF_2Br. These observations indicate that the preferential mode of reaction is with the bromine atom, as predicted from the current spectroscopic measurements based on the dangling bond shift.

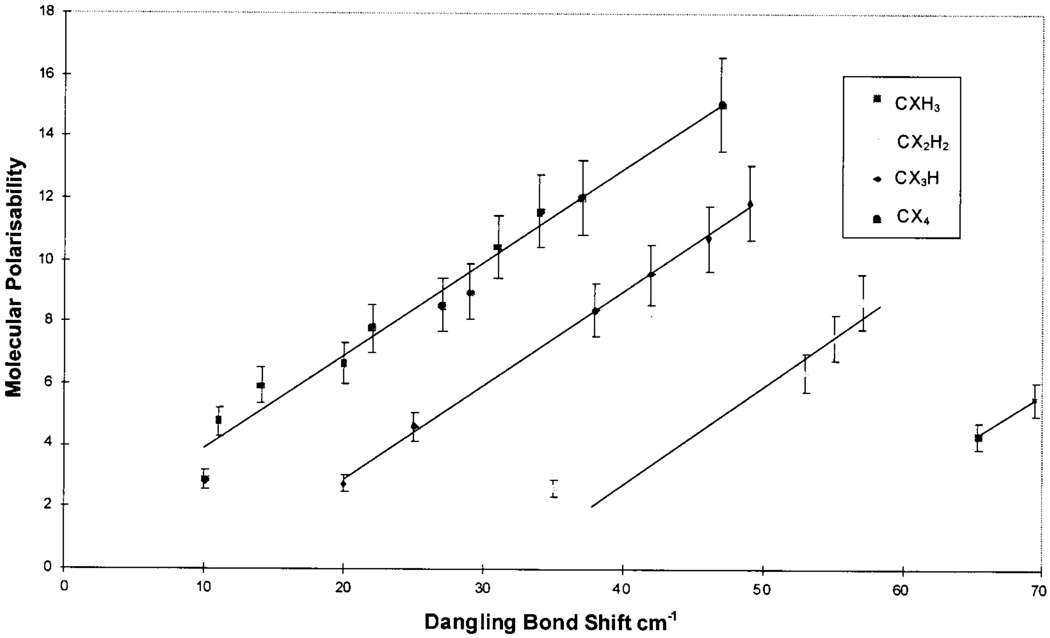

Figure 4. Graph of molecular polarizability of the halomethanes against "dangling bond" IR shift.

TABLE 2. Comparison between Molecular Polarizability and the "Dangling Bond" IR Shift for the Halogenocarbons

compound	molecular polarizability[25]	dangling bond shift cm^{-1}
CF_4	2.88	10
CF_3H	2.74	20
CF_2H_2	2.60	34
CCl_4	10.48	31
CCl_3H	8.44	38
CCl_2H_2	6.40	48
$CClH_3$	4.36	65
CBr_4	16.40	47
CBr_3H	12.88	49
CBr_2H_2	9.36	58
$CBrH_3$	5.84	70
$CClF_3$	4.78	11
$CBrF_3$	6.26	14
CCl_2F_2	6.68	20
CBr_2F_2	9.64	29
CBr_3F	13.02	37
$CFCl_3$	8.58	27
$CBrCl_3$	11.96	34
CF_2ClH	4.64	25
CCl_2BrH	9.92	42
$CClBr_2H$	11.40	46
$CClBrH_2$	7.88	55
CF_2ClBr	8.16	22

The relationship between molecular polarizability and dangling bond shift has also been explored in the current study: Table 2 and Figure 4 show summaries of the results obtained. The four profiles shown in the diagram represent (i) full halogenation, (ii) tri-halogenation, (iii) bi-halogenation, and (iv) mono-halogenation. The most important observation is that the best-fit lines give linear trends with similar gradients for each grouping. Further inspection of the data indicate that for the fully halogenated compounds, the most polarizable molecules exhibit the largest shift in the dangling bond; a similar trend is found for the trihalogenated methanes. Furthermore the shift observed is larger for the trihalomethanes than for the tetrahalomethanes of the same molecular polarizability. The fact that the gradients of the lines for the two series is the same indicates that the mode of interaction for the trihalomethanes with water-ice is identical to that observed for the tetrahalomethanes. Fewer data points are available for the mono- and di-substituted methanes, but the data for both series suggests that the interactions are again the same.

The observations that the wavenumber and molecular polarizability gaps between the best-fit lines increase as a function of the number of hydrogen atoms present in the molecule suggest that an increase in electron density on the halogen atom occurs with each hydrogen substitution as predicted by Bruns and Guadagnini.[19,20] The effect is to increase the strength of the hydrogen-bonding interaction between the halogen atom and the surface water.

If either of the plots of atomic charge or molecular polarizability versus dangling bond shift is used to predict the shift expected for methyl fluoride, the values obtained are remarkably similar. In the case of the molecular polarizability, the calculated value of 2.46 produces a shift in the dangling bond of 58 cm^{-1}. When the value of $-0.55e$, as calculated by Guadagnini and Bruns,[19] is used in the plot of atomic charge versus dangling bond shift, the shift predicted from Figure 3 is 57 cm^{-1}. A single, combined model can be invoked to explain this phenomenon, where the extent of the electronic interaction is dependent on both the charge and the polarizability within the heterogeneous system. The charge on the halogen atoms in the individual methane is controlled by two factors—the nature of the halogen atoms and the number of hydrogen atoms in the molecule. As discussed already, the higher charge density on the fluorine atom as compared to the chlorine and bromine atoms does not control the site of the reaction. Therefore the nature of the halogen would be predicted to have little effect on the interaction strength. In contrast, however, the increased charge on the halogen atom(s) resulting from hydrogen atom replacement of the halogen atom by a hydrogen atom would be expected to influence the interaction, as confirmed by Figure 3. The "parameter strength" of the interaction for a specific halomethane is hence calculable from the sum of its molecular polarizability and a charge term. The latter is only dependent upon the number of hydrogen atoms in the molecule; its specific contribution is calculated from the average increase in charge on the halogens accompanying hydrogen atom replacement. As can be seen in Figure 5, when this combined interaction parameter is plotted against the dangling bond shift, a straight line results. The excellent correlation between the dangling bond

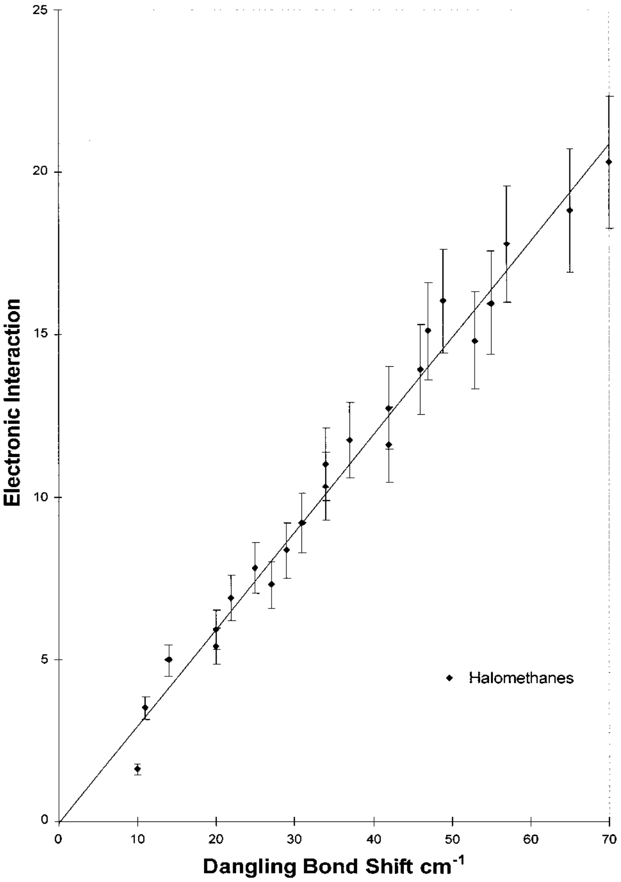

Figure 5. Graph of combined electronic effects of the halomethanes against “dangling bond” IR shift.

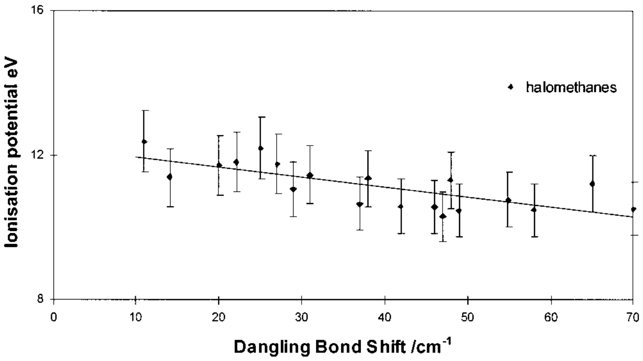

Figure 6. Graph of ionization potential of the halomethanes against “dangling bond” IR shift.

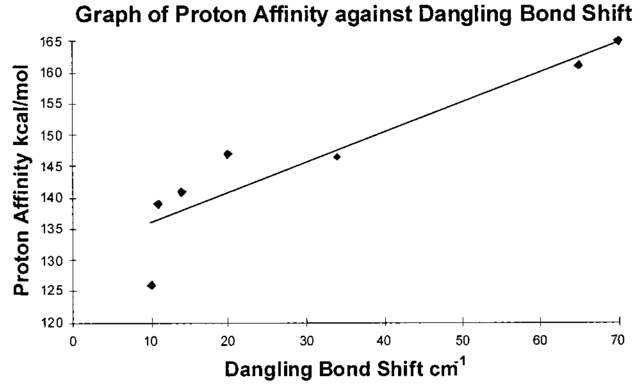

Figure 7. Graph of proton affinities of the halomethanes versus “dangling bond” shift.

shift and the interaction parameter linearity of the plot confirms the prediction that the interaction between the halomethanes and water is based on a combination of atomic charge and molecular polarizability.

In summary: it is clear from the consistency and linear nature of the data plotted in Figure 4 that the measurement of the shift in the dangling bond can provide accurate molecular polarizability values for the halomethanes. Furthermore, the dangling bond data can be fitted to a single model combining contributions from both Coulombic and molecular polarizability terms.

Methods for Predicting Ionization Potentials and Proton Affinities of the Halogenocarbons and Related Compounds Using Dangling Bond Shift Data. The ionization potential of a halomethane provides a good indication of the ease with which its electrons are surrendered and should therefore correlate well to the dangling bond shift. Indeed, if the ionization potentials of the nineteen chloro- and bromo-compounds studied here are plotted against the dangling bond shifts (shown in Figure 6) a straight line results with all data located within 7% of the best fit. Thus, for these classes of halogenocarbon the measurement of the dangling bond shift on water-ice would appear to represent a simple and accurate method of predicting their respective ionization potentials.

Hunt and Andrews[17] postulated that bond shifts could also provide information about the relative proton affinities of the halomethanes. In the extreme case the interaction would effect proton abstraction from water by the halomethane, e.g., reaction 2:

$$CX_4 + H_2O \rightarrow CX_4H^+ + OH^- \qquad (2)$$

In the present study, the increase observed in the dangling bond shift from CF_4 to CCl_4 to CBr_4 is consistent with the development of positive charge on the carbon in the complex as would be expected if donation from the halomethane molecule to the water occurred.

Proton affinities are available for only seven of the molecules studied in this work namely CF_4, CF_3H, CF_2H_2, $CClH_3$, $CBrH_3$, $CClF_3$, and $CBrF_3$. Our values for the proton affinities for the chloromethane series CCl_4−$CClH_3$ do not agree with those predicted by Hunt and Andrews using the shift in the HF stretching frequency.[17] Furthermore, if the shifts in the HF stretching frequency are plotted against the values for atomic charge,[19] the data do not lie on a straight line. It would appear therefore that the use of H−F shifts to calculate proton affinities is invalid. By contrast, if the values are plotted against the shift in dangling bond (shown in Figure 7) excellent correlation, i.e., within 5% from the best-fit lines are observed for six of the compounds. The exception is CF_4, and in this case the wavenumber shift observed in the present study would predict a proton affinity some 10−15% higher than has been calculated. The reasons for the anomaly are unclear but Devlin[2] has commented previously on the hydrophobic nature of tetrafluoromethane and found that it did not produce a shift in the dangling bond when deposited below 55 K. This observation is consistent with the results of the present study because a shift in the dangling bond was observed only after the tetrafluoromethane-D_2O film was annealed to 80 K.

Because so little proton affinity data is available in the literature for the halogenocarbons the graphical model displayed in Figure 7 can only be used to make tentative correlations, but Table 3 summarizes the predicted proton affinities of the halomethanes based on the dangling bond shift observed here. However, it is apparent that if the values predicted for the dangling bond shift of methyl fluoride are used to estimate the proton affinity the agreement with the literature value is not so

TABLE 3: Summary of the Proton Affinities Predicted from the "Dangling Bond" IR Shifts

compound	dangling bond shift cm^{-1}	measured/calculated proton affinities kcal mol^{-1} [26]	predicted proton affinities kcal mol^{-1}
CF_4	10	126	136
CF_3H	20	147	141
CF_2H_2	34	146.5	147
CCl_4	31		146
CCl_3H	38		149
CCl_2H_2	48		154
$CClH_3$	65	161	162
CBr_4	47		154
CBr_3H	49		155
CBr_2H_2	58		159
$CBrH_3$	70	165	165
$CClF_3$	11	139[21]	136
$CBrF_3$	14	141[21]	138
CCl_2F_2	20		141
CBr_2F_2	29		145
CBr_3F	37		149
$CFCl_3$	27		144
$CBrCl_3$	34		147
CF_2ClH	25		143
CCl_2BrH	42		151
$CClBr_2H$	46		153
$CClBrH_2$	55		157
CF_2ClBr	22		141

accurate as that predicted from the molecular polarizability correlation. The two points (56.8 and 58.6 cm^{-1}) provide values of 157 and 158 kcal mol^{-1} for the proton affinity of methyl fluoride, compared to the experimental value of 148 ± 2 kcal^{-1} measured by McMahon and Kebarle.[24]

One final observation regarding the IR data can be made: coincident with the weakening of the O−D stretch in D_2O the interaction between the halomethanes and water leads to stretching frequencies of the halomethanes, which also shift to lower wavenumbers. However these data cannot be used in any predictive sense at this stage because the exact structures of the halomethane−D_2O complexes are not known.

Conclusion

The infrared spectra of a series of twenty-three halogenocarbon compounds deposited onto water-ice held at 12 K have been investigated. Perturbations to the water (D_2O) sites which are not saturated in the absence of guests show distinct trends depending on the type and extent of halogen substitution in the occluded molecules. The data are quantified in terms of the IR spectral positions of the so-called "dangling bond" of water. Interaction also lead to changes in the halogenocarbon compound IR spectra. It is clear from the results that the halomethanes interact through lone pair donation from a halogen atom to a deuterium atom in the water molecule. It has been demonstrated that within each of the series CX_nH_{4-n}, for compounds with the same number of hydrogen atoms, a high level of correlation is found between the shift in the dangling bond and the molecular polarizability. As the halogen atoms are replaced by hydrogen atoms, a similar relationship is established although the dangling bond shifts to lower wavenumber due to an inductive effect from the CY_3 grouping. It is shown that the IR data can be used to predict ionization potentials and molecular polarizabilities of the Br- and Cl-containing halogenocarbons with high levels of accuracy. When a combined polarizability/charge interaction parameter is plotted against the dangling bond shift, a straight line with predictive capabilities results. These observations confirm that the interaction between the halomethanes and water is based on a combination of atomic charge and molecular polarizability.

Correlations of dangling bond IR shift with proton affinity are shown to be less predictively useful, although linear trends are obtained.

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References and Notes

(1) (a) Solomon, S.; Garcia, R. R.; Rowland, F. S.; Wuebbles, D. J. *Nature* **1986**, *321*, 755. (b) Molina, M. J.; Tso, T.-L.; Molina, F. T.; Wang, F. C−Y. *Science* **1987**, *238*, 1253. (c) Koch, T. G.; Banham, S. F.; Sodeau, J. R.; Horn, A. B.; McCoustra, M. R. S.; Chesters, M. A. *J. Geophys. Res. D* **1997**, *102*, 1513.

(2) Devlin, J. P. *J. Am. Chem. Soc.* **1992**, *96*, 6185.

(3) Buch, V.; Devlin, J. P. *J. Chem. Phys.* **1993**, *98*, 4195.

(4) Delzeit, L.; Powell, K.; Uras, N.; Devlin, J. P. *J. Phys. Chem.* **1997**, *101*, 2327.

(5) Sadlej, J.; Rowland, B.; Devlin, J. P.; Buch, V. *J. Chem. Phys.* **1995**, *102*, 4804.

(6) Blanchard, J. L.; Roberts, J. T. *Langmuir* **1994**, *10*, 3303.

(7) Horn, A. B.; Chesters, M. A.; McCoustra, M. R. S.; Sodeau, J. R. *J. Chem. Soc., Faraday Trans. 2* **1992**, *88*, 1077.

(8) Rowland, B.; Devlin, J. P. *J. Chem. Phys.* **1991**, *94*, 812.

(9) Rowland, B.; Fisher, M.; Devlin, J. P. *J. Chem. Phys.* **1991**, *95*, 1378.

(10) Hixson, H. G.; Wojcik, M. J.; Devlin, M. S.; Devlin, J. P. *J. Chem. Phys.* **1992**, *97*, 753.

(11) Andrews, L.; Arlinghaus, R. T.; Johnson, G. L. *J. Chem. Phys.* **1983**, *78*, 6347.

(12) Schaff, J. E.; Roberts, J. T. *J. Phys. Chem.* **1994**, *98*, 6900.

(13) Holmes, N. S. Ph.D. Thesis, University of East Anglia, 1998.

(14) Devlin, J. P.; Buch, V. *J. Phys. Chem.* **1995**, *99*, 16534.

(15) Hobza, P.; Sandorfy, C. *Can. J. Chem.* **1984**, *62*, 606.

(16) Hobza, P.; Mulder, F.; Sandorfy, C. *J. Am. Chem. Soc.* **1981**, *103*, 1360.

(17) Hunt, R. D.; Andrews, L. *J. Phys. Chem.* **1992**, *96*, 6945.

(18) Del Bene, J. E.; Mettee, H. D. *J. Phys. Chem.* **1993**, *97*, 9650.

(19) Guadagnini, P. H.; Bruns, R. E. *J. Am. Chem. Soc.* **1995**, *117*, 4144.

(20) Bruns, R. E., Guadagnini, P. H. Private communication.

(21) Bradley, J. N.; Whytock, D. A.; Zaleski, T. A. *J. Chem. Soc., Faraday Trans.* 1 **1976**, *72*, 2284.

(22) Westenberg, A. A.; De Haas, N. *J. Chem. Soc.* **1977**, *67*, 2388.

(23) Skinner, G. B.; Ringrose, G. H. *J. Chem. Soc.* **1965**, *43*, 4129.

(24) McMahon, T. B.; Kebarle, P. *Can. J. Chem.* **1985**, *63*, 3160.

(25) Dewar, M. J. S.; Stewart, J. J. P. *Chem. Phys. Lett.* **1984**, *111*, 416.

(26) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.