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ARTICLES

What Can C1s Photoelectron Spectroscopy Tell about Structure and Bonding in Clusters of Methanol and Methyl Chloride?

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Single-component clusters of methanol and methyl chloride have been produced by adiabatic expansion, and their carbon 1s photoelectron spectra were recorded using synchrotron radiation and a high-resolution electron analyzer. The experimental spectra are interpreted by means of theoretical models based on molecular dynamics simulations. The data are used to explore to what extent core-level photoelectron spectra may provide information on the bonding mechanism and the geometric structure of clusters of polar molecules. The results indicate that the cluster-to-monomer shift in ionization energy and also the width of the cluster peak may be used to distinguish between hydrogen bonding and weaker electrostatic interactions. Moreover, the larger width of the cluster peak in methanol clusters as compared to methyl chloride clusters is partly due to the structured surface of methanol clusters. Theoretical modeling greatly facilitates the analysis of core-level photoelectron spectra of molecular clusters.

I. Introduction

Molecular clusters are conglomerates of molecules such that the diameter of the cluster typically lies in the range of 1−100 nm. The clusters are held together by three main mechanisms of intermolecular bonding: dispersion interactions, electrostatic interactions, and hydrogen bonding.[1,2] Whereas dispersion is purely attractive and arises due to instantaneous fluctuations of the charge densities of molecules, the electrostatic force between two molecules arises from Coulomb interactions between the charge distributions of the molecules.[1] It comprises both static and dynamic (induction) terms, and the latter is due to distortion of the charge density of a molecule in the electric field of its neighbors. Hydrogen bonding is the strongest among intermolecular forces and receives important contributions not only from electrostatic interactions but also from dispersion and charge transfer.[3]

Molecular clusters are of interest because they form a sensitive testing ground for our understanding of molecular interactions at interfaces, in the bulk, and in the transition zone between these. Moreover, the study of the geometric structure and stability of molecular clusters, as a function of size, may give important information on nucleation and crystal-growth phenomena.[4,5] Most of the experimental studies on molecular clusters employed simple experimental techniques, such as mass-abundance spectroscopy, infrared (IR) spectroscopy, and ionization-energy studies.[2,6] The results provide information on the size, stability, and electronic structure of clusters but rarely give direct information about their geometric structures.

Core-level spectroscopy appears as a promising tool for the

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exploration of structure and properties of atomic and molecular clusters.[7−17] This class of techniques include X-ray Absorption Spectroscopy (XAS), Auger Electron Spectroscopy (AES), and X-ray Photoelectron Spectroscopy (XPS). Core-level XPS is particularly promising for a number of reasons. First, the spectra are less complicated than for the other core-level spectroscopies. Second, it is sensitive to the local surroundings of the ionization site, thereby allowing for site-specific investigation of structure and other properties.[18] Third, since chemical shifts in core-level spectra of clusters are generally perceived to be dominated by final-state charge relaxation,[19] the experimental spectra can be used to validate the polarization models used in theoretical studies.

Differences between the photoelectron spectrum of a gas-phase molecule and that of a cluster made up from the same kind of molecules obviously reflect the intermolecular interactions in the cluster. The primary observables in the spectrum include chemical shifts in ionization energies, line widths, and, possibly, shoulders and other features in the line shapes. The mean chemical shift between the cluster and the monomer is found to provide information about the size of the cluster[20−22] and possibly also the geometric structure.[23,24] The line width of a cluster spectrum is dominated by the distribution of ionization energies within the cluster and provides information on the variation of local structure. There are also contributions from inter- and intramolecular normal modes of vibration as well as the distribution of cluster sizes. Apart from monomer properties such as spin−orbit coupling and molecular vibrations, the presence of distinct features in the cluster line shape may reflect substructures in the cluster with unique shifts in ionization energy. An example of this is the so-called bulk-surface splitting, i.e., molecules in the bulk and at the surface may, due to the difference in mean coordination number,[13] have sufficiently different ionization energies to give separated peaks[20,22] or shoulders[25] in photoelectron spectra.

In order to extract information about clusters from photoelectron spectra, it may be useful to combine experimental information with theoretical models. In recent work on methane clusters,[25] the experimental C1s photoelectron spectrum was found to exhibit well-resolved bulk and surface features as well as vibrational structure. With this amount of detailed information available from the spectrum itself, only simple theoretical models were needed to complement the experimental results. In the case of methanol clusters, however, the experimental C1s spectrum consists of a fairly featureless peak, characterized by the mean ionization energy and the line width.[23,24] By combining theoretical modeling and experimental spectra recorded under different conditions, it was still possible to analyze the spectrum in terms of different cluster sizes.[24]

In the current contribution we use core-level photoelectron spectroscopy in combination with theoretical modeling to explore intermolecular interactions in clusters. The main goal of the study is to investigate to what extent core-level photoelectron spectroscopy is sensitive to the bonding mechanism in the cluster. To this end, we focus on a comparison between methanol and methyl chloride clusters, based on carbon 1s photoelectron spectra and line shape modeling. These molecules are isoelectronic and possess similar gas-phase dipole moments: 1.87 D for methyl chloride and 1.70 D for methanol.[26] Whereas both compounds may engage in dipole−dipole interactions, they differ in that only methanol is capable of forming strong hydrogen bonds. A main topic is therefore to what extent differences in the cluster spectra of methanol and methyl chloride reflect the bonding mechanisms: hydrogen bonding vs dipole−dipole interactions. Apart from an IR study of dimers of methyl chloride,[27] we have not found previous reports on pure clusters of methyl chloride. However, we are aware of a concurrent study of these clusters, in which the C1s XPS data presented in this work are supplemented by Cl2p XPS and also valence photoelectron spectra.[28]

A problem when comparing experimental spectra of clusters is that, a priori, it cannot be ruled out that observed differences are due to differences in cluster size. In order to reduce this uncertainty, we will initially base our comparison on theoretical spectra that pertain to clusters that contain the same number of molecules. The theoretical spectra will be computed according to the recipe laid out in ref 23, whereby molecular dynamics (MD) is used for obtaining cluster geometries and a polarizable force field[29,30] is used for computing chemical shifts in ionization energy. Having established the agreement between our model spectra and the experimental data, we use the theoretical models to explore the relationship between the core-level spectra and mechanisms of intermolecular bonding.

II. Experimental Methods

Clusters are optically thin samples, and in order to study them with electron spectroscopy it is necessary to use cluster sources that produce intense cluster beams. Clusters of methanol and methyl chloride were produced in a supersonic (free jet) condensation source.[2,31] The mean cluster size obtained in supersonic expansion experiments is governed by the nozzle geometry and temperature, the stagnation pressure, and the sample compound. In our experiments, a nozzle with an opening diameter of 150 μm and a total opening angle of 20° was used. During the methanol experiment, the temperature of the nozzle was maintained in the range of 135−145 °C, and the stagnation pressure was 1.4−1.5 bar. Helium was used as a seeding gas in order to enhance the condensation process. From comparison to previously analyzed carbon 1s photoelectron spectra that pertain to different size regimes,[23,24] the mean cluster size is deduced to be in the range of a few hundred molecules. During the methyl chloride experiment, the temperature of the nozzle was maintained in the range 20−30 °C, and the stagnation pressure was about 1.4 bar. No seeding gas was used. At these conditions, the mean cluster size has been estimated to be several hundred molecules.[28]

Carbon 1s photoelectron spectra of methyl chloride clusters (shown in Figure 1) were recorded in February 2005 at beamline I411 at MAX-Lab, in Sweden,[32] using a photon energy of 349 eV. The finite experimental resolution may be represented by a Gaussian distribution with a full width at half maximum (fwhm) of 115 meV which includes the contribution from both the monochromator and the electron energy analyzer. In order to ensure optimal conditions for a comparison between methanol and methyl chloride, the C1s spectrum of methanol was remeasured in February 2006, using the same setup and instrumental settings as described for methyl chloride. The methanol spectrum reported here has significantly better instrumental resolution and statistics than those reported earlier.[23,24]

The data acquisition was done in collaboration with the authors of ref 28.

III. Computational Details

Methanol and methyl chloride clusters, containing about 200 molecules each, were propagated in time using molecular dynamics (MD) simulations as implemented in the TINKER molecular modeling package.[33] The force-field parameters used in the simulation of methanol spectra are given in ref 23, while

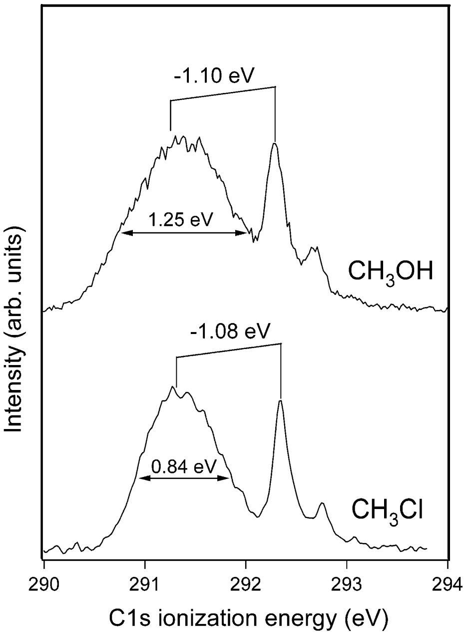

Figure 1. Experimental carbon 1s photoelectron spectra of clusters and free monomers of methanol (top) and methyl chloride (bottom). Calibration of the ionization-energy scale was obtained by assigning the energy of the adiabatic peak of the monomer subspectrum and by combining the vertical ionization energy, i.e., 292.42 eV for methanol[42] (292.48 eV for methyl chloride[43]), with the mean vibrational excitation energy computed from the Franck−Condon profile of the gas-phase molecule (0.14 eV for both molecules).

those for methyl chloride are given as Supporting Information. During MD simulation of the methyl chloride cluster, the quadrupole moments were not used, and the polarization energy term was turned off. First, MD simulations of methanol and methyl chloride clusters were run at 298 and 250 K, respectively, for 0.1 ns. Then, a simulated annealing protocol employing Groningen coupling to an external bath[34] was used to bring the temperatures down to 50 K. At 50 K, the methanol (methyl chloride) cluster was equilibrated for 0.4 ns (2.0 ns).

Line shape modeling was based on analysis of the trajectories from the production phase, which lasts for about 200 ps for each trajectory. For each MD frame we compute a model spectrum, and the final spectrum is obtained as a time average over such “snapshot” spectra.[23]

IV. Results

Figure 1 shows the experimental carbon 1s photoelectron spectra of clusters and free monomers of methanol and methyl chloride, respectively. In these spectra, the monomer contributions appear as sharp peaks at high ionization energy, to the right in the figure. The broad bands at lower ionization energy in the two spectra correspond to signals from the clusters. In general, the two spectra are quite similar; each of the monomer bands show a main peak and a progression due to vibrational excitation of the symmetric C−H stretching mode. Moreover, the parts of the spectra that correspond to clusters are broad and featureless. A closer look reveals that the signal pertaining to methanol clusters is significantly broader than that of methyl chloride clusters. Regarding cluster-to-monomer chemical shifts, we obtain values of −1.10 eV for methanol and −1.08 eV for methyl chloride clusters, from fits to experimental spectra based on the line shape of the free monomers.

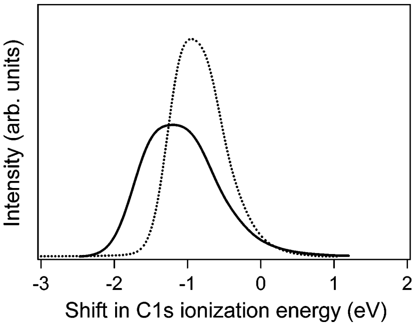

Figure 2. Theoretical carbon 1s photoelectron spectra that pertain to clusters of methanol (solid line) and methyl chloride (dotted line), based on molecular dynamics simulations at 50 K. The spectra have been normalized to the same area. The chemical shifts in ionization energies are computed relative to the adiabatic ionization energies of the free monomers.

TABLE 1: Mean Cluster-to-Monomer Chemical Shifts (ΔIE) of Spectra Pertaining to Methanol and Methyl Chloride Clusters as Obtained from Theoretical Calculations and Experimental Spectra[a]

		theoretical		
cluster	exptl ΔIE	ΔIE	ΔM	ΔP
methyl chloride	−1.08(3)[b]	−0.97	−0.14	−0.83
methanol	−1.10(3)[b]	−1.14	−0.52	−0.62

[a] The contributions to ΔIE from permanent multipoles (ΔM) and polarization (ΔP) are also given. All values are given in units of eV. [b] Estimated uncertainty in last digit.

TABLE 2: Total Line Widths (fwhm) of Spectra Pertaining to Methanol and Methyl Chloride Clusters as Obtained from Theoretical Calculations and Experimental Spectra[a]

		theoretical			
cluster	exptl total	total	$\Sigma_{\Delta \mathrm{IE}}$	$\Sigma_{\Delta M}$	$\Sigma_{\Delta P}$
methyl chloride	0.85(2)[b]	0.84[c]	0.58	0.36	0.49
methanol	1.25(2)[b]	1.25[c]	0.96	0.74	0.37

[a] The widths of the theoretical distributions of chemical shifts ($\Sigma_{\Delta \mathrm{IE}}$) are also given and broken down into contributions from permanent multipoles ($\Sigma_{\Delta M}$) and polarization ($\Sigma_{\Delta P}$). All values are given in units of eV. [b] Estimated uncertainty in last digit. [c] Including contribution from the monomer line shape.

In Figure 2, we show theoretical spectra that pertain to methanol and methyl chloride clusters of size $N \approx 200$ molecules. The computed cluster-to-monomer chemical shifts and total line widths of the cluster peaks are compared to the experimental values in Tables 1 and 2. Theory predicts, in agreement with experiment, that the cluster peak in the methanol spectrum is significantly broader than that of methyl chloride.

Turning to chemical shifts, in the case of methanol clusters the theoretically computed cluster-to-monomer shift agrees well with the experimental result. In the case of methyl chloride, the theoretically computed shift is smaller than the experimental value by 0.11 eV. When investigating possible explanations for this, we found the presently adopted force field to predict a density of solid methyl chloride that is too low by about 5% (at 138 K). Assuming that the main impact from the cluster density on the mean ionization energy comes from charge−induced-dipole interactions in the ionized state, a simple polarization model[19,35] suggests that underestimating the density by 5% would lead to a cluster-monomer shift that is too small by 0.06 eV. The corrected cluster-to-monomer shift thus becomes −1.03 eV in the case of methyl chloride which agrees quite well with what is observed. The remaining discrepancy between theory and experiment is probably within the combined error bars of the two approaches. An additional source of discrepancy, acting in the observed direction, would be the

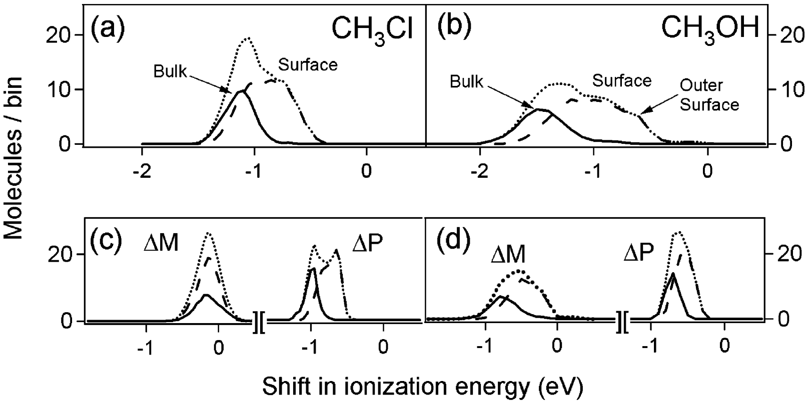

Figure 3. Distributions of chemical shifts in clusters of methyl chloride (left column) and methanol (right column) split into permanent-multipole (ΔM) and polarization (ΔP) terms. The dotted lines correspond to all molecules, solid lines to bulk molecules, and dashed lines to surface molecules.

experimental beam consisting of clusters significantly larger than the 200 molecules used in the simulations.

In the rest of this paper, we focus on an important and little discussed issue, namely the effect of intermolecular interactions on core-level photoelectron spectra of clusters. Having established an agreement between the theoretical models and the experimental spectra, the models are used to explore the connection between the information contents of core-level spectra, i.e., chemical shifts and line widths, and the strength of intermolecular interactions. In particular, we would like to understand why methanol and methyl clusters show very similar cluster-to-monomer chemical shifts, despite the molecular polarizability of methyl chloride being more than 35% larger than that of methanol (4.5 vs 3.3 Å^3)[36] and the density of liquid methyl chloride being almost 30% larger than that of liquid methanol (1.00 vs 0.79 g/mL).[37,38] In the absence of specific interactions, both of these factors should contribute to a significantly large cluster shift for methyl chloride than methanol. Moreover, the cluster peak is much broader in the methanol case than for methyl chloride clusters. We will be looking for how to interpret these observations in terms of the different bonding mechanisms at work: hydrogen bonding vs dipole−dipole interactions.

1. Chemical Shifts. The distribution of C1s ionization energies as computed for 208 molecules making up a methyl chloride cluster is shown as Figure 3a (dotted line). Based on the spherical-cluster model,[2] a fraction $f_S = 4N^{-1/3}$ of the molecules may be regarded as constituting the surface of the cluster. In MD simulations, this may be used to classify each molecule as belonging to the bulk or surface of the cluster, depending on its distance from the center-of-mass of the cluster, and, in turn, this allows for the formation of separate distributions of ionization energies within the bulk and surface fractions. In the figure, the distribution associated with bulk molecules may be seen at low ionization energies (full line), whereas the one associated with surface molecules appears at higher ionization energy (dashed line). The same information is provided for a methanol cluster of 204 molecules in Figure 3b. For both systems, the combined surface+bulk distributions (dotted lines in Figure 3a,b) are quite broad and yet show high-energy shoulders indicative of a bulk-surface splitting. This shoulder is broader and constitutes a larger part of the distribution in the case of methanol than it does for methyl chloride. However, the process of going from a distribution of ionization energies to a photoelectron spectrum entails convolution with various broadening functions[20] such as due to intramolecular vibrations, a finite lifetime, and instrumental resolution, the net effect of which is to camouflage the surface-bulk splitting in the model spectra in Figure 2.

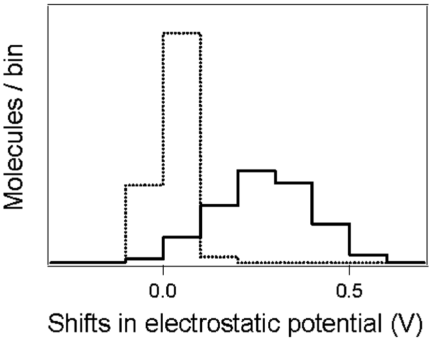

Figure 4. The contribution from induced dipoles to the shifts in electrostatic potential at the carbon site in neutral clusters of methanol (solid line) and methyl chloride (dotted line), relative to those in the respective monomers.

It is instructive to analyze chemical shifts (ΔIE) in terms of permanent multipole (ΔM) and polarization interactions (ΔP), such that $\Delta \mathrm{IE} = \Delta M + \Delta P$. ΔM would be the ionization energy (relative to the free monomer) in the absence of induced dipoles in either the neutral or ionized states. It is dominated by the interaction of the added positive charge in the ionized molecule with permanent dipoles in the surrounding molecules. It does however include the effect of redistribution of charge within the ionized molecule and hence permanent multipole moments that differ from those of the neutral molecules. The polarization term arises due to changes to the induced dipoles at atomic sites outside the ionized monomer, due to the electric field of the ion. In Figure 3c, the distribution of ionization energies in the methyl chloride cluster has been broken down into contributions from permanent multipoles and polarization interactions, respectively. As can be seen, the contribution to chemical shifts by the permanent multipoles is small. Hence, the mean shift in ionization energy reported in Table 1 may be understood as a result of polarization interactions. The polarization term, to the right in Figure 3c, shows a bimodal distribution, given by the bulk-surface splitting known for instance from rare-gas clusters.[19] This indicates that induction in the neutral state is negligibly small, which is confirmed by explicit calculations reported in Figure 4. The bulk-surface splitting apparent in the ΔP term is, however, reduced to a shoulder in Figure 3a by the broad distribution of permanent-multipole terms.

Turning to methanol clusters, the resolution of ΔIE into ΔM and ΔP terms is included as Figure 3d. Now it can be seen that the mean cluster-monomer chemical shift is due to permanent

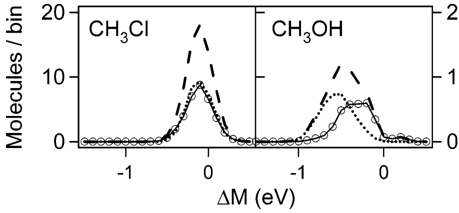

Figure 5. The contribution from molecules at the inner and outer surfaces, respectively, to the permanent-multipole part (ΔM, dashed line) of the chemical shift in C1s ionization energy (relative to that of the monomer) of methyl chloride (left) and methanol clusters (right). The dotted line represents the inner surface, and the line with circles denotes the outer surface.

multipoles and polarization to about equal measures, cf. also Table 1. Focusing on the polarization term, we find that it does not show a bulk-surface splitting but rather a single narrow peak. This is contrary to what we found for the methyl chloride cluster. The reason is that the induced dipoles formed in the initial state display a broad distribution, cf. Figure 4, which is smearing out any features that would be arising from final-state polarization.

2. Line Widths. In addition to factors already present in the monomer spectrum, the total line width of the cluster signal receives contributions from intermolecular vibrational broadening, the distribution of ionization energies among the molecules making up each cluster, and shifts due to a distribution of cluster sizes. Based on a comparison of Figures 2 and 3a,b, the total line widths of the spectra in question are seen to be dominated by the distributions of chemical shifts, in particular those pertaining to the surface fractions. Moreover, from Figure 3c,d and Table 2, which lists explicit contributions to line widths from distributions of ionization energies, it can be seen that the observed large difference in line width between methanol and methyl chloride clusters is mainly caused by the permanent-multipole terms.

To analyze this further, the ΔM part shown in dashed lines in Figure 3c,d has been further resolved into contributions from the outer surface, defined by all molecules in the outermost 3 Å-thick layer, and the contribution from the inner surface, all molecules in the surface fraction that are not part of the outermost layer. This subdivision is shown in Figure 5, with the data for methyl chloride (methanol) to the left (right) in the figure. In the case of methyl chloride, the inner and outer surface layers provide small and almost indistinguishable contributions to the permanent-multipole part of the chemical shift.

The situation is quite different in the case of methanol, however. At the right of Figure 5, it may be seen that the molecules at the outer surface have their permanent-multipole term (ΔM) shifted upward in energy by about 0.2 eV compared to those at the inner surface. Visual inspection of MD structures of the methanol cluster, cf. Figure 6, shows that molecules at the outer surface are oriented with their methyl groups extending outward from the cluster. It may be noted that the direction of the difference in ΔM terms between the outer and inner surfaces is consistent with alignment of molecular dipoles in the surface layer, with the positive ends of the dipoles pointing out of the cluster. No such orientational order was found for the methyl chloride cluster.

V. Discussion

In recent years, a number of studies have appeared on the cluster-to-monomer shift in core-level ionization energies of van der Waal bonded clusters.[17,19,21,22,25,39] The cluster-to-monomer chemical shift has been explained in terms of final-state polarization, and the magnitude of the shift has indeed been found to increase with the atomic (molecular) polarizability of the constituent particles. In light of these results, one would expect methyl chloride to show a larger cluster-to-monomer chemical shift than methanol, simply because it has a larger molecular polarizability than does methanol. Moreover, according to our MD simulations, methyl chloride forms denser clusters than does methanol, which would pull in the same direction. However, both calculations and experiments show approximately the same cluster-to-monomer shift for methanol and methyl chloride clusters of sizes in the same range. This indicates that the permanent multipole term plays an important role in the chemical shift of either methanol or methyl chloride but not for both. From the further analysis presented in Figure 3, it becomes clear that in methanol clusters and, by extension, in other hydrogen-bonded molecular clusters the mean ionization energy is strongly affected by the molecular permanent multipole moments. For the methanol cluster, the permanent multipole term contributes up to 50% of the cluster-to-monomer chemical shift. For the methyl chloride cluster, however, the contribution to chemical shifts from permanent multipole interactions is less than 20%. This can be understood if we recognize that in the condensed phase, methanol forms shorter and stronger intermolecular bonds than does methyl chloride. This can be exemplified by the structure and binding energy of the dimer, obtained from calculations at the second-order Møller−Plesset level of theory in conjunction with the 6-311++G(2d,2p) basis set.[40] The methanol dimer has an O···H bond length of about 1.9 Å and a binding energy of 4.8 kcal/mol, whereas the methyl chloride dimer has a Cl···H bond length of about 3.3 Å and a binding energy of 2.8 kcal/mol.

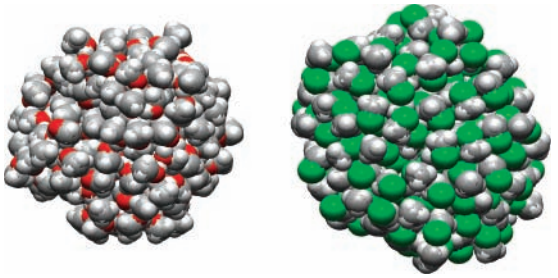

Figure 6. Snapshots of methanol (left) and methyl chloride (right) clusters of size $N = 204$ and 208 molecules, respectively, as obtained from molecular dynamics simulations.

Turning to line widths in core-level photoelectron spectra, previous studies of rare-gas clusters[17,19,22,39] have shown that the line width of a cluster signal arises due to variations in the coordination number through the polarization energy in the final state. For the polar systems studied here, the permanent multipole terms make significant contributions to the total line widths. Moreover, the permanent-multipole terms are also the main cause of the observed difference in C1s line widths between methyl chloride and methanol clusters. This indicates that the fluctuations in the permanent-multipole term scales with the strength of intermolecular bonding, i.e., larger line widths in systems with hydrogen bonding than for systems with only dipole−dipole interactions. The example provided by methanol and methyl chloride demonstrates that the spectral line width is sensitive not only to coordination number but also to the orientation of molecules in the cluster, which is driven by the intermolecular forces.

Figure 3c shows that in the methyl chloride cluster, the contributions from the permanent-multipole term to the chemical shifts in the bulk and surface fractions, respectively, are very similar. This indicates that the local structure does not change appreciably between the bulk and the surface part of the cluster. From molecular dynamics simulations, the most abundant substructures are dimers with either antiparallel or linear configurations. However, there is orientational freedom of molecules within the coordination shell, which gives rise to dimer structures other than those described. These results agree with Monte Carlo simulations performed for liquid methyl chloride.[37]

By comparing Figure 3d and the part of Figure 5 that pertains to methanol, it becomes apparent that the contribution from the permanent-multipole term to chemical shifts in the methanol cluster is different for bulk and surface molecules and, moreover, different between molecules in the inner and outer surface layers. In turn, this suggests that the local structure in the bulk is different from that at the surface and that the surface develops a radial substructure. Analysis of MD trajectories shows that methanol molecules in the bulk tend to arrange in long chains, whereas those at the surface form cyclic structures as well as hydrogen-bonded combinations of cycles and chains.[23] Moreover, molecules in the outermost surface layer tend to align radially with the methyl groups extending outward. Similar results were reported by Wilson and co-workers in an experimental study of microdroplets of methanol.[41]

In a recent study of small-size krypton clusters,[17] the authors show that different surface sites in a cluster can be distinguished by the substantial difference in the associated Kr3d ionization energies, which give rise to structures in the photoelectron spectrum. This study represents a particularly favorable case for studying the geometric structure of clusters by core-level photoelectron spectroscopy. This derives from the fact that rare-gas atoms display narrow line shapes upon core ionization and that the cluster line shape is completely dominated by final-state polarization energy, which depends greatly on the number of nearest neighbors. The situation, however, may be more complicated for molecular clusters because of the possibility of pronounced nuclear dynamics following the ionization process and the possibility of having complex intermolecular bonding patterns, e.g. involving permanent and induced multipole interactions. In ref 25, carbon 1s photoelectron spectra of medium-size methane clusters were investigated. Methane is a good candidate for studying the effect of molecular vibrations on core-level spectra of molecular clusters, because the gas-phase spectrum shows a single progression of well-separated peaks (by $\omega \approx 0.40$ eV), and because the intermolecular interactions in a methane cluster are similar to those in a rare-gas cluster. Still, methane clusters display C1s photoelectron spectra with less pronounced bulk-surface splitting than what is common for rare-gas clusters, partly due to internal molecular vibrations. In the present work, we focus on core-level spectra of molecules with similar vibrational structures and yet different bonding mechanisms. The spectra in question correspond to medium-size clusters and show no structural features at all. Results from the model calculations indicate that different bonding mechanisms lead to different contributions to chemical shifts in carbon 1s ionization energy. Moreover, different bonding regimes in a cluster, including orientational order at the cluster surface, may be distinguished from each other by the substantial difference in their permanent-multipole (ΔM) contributions to the chemical shifts. However, even though the distribution of chemical shifts shows evidence of different bonding regimes, the process of going from a distribution of chemical shifts to a photoelectron spectrum entails convolution with the vibrational profile of the monomer and other broadening mechanisms which will tend to smear out characteristic features. Although it may well be possible to obtain detailed information about the geometric structure in core-level spectra of small clusters,[17,24] for medium-to-large-size molecular clusters this will rarely be possible from the spectra alone. By the aid of molecular modeling, however, a photoelectron spectrum may support or invalidate suggested models of the geometric structure.

VI. Conclusions

At first glance, the similarity of the cluster-to-monomer shifts in C1s photoelectron spectra of methanol and methyl chloride clusters, respectively, seem to indicate that this shift is not related to the strength of intermolecular interactions in the cluster. In the methyl chloride case, this shift is heavily dominated by polarization effects in the ionized state, despite the significant dipole moment of the molecule. In methanol clusters, however, the ability to form strong and directionally specific hydrogen bonds changes this picture, and a significant contribution to the cluster-to-monomer shift originates from permanent electrostatic terms. Hence, by comparing the observed chemical shift to what one might have expected based on final-state polarization alone, the cluster-to-monomer shift may be indicative of strong, specific interactions in the cluster.

The line width of the cluster peak is found to be significantly larger for methanol than for methyl chloride, and this difference is identified with larger fluctuations in the permanent-multipole terms in the hydrogen-bonded system. In particular, a partial ordering of the outer surface of methanol clusters is responsible for a significant part of the additional line broadening seen in the C1s spectrum of methanol clusters. Hence, the large width of the cluster peak may be seen as evidence for substructures in the methanol cluster. It appears that either theoretical modeling or some means of depth profiling would be needed to identify this substructure as due to orientational order in the outer surface. Clearly, theoretical modeling greatly facilitates the analysis of core-level photoelectron spectra of molecular clusters, in particular with respect to structural information.

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Supporting Information Available: Detailed account of the polarizable force field developed for neutral and C1s-ionized methyl chloride, including functional forms and parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Stone, A. J. *The Theory of Intermolecular Forces*; Oxford University Press: 2000.

(2) Johnston, R. L. *Atomic and Molecular Clusters*; Taylor and Francis: New York, 2002.

(3) Rashin, A. A.; Topol, I. A.; Tawa, G. J.; Burt, S. K. *Chem. Phys. Lett.* **2001**, *335*, 327.

(4) Bartell, L. S. *J. Phys. Chem.* **1995**, *99*, 1080.

(5) Bartell, L. S. *Annu. Rev. Phys. Chem.* **1998**, *49*, 43.

(6) *Clusters of Atoms and Molecules I & II*, Vol. 52 of *Springer Series in Chemical Physics;* Haberland, H., Ed.; Springer: Berlin, 1994−1995.

(7) Flesch, R.; Kosugi, N.; Bradeanu, I. L.; Neville, J. J.; Rühl, E. *J. Chem. Phys.* **2004**, *121*, 8343.

(8) Bradeanu, I. L.; Flesch, R.; Kosugi, N.; Pavlychev, A. A.; Rühl, E. *Phys. Chem. Chem. Phys*. **2006**, *8*, 1906.

(9) Pavlychev, A. A.; Flesch, R.; Rühl, E. *Phys. Rev. A* **2004**, *70*, 015201.

(10) Björneholm, O.; Federmann, F.; Kakar, S.; Möller, T. *J. Chem. Phys.* **1999**, *111*, 546.

(11) Öhrwall, G.; Tchaplyguine, M.; Lundwall, M.; Feifel, R.; Bergersen, H.; Rander, T.; Lindblad, A.; Schulz, J.; Peredkov, S.; Barth, S.; Marburger, S.; Hergenhahn, U.; Svensson, S.; Björneholm, O. *Phys. Rev. Lett.* **2004**, *93*, 173401.

(12) Barth, S.; Joshi, S.; Ulrich, V.; Lindblad, A.; Öhrwall, G.; Björneholm, O.; Hergenhahn, U. *J. Chem. Phys.* **2005**, *122*, 241102.

(13) Stapelfeldt, J.; Wörmer, J.; Möller, T. *Phys. Rev. Lett.* **1989**, *62*, 98.

(14) Hergenhahn, U.; Kolmakov, A.; Riedler, M.; de Castro, A. R. B.; Löfken, O.; Möller, T. *Chem. Phys. Lett.* **2002**, *351*, 235.

(15) Flesch, R.; Tappe, W.; Rühl, E.; Pavlychev, A. A. *Surf. Rev. Lett.* **2002**, *9*, 99.

(16) Kakar, S.; Björneholm, O.; Löfken, J. O.; Federmann, F.; Soldatov, A. V.; Möller, T. *Z. Phys. D* **1997**, *40*, 84.

(17) Hatsui, T.; Setoyama, H.; Kosugi, N.; Wassermann, B.; Broadeanu, I. L.; Rühl, E. *J. Chem. Phys.* **2005**, *123*, 154304.

(18) Hergenhahn, U. *J. Phys. B: At., Mol. Opt. Phys.* **2004**, *37*, 89.

(19) Björneholm, O.; Federmann, F.; Fössing, F.; Möller, T.; Stampfli, P. *J. Chem. Phys.* **1996**, *104*, 1846.

(20) Bergersen, H.; Abu-samha, M.; Harnes, J.; Björneholm, O.; Svensson, S.; Sæthre, L. J.; Børve, K. J. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1891.

(21) Tchaplyguine, M.; Marinho, R. R.; Gisselbrecht, M.; Schulz, J.; Mårtensson, N.; Sorensen, S. L.; de Brito, A. N.; Feifel, R.; Öhrwall, G.; Lundwall, M.; Svensson, S.; Björneholm, O. *J. Chem. Phys.* **2004**, *120*, 345.

(22) Amar, F. G.; Smaby, J.; Preston, T. J. *J. Chem. Phys.* **2005**, *122*, 244717.

(23) Abu-samha, M.; Børve, K. J.; Sæthre, L. J.; Öhrwall, G.; Bergersen, H.; Rander, T.; Björneholm, O.; Tchaplyguine, M. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2473.

(24) Bergersen, H.; Abu-samha, M.; Lindblad, A.; Marinho, R. R. T.; Öhrwall, G.; Tchaplyguine, M.; Børve, K. J.; Svensson, S.; Björneholm, O. *J. Chem. Phys.* **2006**, *125*, 184303.

(25) Bergersen, H.; Abu-samha, M.; Lindblad, A.; Marinho, R. R. T.; Céolin, D.; Öhrwall, G.; Sæthre, L. J.; Tchaplyguine, M.; Børve, K. J.; Svensson, S.; Björneholm, O. *Chem. Phys. Lett.* **2006**, *429*, 109.

(26) *Handbook of Chemistry and Physics*, 66th ed.; Weast, R. C., Astle, M. J., Beyer, W. H., Eds.; CRC Press: Florida, 1985−1986.

(27) Futami, Y.; Kudoh, S.; Ito, F.; Nakanaga, T.; Nakata, M. *J. Mol. Struct.* **2004**, *690*, 9.

(28) Rosso, A.; Lindblad, A.; Lundwall, M.; Rander, T.; Svensson, S.; Tchaplyguine, M.; Öhrwall, G.; Björneholm, O. *J. Chem. Phys.* **2007**, *127*, 024302.

(29) Ren, P.; Ponder, J. W. *J. Phys. Chem. B* **2003**, *107*, 5933.

(30) Ren, P.; Ponder, J. W. *J. Comput. Chem.* **2002**, *23*, 1497.

(31) Tchaplyguine, M.; Feifel, R.; Marinho, R. R. T.; Gisselbrecht, M.; Sorensen, S. L.; de Brito, A. N.; Mårtensson, N.; Svensson, S.; Björneholm, O. *Chem. Phys.* **2003**, *289*, 3.

(32) Bässler, M.; Forsell, J. O.; Björneholm, O.; Feifel, R.; Jurvansuu, M.; Aksela, S.; Sundin, S.; Sorensen, S. L.; Nyholm, R.; Ausmees, A.; Svensson, S. *J. Electron Spectrosc. Relat. Phenom.* **1999**, *101−103*, 953.

(33) Ponder, J. W. *Tinker 4.2*. http://dasher.wustl.edu/tinker/ (accessed 2004).

(34) *Groningen molecular simulation (gromos) library manual*; van Gunsteren, W., Berendsen, H., Eds; University of Groningen: 1987.

(35) Stampfli, P. *Phys. Rep.* **1995**, *255*, 1.

(36) van Duijnen, P. T.; Swart, M. *J. Phys. Chem. A* **1998**, *102*, 2399.

(37) Cabral, B. J. C.; Rivail, J. L.; Bigot, B. *J. Chem. Phys.* **1987**, *86*, 1467.

(38) Pereira, J. C. G.; Catlow, C. R. A.; Price, G. D. *J. Phys. Chem. A* **2001**, *105*, 1909.

(39) Lundwall, M.; Tchaplyguine, M.; Öhrwall, G.; Feifel, R.; Lindblad, A.; Lindgren, A.; Sorensen, S.; Svensson, S.; Björneholm, O. *Chem. Phys. Lett.* **2004**, *392*, 433.

(40) Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1984**, *80*, 3265.

(41) Wilson, K. R.; Cavalleri, M.; Rude, B. S.; Schaller, R. D.; Catalano, T.; Nilsson, A.; Saykally, R. J.; Pettersson, L. G. M. *J. Phys. Chem. B* **2005**, *109*, 10194.

(42) Drake, J. E.; Riddle, C.; Henderson, H. E.; Glavincevski, B. *Can. J. Chem.* **1977**, *55*, 2957.

(43) Perry, W. B.; Jolly, W. L. *Inorg. Chem.* **1974**, *13*, 1211.