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## Neutral CH<sub>3</sub>Cl and CH<sub>3</sub>Br clusters studied by X-ray photoelectron spectroscopy and modeling: Insight to intermolecular interactions and structure

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### ABSTRACT

Single-component clusters of methyl chloride and methyl bromide have been produced by adiabatic expansion and their C 1s, Cl 2p and Br 3d photoelectron spectra recorded using synchrotron radiation and a high-resolution electron analyzer. The experimentally observed cluster-to-monomer shifts in core-level ionization energies are interpreted in terms of theoretical models based on molecular dynamics (MD) in conjunction with polarizable force fields developed and validated in the course of this work. MD simulations have also been used to explore the global and local structure of the clusters, providing evidence for a predominance of anti-parallel, head-to-tail arrangement of neighboring molecules. Whereas the cluster-to-monomer shifts are strongly dominated by polarization effects, the polarization contribution is very similar for ionization of carbon and the halogen, respectively. The *difference* in cluster shifts between the two ionization sites within the same molecule, C vs. Cl or C vs. Br, is thus determined by permanent electrostatic moments, i.e. the magnitude and direction of the permanent dipole moment and the local alignment of dipoles.

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### 1. Introduction

The nonideality of a gas is caused by intermolecular interaction, without which condensation would not take place and molecular matter would remain gaseous. Condensation and cluster formation involve nucleation and subsequent growth, and molecular clusters constitute interesting model systems for nucleation phenomena, for phase changes in condensed phases [1,2], and for testing our understanding of molecular interactions in general; at interfaces, in the bulk, and in the transition zone between these [3].

The main contributions to intermolecular interactions are electrostatic, induction, charge transfer and van der Waals (vdW) terms [4]. Here, electrostatics is restricted to interactions between permanent electric multipoles, while induction includes interaction between induced electric moments as well as between induced and permanent electric moments. Hydrogen bonding receives contributions from all of these four categories, although it is often considered a separate class of intermolecular interactions [5]. While vdW and induction interactions have only weak orientational effects, interactions between permanent multipole moments, in particular that between permanent dipoles, display a strong orientational effect on molecules.

The two most favorable arrangements of two dipoles are linear and anti-parallel (side-by-side) head-to-tail orientation, respectively, with the relative energy ordering depending on packing, i.e. intermolecular distances [6]. This can be exemplified by the methyl halides, for which the most stable structure of the respective dimers show anti-parallel head-to-tail orientation, shifted along the dipolar axis [7]. This carries partly over to the molecular liquids of CH<sub>3</sub>Cl and CH<sub>3</sub>I, for which molecular dynamics (MD) and Monte Carlo (MC) simulations [8,9] show predominance of the anti-parallel and linear head-to-tail structures and also perpendicular orientation of neighboring molecules. The fractions of anti-parallel and linear orientations increase with decreasing temperature [8,9]. Interestingly, the crystalline phase of CH<sub>3</sub>Cl [10], which is isomorphous to the high-temperature  $\alpha$ -phase of CH<sub>3</sub>Br, [11], does not feature anti-parallel orientation of neighboring molecules, although the low-temperature  $\beta$ -phase of CH<sub>3</sub>Br does [11]. Parallel dipoles that are displaced relative to one another in the direction of the dipole is, however, an important motif in both modifications of crystalline methyl bromide and also crystalline methyl chloride.

One appealing aspect of clusters is the ability to follow the evolution of structure with size, and in two recent reports [12,13] the local structures of free, neutral clusters of methyl bromide and methyl chloride were investigated by means of valence and inner-shell photoelectron spectroscopy (UPS, XPS). The latter technique is particularly well suited to probe the local structure in molecules and supramolecular structures due to the highly localized

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character of the core orbitals and the sensitivity of inner-shell ionization energies to the chemical environment. In Refs. [12,13], the results for clusters of methyl chloride and bromide were in both cases interpreted purely within a model of local anti-parallel head-to-tail orientation of molecules. The diversity in the local structure of liquid methyl chloride and also the presence of two modifications with different local structures in crystalline methyl bromide, suggest that other local arrangements than anti-parallel head-to-tail may be important in the clusters. Alternatively, if one is able to confirm a highly uniform local structure of the clusters, this may indicate that the clusters are crystalline. The freezing point has been found to vary considerably with size for many cluster systems [14–16], although information regarding clusters of polar molecules is scarce [17]. A main aim of the present work is to perform molecular dynamics simulations of clusters of methyl chloride and bromide, respectively, in order to analyze the local structure. Moreover, the resulting cluster geometries will be used as basis for theoretical models of inner-shell photoelectron spectra, to be compared to the experimental observations for consistency checks. In addition to reanalyzing previously published spectra, the Br 3d photoelectron spectrum has been remeasured with much improved statistics.

A second aim of this work is to explore the validity of the polarization model for analyzing cluster–monomer shifts in core-level photoelectron spectra. This model only takes into account polarization about the site of ionization in order to explain the difference in ionization energy between an isolated molecule and a molecule in a cluster, and thus neglects any contributions from the cluster surrounding to the electrostatic potential at the site of ionization. The polarization model is fully justified in the case of apolar cluster constituents such as the rare gases and methane [18–22]. Moreover, in methyl chloride, only 13% of the C 1s monomer–cluster shift is due to permanent dipole moments [3]. This picture does not necessarily apply when comparing cluster shifts at two inequivalent sites of ionization. Using methyl chloride as an example, the polarization contributions to the monomer–clusters shifts in Cl 2p and C 1s ionization energies may in fact be expected to be almost the same. This follows from the close agreement between the respective group polarizabilities ( $\text{CH}_3$ :  $2.222 \text{ \AA}^3$ ; Cl  $2.315 \text{ \AA}^3$ ) [23] and opens for the possibility that the *difference* between the two cluster shifts may receive important contributions from the permanent electrostatic potential. It is therefore pertinent to explore the validity of a polarization-only approach for drawing conclusions regarding the local structure based on differences in monomer–cluster shifts in ionization energies. The larger polarizability of bromine ( $3.013 \text{ \AA}^3$ ) [23] makes methyl bromide a very good comparison to methyl chloride in this respect.

Finally, in order to address the said issues, there is a need for accurate force fields for methyl chloride and methyl bromide. The force field used for simulations of liquid methyl chloride in Ref. [8] does not provide realistic oligomer structures, and for this system we will be using a recently published polarizable force field that is well balanced between oligomer and condensed structures of methyl chloride [3]. Here, we go on to develop a similar force field for methyl bromide and also report on validation studies of both of these potentials.

## 2. Experimental

Neutral free clusters of methyl chloride and methyl bromide were produced in a free-jet condensation source [24]. The mean cluster size obtained in supersonic expansion experiments depends on the sample compound and the stagnation pressure, in addition to the temperature and geometry of the nozzle through which the gas expands [25]. In our case, the nozzle was conical with an open-

ing diameter of  $150 \mu\text{m}$  and a total opening angle of  $20^\circ$ . No seeding gas was used.

In the methyl chloride experiment, the temperature of the nozzle was maintained in the range  $20\text{--}30^\circ\text{C}$  and the stagnation pressure was about 1.4 bar. At these conditions, the mean cluster size is estimated to several hundred molecules [13]. Methyl bromide clusters were produced at a stagnation pressure of 1.7 bar and with the nozzle temperature kept at  $35\text{--}37^\circ\text{C}$ . The higher stagnation pressure used in the case of methyl bromide is likely to favor the formation of larger  $\text{CH}_3\text{Br}$  clusters than  $\text{CH}_3\text{Cl}$  clusters [5,26,27], as is the higher boiling point of  $\text{CH}_3\text{Br}$  (276.1 K) compared to that of  $\text{CH}_3\text{Cl}$  (248.9 K) [26,28,29].

Refs. [30,5] show that there exists a relation between the cluster temperatures and the dimer well depths. Based on Klots's formula [31] in combination with Trouton's rule [2], one obtains cluster temperatures based on evaporative cooling of 103 K ( $\text{CH}_3\text{Cl}$ ) and 115 K ( $\text{CH}_3\text{Br}$ ). The temperature estimates given in Refs. [12,13] of  $120\text{--}130 \text{ K}$  for  $\text{CH}_3\text{Cl}$  clusters and  $130\text{--}140 \text{ K}$  for  $\text{CH}_3\text{Br}$  clusters were obtained as half the boiling temperature of the respective liquids and are in reasonable agreement with the preceding values.

The present core-level photoelectron spectra of methyl chloride and methyl bromide clusters were recorded in February 2005 at beamline I411 at MAX-Lab, Sweden. Carbon 1s photoelectron spectra of methyl chloride and methyl bromide clusters were obtained 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 112 meV which includes the contribution from both the monochromator and the electron energy analyzer. Chlorine 2p spectra of methyl chloride clusters were recorded at a photon energy of 250 eV and a resolution given by  $\text{fwhm} \approx 85 \text{ meV}$ . Bromine 3d spectra of methyl bromide clusters were recorded at a photon energy of 134 eV and a resolution of  $\approx 83 \text{ meV}$ . The pass energy was 50 eV in all cases. The monochromator slit was  $15 \mu\text{m}$  when recording the C 1s and Cl 2p spectra and  $40 \mu\text{m}$  for the Br 3d spectrum.

The C 1s spectrum of  $\text{CH}_3\text{Cl}$  was published in Ref. [3]. Our Cl 2p spectrum for  $\text{CH}_3\text{Cl}$  forms part of the basis of Fig. 1 in Ref. [13], which in addition also includes data recorded at another stagnation pressure (1.9 bar). The C 1s spectrum of  $\text{CH}_3\text{Br}$  is earlier published in Ref. [12]. The Br 3d spectrum of  $\text{CH}_3\text{Br}$  which is reported in this work has significantly better statistics than the spectrum reported in Ref. [12].

### 2.1. Fitting models

Photoelectron spectra of the cluster beam contain signals from uncondensed molecules, i.e. monomers, as well as clusters. When analyzing such spectra, the monomer contribution is modeled either by gas-phase spectra recorded in separate experiments, or by theoretical models that include vibrational structure (Franck–Condon profile), Lorentzian lifetime broadening and asymmetric distortion from the Lorentzian lineshape due to post-collision interactions, as well as convolution by a Gaussian distribution to account for instrumental broadening. The post-collision interaction is modeled according to eq. 12 in Ref. [32] and quantified in terms of an asymmetry factor ( $\beta$ ). This parameter is computed in each case from the kinetic energy of the photoelectron and the main Auger transition energies for the decay process. The instrumental broadening is computed from the experimental conditions (i.e. the pass energy of the electron analyzer and the width of the monochromator slit).

The cluster contribution to the spectrum is modeled by the monomer spectrum (experimental or theoretical, as detailed above), subject to convolution with a second Gaussian distribution to account for the variation in ionization energy among the

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