Supplementary information for
The structure of mixed methanol/chloroform clusters from core-level photoelectron spectroscopy and modeling

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1 Detailed account of polarizable force fields for neutral and carbon-1s-ionized chloroform

A polarizable force field has been developed for chloroform, following the approach previously documented for methanol [1]. Valence potential expressions and force constants were taken from the MM3 force field [2] as included in the TINKER molecular modeling package (version 5.1) [3]. Bond distances and bond angles were obtained from the geometry optimized at the *ab initio* MP2 level of theory in conjunction with 6-311++G(2d,2p) basis set [4].

The non-bonding part of the force field contains an electrostatic model based on distributed multipoles, a self-consistent polarization model based on atomic polarizabilities, and van der Waals (vdW) interaction terms. Permanent multipoles up to the quadrupole moment were computed for all atomic sites in both neutral and carbon-1s-ionized molecules, via the distributed multipole procedure as implemented in the GDMA 2.2.03 program [5]. The program takes as input atomic radii, and the molecular geometry and electron density. For the neutral molecule, we used the MP2-optimized geometry and associated electron density described above. For the ionized state, the electron density was obtained from MP2 calculations performed in the geometry of the neutral molecule, with the ionized carbon core represented by an effective core potential [6]. The default relative atomic radii were used in the GDMA procedure.

Polarization is described by mutual induction of dipoles at atomic centers [7,8]. Starting from the atomic polarizabilities given in ref. 9, the final atomic polarizabilities were adjusted to reproduce the mean molecular polarizability of 8.53 Å^3.[9]

Van der Waals (vdW) interactions are included in terms of the buffered 14-7 potential proposed in Ref. 10. The vdW parameters (R^* and ε) are optimized for all atomic sites in the molecules. Starting out from the parameter values given in ref. 10, the parameters (cf. Table 1) were parametrized against the density of the crystalline structure of chloroform at 185 K, i.e. 1.91 g/ml from ref. 11. Crystal simulations at 185 K show that the force field reproduces the experimental density to within 1%.

Moreover, at the MP2 level of theory in conjunction with the 6-311++G(2d,2p) basis set and inclusion of corrections due to basis set superposition error (BSSE), the most stable dimer geometry was the antiparallel C_{2h} symmetry structure. This isomer has a binding energy of -3.06 kcal/mol and a C-C distance of 3.98 Å. The correction due to basis set superposition error is 2.18 kcal/mol. The force field predicts a binding energy of -2.33 kcal/mol for this geometry. However, the most stable dimer geometry at the force field level of theory has a binding energy of -3.38 kcal/mol and a C-C distance of 3.68 Å. The force-field-optimized dimer geometry can be described as an antiparallel dimer with a structure close to C_{2h} symmetry.

2 On the accuracy of the force field predictions of monomer–cluster chemical shifts

For the pure chloroform and methanol clusters, we computed average monomer–cluster shifts in carbon 1s ionization energies $<\Delta IE>$ and standard deviations among molecules in oligomers ranging in size from dimers to the $N = 12$ for chloroform (Table 2) and up to the $N = 20$ for methanol (Table 3). The shifts are computed using either density functional theory (DFT), second-order Møller-Plesset perturbation theory (MP2) or the present force field (MM) approach. All *ab initio* calculations were carried out using the Gaussian 09 suite. [13] The DFT calculations were performed with the M06-2X [14] and the B3LYP [15,16] hybrid functionals. The calculations are performed in conjunction with the cc-pVTZ, aug-cc-pVTZ and the aug-cc-pVQZ basis sets [17,18].

In general, DFT calculations with the M06-2X functional are in better agreement with the MP2 results than are DFT calculations with the B3LYP functional. For chloroform, the force-field predictions are in good agreement with the MP2 results. Regarding methanol, the force field overestimate the shifts compared to the MP2 results. Based on a least-squares fit of the fore-field derived ΔIE values toward those computed

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Table 1 Electrostatic moments, atomic polarizabilities and vdW parameters for neutral and C1s-ionized chloroform. The atomic dipoles and quadrupoles are defined with respect to a local reference frame defined by neighboring atoms (z-then-x)[12]. Electrostatic moments are given in atomic units, polarizabilities (α) in Å^3, vdW radii (R^*) in Å, and well depths (ε) in units of kcal/mol. q, μ and Θ refer to the atomic charge, dipole, and quadrupole. Additionally, for hydrogen, a reduction factor of 0.94 is used. This means that for hydrogen, the vdW site is shifted by a factor of 0.06 of the carbon-hydrogen bond length toward the carbon atom compared to the corresponding atomic sites.

Parameter	Cl	H	C
z-axis	C	C	C
x-axis	H	Cl	Cl
α	2.485	0.52	1.49
R^*	3.50	2.90	3.10
ε	0.276	0.016	0.068

Electrostatic multipole moments

	Neutral $CHCl_3$		
q	0.2166	0.11147	-0.7613
μ_x	-0.0240		
μ_z	0.6242	0.1060	0.4622
θ_{xx}	-1.0713	-0.0800	-0.3685
θ_{yy}	-1.0714	-0.0800	-0.3683
θ_{zz}	2.1427	0.1600	0.7368
θ_{xz}	-0.0101		

	C1s-ionized $CHCl_3$		
q	0.4938	0.2784	-0.7599
μ_x	-0.0196		
μ_z	0.3946	0.0173	0.4830
θ_{xx}	-1.1272	-0.0760	-0.3769
θ_{yy}	-1.1615	-0.0760	-0.3768
θ_{zz}	2.2887	0.1520	0.7538
θ_{xz}	0.0191		

with the MP2 (aug-cc-pVTZ), we arrive at the following expression

$$\Delta IE_{\mathrm{MP2}} = \Delta IE_{\mathrm{FF}} + 0.04\ \mathrm{eV}. \tag{1}$$

Eq. 1 is used to correct force field shifts for pure methanol clusters ranging in size from 13 to 52 molecules.

To validate the force field results for the mixed chloroform-methanol clusters, in Table 4 we provide $< \Delta IE >$ and standard deviations among molecules in a mixed 49-molecule cluster containing 13 methanol molecules and 39 chloroform molecules. The force field performance is validated against QM/MM calculations where the QM part employs the M06-2X functional. In the QM/MM model, the chemical shift is computed as $\Delta IE_{\mathrm{DFT/FF}} = \Delta IE_{\mathrm{FF}} + (\Delta IE_{\mathrm{DFT,\ subcluster}} - \Delta IE_{\mathrm{FF,\ subcluster}})$, where the subcluster contains the ionized molecule and all its neighbours within a carbon-carbon distance of 5 Å. The cluster geometry is obtained from the production phase of molecular dynamics simulations. The force field calculations are in good agreement with *ab initio* calculations, see Table 4.

3 The cluster temperature

Contrasted to a supersonic beam with negligible clustering which provides a very low temperature environment for the small clusters, the heat of condensation that is released in a heavily condensing beam increases the temperature of the growing clusters until they are ”boiling hot”. [19] While the initial phase of the expansion can be well described by thermodynamic equilibrium and steady flow conditions, there is an increasing rarefaction with increasing distance from the nozzle, finally leading to the so-called free-molecular flow regime. In the intermediate and finale stages of the expansion, evaporation is the main cooling mechanism. The terminal temperature in the expansion can then be described by the evaporative cluster temperature [20,21], $T_e = 0.4T_b$, where T_b is the boiling temperature of the compound at standard conditions. Based on the calculated T_e values and by comparing methanol and chloroform clusters with the temperature of several large clusters made of different compounds [19], we chose to simulate the clusters at 150 K. This temperature is high enough to enable diffusion of molecules within the clusters such that clusters with low-energy structures can be obtained.

4 On inelastic scattering of photoelectrons

Due to the effect of inelastic scattering, a photoelectron that is emitted from the interior of the cluster has a lower probability to reach the detector than a photoelectron that is emitted from the surface of the cluster. Additionally, the path that the photoelectron travels inside the cluster is extended due to elastic

Table 2 Comparison of mean values and standard deviations of computed cluster-to-monomer shifts in carbon 1s ionization energies of a chloroform dimer, tetramer and a 12-molecule clusters, using the present force field (FF) and quantum chemistry calculations using DFT (M06-2X[14]; B3LYP[15,16]) and MP2 in conjunction with the cc-pVTZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets[17,18]. The dimer structure is obtained with MP2 calculations using the 6-311++G(2d,2p) basis set, and accounting for basis set superposition error. For the tetramer and the 12-molecule clusters, the geometries are obtained from force field optimization and molecular dynamics simulations, respectively. Standard deviations among the ΔIE's are given within the parentheses.

Basis set	B3LYP	M06-2X	MP2	FF
		dimer		
cc-pVTZ	-0.03/0.17	-0.06/0.14	-0.05/0.14	
aug-cc-pVTZ	-0.01/0.19	-0.03/0.16	-0.03/0.16	-0.03/0.14
		tetramer		
cc-pVTZ	-0.41(0.24)	-0.32(0.26)	-0.31(0.26)	
aug-cc-pVTZ	-0.44(0.23)	-0.38(0.25)	-0.34(0.25)	-0.33(0.29)
		12-mer		
cc-pVTZ	-0.51(0.14)	-0.36(0.14)		
aug-cc-pVTZ		-0.53(0.14)		
				-0.47(0.12)

scattering. For each molecule, the calculated ionization energy has to be given a weight factor proportional to the probability that the emitted photoelectron escapes from the cluster without loss of energy. Here, the exponentially decaying attenuation model described in refs. 22,23 is adapted. The effective mean free path, λ, between two inelastic collisions is an input parameter into the attenuation model. For methanol, λ is determined based on classical Monte Carlo simulations[24] of the electrons propagating through an $N = 52$ cluster. Both elastic and inelastic scattering events are taken into account. However, the effect of excitations (and de-excitations) of rotational degrees of freedom is not included in the simulations due to uncertainties regarding the transferability of the rotational excitation cross section from the gas phase to the condensed phase. Mean free paths between elastic ($\lambda_e = \frac{1}{n\sigma_e}$) and inelastic ($\lambda_i = \frac{1}{n\sigma_i}$) scattering events are obtained from the total elastic cross section (σ_e) and the difference between the total cross section and the total elastic cross section ($\sigma_i = \sigma_t - \sigma_e$), respectively.[25]

In this work, two different photon energies were used, i.e. 330 eV and 440 eV, based on the adiabatic carbon 1s ionization energy for chloroform of 295.09 eV[26], the adiabatic carbon 1s ionization energy for methanol was determined to be 292.34 eV, leading to photoelectrons with roughly 40 eV and 150 eV kinetic energy, respectively. The number density ($n = 0.0191$ mol cm^{-3})[27] is taken to be that of the solid at 160 K, leading to $\lambda_{e,40eV} = 4.6$Å, $\lambda_{e,150eV} = 11.5$Å, $\lambda_{i,40eV} = 9.8$Å and $\lambda_{i,150eV} = 11.7$Å. The differential cross sections (DCS) for elastic electron scattering was obtained from ref. 28. While the DCS for 40 eV photoelectrons was obtained as interpolated values between the 30 eV and the 50 eV data, since the highest electron energies used in ref. 28 was 100 eV, the DCS for 150 eV photoelectrons was taken to be that of the 100 eV data. The resulting probability distribution from the Monte Carlo simulations was compared to probability distribution calculated by usage of the exponential decaying attenuation model[22,23] and the effective attenuation length was determined to be $\lambda_{40eV}/\text{Å} = 7 \pm 2$ and $\lambda_{150eV}/\text{Å} = 10 \pm 2$. Here the effect of excitation of rotational degrees of freedom is approximated by reducing the final λ values by 1 Å and addition of 1Å to the uncertainties. These values are significantly larger than the corresponding values for the inelastic mean free path, $\lambda_{i,40eV}$=4.1Å and $\lambda_{i,150eV}$=7.9Å, given by the universal predictive $G1$ equation[29]. Since the effect of elastic scattering is most important for the larger clusters, the calculated λ values are likely to show a weak size dependency. The adiabatic carbon 1s ionization energy for chloroform is 295.09 eV[26], leading to photoelectrons with 35 eV and 145 eV for the 330 eV and the 440 eV experiment, respectively. However, contrasted to methanol, less information about the electron scattering cross sections is found. Therefore, based on the values obtained by usage of the predictive equation given in ref. 29

Table 3 Comparison of mean values and standard deviations of computed cluster-to-monomer shifts in carbon 1s ionization energies of a methanol dimer, trimer, heptamer, $N = 13$ and $N = 20$ clusters, using the present force field (FF) and quantum chemistry calculations using DFT (M06-2X[14]; B3LYP[15,16]) and MP2 in conjunction with the cc-pVTZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets[17,18]. The dimer, trimer and heptamer geometries are obtained from force field optimization. The geometries of the 13- and 20-molecule clusters are obtained from molecular dynamics simulations at the force-field level. Standard deviations among the ΔIE's are given within the parentheses.

Basis set	B3LYP	M062X	MP2	FF
		dimer		
cc-pVTZ	-0.67/0.39	-0.66/0.39	-0.65/0.39	
aug-cc-pVTZ	-0.67/0.36	-0.66/0.37	-0.65/0.36	
aug-cc-pVQZ	-0.67/0.36	-0.66/0.37	-0.65/0.36	
				-0.70/0.38
		trimer (cyclic)		
cc-pVTZ	-0.21/-0.24/-0.16	-0.20/-0.22/-0.14	-0.19/-0.21/-0.14	
aug-cc-pVTZ	-0.24/-0.27/-0.19	-0.22/-0.25/-0.17	-0.22/-0.25/-0.17	
aug-cc-pVQZ		-0.22/-0.25/-0.17		
				-0.24/-0.28/-0.19
		heptamer (cyclic)		
cc-pVTZ	-0.42(0.09)	-0.40(0.09)	-0.39(0.10)	
aug-cc-pVTZ	-0.46(0.09)	-0.43(0.09)	-0.43(0.09)	
				-0.45(0.12)
		13-mer (cyclic 6-mer + cyclic 7-mer)		
cc-pVTZ	-0.56(0.25)	-0.53(0.25)	-0.51(0.25)	
aug-cc-pVTZ	-0.60(0.25)	-0.57(0.25)		
				-0.62(0.24)
		20-mer structure 1		
cc-pVTZ		-0.71(0.29)		
				-0.77(0.29)
		20-mer structure 2		
cc-pVTZ		-0.62(0.26)		
				-0.71(0.27)

Table 4 Comparison of mean values and standard deviations of computed cluster-to-monomer shifts in carbon 1s ionization energies, ΔIE, of a mixed methanol-chloroform cluster containing 13 methanol molecules and 36 chloroform molecules. The ΔIE values are calculated using the given force field (FF) or by a QM/MM model where the ionized molecule and its nearest neighbours are studied with the M06-2X[14] and B3LYP[15,16] hybrid functionals while the remaining part of the cluster are treated by usage of the given force field (see text). Standard deviations among the ΔIE's are given within the parentheses.

Ionized molecule	B3LYP/FF	M062X/FF	FF
CH_3OH	-0.69(0.36)	-0.60(0.34)	-0.59(0.29)
$CHCl_3$	-0.85(0.27)	-0.77(0.27)	-0.79(0.23)

Table 5 Average monomer–cluster shifts (ΔIE) and fwhm (Γ_G) computed for single-component chloroform clusters of size N, based on distributions of ionization energies. For large clusters, ΔIE and Γ_G are computed at two different λ values to simulate the experimental measurements at 330 eV and 440 eV. The shifts are computed for geometries obtained from MD simulations at 150K.

N	λ(Å)	ΔIE (eV)	Γ_G (eV)
10	∞	-0.43(0.02)	0.43(0.02)
54	8	-0.68(0.04)	0.50(0.02)
	12	-0.69(0.04)	0.50(0.02)
146	8	-0.81(0.05)	0.54(0.02)
	12	-0.83(0.03)	0.54(0.02)
323	8	-0.93(0.06)	0.57(0.02)
	12	-0.95(0.02)	0.59(0.02)
545	8	-1.02(0.05)	0.67(0.04)
	12	-1.06(0.03)	0.69(0.02)

and the comparison towards methanol, only rough estimates are given: $\lambda_{35eV}/\text{Å} = 8 \pm 4$ and $\lambda_{145eV}/\text{Å} = 12 \pm 4$. Here, the number density ($n = 0.0266$ mol cm^{-3})[11] of the crystalline structure of chloroform at 185 K is used.

For the purpose of comparing to the experimental measurements, the average monomer–cluster shift and fwhm are shown in Table 5 for pure chloroform clusters and in Table 6 for pure methanol clusters. In the Tables, the uncertainties in shift and width values are due to uncertainty in determing the effective attenuation length (λ).

Table 6 The same as Table 5 for pure methanol clusters.

N	λ(Å)	ΔIE (eV)	Γ_G (eV)
6	∞	-0.37(0.02)	0.28(0.03)
13	∞	-0.60(0.02)	0.43(0.03)
20	∞	-0.68(0.02)	0.59(0.03)
52	7	-0.81(0.03)	0.66(0.07)
	10	-0.83(0.02)	0.73(0.04)
147	7	-0.93(0.04)	0.92(0.06)
	10	-0.97(0.02)	0.97(0.03)

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