Predictive simulations of core electron binding energies of halogenated species adsorbed on ice surfaces from relativistic quantum embedding calculations

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We report an investigation of the suitability of quantum embedding for modeling the effects of the environment on the X-ray photoelectron spectra of hydrogen chloride and the chloride ions adsorbed on ice surfaces, as well as of chloride ions in water droplets. In our approach, we combine a density functional theory (DFT) description of the ice surface with that of the halogen species with the recently developed relativistic core-valence separation equation of motion coupled cluster (CVS-EOM-IP-CCSD) via the frozen density embedding formalism (FDE), to determine the K and L\textsubscript{1,2,3} edges of chloride. Our calculations, which incorporate temperature effects through snapshots from classical molecular dynamics simulations, are shown to reproduce the experimental trends for L edges of the species on ice surfaces, with respect to changes in temperature as well as the decrease in core binding energies in Cl\textsuperscript{−} with respect to HCl. Finally, we find that in contrast to the L edges, we strongly underestimate the environmental effects on the K edges. We trace this behavior to the inability of the embedding potential obtained with the FDE approach to faithfully reproduce the Kohn-Sham potential of the analogous DFT calculation on the whole (supermolecular) system, and provide an \textit{ad hoc} correction to the CVS-EOM-IP-CCSD energies, based on ground-state DFT calculations, that yields binding energies with similar accuracy to that observed for the L edges.

I. INTRODUCTION

Ice is everywhere in the environment and its peculiar structure and properties make it a subject of intense scientific research. Studies connected to ice indicate that it hosts reactions that can influence climate, air quality, biology systems and initiate ozone destruction\cite{1,2,3}. Hydrogen Bonding (HB) between ice and trace gases is the first step towards their interaction\cite{4}. Investigations into the bound state of strong acids\cite{5} interaction with ice indicate that strong acids lead to modification in the HB network of the liquid-like layer on ice surface. It has been shown however that, weak acids adsorption on ice surface does not produce any significant changes in the electronic properties of solvated halide/halide ions\cite{6,7}, and among these X-ray Photoelectron Spectroscopy (XPS) stands out as a particularly powerful technique\cite{8} due to its high specificity, and the great sensitivity of core binding energies (BEs) to small perturbations to the surroundings of the atoms of interest\cite{9,10,11}.

The surface sensitivity and chemical selectivity of radiations from XPS has made it possible to investigate the loss of gas-phase molecules as well as their behavior and transformation in complex reactions or solvent mediums\cite{11,12,13,14,15}.

This is illustrated in recent investigations of the electronic structure of halogen-related systems interacting with solvent environment\cite{4,14,24}, for which the evidence from XPS suggests the dependence of chemical and solvent binding energy induced shifts on the HB network configuration of the solvent to the halide systems. In a pioneering work by McNeill et al. it has been shown that the quasiliquid layer (QLL) plays an essential role in influencing the sorption behavior of HCl and on the chemistry of environmental ice surfaces\cite{25,26}, for which the evidence of XPS suggests that the dissociated form of HCl perturbs the HB network of the liquid-like layer on ice by forcing them into solvation\cite{4,27}. From these studies, it is observed that the ionization of HCl on ice surfaces follow a janus-like behavior, where molecular HCl is formed on the ice surface and its dissociated form is observed at the uppermost bulk layer of the ice surface. In addition, there is a long-standing debate on whether the dissociation of HCl on ice surfaces is temperature dependent. While some studies show that the dissociation occurs only at high temperatures\cite{28,29}, other studies indicate that this mechanism can occur even at low temperatures\cite{4,30}.

As the physical and chemical processes at play (with respect to the interaction between adsorbed species and

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the ice surface, as well as the interaction between the incoming X-rays and the sample) are quite complex, it is difficult to make sense of the experimental results without the help of theoretical models. Such models invariable which encompass representations for both a spatial (the arrangement of the atoms) and an electronic structure components.

From the electronic structure standpoint, two mains questions have to be addressed, how to determine the core binding energy for a particular atom and edge, and how to incorporate the effect of the environment—which may go well beyond the immediate surroundings of the atoms of interest, and may be quite severely affected by the structural changes mentioned above.

On the first question, in contrast to valence ionizations, estimating core ionization energies from ground-state quantities of the non-ionized system through Koopman’s theorem is a poor choice, since large orbital relaxation effects that come into play upon the creation of the core hole(s) are not taken into account. Relaxation is, on the other hand, quite well described in the ∆-SCF method50,31 (and its generalizations to DFT52 and other correlated approaches33–35. Though computationally relatively inexpensive, ∆-SCF and ∆-DFT have as non-negligible downsides the requirement of converging different open-shell states for targeting different edges, which can be a daunting task in difficult open shell cases, or require a great number of calculations in cases of systems with the same element in different chemical environments.

In this work we shall consider an alternative route, in which core BEs are obtaining via the diagonalization of the same Hamiltonian for the ground and ionized states. The development of such approaches is currently a very active area of research, and different ansätze have been discussed in the literature32,36–55. Here however we shall focus exclusively on the use of the relativistic (4-component based) equation of motion (EOM) coupled cluster (CC) for ionization energies within the core-valence (CVS) approximation (CVS-EOM-IP-CC)56.

This is due, first, to EOM-based approaches being capable of both providing a balanced description of the ground and ionized states, with CC wavefunctions being known to account for a great deal of relaxation effects. Second, EOM approach provides us with a way to target several ionized states at once and does not require the definition of active/model spaces. Third, the physically motivated CVS approximation54 allows one to target core states in an efficient manner with little modification to standard diagonalization approaches that target exterior roots43–46,56, in spite of the fact that the core states are embedded in a continuum of states arising from valence excitations and ionizations.

Finally, the use of relativistic Hamiltonians65 allows one to capture the changes in core BEs due to scalar relativistic and spin-orbit coupling effects, the latter being responsible for the splitting of the L, M and N edges. The higher computational cost associated with 4-component relativistic Hamiltonians has motivated the development of efficient 2-component approaches. Among the latter, the superior accuracy of approaches which define the transformation to 2-component based on 4-component atomic or molecular calculations makes them particularly useful for correlated calculations such as those with CC approaches66–68.

Due to the correlated electronic structure methods’ steep computational scaling with system size \( O(N^6) \) for CCSD-based methods, the incorporation of the environment surrounding the species of interest on the calculations is in general not possible beyond a few nearest neighbors, without requiring the introduction of approximations to the correlation methods themselves via localization methods69–74. Embedding approaches, in which a system is partitioned into a collection of interacting subsystems, allow one to select the most cost-effective approach to treat each subsystem, with either classical or quantum-mechanical approaches.

Classical embedding (QM/MM) models (continuum models, point-charge embedding, classical force fields etc) are computationally very efficient but at the cost of foregoing any prospect of extracting electronic information from the environment, and will be bound by the limitations of the classical models (e.g. the difficulties of continuum models to account for specific interactions such as hydrogen bonding). Purely quantum embedding approaches (QM/QM), on the other hand, may be more costly but with the advantage of permitting one to extract information from the electron density or wavefunctions of the environment and as such have been used to study absorption75 and reaction energies76, electronically excited77–83 and ionized84,85 states of species of experimental interest.

Among QM/QM embedding methods, the frozen density embedding (FDE) approach is particularly interesting since it provides a framework to seamlessly combine CC and DFT approaches (CC-in-DFT) for both ground and excited states69,77,82,86, and recently has been shown to successfully tackle the calculation of valence electron BEs of halogens in water droplets84, while providing rather accurate of valence water binding with no additional effort that necessary to represent the system of interest.

Such an approach would be particularly interesting for addressing XPS spectra, as it would allow the calculation of the core spectra with correlated approaches for the species of interest while at the same time providing information on the valence band of the environment (which is often used as a reference). However, to the best of our knowledge to date there have been no studies of XPS spectra with CC-in-DFT, though we note a recent study of excitation, electron attachment and detachment (including core) with EOM-CC employs a projection-based QM/QM embedding approach similar to FDE, but for relatively simple environments.

Thus, in this contribution, we aim to extend the CC-in-DFT based computational protocol of Bouachra et al.84.
to core ionized states, and investigate the performance of CC-in-DFT in the determination of chlorine (Cl) core electron BEs, and associated chemical shifts, for hydrogen chloride (HCl) and ionic chloride (Cl⁻) adsorption on ice surfaces. We shall also profit of this investigation and determine the ionic chloride BEs on the water droplet model employed in ref. 84.

The manuscript is organized as follows: the basic theoretical aspects of DFT-in-DFT and CC-in-DFT embedding are outlined in section II, with a description of the structural models (alongside the details of the calculations) provided in section III. The discussion of our results, and conclusions are presented in sections IV and V, respectively.

II. THEORETICAL APPROACHES

A. Frozen density embedding (FDE) method

The main idea of FDE, is the separation of the total electron density of a system into a number of density sub-systems. Two sub-systems are considered in our case and the whole system is represented as the sum of the density of the sub-system of interest, ρα and subsystem of the environment, ρβ (i.e. ρtot = ρα + ρβ). The ρβ is considered to be frozen in this approximation. The corresponding total energy of the whole system is based on the electron densities of the sub-systems and can then be written as

\[ E_{\text{tot}}[\rho_{\text{tot}}] = E_{\alpha}[\rho_{\alpha}] - E_{\beta}[\rho_{\beta}] + E_{\text{int}}[\rho_{\alpha}, \rho_{\beta}] \]  

where \( E_{\text{int}}[\rho_{\alpha}, \rho_{\beta}] \) is the energy obtained from the interaction of the two sub-systems, which is known as the interaction energy of the system. The interaction energy is given as

\[ E_{\text{int}}[\rho_{\alpha}, \rho_{\beta}] = E^{NN}_{\text{int}} + \int \rho_{\alpha}(r)\rho_{\beta}(r)\rho_{\text{nu}}(r) + \rho_{\beta}(r)\rho_{\text{nu}}(r) \]  

\[ + \int \frac{\rho_{\alpha}(r)\rho_{\beta}(r')}{|r - r'|} d^3r d^3r' + E_{\text{xc}}^{\text{nadd} |\rho_{\alpha}, \rho_{\beta}] + T_{s}^{\text{nadd} |\rho_{\alpha}, \rho_{\beta}] \]  

where \( E^{NN}_{\text{int}} \) is the nuclear repulsion energy between sub-systems, \( \rho_{\alpha}^{\text{nu}} \) and \( \rho_{\beta}^{\text{nu}} \) are the electrostatic potential of the nuclei in sub-systems \( \alpha \) and \( \beta \) respectively. \( E_{\text{xc}}^{\text{nadd} |\rho_{\alpha}, \rho_{\beta}] \) and \( T_{s}^{\text{nadd} |\rho_{\alpha}, \rho_{\beta}] \) are the non-additive contributions due to exchange-correlation and kinetic energies respectively as defined as

\[ E_{\text{xc}}^{\text{nadd} |\rho_{\alpha}, \rho_{\beta}] = E_{\text{xc}}[\rho_{\alpha} + \rho_{\beta}] - E_{\text{xc}}[\rho_{\alpha}] - E_{\text{xc}}[\rho_{\beta}] \]

\[ T_{s}^{\text{nadd} |\rho_{\alpha}, \rho_{\beta}] = T_{s}[\rho_{\alpha} + \rho_{\beta}] - T_{s}[\rho_{\alpha}] - T_{s}[\rho_{\beta}] \]  

The non-additive kinetic energy and the non-additive exchange-correlation energy take into consideration non-classical contributions to the energy. The non-additive kinetic energy prevents spurious delocalization among the sub-systems as observed by balancing the attractive interaction in the nuclear framework of one sub-system and the electron density of another sub-system. The FDE uses only the electron density in the calculation of interaction between sub-systems without the sharing of orbital information among the sub-systems. Minimization of the total energy of the system with respect \( \rho_{\alpha} \) yields an Euler-Lagrangean equation that keeps the number of electrons in the sub-system of interest fixed.

The application of the Euler-Lagrangean equation in the FDE allows the molecular system to be subdivided into smaller interacting fragments and each of them being treated at the most suitable level of theory. Although based on DFT, the FDE scheme also allows treatment of one of the sub-systems with wave function method and the rest of the sub-systems with DFT (WFT-in-DFT) or treating all the sub-systems with wave function (WFT-in-WFT). Several literatures have implemented such WFT-in-DFT, in particular coupling of CC with DFT to accurately probe the excitation energies and ionization energies of numerous molecules.

To obtain the electron density of the sub-system of interest in Kohn-Sham (KS) DFT, the total energy, \( E_{\text{tot}}[\rho_{\text{tot}}] \) is minimized concerning \( \rho_{\alpha} \), while the electron density of the sub-system of the environment is kept frozen. It is performed under the restriction that the number of electrons in sub-system \( \alpha \) is fixed, with the orbitals of the embedded system generated from a set of KS-like equations,

\[ T_{s}(i) + v_{\alpha}^{KS}[\rho_{\alpha}] + v_{\text{int}}^{\alpha}[\rho_{\alpha}, \rho_{\beta}] \]  

where \( T_{s}(i) \) and \( v_{\alpha}^{KS}[\rho_{\alpha}] \) are the KS kinetic energy and effective potential of the isolated sub-system of interest respectively. The embedding potential which describes the interaction between sub-system \( \alpha \) and the frozen sub-system \( \beta \) is

\[ \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(r)}|_{\rho=\rho_{\text{tot}}} + \frac{\delta T_{s}[\rho]}{\delta \rho(r)}|_{\rho=\rho_{\text{tot}}} + \frac{\delta T_{s}[\rho]}{\delta \rho(r)}|_{\rho=\rho_{\alpha}} = 0 \]  

B. Core-Valence Separation (CVS) Equation-of-motion coupled cluster (CVS-EOM-CC) theory

In the CVS-EOM-IP-CCSD method, the BEs are obtained from the solution of the projected eigenvector and its corresponding eigenvalue equation of

\[ P_{c}^{\alpha}(\hat{H}P_{c}^{\alpha}R_{k}^{P}) = \Delta E_{k}P_{c}^{\alpha}R_{k}^{P} \]  

where \( \Delta E_{k} \) is the ionization energy of the system, \( \hat{H} = e^{-T}\hat{H}e^{T} \) is a similarity transformed Hamiltonian including equation 5, \( P_{c}^{\alpha} \) is a projector introduced to restrict
all elements of valence orbitals to zero and \( R_k^{IP} \) is the operator that transforms the coupled-cluster ground-state to electron detachment states. \( R_k^{IP} \) is given as

\[
R_k^{IP} = \sum_i r_i \{a_i\} + \sum_{i>j,a} r_{ij}^a \{a_i^\dagger a_j a_i\} \quad (7)
\]

III. COMPUTATIONAL DETAILS

A. Electronic structure calculations

All DFT\textsuperscript{90} and DFT-in-DFT\textsuperscript{91} calculations have been performed with the 2017 version of the ADF code\textsuperscript{92}, employing the scalar relativistic zeroth-order regular approximation (ZORA)\textsuperscript{63} Hamiltonian\textsuperscript{63} and triple zeta basis sets with polarization function (TZP)\textsuperscript{93}. In the case of single-point calculations and in the determination of embedding potentials, the statistical average of orbital potentials (SAOP)\textsuperscript{94} model potential\textsuperscript{95,96} was used for the exchange-correlation potential of the subsystems, whereas the PBE\textsuperscript{97} and PW91\textsuperscript{98} density functionals were employed for the non-additive exchange-correlation and kinetic energy contributions, respectively. In embedding calculations no frozen cores were employed. In the case of geometry optimizations, the PBE functional was used, along with the large core option. All integration case of geometry optimizations, the PBE functional was employed for the non-additive exchange-correlation interaction to DC (\( M \)) Hamiltonians. For the latter, the Gaunt-type \( \sum_i a_i^\dagger a_i \) has been taken from the original reference. Each droplet contains 50 water molecules, and the halogen position has been constrained to be at the center of mass of the system.

Initial structures of the halogens adsorbed on the ice surfaces have been taken from Woittequand et al.\textsuperscript{106}, which are based on CMD simulation of HCl adsorbed on the ice surfaces with a non-polarizable force field\textsuperscript{107} at 210 K. We have considered 25 snapshots, each containing 216 water molecules. It should be noted that this set of structures account for the disorder at the air-ice interface associated with the ice quasi-liquid layer.

Due to the nature of the force field, structures for Cl\textsuperscript{−} were not available for the same surface, and we have therefore started out from the HCl snapshots, removed a proton and proceeded to optimizations of the ion position while constraining the water molecules of the ice surface to keep their original positions. As such, the adsorption site is slightly altered with respect to the original HCl-ice system, but not the surface on which adsorption takes place.

Furthermore, to assess the importance of HCl-water interactions not captured by the classical force field, we have applied a constrained optimization to the HCl species as well, in a similar vein as outlined above, for all CMD snapshots. We have considered two situations: one in which only the position of HCl was allowed to change (thus allowing both changes in H-Cl bond distance and in relative position of H and Cl with respect to the surface), and another in which the atoms for the six waters closest to HCl were also allowed to change position.

B. MD-derived structures

The structures for Cl\textsuperscript{−} in water droplets simulated at temperature of 300 K have been taken from Bouchafra et al.\textsuperscript{84}, and originate from classical molecular dynamics (CMD) simulations employing polarizable force fields\textsuperscript{108}. Here we have have considered the same 100 snapshots as in the original reference. Each droplet contains 50 water molecules, and the halogen position has been constrained to be at the center of mass of the system.

For Cl\textsuperscript{−} in water droplets a single embedding model is used, in which two subsystems are defined: the active subsystem (treated with CC), containing the halogen, and the environment (treated with DFT) containing the 50 waters. Further details can be found in\textsuperscript{84} for our discussion of the halogens adsorbed on ice we have considered three models: the first represents electronic states with main contributions arising from holes in the 1s, 2s, 2p\textsubscript{1/2} and 2p\textsubscript{3/2} spinors, respectively.

All the datasets associated with this study are available at https://doi.org/10.5281/zenodo.5729761.

C. Embedding models

For Cl\textsuperscript{−} in water droplets simulated at temperature of 300 K, we have employed the usual approximation of the energy contribution from (SS\{SS\})-type two-electron integrals by a point-charge model.\textsuperscript{107} In CC-in-DFT calculations, the embedding potential obtained (with ADF) at DFT-in-DFT level is included in DIRAC as an additional one-body operator to the Hamiltonian, following the setup outlined in\textsuperscript{77}.

Unless otherwise noted, all occupied and virtual spinors were considered in the correlation treatment. The core binding energy calculations with CVS-EOM-IP-CCSD\textsuperscript{56} were performed for the K, L\textsubscript{1}, L\textsubscript{2} and L\textsubscript{3} edges of the chlorine atom. The energies so obtained represent electronic states with main contributions arising from holes in the 1s, 2s, 2p\textsubscript{1/2} and 2p\textsubscript{3/2} spinors, respectively.
FIG. 1: Perspective views for cluster models of halogens adsorbed ice surfaces (represented by 200 water molecules): without a partition into subsystem (SM, left), with an active subsystem containing only the halogen (EM1, center) and with an active subsystem containing the halogen and 6 nearest water molecules (EM2 right). Boxes A, B and C represent the system HCl-ice whereas boxes D, E and F represent the system Cl\(^{-}\)-ice.

Considered, the first (referred to as model EM1 in the following) is similar to the droplet one in that only the species containing the halogen is contained in the active subsystem, and all water molecules make up the environment. In the second model (referred to as model EM2 in the following), we include a number of water molecules (the nearest neighbors to the halogen species) in the active subsystem, and the remaining water molecules make up the environment.

These models are pictorially represented in figure 1, for a case in which we considered only 50 water molecules, which together with model EM1 will be our working model when considering CC-in-DFT calculations for different snapshots, given its best cost/accuracy ratio, which will be discussed below. For such systems, and for a single snapshot, we have investigated the effect of relaxing the density of the \(n\) (\(n = 0, 10, 20, 30, 40\) for EM1 and EM2, and also \(n = 50\) for EM1) water molecules closest to the active subsystem, via freeze-thaw iterations, on the DFT and DFT-in-DFT orbital energies.

If orbital energies provide a poor model for comparing to experiment due to the lack of orbital relaxation, they are well-defined quantities, are obtainable for all model sizes and provide a qualitatively correct picture of the changes in electrostatic interaction between the surface and the halogens as the number of water molecules is increased.

Before arriving at this choice of system size, we have investigated, also for a single snapshot, the effect of the number of water molecules on the BEs for systems containing 50, 100, 150 and 200 water molecules for model EM1. Due to constraints in our computational resources, and also in the perspective of performing both DFT-in-DFT and CC-in-DFT calculations, we have employed a variant of model EM2 (denoted by EM2\(^V\)), in which only the nearest water molecule to the halogen is added to the active subsystem.

In the CC-in-DFT calculations associated with such tests, we have restricted the virtual spinor space to include only those with energies up to 100 Hartree, and therefore exclude high-lying virtual spinors which are very important for obtaining accurate EOM-CC BEs. As such, our results here should be viewed as semiquantitative at best.

IV. RESULTS AND DISCUSSION

As indicated in section IV A, we have performed benchmark calculations on the accuracy of the different Hamiltonians to predict chlorine core ionization energies of gas-phase HCl and Cl\(^{-}\). First, the accuracy of the ZORA Hamiltonian to obtain ground-state core orbital energies and making approximations to predict core ionization potential at the DFT level is discussed. We then evaluated the performance of the different Hamiltonians in conjunction with Hartree-Fock (HF), Delta HF (\(\Delta\) HF) and CVS-EOM-IP-CCSD methods to check their influence on the probed core ionized-states at the chlorine
edges. The Hamiltonian producing the most accurate results is compared with reference experimental core ionization potential and some selected theoretical estimated core BEs at the gas-phase level. In addition, we investigated the performance of our two embedding models (EM1 and EM2) and compared them with a reference supermolecule model (SM) at the DFT level utilizing the ZORA Hamiltonian, in which we discussed their accuracy from different perspectives. Finally, we selected the ZORA Hamiltonian and the Hamiltonian that gives the most accurate results for the gas-phase species at the CC level of theory to perform our embedding calculations on the HCl (or Cl\textsuperscript{−}) adsorbed on ice surfaces and Cl\textsuperscript{−} interacting with the bulk layer of droplets at relevant environmental conditions. The ZORA with other parameters is employed to obtain an embedding potential at the ground-state embedding potential between the halogens and solvent environment at the DFT level, while the ionization energies are treated with the most accurate set-up at the CC level. See section III of this study for more details about how the embedding calculations are performed. Moreover, the influence of water cluster size on the core orbitals and BEs and their convergence trends as we move from the surface to the bulk layer are analyzed.

Hereinafter, basis sets’ influence on the chlorine core BEs is discussed for the gas-phase species using the ∆ HF and CVS-EOM-CCSD method and their adsorption on the solvent environment using the CVS-EOM-CCSD method. For both the gas-phase and embedding calculations, the basis sets effect are discussed between the methods used in our calculations and also to some reference experimental expectation values.

A. Benchmark calculations

1. Ionization Potential: The performance of density functional theory, Hartree-Fock, Delta HF and core-valence separation equation of motion coupled cluster for molecular HCl and ionic chloride in gas phase.

To begin, we draw our attention to the performance of different levels of theories in probing the chlorine core BEs of HCl and its dissociated form, Cl\textsuperscript{−} in the gas-phase. The results from the DFT ZORA and CVS-EOM-IP-CCSD are shown in table I, while the HF and ∆ HF calculations are displayed in table III. We have evaluated the influence of different Hamiltonians and basis sets in the prediction of the chlorine core BEs at the ∆ HF and CVS-EOM-IP-CCSD level of theory. As a first observation, what emerges from the DFT ZORA calculation is that DFT is a ground-state theory and approximating the core BEs as the negative value of the ground-state orbital energy is significantly off the reported experimental values given by reference\textsuperscript{111–113} for all the chlorine edges in both the neutral and ionic species. The possible error in this calculation is the neglect of orbital relaxation\textsuperscript{114} in the DFT method in addition to the lack of first-order correction in the ZORA Hamiltonian. In the case of the HF, our calculations in table III showed to always overestimate the experimentally reported values displayed in table I. We attribute this overestimation in the HF calculations to the lack of correlation in the method. For core BEs, treating orbital relaxation and correlation is essential and their neglect in these two methods could be the source of such deficiencies in comparison to their ∆ HF and CVS-EOM-IP-CCSD counterparts. However, valence ionization where correlation and orbital relaxation cancel out the DFT ZORA has been shown to give reasonable results in comparison with equation of motion coupled cluster (EOM-IP-CCSD).\textsuperscript{84} It is interesting to point out that, the frameworks of ∆ HF and CVS-EOM-IP-CCSD in our calculations, yielded results that are almost in excellent agreement with the experimental measurement values. We attribute this improvement to the treatment of electron correlation and orbital relaxation on the same footing through separate orbital optimizations for core-ionized or excited states in the ∆ HF method and the coupling of single- and double-excitation manifolds\textsuperscript{115} in the CVS-EOM-IP-CCSD approach. The performance of ∆ HF and CVS-EOM-IP-CCSD showed to provide a slight improvement in comparison to the theoretical method used for 1s core ionized state of Cl\textsuperscript{116} and showed to agree with the 2p ionized state of Cl in HCl from literature.\textsuperscript{117} For 2p ionized state of Cl\textsuperscript{−}, we make a comparison with the theoretical method from literature.\textsuperscript{117} The results showed to agree with a slight difference of a few electron-volts as shown in table II. To the best of our knowledge, we could not find any available reference experimental data, making it very hard to deduce the accuracy of the calculated value of the 1s, 2s ionized states of Cl in HCl as well as the 2s and 2p ionized state of chlorine. Practically, the choice of Hamiltonian either the parent 4-component or 2-component models for computational efficiency and accuracy is essential. The 2-component Hamiltonian employing molecular mean-field (X2Cmmf) formalism is compared with the parent 4-components Dirac-Coulomb (DC) Hamiltonian as depicted in table I. We observed that transforming from the DC to the X2Cmmf Hamiltonian gives almost identical results in conjunction with the CVS-EOM-IP-CCSD method. The inclusion of Gaunt term in the X2Cmmf Hamiltonian, however, showed to reduce the BEs approximately by 1.9 eV at the chlorine K edge and 0.1 eV at the L edges. In the case of the ∆ HF, the inclusion of the Gaunt term showed to reduce the BEs approximately by 2.0 eV at the K edge, and in the range of 0.1 - 0.2 eV at the L edges. The inclusion of the Gaunt term which contains spin-other-orbit (SOO) interaction showed to be essential for spin-orbit splitting as well as treating chlorine core electron BEs. So the source of the remaining error in the ∆ HF and CVS-EOM-IP-CCSD calculations compared to the experimental expected values must be sought in some part of the electron-electron operator in the relativistic Hamiltonian (i.e. accounting...
for the first order correction such as the retardation effect in the Breit interaction) or by including triple excitations in the wave function in the case of the CVS-EOM-IP-CCSD.

TABLE I: CVS-EOM-IP-CCSD chlorine core binding energies (in eV) for HCl and Cl\(^-\) in gas-phase, for the Dirac-Coulomb (DC), 2-component molecular mean-field X2C (\(^2\text{DC}^M\)) and 2-component molecular mean-field X2C including the Gaunt interaction (\(^2\text{DCG}^M\)) Hamiltonians. In addition to those, for the spin-orbit ZORA Hamiltonians we show orbital energies from SAOP.

| Species | Method | K   | L\(_1\) | L\(_2\) | L\(_3\) |
|---------|--------|-----|---------|---------|---------|
| HCl     | ZORA   | 2764.58 | 253.94  | 194.08  | 192.41  |
|         | DC     | 2835.79 | 280.77  | 210.18  | 208.48  |
|         | \(^2\text{DC}^M\) | 2835.78 | 280.77  | 210.18  | 208.48  |
|         | \(^2\text{DCG}^M\) | 2833.90 | 280.69  | 210.02  | 208.39  |
|         | Exp.\(^{112}\) |         | 208.70  | 207.1   |         |
|         | Exp.\(^{113}\) |         | 209.01  | 207.38  |         |
| Cl\(^-\) | ZORA   | 2754.42 | 243.88  | 184.02  | 182.35  |
|         | DC     | 2826.06 | 270.81  | 200.26  | 198.56  |
|         | \(^2\text{DC}^M\) | 2826.05 | 270.81  | 200.26  | 198.56  |
|         | \(^2\text{DCG}^M\) | 2824.17 | 270.73  | 200.10  | 198.47  |
|         | Exp.\(^{111,118}\) |         | 2822.3,2822.4 |         |         |

TABLE II: Selected theoretically estimated chlorine core binding energies (BE, in eV) from literature for HCl and Cl\(^-\) using the Δ B3LYP approach, Koopman, Scaled Configuration Interaction Singles and Doubles CIS(D) and ΔSCF.

| Species | Method | K (2p)\(^{-1}\) | Cl in HCl | Cl\(^-\) |
|---------|--------|-----------------|-----------|----------|
|         | Δ B3LYP | 2817.8\(^{116}\) |           |          |
|         | Koopman | 2855.0\(^{116}\) |           |          |
|         | CIS(D)  | 2810.1\(^{116}\) |           |          |
|         | Δ SCF   | 208.92\(^{117}\) | 197.07\(^{117}\) |          |

B. Basis set effects on gas-phase HCl and Cl\(^-\)

We start our discussion with a not-so-detailed comparison of the computed ionization energy values using both the Δ HF and CVS-EOM-IP-CCSD methods. Different basis sets are discussed and their accuracy to each other is compared. To this end, we plot in figure 2 the errors as we move from double zeta (dz) basis set to quadruple zeta (qz) basis set limit in the series of d-aug-dyall.acvxz (where x=2 (dz), x = 3 (tz) and x= 4 (qz)) considered for the ionization energies. For the two methods used in our calculations, we observed an almost decreasing error trend for the chlorine K and L edges as we move from the dz basis set to the qz basis set. For the CVS-EOM-IP-CCSD method, little difference in the range of 0.02 - 0.1 eV is observed between the triple zeta (tz) and qz results at the chlorine edges for both the neutral and ionic species. In the case of the double and quadruple zeta, a difference in the range of 0.2 - 0.3 eV is observed.

For the Cl K and L edges in HCl and Cl\(^-\), the difference between the Δ HF results obtained for x=3 (tz) and x=4 (qz) in the series of d-aug-dyall.acvxz, are always in the range of 0 - 0.01 eV for both the gas phase HCl and Cl\(^-\). Changing from x=2 to x=4 leads to a difference in the range of 0.1 to 0.2 eV. Cl\(^-\). The influence of basis sets on the core BEs of the gas phase neutral and ionic species is minor, making the corrections due to basis set incompleteness so small that it can be neglected.

Regarding the chlorine edges in HCl and Cl\(^-\) with which experimental data exist, the CVS-EOM-IP-CCSD model showed to systematically overestimate the core ionization energies. The Δ HF method on the other hand showed to underestimate the core ionization energies and the estimated values for both methods could be shifted in comparison to their experimental counterparts.

1. The Accuracy of the Embedding models to the Supermolecule model

Herein, we first established the reliability of our embedding models (EM1 and EM2) to a reference supermolecule model (SM) at the DFT level of theory. We analyzed relaxation of the density of some or all the water molecules on ice influence on the adsorbed HCl/Cl\(^-\) ground-state orbital energies and then investigated how the accuracy of the embedding models after absolute localization of the subsystems’ orbitals in a freeze-and-thaw optimization approach the supermolecule model. We have analyzed the embedding calculations of Cl 1s, 2s, and 2p orbital energies of HCl/Cl\(^-\) adsorption on ice from several perspectives. The reference supermolecule calculations, which include the explicit addition of all the water molecules to the HCl/Cl\(^-\) are used to assess the quality of embedding models EM1 and EM2 at the DFT level of theory, which is shown in figure 3. First, we noticed for all the edges of Cl in HCl, the orbital energies obtained in EM1 model consistently approach the corresponding reference SM model with a difference of 0.2, 0.1, and 0.1 eV for the 1s, 2s, and 2p respectively, as EM2 yields orbital energies that are shifted by about 0.6, 0.3 and 0.3 eV. In the case of the ionic chloride, EM2 showed to be in good agreement with the supermolecule calculations with a difference of 0.6 eV for the 1s and 0.5 eV for both the 2s and 2p, while EM1 shifted the orbital energies by about 0.7 eV for the 1s and 0.6 eV for the 2s and 2p. The energy shifts between model EM1 and EM2 are approximately in the range of 0.1 to 0.4 eV for both the neutral and ionic species. This reflects the accuracy of the embedding models to the reference model. The orbital energies in both models displayed strong depen-
TABLE III: Δ HF chlorine core binding energies (in eV) for HCl and Cl⁻ in gas-phase, for the Dirac-Coulomb (DC), Dirac-Coulomb including the Gaunt interaction (DCG) and Dirac-Coulomb including the Gaunt interaction (DCG) as well as the addition of small integrals (DCG(SS—SS) Hamiltonians. In addition to those, we show orbital energies from Hartree-Fock.

| Species | Method   | K    | L₁   | L₂    | L₃    | HF   | Δ HF | HF   | Δ HF | HF   | Δ HF |
|---------|----------|------|------|-------|-------|------|------|------|------|------|------|
| HCl     | DC       | 2864.16 | 2832.28 | 289.61 | 279.33 | 220.12 | 208.72 | 218.25 | 207.02 |
|         | DCG      | 2862.27 | 2830.25 | 289.53 | 279.25 | 219.85 | 208.55 | 218.16 | 206.93 |
|         | DCG(SS—SS) | 2862.27 | 2830.25 | 289.53 | 279.25 | 219.85 | 208.55 | 218.16 | 206.93 |
| Cl⁻     | DC       | 2854.83 | 2821.63 | 280.23 | 268.79 | 210.64 | 198.19 | 208.88 | 196.48 |
|         | DCG      | 2852.94 | 2819.61 | 280.15 | 268.71 | 210.48 | 198.03 | 208.78 | 196.39 |
|         | DCG(SS—SS) | 2852.93 | 2819.60 | 280.15 | 268.71 | 210.48 | 198.03 | 208.79 | 196.39 |

FIG. 2: Basis set influence (Dyall basis sets) on the core binding energies of gas phase HCl and Cl⁻ using the Δ HF and CVS-EOM-IP-CCSD approaches.

dence with the number of relaxed densities of subsystem β for the ionic chloride. Of course, agreement with the supermolecule calculation is obtained when the density of more water molecules in subsystem β are relaxed together with the density of subsystem α in a freeze-and-thaw optimization. This ensures the absolute localization of the subsystems orbitals compared to the frozen density approximation in subsystem β. In the molecular HCl
FIG. 3: Variation of the approximate $K$, $L_1$ and $L_{2,3}$ core binding energies of chlorine in HCl (left) and Cl$^-$ (right), obtained from scalar ZORA calculations with the SAOP model potential, with respect to the number of water molecules whose density is relaxed (in the ground state) via freeze-thaw cycles, for models EM1 (squares) and EM2 (circles). For comparison, the corresponding orbital energies obtained for model SM are provided as a reference (dashed line). The $L_{2,3}$ values are not split as calculations do not include spin-orbit coupling.

Calculations, the orbital energies showed to be less sensitive to the relaxed densities of the environment. These results are unexpected and speculatively we attribute it to the covalent character of the HCl in the presence of the water environment. It is clear that localizing the subsystems’ orbitals followed by iterative optimization provides core orbitals energies that are close to the supermolecule while improving the computational efficiency as well.\textsuperscript{119}

Hence, the remaining source error in the embedding models compared to the supermolecule model must be considered in some other parts of the embedding schemes, in particular improvement in the approximate non-additive kinetic energy functional, which is not always accurate enough to avert electron-leak problem thoroughly\textsuperscript{70} may be needed to reduce the errors.
C. Calculation of chlorine core binding energies of Hydrogen Chloride and ionic Chloride on ice surface at 0 K and investigation of the convergence behavior with increasing solvent-induced environment.

As shown in the figure 5, we have tested the sensitivity of the core electron BEs for increasing cluster sizes in subsystem $\beta$ at the CC-in-DFT embedding scheme. The accuracy of model $\text{EM1}$ is compared to that of model $\text{EM2}$. From table VIII, IX, X, and XI, we observed small changes in the orbital energies when model $\text{EM1}$ is compared with that of $\text{EM2}$ for both the neutral and ionic species. We found that the results showed to be sensitive, but with only small shifts in the energies. This suggests that the explicit addition of more water molecules to subsystem $\alpha$ at both the DFT and WFT levels could lead to a further shift in the core electron BEs. The response of the energies to the long-range influence of the water environment showed to be in the range of 0.1 - 0.5 eV for the molecular HCl, while for the ionic chloride, variations are found in the range of 0.2 - 1 eV for all the chlorine edges. The size of the shift estimated showed to be consistent in both models. The shifts in the ground-state orbital energies trend with increasing cluster size at the DFT-in-DFT depicted in table V, VI, VII is observed to be consistent with the core-ionized state energies trends at the CC-in-DFT scheme. This supports the reliability of DFT to provide ground-state density and potential to account for solvent environment influence at the WFT level and solidifies the non-negligible effect of the non-additive kinetic energy functional in the embedding potential. In terms of the electron BEs, while the ionic chloride seemed to respond strongly to the potential of the solvent environment, the adsorbed HCl showed not to experience much of the potential from the water molecules on the ice surface even with an increased water cluster size. We attribute the possible source of errors to the starting structures. The calculations are started from a rigid or fixed configuration with only the internal coordinates relaxed and the lack of polarization of the non-optimized geometries and environmental densities for each other results in the HCl neglecting the environmental potential.

TABLE IV: Calculated chlorine orbital energies (in eV) of HCl + (H$_2$O)$_n$ clusters with DFT-in-DFT embedding scheme.

| Cl in HCl | No. of H$_2$O (n): K | L$_1$ | L$_2$ |
|-----------|----------------------|------|------|
| 50        | 2754.51 253.98 193.02 |
| 100       | 2754.52 253.99 193.03 |
| 150       | 2754.30 253.77 192.81 |
| 200       | 2754.34 253.81 192.85 |

TABLE V: Calculated chlorine orbital energies (in eV) of Cl$^-$ + (H$_2$O)$_n$ clusters with DFT-in-DFT embedding scheme.

| Cl$^-$ | No. of H$_2$O (n): K | L$_1$ | L$_2$ |
|--------|----------------------|------|------|
| 50     | 2745.26 244.76 183.83 |
| 100    | 2745.40 244.91 183.97 |
| 150    | 2745.27 244.78 183.84 |
| 200    | 2745.21 244.71 183.78 |

TABLE VI: Calculated chlorine orbital energies (in eV) of Cl(H$_2$O)$_n$ clusters with DFT-in-DFT embedding scheme.

| Cl$^-$ | No. of H$_2$O (n): K | L$_1$ | L$_2$ |
|--------|----------------------|------|------|
| 49     | 2745.35 244.9.0 183.96 |
| 99     | 2745.33 244.87 183.934 |
| 149    | 2745.15 244.69 183.76 |
| 199    | 2745.09 244.63 183.69 |

TABLE VII: Calculated chlorine orbital energies (in eV) of Cl(H$_2$O)$_{1+}$ (H$_2$O)$_n$ clusters with DFT-in-DFT embedding scheme.

| Cl$^-$ | No. of H$_2$O (n): K | L$_1$ | L$_2$ |
|--------|----------------------|------|------|
| 50     | 2833.84 2823.94 280.83 210.18 208.55 |
| 100    | 2833.85 2823.96 280.84 210.19 208.56 |
| 150    | 2833.62 2823.73 280.61 209.97 208.34 |
| 200    | 2833.66 2823.77 280.65 210.01 208.38 |
FIG. 4: Calculated chlorine 1s, 2s and 2p orbital energies of HCl and Cl− adsorbed on different water cluster systems on ice surface at 0 K using the DFT-in-DFT embedding scheme. The blue lines represent X + (H$_2$O)$_x$, x=0, 50, 100, 150, 200, (X = HCl and Cl−) and that of the red lines represent X(H$_2$O)$_1$ + (H$_2$O)$_x$, x=0, 49, 99, 149, 199, (X = HCl and Cl−).

TABLE IX: Calculated chlorine orbital energies (in eV) of HCl(H$_2$O)$_1$ + (H$_2$O)$_n$ clusters with CC-in-DFT embedding scheme. K and K$_c$ are the original and corrected mean values of CC-in-DFT core binding energies (BE, in eV) at the chlorine K edge respectively.

| Cl in HCl | No. of H$_2$O (n): | K   | K$_c$ | L$_1$ | L$_2$ | L$_3$ |
|-----------|-------------------|------|-------|-------|-------|-------|
| 49        |                   | 2833.78 | 2823.89 | 280.76 | 210.11 | 208.48 |
| 99        |                   | 2833.79 | 2823.90 | 280.77 | 210.12 | 208.49 |
| 149       |                   | 2833.57 | 2823.68 | 280.55 | 209.90 | 208.27 |
| 199       |                   | 2833.61 | 2823.72 | 280.59 | 209.94 | 208.31 |

TABLE X: Calculated chlorine orbital energies (in eV) of Cl− + (H$_2$O)$_n$ clusters with CC-in-DFT embedding scheme. K and K$_c$ are the original and corrected mean values of CC-in-DFT core binding energies (BE, in eV) at the chlorine K edge respectively.

| Cl$^-$ | No. of H$_2$O (n): | K   | K$_c$ | L$_1$ | L$_2$ | L$_3$ |
|--------|-------------------|------|-------|-------|-------|-------|
| 50     |                   | 2824.95 | 2815.58 | 271.70 | 201.09 | 199.46 |
| 100    |                   | 2825.16 | 2815.79 | 271.91 | 201.30 | 199.67 |
| 150    |                   | 2824.94 | 2815.57 | 271.68 | 201.07 | 199.45 |
| 200    |                   | 2824.99 | 2815.62 | 271.73 | 201.12 | 199.50 |
FIG. 5: Calculated chlorine 1s, 2s and 2p core binding energies of HCl and Cl\(^-\) adsorbed on different water cluster systems on ice surface at 0 K using the CC-in-DFT embedding scheme. The blue lines represent X + (H\(_2\)O)\(_x\), x=0, 50, 100, 150, 200, (X = HCl and Cl\(^-\)) and that of the red lines represent X(H\(_2\)O)\(_1\) + (H\(_2\)O)\(_x\), x=0, 49, 99, 149, 199, (X = HCl and Cl\(^-\)).

TABLE XI: Calculated chlorine orbital energies (in eV) of Cl(H\(_2\)O)\(_1\) + (H\(_2\)O)\(_x\) clusters with DFT-in-DFT embedding scheme. K and K\(_c\) are the original and corrected mean values of CC-in-DFT core binding energies (BE, in eV) at the chlorine K edge respectively.

| No. of H\(_2\)O (n) | K        | K\(_c\)    | L\(_1\)    | L\(_2\)     | L\(_3\)     |
|---------------------|----------|------------|------------|-------------|-------------|
| 49                  | 2824.89  | 2815.52    | 271.63     | 201.02      | 199.40      |
| 99                  | 2824.93  | 2815.56    | 271.68     | 201.07      | 199.44      |
| 149                 | 2824.67  | 2815.30    | 271.41     | 200.80      | 199.17      |
| 199                 | 2824.71  | 2815.34    | 271.46     | 200.85      | 199.22      |

D. Relaxed Configurations: Basis sets influence on the chlorine core binding energies of Hydrogen Chloride and Ionic Chloride Adsorption on ice surfaces at 210 K

We start our discussion with the basis sets effect on the chlorine computed core ionization energy values for HCl and Cl\(^-\) adsorbed on ice surfaces using the CVS-EOM-IP-CCSD methods. Different basis sets are discussed and their accuracy to each other is compared. To this end, we plot in figure 6 the errors as we move from double zeta basis set to quadruple zeta basis set limit considered for the core ionization energies. The full set of numerical values of the core ionization energies are displayed in table XII. As depicted in figure 6, except for the K edge we observed an almost decreasing error trend for all the chlorine edges in the molecular HCl as we move from double zeta basis set to quadruple zeta basis set. A difference in the range of 0.5 - 0.7 eV is observed between the triple and quadruple zeta results. In the case of the double and quadruple zeta, a difference in the range of 0.2 - 0.7 eV is observed.

For the ionic species, the difference between x=3 (tz) and x=4 (qz) in the series of d-aug-dyall.acvz, are observed in the range of 0.1 - 1.1 eV. Changing from x=2 to x=4 leads to a difference in the range of 2.9 to 3.2 eV. The influence of basis sets on the chlorine core BEs of the adsorbed neutral and ionic species on the ice surface is significant, hence corrections due to basis set incompleteness can not be neglected.

For Cl in HCl core ionization energies, calculations using triple zeta basis set showed to systematically approach the reference experimental data than the double
TABLE XII: Mean values of CC-in-DFT chlorine core binding energies (BE, in eV) averaged over structures from CMD simulations for models with 50 water molecules. The molecular structures correspond to optimization of the halogen system coordinates, keeping the ice surface constrained to the CMD structure. For the ice surface systems, calculations correspond a temperature of 210 K (experimental results at 253 K are provided for comparison)

| System | Environment | Edge | BE(A) | ΔγBE(A) | BE(B) | ΔγBE(B) | BE(C) | ΔγBE(C) |
|--------|-------------|------|-------|----------|-------|----------|-------|----------|
|        |             | d-aug- |       | acv2z    |       | acv3z    |       | acv4z    |
| HCl    | ice         | K     | 2833.73 | -0.40 | 2833.40 | -0.50 | 2833.94 | 0.06    |
|        |             | L_1   | 280.09  | -0.45 | 280.15  | -0.54 | 280.75  | -0.01   |
|        |             | L_2   | 209.52  | -0.44 | 209.49  | -0.53 | 210.13  | 0.01    |
|        |             | L_3   | 207.90  | -0.44 | 207.86  | -0.53 | 208.54  | 0.04    |
| Cl^-   |             | K     | 2825.89 | 1.48 | 2827.70 | 3.28 | 2828.79 | 4.64    |
|        |             | L_1   | 271.86  | 1.29 | 274.90  | 4.17 | 275.07  | 4.27    |
|        |             | L_2   | 201.31  | 1.26 | 204.41  | 4.31 | 204.47  | 4.26    |
|        |             | L_3   | 199.68  | 1.24 | 202.70  | 4.23 | 202.91  | 4.33    |

FIG. 6: Basis set influence (Dyall basis sets) on the core binding energies of HCl and Cl^- adsorbed on ice surfaces at a temperature of 210 K using the CVS-EOM-IP-CCSD approaches. The calculations are average of 25 snapshots.
and quadruple zeta basis sets. In the case of Cl\(^{-}\), the results from d-aug-dyall.acv2z basis set showed to give reasonable results and systematically approach the reference experimental value than the d-aug-dyall.acv2z and d-aug-dyall.acv4z basis set. In this respect, we can propose that while using more basis functions for the neutral species may be important. In the case of the ionic species, it can be neglected.

One essential finding that can not be overlooked is that when we change from smaller basis sets to much larger basis sets, changes in the chlorine core binding energy at the K edge showed to be somehow small in comparison to the L edges. This shows a strong dependence of the accuracy of the results on the basis used for the K and L edges of the chlorine in the molecular HCl and the ionic Cl\(^{-}\). With this, we speculate that the reliability of our results at the Cl edges is dependent on factors like the quality of the basis sets, approximate treatment of the non-additive kinetic energy functional in the embedding potential at the ground-state, and the truncation in the cluster operator.

E. Calculation of chlorine core binding energies of Hydrogen Chloride and Chloride ion Adsorption on ice surfaces at 210 K

CC-in-DFT embedding scheme has allowed evaluating chlorine core level electron BEs of molecular HCl and ionic chloride adsorption on ice surfaces. The results give clear theoretical evidence that chemical properties shifts across the air-ice interface and that chemical properties are determined by the stretching of the HCl bond length, the geometric distances between the adsorbate and the adsorbent, and the electron densities generated from their interaction. Supporting DFT-in-DFT orbital energy at the chlorine edges reveals perturbations to the chlorine orbitals by the water molecules. It is observed that a slight shift in the HCl bond length away from the equilibrium position and changes in the HCl/Cl\(^{-}\)-water molecules geometric distance influence the chlorine ground-state orbitals and allowed us to link them to how strongly the adsorbed HCl/Cl\(^{-}\) experience the surface potential imposed by the water molecules at the air-ice interface.

Table XIII shows the core BEs of both the covalent and ionic states directly estimated with the CC-in-DFT embedding scheme at the air-ice interface. The Cl 1s core ionized state associated with the rigid HCl, optimized HCl structures and optimized ionic chloride ion on the ice surfaces is well estimated. Two spin-orbit doublets representing HCl and Cl\(^{-}\) as shown in figure 7, 8 and 9 are well estimated for the Cl 2p core ionized state. The calculated energy splitting between the 2p\(_{3/2}\) and 2p\(_{1/2}\) approximately around 1.7 eV for both the neutral and ionic species, which are in excellent agreement with the experimental reported value of 2.1 eV carried at 253 K.\(^{26}\)

The chemical shift in the BEs of approximately 6.0 eV between the rigid molecular HCl and ionic chloride calculated at the Cl 1s and 2s singlets and Cl 2p doublets are in line with XPS measurements, however, there is an overestimation of about 4.0 eV. Possible attribution to the overestimation of the experimental values likely appears to be: 1) the temperature differences in the ice structure and 2) the lack of surface potential experienced by the adsorbed molecular HCl as seen in the BEs. The reason is that the calculations are performed on structures where both the HCl and ice are considered to be rigid, with only the internal coordinates relaxed.

We indicate that this constrain on the HCl molecule is too restrictive and we propose that the Cl does not experience much of the ice surface potential since the coordination between the HCl and closest water molecules is neglected. The error attributed to the negligence of the H\(_2\)O surface potential by the adsorbed HCl has allowed the analyzes of the Cl core BEs with regards to the stretching of the HCl bond length away from the equilibrium and the stability of the energies of gas-phase and micro-solvated HCl. The results are discussed in section supplementary information.

F. Relaxed Configurations: Calculation of chlorine core binding energies of Hydrogen Chloride and ionic Chloride Adsorption on ice surfaces at 210 K

Now that we have established that starting from rigid configurations overestimate the experimentally measured values, we turn to analyze the results of an optimized HCl on a constrained ice environment, shown in the table XIII and figure 8. We observed that the results improved upon the calculations performed on the initial rigid HCl on ice configuration with a shift of approximately 0.6 eV for the Cl 1s and 2s and 0.7 eV for the 2p BEs as well as the chemical shifts in the BEs towards the experimental values. This justifies the observation in our previous calculations that the HCl neglected the effects of the environmental density. It is evident now that not relaxing the HCl to the ice environment neglects the response of the water ice and amounts to errors in the core BEs and chemical shift at all the Cl in HCl edges.

From the table XIII and figure 9, we find that seemingly optimizing the HCl together with the four closest water molecules shifts the BEs by 0.1 eV and closer to the experimental expectation value. This observation calls into question the effect of the response of the nearest water molecules to get an accurate description of the core BEs can be proposed that the largest source of error in the rigid configuration is the inadequate description of the closest water molecules (possibly the neglect of their response). Hence, the inclusion of more water molecules to the HCl in the optimization process should yield better results. Nonetheless, we observed that the small stretching of HCl bond length makes it slightly unstable, but dissociation does not occur at this point. Therefore, the stability of the geometric structure is not altered that
TABLE XIII: Mean values of CC-in-DFT chlorine core binding energies (BE, in eV) averaged over structures from CMD simulations for models with 50 water molecules, and the difference of BEs and those calculated for the gas phase ($\Delta g$BE, in eV). The molecular structures correspond to (A) the original CMD snapshots for water droplets and ice surfaces; (B) optimization of the halogen system coordinates, keeping the ice surface constrained to the CMD structure; (C) optimization of the halogen system coordinates and four nearest neighbor waters, keeping the remaining of the ice surface constrained to the CMD structure. For the ice surface systems, calculations correspond a temperature of 210 K (experimental results at 253 K are provided for comparison). For water droplets, calculations correspond a temperature of 300 K.

| System  | Environment | Edge | BE(A) | $\Delta g$BE(A) | BE(B) | $\Delta g$BE(B) | BE(C) | $\Delta g$BE(C) | Experiment |
|---------|-------------|------|-------|-----------------|-------|-----------------|-------|-----------------|------------|
| HCl     | ice         | K    | 2834.03 | 0.13            | 2833.40 | -0.50          | 2833.29 | -0.61          | 2817.6     |
|         |             | L1   | 280.84 | 0.15            | 280.15 | -0.54          | 280.04 | -0.65          |            |
|         |             | L2   | 210.18 | 0.15            | 209.49 | -0.53          | 209.38 | -0.64          | 204.9      |
|         |             | L3   | 208.54 | 0.15            | 207.86 | -0.53          | 207.75 | -0.64          | 202.8      |
| Cl$^-$  | K           |      |        |                 | 2827.70 | 3.53           |        | 2815.4         |            |
|         |             | L1   |       | 274.90 | 1.17          |        | 273.78 | 1.17          |            |
|         |             | L2   |       | 204.41 | 4.31          |        | 200.03 | 4.31          |            |
|         |             | L3   |       | 202.70 | 4.23          |        | 200.03 | 4.23          |            |
| Cl$^-$  | droplet     | K    | 2829.97 | 6.66           |        |                |        |                |            |
|         |             | L1   | 276.63 | 5.90           |        |                |        |                |            |
|         |             | L2   | 205.99 | 5.89           |        |                |        |                |            |
|         |             | L3   | 204.36 | 5.89           |        |                |        |                |            |

TABLE XIV: Original and Corrected mean values of CC-in-DFT chlorine core binding energies (BE, in eV) at the K edge (K and $K^c$ respectively) averaged over structures from CMD simulations for models with 50 water molecules, and the difference of BEs and those calculated for the gas phase ($\Delta g$BE, in eV). The molecular structures correspond to (A) the original CMD snapshots for water droplets and ice surfaces; (B) optimization of the halogen system coordinates, keeping the ice surface constrained to the CMD structure (this work); (C) optimization of the halogen system coordinates and four nearest neighbor waters, keeping the remaining of the ice surface constrained to the CMD structure (this work). For the ice surface systems, calculations correspond a temperature of 210 K (experimental results at 253 K are provided for comparison). For water droplets, calculations correspond a temperature of 300 K.

| System Env. | Edge | BE(A) | $\Delta g$BE(A) | BE(B) | $\Delta g$BE(B) | BE(B) | $\Delta g$BE(B) | BE(B) | $\Delta g$BE(B) | BE(B) | $\Delta g$BE(B) | Exp. |
|-------------|------|-------|-----------------|-------|-----------------|-------|-----------------|-------|-----------------|-------|-----------------|------|
|             |      | d-aug- | d-aug- | d-aug- | d-aug- | d-aug- | d-aug- | d-aug- | d-aug- | d-aug- | d-aug- |       |
|             |      | acv3z | acv2z | acv3z | acv3z | acv4z | acv3z | acv3z | acv3z | acv3z | acv3z |       |
| HCl         | ice  | K     | 2834.03 | 0.13 | 2833.40 | -0.50 | 2833.29 | -0.61 | 2817.6     |       |       |       |
|             |      | K$^c$ | 2824.14 | -9.76 | 2823.84 | -10.39 | 2824.05 | -10.50 | 2817.6     |       |       |       |
| Cl$^-$      | K    | 2825.89 | 1.48 | 2827.70 | 3.53 | 2828.79 | 4.64 |        |       |       |       |       |
|             | K$^c$ | 2816.52 | -7.89 | 2818.33 | -5.84 | 2819.42 | -4.73 |        |       |       |       |       |
| Cl$^-$      | droplet K | 2829.97 | 6.66 |        |       |       |       |       |       |       |       |       |
|             | K$^c$ | 2820.06 | -3.17 |        |       |       |       |       |       |       |       |       |

much with improvement in BEs compared to the non-relaxed or rigid potential energy surface (PES), albeit not very different from the relaxed one.

Furthermore, based on the depth at which the HCl and Cl$^-$ are adsorbed on the ice surface, we indicate that the ionic Cl$^-$ experiences strongly the surface potential imposed by the water molecules than the molecular HCl. The explicit treatment of solvent may be important to predict accurate results since chemical shifts are very sensitive to the solvent interactions or we may need to use wave function to polarize the environment. One essential observation that can not be overlooked is that our embedding potentials from the DFT-in-DFT calculations are generated from unscaled ZORA Hamiltonian instead of a scaled ZORA Hamiltonian and while the L edges orbital energies are shown to give almost identical results for both Hamiltonians, the values from the unscaled ZORA showed to overestimate the K edge by...
FIG. 7: Average calculated chlorine 1s, 2s and 2p core binding energies of rigid HCl interacting with constrained ice surfaces at 210 K (25 snapshots using the CC-in-DFT scheme. The systems are considered as $X + (H_2O)_{50}$ ($X = \text{HCl}$) with d-aug-kyally-acv3z.

FIG. 8: Average calculated chlorine 1s, 2s and 2p core binding energies of optimized HCl and Cl$^-$ interacting with constrained ice surfaces at 210 K (25 snapshots) using the CC-in-DFT scheme. The systems are considered as $X + (H_2O)_{50}$ ($X = \text{HCl and Cl}^-$) with d-aug-kyally-acv3z.
9.9 eV and 9.4 eV for the Cl and HCl and Cl$^-$ respectively. In this respect, the introduction of this embedding potential in the coupled-cluster calculations leads to an overestimation of the Cl core BEs by approximately 10 eV in comparison to the reference experimental value. Taking account of this correction in the core BEs shifts the results closer to the experimental expectation values as displayed in table XIV. It should be pointed out that the errors arising due lack of first-order corrections in the ZORA Hamiltonian cannot be neglected at the Cl K-edge.

To ameliorate the problem, we may need to improve the approximate non-additive kinetic-energy functional in our embedding potential, which has shown to be a major source of error in the generation of embedding potential and perhaps the inclusion of coupled-cluster triples. These calculations provide theoretical evidence of the presence of chemical shifts between molecular HCl and ionic Cl$^-$ upon adsorption on ice surfaces.

1. Investigation of the influence of HCl bond lengths, and HCl-water intramolecular and intermolecular distance on chlorine core binding energies

This discussion shows changes in the chlorine core BEs, HCl bond length, intra- and inter-molecular distances between the HCl and the ice environment as we compare a rigid HCl on ice configuration to optimizing HCl on constraint ice as well as optimizing HCl with the four nearest water molecules on the ice surface and constraining the rest. The results are displayed in figure 10.

In the starting configuration, where all the atoms of the H$_2$O and HCl molecules are kept rigid 10 (Å) the estimated BEs take the form of gas-phase species with only minor variations as shown in table I. This is an indication that the electron density and the corresponding surface potential of the H$_2$O molecules impose a little effect on the chlorine core level BEs, even though our calculations are started from a stable adsorbate and adsorbent structure. We attribute this to the fact that the constrain on the Cl in the HCl molecule is too restrictive and we propose that the electrostatic potential from the attraction and repulsion between the density of the HCl and water molecules is almost neglected.

On the other hand, when all the atoms of the H$_2$O are kept fixed and optimize the HCl to ice, we see a decrease in the core BEs. Notwithstanding, we observed that the increase in the HCl bond after optimization leads to much coordination between the atoms of both species, shifting their interaction to lower BEs as shown in figure 10 (B). These shifts could be attributed to modification in the coordination environment of the intra- and inter-molecular distances between the HCl and the H$_2$O molecules on the ice surface.

From this observation, the shift in the energies with the decreasing molecular distances between the HCl-H$_2$O may be understood as an alteration in the intramolecular HCl distance by some part of the ice environment, making the electrostatic potential between the density of the HCl and water molecules to be non-trivial compared to the rigid configuration. It should be noted that the adsorption site of the HCl on ice does not change as a result of the optimization to the constrained H$_2$O, however, there is a slight increase in the HCl bond length from the equilibrium distance of 1.274 Å as shown in figure 10 (D). Further, a decrease in the BEs is observed as we optimize the HCl with some of the nearest water molecules on the ice surface. It should be noted that the systematic decrease in the BEs is translated from further stretching of the H-Cl bond length away from the equilibrium position by the water molecules and much coordination between...
FIG. 10: Estimated chlorine 2p core binding energies as a function of HCl-H\textsubscript{2}O intra- and inter-molecular distances of HCl adsorbed on ice surfaces at 210 K (25 snapshots) A) Rigid HCl on ice surfaces B) Optimized HCl on a constrained ice surfaces, C) HCl optimized together with the four nearest water molecules on the ice surface and the rest constrained and D) Changes in the HCl bond lengths in A, B and C.

FIG. 11: Average calculated chlorine 1s, 2s and 2p core binding energies of Cl\textsuperscript{−} interacting with the bulk layer of droplets at 300 K (100 snapshots) using the CC-in-DFT scheme. The systems are considered as X + (H\textsubscript{2}O)\textsubscript{100} (X = Cl\textsuperscript{−}) with d-aug-dyall-acv3z.

FIG. 12: Calculated Cl 1s, 2s and 2p core binding energies of ionic Chloride adsorbed on ice surfaces at 210 K (25 snapshots) and within the bulk layer of droplets at 300 K (100 snapshots) using the CC-in-DFT scheme. The systems are considered as X + (H\textsubscript{2}O)\textsubscript{25,100} (X = Cl\textsuperscript{−}) with d-aug-dyall-acv3z.
the atoms of the HCl and the water molecules as well as the slight changes in the intermolecular distances as shown in figure 10 (C).

G. Estimation of solvent-Induced core binding energy shifts of ionic Chloride interacting with ice at 210 K and bulk water at 300 K

In this section, we will concentrate on the core level BEs and solvent-induced binding energy shifts on the chlorine 1s, 2s, and 2p ionized-states. The discussion is focused on the evolution of the Cl core BEs in the presence of the solvent environment and investigated temperature effects. From the estimated Cl core BEs of gas-phase Cl−, shown in table I to its adsorption on the uppermost bulk ice layer in table XIII, a solvent-induced shift in the BE of approximately 5.0 eV is estimated for the Cl 1s and 4.0 eV for both the Cl 2s and 2p. In the case of the Cl− adsorbed within the bulk layer of droplets, a shift in the Cl core BEs around 4.0 eV is estimated for the Cl 1s and 6.0 eV for both the Cl 2s and 2p. In all cases, the chlorine core ionized states exhibited highly non-negligible variations in the presence of the solvent environment. These solvent-induced shifts are an indication that the water molecules within the interfacial region are mobile enough to influence the chlorine electronic properties of the adsorbed Cl−. We noticed that as we move to higher temperatures and into the bulk layer, the solvent-induced shift in the binding energy decreases for the Cl 1s, while in the case of the Cl 2s and 2p it showed to increase. Overall, an approximately 2.0 eV shift in the absolute BEs is observed as we move to the bulk layer and at higher temperatures. The large solvent effects observed for the adsorbed halide ion at different temperatures are well captured by the embedding scheme. From figure 12, we see that the different nature of the hydrogen bonding network, temperature in the two structures in addition to the point of interaction (at the surface or within the bulk layer) could be the possible source of the shift in energies at the Cl edges.

V. CONCLUSION

In this article, we have reported for the first time the application of the coupling of DFT and WFT schemes to predict core electron BEs and chemical shifts of halogenated species in gas-phase and their interaction with solvent environments. The calculations on the gas-phase species are performed with DFT using the approximate ZORA Hamiltonian, HF, Δ HF, and CVS-EOM-IP-CCSD using the DC and X2Ccmnf Hamiltonian. It is without a doubt that quantum chemical calculation for large-sized molecular systems is very difficult especially when probing core-level states. Among the different embedding methods available, we have utilized the so-called FDE embedding framework, where the reasonable computational cost of DFT can be coupled with expensive yet highly accurate CCSD method. The means to conduct the calculations are through the ADF DFT and Dirac electronic structure code. The Calculations are performed at the DFT level to obtain an effective embedding potential, which is local. This embedding potential is then introduced as an external potential into CC calculations to account for the effects of the ice/liquid on the halide/halide ion. The FDE calculations are performed in freeze-and-thaw iterations, which allows ground-state polarization to be taken into consideration. This makes the polarization of the halide/halide ion by the water molecules to be included at the ground-state. This scheme retains the full electron density of the solvent environment and has allowed the treatment of core ionized state properties of the adsorbed species. We note that the predicted core level BEs based on this embedding scheme are in good agreement with experimental observations with minor deviations. Chemical and solvent-induced shifts in BEs are observed, indicating the influence of different chemical environments and bonding at the air-ice/liquid interface. Finally, the embedded calculation predicted with accuracy splitting of the 2p ionized states under relativistic effects. We have shown that the use of a fully quantum mechanical embedded method to treat solute-solvent systems is computationally efficient, yet accurate enough to interpret experimental XPS spectra. Our calculations showed that the inclusion of the Gaunt term in the Hamiltonian, which is essential for spin-orbit coupling provides results that approach the experimental values. In addition, the probed Cl core ionized states are dependent on the quality of the basis sets and can not be neglected. We attribute the few errors encountered in our calculations in comparison to experimental values to factors like working at different environmentally relevant conditions, slight deficiencies in the approximation of the kinetic energy part used to estimate our embedding potential, and the lack of first-order correction (retardation effect) in our Hamiltonian. These results have essential implications for understanding the role of ice as a catalyst for reactive trace gas emissions in the atmosphere and the loss of gas-phase molecules. In terms of computation cost, the DFT calculations take about 24 hours while the CVS-EOM-IP-CCSD calculations take about 18 hours for a single snapshot on 1 node with 48 n-processors.

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