Electronic Structure of Solvated Molecular Ions

ICl⁻(CO₃)₄

Authors:

James Faeder,
faeder@jarrett.colorado.edu
Paul Maslen,
maslen@jila02.colorado.edu
Robert Parson,
rrparson@jila02.colorado.edu

Department of Chemistry and Biochemistry, University of Colorado, and JILA,
University of Colorado and National Institute of Standards and Technology, Boulder,
Colorado 80309-0440


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http://jarrett.colorado.edu/~rrparson/iclinus.html

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Introduction

By studying chemical reactions in small clusters, experimentalists can extract detailed information about the effects of a condensed phase environment upon the reaction dynamics. Ionic clusters offer several experimental advantages over the corresponding neutral clusters since they can be readily mass-selected and mass-analyzed. However, the strong electrostatic forces that prevail in ionic clusters (and in ionic solutions as well) offer a serious challenge to theory. It is not uncommon for the solvent–solute interaction energy to be of the same order of magnitude as the chemical bond energies involved in the reaction. In such circumstances one cannot expect empirical potential energy surfaces constructed from pairwise interactions to provide even a qualitatively correct description of the true potential energy surface. It is necessary to calculate explicitly the effect of the solvent upon the solute electronic structure. Since the solvent has many degrees of freedom, this will in general require us to carry out an electronic structure calculation while simulating the nuclear motion.
In the remaining sections of this paper we describe our methods, and then present an application to ICl– solvated by 1–6 CO2 molecules, a system for which interesting experimental results have been obtained by Carl Lineberger’s group.

Requirements

Our electronic structure calculation must be a simple one, since we need to carry it out inside a molecular dynamics or Monte Carlo simulation. Nevertheless it must be:

- Able to handle dissociating molecules (rules out SCF, local density)
- Able to treat excited states and strong spin orbit coupling.
- Capable of yielding nonadiabatic transition matrix elements as well as energies and forces (energy gradients).

Model Hamiltonian

Our fundamental assumption is to ignore electron exchange between solute and solvent. We can fit the electrostatic multipole moments of each solvent molecule to a set of distributed point charges. The solvent then generates a nonuniform, time-variation electric field that perturbs the solute electronic structure. (For the time being we neglect the electronic polarizability of the solvent molecules.)

We choose ab initio electronic eigenfunctions of the isolated solute molecule as basis functions for a Hamiltonian matrix which describes the effects of the solvent upon the electronic structure of the solute. The matrix elements of the solute–solvent interaction operator in this basis can be expressed in terms of the distributed charges on the solvent molecules and distributed multipoles on the solute.

- For a more detailed description of the matrix element calculation, click here (postscript).

For any particular geometry of solvent molecules, the eigenvalues of the Hamiltonian matrix give us the electronic energy of the solute — in other words, they give us a single point on each of the multidimensional potential energy surfaces. The corresponding eigenvectors give us the electronic wave functions, which are used to calculate the nonadiabatic transition matrix elements. At each step of a Molecular Dynamics or Monte Carlo trajectory the matrix elements are evaluated, the Hamiltonian Matrix is diagonalized, and the electronic energies and energy gradients determined. For a more detailed discussion, see our recent paper *Solvation of Electronically Excited I2*—in J. Chem. Phys. 101, 5731 (1994); a <postscript version (including figures)> is available on the web.

The remaining terms in the total cluster potential energy — the short-range intermolecular repulsion and the longer-range dispersion attraction — cannot be calculated ab initio without including the electrons on the solvent molecules explicitly. Instead, we use empirical pairwise potentials that have been fit to bulk CO2 data.

Application to ICl–

The electronic spectra and photodissociation dynamics of ICl– embedded in clusters of 0–8 CO2 molecules have been studied by Lineberger and coworkers. They find that the photodissociation products change as the number of solvent molecules increase.

Consider first the isolated ICl– anion.
Since Chlorine is more electronegative than Iodine, we expect the excess charge to be pulled towards the Cl end. Ab initio calculations show that this is indeed the case. In the electronic excited state however, the charge is displaced in the opposite direction, towards the I end, and the experiments show that this electronic state dissociates adiabatically to an I− anion and a Cl atom.

In the cluster, on the other hand, experiments find Cl− products as well as I− products. The relative proportion of Cl− products increases with cluster size:

We have used the methods described above to calculate the minimum energy structures of ICl−(CO2)n in the ground electronic state.

- ICl−(CO2)n=2
- ICl−(CO2)n=4
- ICl−(CO2)n=6

The major feature of these structures is the strong preferential solvation of the Cl end, due largely to the higher electron affinity of Cl over I.

The following estimates provide some insight:

- The electron affinities of I and Cl differ by about 550 meV.
- The solvation energy of ICl− is about 200 meV per CO2 molecule.
I. HAMILTONIAN MATRIX ELEMENTS.

In our model the solvent is approximated as a collection of classical point charges $Q_i$ at positions $R_i$. The Hamiltonian for the cluster is then expressed in terms of the Hamiltonian for the isolated ion, $H^o$, and the interaction of the electrons and nuclei on the ion with all $N_Q$ solvent charges. The interaction of the ion nuclei $Z_j$ at positions $R_j$ with the solvent charges is simply a sum of classical coulomb repulsion terms,

$$\sum_{i,j} Q_i Z_j / |R_i - R_j|$$

and will be omitted in the following. The ion-solvent Hamiltonian is then,

$$H = H^o + \sum_{r=1}^{N_e} \sum_{i=1}^{N_Q} e Q_i / |R_i - r|$$

where $r$ is the position of one of the $N_e$ electrons belonging to the ion. The Hamiltonian matrix for the cluster is constructed in a basis of eigenfunctions $\psi^o_i$ of $H^o$ with corresponding eigenvalues $E^o_i$,

$$\langle \psi^o_i | H^o | \psi^o_m \rangle = E^o_i \delta_{i,m}$$

Each matrix element of the ion-solvent interaction, $\langle \psi^o_i | H - H^o | \psi^o_m \rangle$, is expanded\(^1\) in terms of the multipoles of the isolated ion. The first multipole is the electronic charge corresponding to states $\psi^o_i$ and $\psi^o_m$, $\langle \psi^o_i | 1 | \psi^o_m \rangle$, and is zero unless $\psi^o_i = \psi^o_m$. Its contribution to $\langle \psi^o_i | H - H^o | \psi^o_m \rangle$ is the familiar coulomb interaction,

$$\langle \psi^o_i | 1 | \psi^o_m \rangle \sum_{i=1}^{N_Q} Q_i / |R_{ion} - R_i|$$

where $R_{ion}$ is the origin of the multipole expansion. The second multipole is the z-dipole, $\langle \psi^o_i | z | \psi^o_m \rangle$, and its contribution to the ion-solvent interaction is,

$$- \langle \psi^o_i | z | \psi^o_m \rangle \sum_{i=1}^{N_Q} Q_i \left[ \frac{\bar{z} \cdot (\bar{R}_{ion} - \bar{R}_i)}{|R_{ion} - R_i|^3} \right]$$

The higher multipoles are formally defined as the matrix elements $\langle \psi^o_i | Y_{l,M_J} | \psi^o_m \rangle$, where $Y_{l,M_J}$ is a spherical harmonic function. For example, the matrix element of $Y_{00}$ gives the charge while $Y_{10}$ gives the z-dipole. The complete expansion of $\langle \psi^o_i | H | \psi^o_m \rangle$ can be compactly represented as an inner product involving the solvent charges $Q_i$, a vector $\mathbf{q}_m$ containing the ion multipoles, and a vector $\mathbf{T}_i$ which is a function of the geometry of both the ion and solvent charge $Q_i$.

$$\langle \psi^o_i | H | \psi^o_m \rangle = E^o_i \delta_{i,m} + \mathbf{q}_m \cdot \sum_{i=1}^{N_Q} \mathbf{T}_i Q_i$$

Both $\mathbf{T}_i$ and $Q_i$ are independent of $l$ and $m$.

ICI- Photofragmentation Products

% Yield

Number of CO2 Solvent Molecules

- - - ▲ I- Products
△ △ △ △ △ △ Cl- Products
○ ○ ○ ○ ○ ○ ○ ICI- products
I\text{-}e^{-} (\text{CO}_2)_2
\[ \text{I} (\text{Cl}, \text{O}_2)_4 \]
The solvation energies of I– surrounded by 4 CO2 molecules, and Cl– surrounded by four CO2 molecules, differ by about 336 meV.

Thus we see that solvation energies are of the same order of magnitude as the difference in electron affinities, so that it is not surprising that solvation can strongly influence the electronic charge distribution in the solute.

In order to explore this idea we introduce a "free energy surface" for solvated ICl–—an energy function that depends upon an effective solvent coordinate as well as upon the I – Cl bond length.

Minimum Energy Surface

The potential energy of the system depends upon all of the nuclear degrees of freedom. We wish to separate out two degrees of freedom that we believe are especially "relevant" to the reaction dynamics, and to suppress the remainder. One relevant degree of freedom is surely the solute bond length—in the absence of the solvent, this would be the only reaction coordinate. Our second degree of freedom will then be some sort of "solvent coordinate."

Our choice for a solvent coordinate is motivated by the Marcus theory of electron transfer in solution. In that theory one envisions the electron as tunnelling from one site to another when the solvent temporarily brings the two sites into energy resonance with each other. The relevant solvent coordinate is then the difference between the electrostatic energies of the two sites. Symmetric solvation, a more-or-less uniform distribution of CO2 molecules around the solute anion, corresponds to a solvent coordinate value close to zero; asymmetric solvation, in which the solvent is clustered around one end of the solute or the other, corresponds to a large positive or negative value of the solvent coordinate.

We then define our minimum—energy surface in terms of the set of minimum—energy structures that the cluster can take on for specified values of bond length r and solvent coordinate s. That is, for each value of r and s, we search for that structure whose energy is a minimum. Each electronic state of the solute gives rise to its own minimum—energy surface. Slicing the surface with a plane parallel to the r axis tells us how the potential energy curves of the solute are affected by a fixed solvent geometry; slicing the surface with a plane parallel to the s axis at large r gives us a picture reminiscent of the classical Marcus theory, in which the only relevant coordinate is the solvent.
Figure: Minimum energy surface with excited state energies for ICl–(CO2)4. Black circles show the approximate Franck–Condon region for the excitation from the ground state (see text below).

The figure above shows the minimum energy surface for the ground state of ICl– surrounded by four CO2 molecules, together with an energy surface for the excited state that is prepared in the experiment. Since we are interested in electronic transitions, which are usually thought of as taking place at a fixed nuclear geometry ("Franck–Condon Principle"), we want vertically related points on the ground and excited surfaces to correspond to the same nuclear configuration. We therefore carry out the minimization procedure described above only on the ground state; the excited state surface then gives the excited state electronic energy at the same set of nuclear geometries. Negative values of the solvent coordinate correspond to solvation at the Cl end, and positive values to solvation at the I end. The ground state surface exhibits a deep well corresponding to ICl– with the CO2 molecules gathered around the Cl– end and a rather indistinct "shelf" at about s=+.02 corresponding to CO2 molecules clustered at the I end. The excited state shows shallow wells for both positive and negative s and only a small barrier between, suggesting that motion in the solvent coordinate is easier in the excited state than in the ground state. The most notable feature of the surfaces, however, is the apparent avoided–crossing at large r (a nearly dissociated molecule) and large positive s (solvation at the I end.) This suggests that electronic relaxation takes place by means of motion in the solvent coordinate, from Cl solvation to I solvation, followed by an electronic transition in the avoided crossing region. In this fashion the solvent is able to compensate the 0.5 eV energy gap between the ground and excited states in the isolated molecule, and thus to bring about electronic relaxation.

Conclusion

We have described an effective Hamiltonian method for treating the effects of solvation on chemical reactions involving ionic species, and have presented a few preliminary results that provide insight into the photodissociation of ICl– in a cluster of CO2 molecules. In particular, we calculated the equilibrium cluster structures, and a free–energy surface that shows how the cluster energetics depends upon the solute bond length and upon an effective "solvation coordinate."

The next step is to pass from energetics to dynamics. Most of the tools that we need for these calculation are now in place.

The general approach that we have taken should be widely applicable, provided that our fundamental assumption – negligible electron exchange between solute and solvent – remains valid. While it is designed with ionic solutes in mind, it might also be useful for neutral systems whose excited states involve a high degree of (intramolecular) charge transfer, so that as in the ionic systems the reaction coordinate is strongly coupled to the solvent. While we have chosen to focus upon clusters, the approach should be applicable to molecules in bulk condensed phase environments as well.

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