First-Principles Excited-State Molecular Dynamics Simulations: Application to Cluster Photochemistry

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Computer simulations of the real time-evolution of complex chemical systems in their electronically excited states, resulting for example from photoexcitation, represent many challenges for modern computational chemistry. In this contribution, we discuss the application of first-principles molecular dynamics simulations of the excited state dynamics of clusters made up of a halide ion and a number of solvent (water) molecules. The number of difficulties encountered in such simulations is outlined, and preliminary results are reported and discussed in connection with available experimental data. A brief outlook for the future development of the current research is also given in light of recent progress in high-performance computing.

La simulation sur ordinateur de la dynamique de systèmes chimiques complexes et de leur états électroniques excités, résultant par exemple d'une photoexcitation, présente un défi de taille pour la chimie numérique moderne. Dans ce travail, nous décrivons une simulation de dynamique moléculaire des états excités d'amas comportant un ion halogène entouré d'un certain nombre de molécules de solvant (eau). On décrit les difficultés généralement rencontrées dans de telles simulations, et on discute de résultats préliminaires en relation avec les données expérimentales disponibles. Une brève perspective des développements futurs pressentis est donnée, à la lumière des progrès récents dans le domaine du calcul de haute performance.

Introduction

The end of the twentieth century has been marked by scientific breakthroughs of paramount importance for chemistry, physics, biology and many other disciplines. Progress in technological and conceptual tools has made it possible to study chemical reactions with unprecedented time resolution. Femtochemistry [1-3], a new field pioneered by the group of A. Zewail, 1999 Nobel Prize winner, allows to explore the ultrafast dynamics of chemical reactions on the timescale of atomic vibrations, *i.e.* on the femtosecond timescale (1 fs = 10^{-15} s). With ultrafast spectroscopic techniques even such ephemeral species as transitions states of chemical reactions can be probed [4]. If the initial developments of femtochemistry mainly dealt with very simple systems composed of a few atoms, femtochemistry is now expanding into studies of increasingly complex systems, such as macromolecules, molecular clusters and condensed phases. These systems can also be studied now with comparable precision, and on the same timescale, with computer simulations, thanks to recent advances in computational chemistry methods and progress in high-performance computing. Molecular dynamics studies are actually necessary for the interpretation of increasingly complex and convoluted experimental results. In this respect, realistic molecular dynamics simulations, based on potential energy surfaces calculated by first-principles quantum chemical methods are very important, especially for investigating systems evolving in their electronically excited states, following for example photoexcitation.

Of particular interest to us are clusters, *i.e.* agglomerates of two or more molecules bound to each other by intermolecular forces. The properties of clusters can be considered to be intermediate between the gas and condensed phases [5], and for instance, cluster studies are critical for understanding fundamental processes such as solvation in chemical, biochemical, and photochemical reactions. In the field of cluster research, halide-water clusters seem to be particularly important, due to the prevalence of dissolved halide salts in the Earth biosphere, hydrosphere and atmosphere [6]. While the structural and energetic properties of $X^-(H_2O)_n$ clusters (X = F, Cl, Br, I) has been a subject of long-standing interest, very little experimental data had been reported of their photochemical properties till recently. One of the fascinating features of anions dissolved in water, especially halides, is the possibility to photochemically transfer an electron from the ion into the bulk solvent, where it will be stabilized by the field of polar solvent molecules, giving rise to so-called charge-transfer-to-solvent (CTTS) excited states, which can eventually lead to the solvated electron. In 1996, M. Jonhson and co-workers [7] were able to experimentally observe cluster analogs of the bulk CTTS states in clusters of iodide with one to four water molecules. It was found that subsequent relaxation of the excited cluster may lead to the ejection of the neutral iodine atom and formation of a dipole-bound water cluster anion $(H_2O)_n^-$.

Shortly after, D. Neumark and co-workers [8] applied state-of-the-art femtosecond photoelectron spectroscopy techniques to study the relaxation dynamics of photoexcited $I^-(H_2O)_n$ clusters (n= 4–6) on a timescale of 2 ps following photon absorption (Fig. 1). This work revealed interesting dynamical characteristics of the excited electron in clusters of different sizes by measuring the evolution of the electron binding energy throughout the relaxation process. For the smallest cluster investigated $I^-(H_2O)_4$, the

electron binding energy was found to remain constant throughout the measurement time window, and the population of photoexcited clusters decayed exponentially because of the spontaneous ejection of the dipole-bound electron from the vibrationally excited water cluster. On the other hand, clusters with five and six water molecules exhibited much more interesting dynamics: an induction period of *ca.* 500 fs was observed, during which the electron binding energy is constant. The electron binding energy then increases by *ca.* 0.3 eV, suggesting that the cluster undergoes some kind of reorganization which leads to the stabilization of the excited electron. Only after this increase of electron binding energy does the population of excited clusters start decaying until the end of observation time (2 ps or 2000 fs). In order to rationalize their observations, Neumark and co-workers put forward the hypothesis [8,9] that the rise in electron binding energy after the first 500 fs is due to a reorganization of the water molecules in $I^-(H_2O)_5$ and $I^-(H_2O)_6$ clusters. This suggests that the four water molecules in $I^-(H_2O)_4$ are not able to rearrange and efficiently stabilize the excess electron transferred from iodide, while five and six water molecules are known to bind an excess electron in a number of cluster configurations. Therefore, in the 500 fs following photoexcitation, the water molecules in $I^-(H_2O)_5$ and $I^-(H_2O)_6$ clusters are assumed to gain configurations which can support the excess electron much more efficiently than in the initial cluster configuration. This model is based solely on the consideration of solvent dynamics, neglecting the possible role of the neutral iodine atom formed by photoexcitation, and is hereafter referred as the "solvent-driven" relaxation dynamics model.

Recently, Chen and Sheu [10,11] performed a quantum-chemical study in which they propose an alternative interpretation for the femtosecond experiments of Neumark and co-workers: in this model, the stabilization of the excited electron is rationalized by the ejection of the neutral iodine atom from the water cluster. Quantum-chemical calculations show that the presence of the neutral iodine atom can considerably destabilize the excited electron in excited $I^-(H_2O)_n$ clusters, and thus as the iodine atom leaves the water cluster, the electron binding energy must significantly increase. According to this "iodine-driven" model of relaxation dynamics, a cluster with four water molecules undergoes iodine atom ejection on a very fast timescale, *i.e.* less than 100 fs, and only the dynamics of the free $(H_2O)_4^-$ cluster can be monitored. On the other hand, iodine leaves photoexcited clusters with 5 and 6 water molecules more slowly, giving rise to the experimentally observed induction period. The main problem with the latter model is that it is based on static quantum-chemical calculations, which have the water cluster moiety frozen in the geometry of the cluster before photoexcitation.

At this stage, none of the models proposed so far to interpret femtosecond experiments, treats the relaxation of
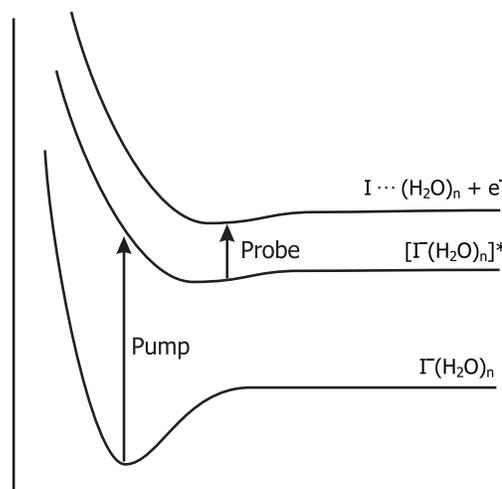

Fig. 1. Schematic representation of femtosecond photoelectron spectroscopy experiments by Neumark and co-workers [8]. The pump laser pulse excites the iodide-water cluster $I^-(H_2O)_n$, and the probe pulse monitors the evolution of the excited state $[I^-(H_2O)_n]^*$ via ejection of the loosely bound excited electron.

iodide-water clusters as a whole, neglecting either the role of the iodine atom or that of solvent reorganization. First-principles molecular dynamics simulations [12] appear to be a method of choice for investigating the time-evolution of photoexcited halide-water clusters. In this approach, the energy and its gradient are calculated "on the fly" during the propagation of the atomic equations of motion by first-principles, or *ab initio*, methods. One should emphasize that the proper theoretical treatment of such complex systems poses several computational chemistry challenges. First, the electronic structure of the ground and excited states must be treated explicitly by high-level quantum chemical methods. This is especially important in the case of dipole-bound excited states of halide-water clusters, where the excited electron spatial distribution is extremely diffuse, which dictates the use of very large, specific, one-electron basis sets augmented by many diffuse basis functions [13]. Further, in order to propagate trajectories on the potential energy surface, both the potential energy and the energy gradient, *i.e.* the forces governing the motion of atoms, must be readily available for the excited states of interest. All these factors make first-principles molecular dynamics simulations of photoexcited iodide-solvent clusters particularly complex and computer-intensive, especially in comparison to routine, conventional static *ab initio* ground-state electronic structure calculations, and dictate the use of advanced software and hardware.

We have recently engaged into *ab initio* excited-state dynamics simulations of the relaxation process of halide-solvent clusters. In the present article we report preliminary results of the $I^-(H_2O)_3$ relaxation dynamics, based on

a few trajectories. In spite of its small size, this cluster possesses the crown-like structure characteristic of $I^-(H_2O)_n$ clusters with $n \leq 6$, and it can thus serve as a good model to gain an insight into complex excited-state relaxation processes in the larger clusters. We will also conclude by an outlook of the impact of high-performance computing on future research, *i.e.* the extension of the current simulations to larger clusters, which will require a large number of trajectories to allow a thorough connection with experiment.

Computational Details

Ground and excited state electronic structure calculations were carried out using the state-averaged (SA) Complete Active Space Self-Consistent Field (CASSCF) formalism [14,15], with the active space consisting of two *p*-orbitals of the iodine atom – which are doubly occupied in the ground state – and the lowest unoccupied orbital – which accommodates the excited electron upon photoexcitation. The basis set used in this work is based on the standard 6-31+G(d,p) basis set by Pople and co-workers [16], which was used in its original form for hydrogen and oxygen atoms. For iodine, we used the LANL2DZ effective core potential (ECP) basis set by Hay and Wadt [17-19], augmented by *d*-polarization functions with the optimized exponents of Check *et al.* [20]. Further, a special set of uncontracted Gaussian basis functions, with diffuse exponents, was added to allow for a proper description of the dipole-bound excited electron. In contrast to static quantum chemical calculations of dipole-bound cluster anions $(H_2O)_n^-$ or dipole-bound $[I^-(H_2O)_n]^*$ excited states, the *ab initio* molecular dynamics simulations demand an even more diffuse basis set, which can describe the excited electron along the whole trajectory, where the cluster structure can change dramatically during the relaxation process. In order to construct a diffuse basis set, flexible enough for dynamical calculations, we added a number of diffuse *sp*-shells centered on the iodine atom, with exponents α_{sp}= 3.0800×10^{-2}, 4.4000×10^{-3}, and 6.2857×10^{-4}. We also centered two *sp*-shells with exponents α_{sp}= 3.6000×10^{-2}, 5.1429×10^{-3} and one *s*-shell with exponent α_s=7.3469×10^{-4} on each of the three "dangling" hydrogen atoms, *i.e.* those that are not involved in water-water hydrogen bonding in the cluster (*cf.* Fig. 2). All quantum-chemical calculations were performed with the MOLPRO suite of *ab initio* programs by H.-J. Werner and P. J. Knowles [21].
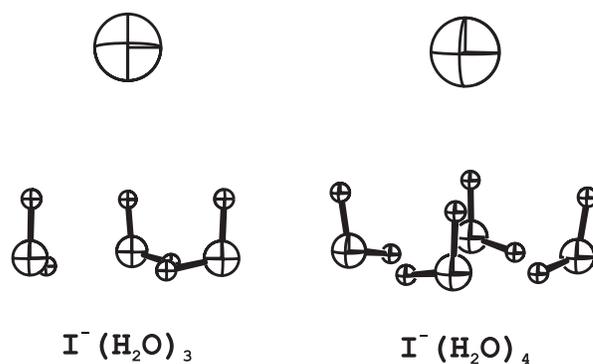

Fig. 2. Equilibrium structures of $I^-(H_2O)_3$ and $I^-(H_2O)_4$ clusters [22]

The classical equations of motion were propagated for all atoms with the standard constant-energy velocity Verlet algorithm [12], with energy and gradient calculated at each time step by the quantum-chemical procedure described above. A time-step of 0.3 fs was used, and the trajectories were propagated for up to 900 fs. Calculations were performed on an AlphaServer ES40 and on a local cluster based on dual-CPU Intel Xeon processors.

Results and Discussion

It is now well established [22,23] that small to medium size iodide-water clusters tend to have so-called surface structures, where the iodide ion tends to sit at the surface of the hydrogen-bonded water network. The smallest clusters have crown-like structures like those shown for $I^-(H_2O)_3$ and $I^-(H_2O)_4$ clusters in Fig. 2 [22]. These structures are governed by a combination of the interaction of the negatively charged I^- with the dipole moment of the entire water network, and the hydrogen-bonding interactions of the "dangling" hydrogen atoms with the iodide ion. We chose $I^-(H_2O)_3$ as an initial, representative, yet computationally feasible, model for excited state dynamics studies of $I^-(H_2O)_n$ clusters. Even though there are no explicit experimental data on the relaxation dynamics for this cluster size, it can be used as a model to gain some insight into general features of the excited state time-evolution of $I^-(H_2O)_n$ species.
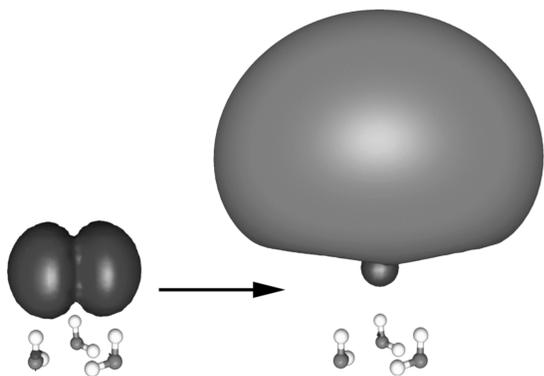
Fig. 3. Electronic density difference between the $I^-(H_2O)_3$ ground and excited states. The negative density difference isosurface is plotted on the left side, and basically shows one of the p orbitals of iodide from where the electron is transferred upon photoexcitation. The positive difference isosurface is plotted on the right side, and shows the diffuse orbital that accommodates the excited electron [24].

The nature of the photoexcitation process in iodide-solvent clusters has been studied in great detail for water and acetonitrile clusters [25,24]. It has been shown that, upon photoexcitation, an electron from I^- is transferred to a very diffuse molecular orbital (*cf.* Fig. 3), where it is supported by the stabilizing interaction with the dipole moment of the solvent network. Further, the excited electron distribution in the excited state of iodide-solvent clusters in the Frank-Condon region has been found to be very similar to the electronic structure of the corresponding dipole-bound solvent cluster anions. The only significant difference between excited $[I^-(S)_n]^*$ and $(S)_n^-$, where S represents water or acetonitrile solvent molecules, is the presence of the neutral iodine atom which destabilizes the excited electron. Moreover, the ion-dipole interactions, which kept the ion and solvent molecules together in the ground state, no longer exist in the excited state. Thus, profound structural changes are expected as the system starts relaxing after photoexcitation.

According to our simulations, the "dangling" hydrogen atoms which formed hydrogen bonds with iodide in the ground state, start moving away from the iodine atom, and in less than 50 fs the structure of the water cluster becomes almost flat (Fig. 4, 48 fs), which is accompanied by a drop in potential energy of the whole system (*cf.* Fig. 5). But because of the kinetic energy acquired, hydrogen atoms keep moving, until the water cluster moiety reaches an "inverted crown" structure (Fig. 4, 96 fs). The latter structure is higher in energy than the "flat" structure, and the hydrogen atoms thus continue their oscillatory motion. In general, the relaxation process involves rapid oscillatory motion of the water molecules which results in abrupt os-

cillations in the system potential and kinetic energies (*cf.* Fig. 6). After the first oscillation, the synchronicity of the water motion appears to be disrupted (Fig 4, 186 fs) as energy is transferred to other cluster vibrational modes and the oxygen atoms and the hydrogen atoms which are involved in the water-water hydrogen bonding start gaining additional kinetic energy (*cf.* Fig. 6). The water network undergoes deformations during the trajectory, and water-water hydrogen bonds break and form back and forth a few times. Meanwhile, the heavy iodine atom is slowly leaving the water cluster: the distance between iodine and the centre of mass of the $(H_2O)_3$ moiety reaches 6.3 Å in less than 900 fs (Fig. 4, 822 fs), while it is only 3.44 Å in the initial Frank-Condon geometry. The fraction of kinetic energy of the heavy iodine atom in the total kinetic energy of the system is not surprisingly very small, with a maximum at 200 fs, and it then slightly decreases, probably due to weak inductive and/or dispersion attractive interactions between the iodine atom and the $(H_2O)_3^-$ cluster (*cf.* Fig. 6). The kinetic energy is thus mainly partitioned into the rotational and vibrational degrees of freedom of water molecules, as evident from Fig. 6.

The main features of the relaxation of photoexcited iodide-water clusters that emerge from this preliminary study are the oscillatory motion of water molecules and the slow recoil motion of the neutral iodine atom. Rapid changes in the relative orientation of the water molecules that result from the interconversion of "crown" and "inverted crown" structures cause rapid changes in the total dipole moment of the $(H_2O)_n$ moiety, and thus, the binding
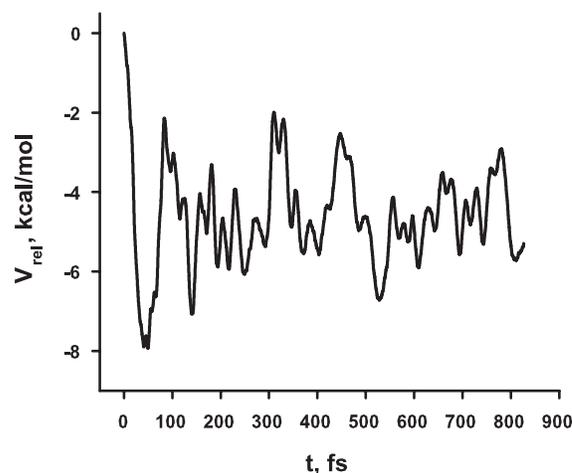

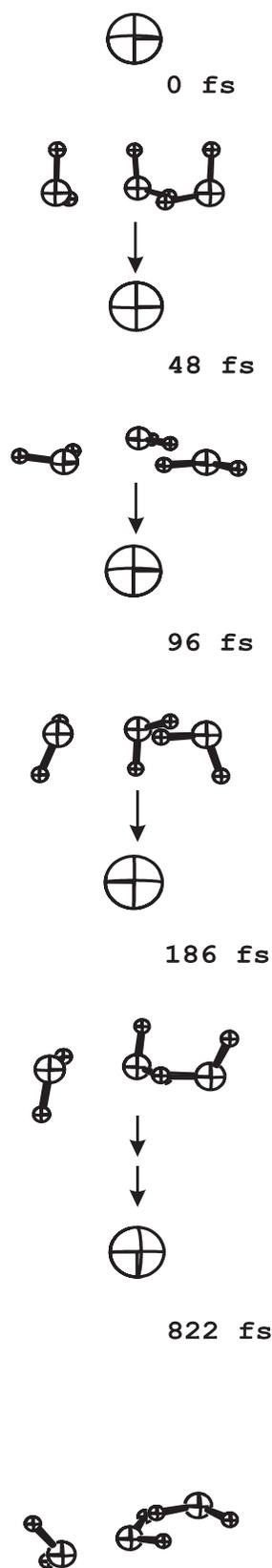**Fig. 5.** Time-evolution of the potential energy for the photoexcited $I^-(H_2O)_3$ cluster

Fig. 4. Snapshots of selected configurations along a typical trajectory of photoexcited $I^-(H_2O)_3$ relaxation.

energy of the excited electron must also undergo oscillatory changes along a given trajectory. However, in the-femtosecond experiments of Neumark and co-workers [8], the measured electron binding energy is changing quite smoothly. This may be explained by the fact that at finite experimental temperatures, ground-state $I^-(H_2O)_n$ clusters exist in various configurations and isomers. The observed experimental signal is an average over the whole *ensemble* of possible initial cluster structures, which may lead to observed smooth changes in ensemble-averaged electron binding energies. A large number of trajectories, starting with many different initial cluster configurations, will thus be needed to make a thorough connection with experiment. However, the present simulations, which include only a few trajectories, already suggest that the relaxation of photoexcited $I^-(H_2O)_n$ clusters is a complex process, where both the role of iodine and solvent motion must be included in order to fully rationalize experimental observations [8].

Concluding Remarks and Outlook

The excited-state dynamics of iodide-solvent clusters represents a challenging, yet very important and fascinating problem in modern chemical physics, and a thorough understanding of $I^-(H_2O)_n$ photoexcitation is not possible without supplementing experimental results with computer simulations. For such a complex system, realistic molecular dynamics simulations must be performed using a reliable potential energy surface, based on high-level quantum-chemical calculations. The preliminary results reported here, suggest that the relaxation of excited $[I^-(H_2O)_n]^*$ clusters is characterized by rapid rotational motion of water molecules, which somewhat supports the "solvent-driven" model of relaxation dynamics. On the other hand, the role of iodine motion may also be critical in determining the time-evolution of the electron binding energy following photoexcitation, which is consistent with the "iodine-driven" model of cluster relaxation dynamics. To thoroughly elucidate the relaxation mechanism of photoexcited $I^-(H_2O)_n$ clusters, more extensive *ab initio* molecular dynamics simulations, which take into consideration various possible initial cluster geometries, combined with accurate calculations of the electron binding energies along trajectories, will be necessary.

Ab initio excited-state molecular dynamics simulations are still very taxing at this point. For instance, propagating a single trajectory for 900 fs for the $I^-(H_2O)_3$ cluster on an AlphaServer ES40 (667 MHz, SPECfp2000 rating 500 [26]) takes 25 days. However, progress in computer hardware will make it possible to perform more extensive simulations in the near future. While it would take *ca.* 17

months to propagate 20 trajectories on the ES40 platform, the computing time decreases to *ca.* 10 months with Intel Xeon-based machines (2.4 MHz, SPECfp2000 rating 803 [26]), and a cluster of 20 Xeon computers will allow to perform the whole simulation is less than 16 days, by simply distributing trajectories to each computer node.

Finally, the quantum-chemical calculations needed at every step of the trajectories typically scale as N^3–N^4, where N is the number of basis functions. If a proper treatment can be achieved for $I^-(H_2O)_3$ with a basis set containing 134 functions, the number of basis functions required for a similar level of accuracy for $I^-(H_2O)_5$ and $I^-(H_2O)_6$, for which detailed experimental data is available, increases to 255 and 301, respectively. This represents an increase in computing time by a factor of *ca.* 10 and 20 respectively. As a result, a detailed investigation of $I^-(H_2O)_6$ relaxation dynamics, involving as many as 100 trajectories, may be performed in 10 months on a distributed cluster of 100 Xeon processors.
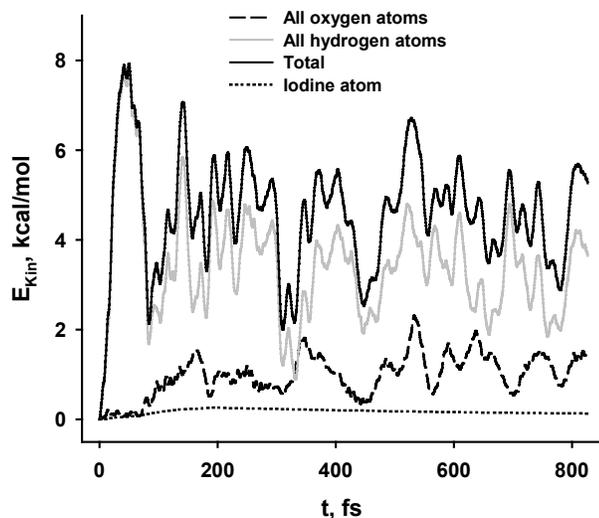

Fig. 6. Time-evolution of the kinetic energy for the photoexcited $I^-(H_2O)_3$ cluster: total kinetic energy, kinetic energy of the iodine atom and kinetic energy of all oxygen and all hydrogen atoms.

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