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Intermolecular Coulombic decay of clusters

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Abstract

Following inner-valence ionization of a cluster, the system can relax by ultrafast electron emission. In contrast to Auger decay this novel process is intermolecular. It is characterized by an efficient Coulombic energy transfer mechanism between monomers in the cluster. As an example, we present an analysis of the hydrogen fluoride trimer, based on extensive ab initio computations. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ionization experiments and their theoretical interpretation make important contributions to the understanding of the quantum structure of matter. Here we would like to focus on clusters, i.e., weakly bound systems consisting of two or more atoms or molecules. Clusters have been receiving a lot of attention for many years [1–3], because they offer the prospect of predicting the macroscopic properties of condensed matter by extrapolating experimental as well as theoretical results obtained for different cluster sizes. In this context it is interesting to investigate whether an ionized, excited species, after

having emitted the primary electron, can give off its excess energy by releasing an additional electron. In particular, is there an electronic decay mechanism that is characteristic of a cluster, *not* amenable to its isolated constituents?

Relaxation by electron emission is well known in the field of core excitation, where this process is commonly referred to as Auger decay [4]. However, ionization energies ranging from a few hundred eV up to several keV are needed to remove a core electron. The excitation energy of the resulting system is so high that even an isolated atomic ion relaxes by electron emission. Auger decay is basically an intraatomic phenomenon and only weakly dependent on neighboring monomers. If one is interested in effects that are sensitive to the molecular environment in the cluster, ionization of the valence shell, which is responsible for the formation of the chemical bond, must be considered.

Recent theoretical investigations accompanied by

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large-scale *ab initio* computations [5–9] addressed this issue. They led to a profound insight. The belief widely held prior to these studies was that valence-ionized molecular systems are electronically stable. The only channels available for energy dissipation were presumed to be vibrational motion and, of course, photon emission. This is true for the outer-valence shell, but, as Cederbaum et al. [5] discovered, in general not for inner-valence states.

2. Intermolecular Coulombic decay

It may be surprising that in the relatively low-energy regime associated with valence ionization, electron emission plays any role at all. However, in the clusters we studied so far, electronic decay was found to be ultrafast, turning out to dominate the overall relaxation behavior. In view of the fact that isolated, inner-valence excited H_2O^+ , for instance, cannot give off its excess energy by electron emission, it may sound even more astonishing that water complexes consisting of two or more monomer units do decay electronically. The novel decay phenomenon is of intermolecular nature, and as such a distinctive feature of clusters.

From our previous work [5–9], the following simplified picture has emerged, which is illustrated

in Figs. 1 and 2. Ionization out of an inner-valence orbital leads to the formation of a hole which is localized at one of the monomers constituting the cluster. An outer-valence electron at this cationic monomer can drop into the inner-valence vacancy. Due to an efficient Coulombic mechanism, the released energy is transferred to neighboring monomers. An indication of this energy transfer process has been observed in a recent experiment by Thissen et al. [10]. As a consequence, an outer-valence electron is ejected in the molecular environment of the initial cation. The resulting final states are characterized by two positive charges distributed over two or more monomers. Thus, Coulomb repulsion of the two holes is reduced, which explains why the electronic decay channels can be energetically accessible (see Fig. 2). This lowering of the double ionization threshold of clusters and condensed matter in comparison to their monomer constituents is experimentally well established [11,12]. Finally, the dicationic cluster undergoes fragmentation caused by the repulsive forces acting between some monomers. For the described process, which is extremely sensitive to the chemical environment, the term *intermolecular Coulombic decay*, abbreviated as ICD, has been introduced [8]. Recent efforts at the Hamburg synchrotron laboratory hint at a first direct experimental verification of our predictions [13].

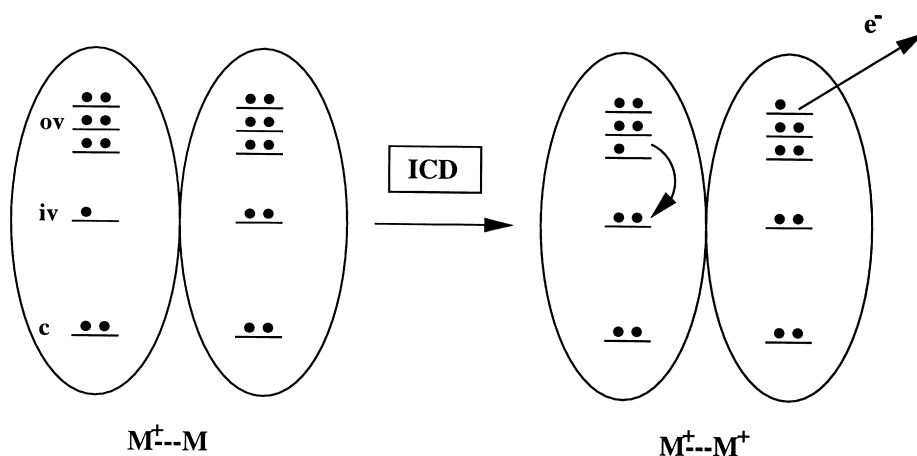


Fig. 1. Schematic representation of the intermolecular Coulombic decay (ICD) of molecular clusters. An inner-valence (iv) hole at one of the monomers decays electronically by transferring its excitation energy to neighboring molecules and ejecting an outer-valence (ov) electron in the cluster environment. Note that core (c) electrons are not involved.

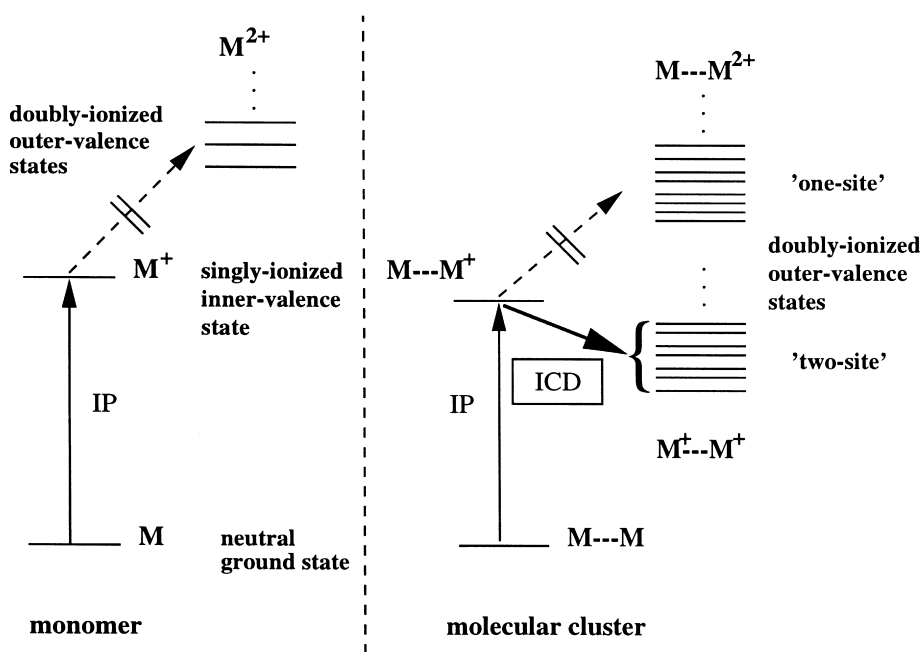


Fig. 2. In isolated monomers, usually all dicationic outer-valence states lie higher in energy than monocationic inner-valence states, which are, therefore, electronically stable. In contrast to the isolated molecules, the inner-valence vacancy in the molecular cluster can efficiently decay by electron emission because of the accessibility of dicationic decay channels with two vacancies localized on neighboring monomers.

3. An example: electronic decay of inner-valence excited $(HF)_3^+$

3.1. Single and double ionization spectra

In order to illustrate the general description of ICD given above, we discuss a concrete example: the intermolecular decay phenomenon in the hydrogen fluoride trimer. In Fig. 3 single and double ionization spectra of HF as well as $(HF)_3$ are displayed [6]. The spectra were calculated by means of Green's function methods [14] at the respective ground state equilibrium geometries [15,16]. More precisely, the ADC(3) approximation of the one-particle Green's function [17] and the ADC(2) scheme for the two-particle propagator [18,19] were used. ADC(n) represents a sophisticated perturbation theoretical approximation of a many-body Green's function, which is complete up to n th order and includes in addition infinite summations over certain classes of expansion contributions. The method is ideally suited for the

investigation of clusters because of its inherent size-consistency.

The spectral intensities in Fig. 3 do not immediately reflect the signal intensity in an experimental photoionization spectrum. We assume that the sudden approximation is valid, i.e., that the incident photon energy is larger by several eV than the binding energy of the primary emitted electron. Under this assumption it is possible to use the spectral intensities given here, and deduce from them photoemission probabilities [20].

As can be seen in Fig. 3, the lowest double ionization energy of isolated HF is larger than 46 eV. This is higher in energy than the cationic inner-valence states in the vicinity of 40 eV, which can therefore not decay by electron emission. In analogy to the isolated molecule, dicationic *one-site* states, where both positive charges are localized at a single molecular monomer, exist in the trimer as well. However, in addition to these there are dicationic *two-site* states available in the cluster, which are

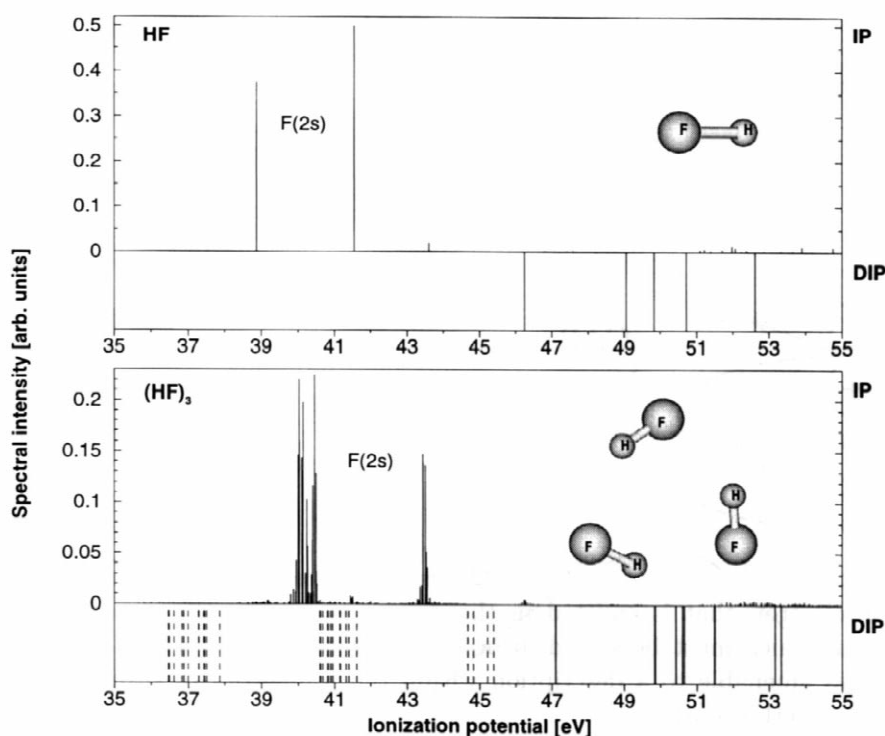


Fig. 3. Single (IP) and double (DIP) ionization potentials of HF and $(\text{HF})_3$. Each stick corresponds to an electronic state. Note that in contrast to the isolated molecule, there are dicationic states of the trimer that are characterizable by a distribution of the two positive charges over at least two monomers. These states are represented by dashed lines. Many of them are lower in energy than those monocationic states which arise from the removal of a 2 s electron. In the clusters these cationic inner-valence states can therefore undergo relaxation by electron emission.

lower in energy than the cationic inner-valence states. Hence, these are resonances, i.e., discrete, quasibound states embedded in and interacting with an electronic continuum. A striking manifestation of this fact are the dense line bundles in the single ionization spectrum of $(\text{HF})_3$ (see Fig. 3). Since ab initio calculations are performed in a finite configuration basis set, the Lorentz profiles resulting from the electronic decay process are approximated by discrete, dense state distributions.

3.2. Calculating the lifetime of electronic resonances

Now that it has been shown that electronic decay channels are energetically accessible, we turn our

attention to the timescale on which electron emission takes place. Computing the lifetime of an electronic resonance is a very difficult issue, because it requires dealing with the wave function of the emitted electron. Such a scattering wave function is not square-integrable and does not reside in a Hilbert space [21]. The methods established in quantum chemistry, being based on Gaussian basis set expansion [22], are therefore not directly applicable.

Several techniques [23–27] are available to remedy the situation. Particularly promising for large-scale calculations of electronic resonances in molecular systems is the complex-absorbing-potential (CAP) method [27]. The underlying idea, illustrated in Fig. 4, is to introduce an absorbing boundary condition in the exterior region of the molecular system. The forced absorption of the outgoing elec-

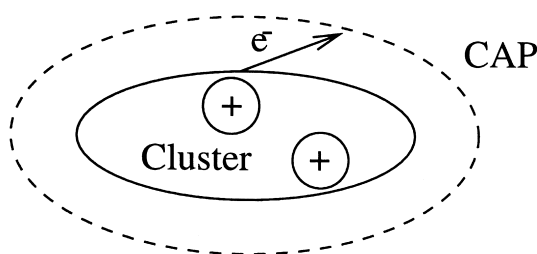


Fig. 4. A complex absorbing potential (CAP) [27] is introduced with the purpose of absorbing the electron that is emitted in the decay process. In this way the scattering problem, which must be solved in order to determine the lifetime of a resonance, becomes amenable to a description within the framework of standard quantum chemistry methods [7,31].

tron renders its wave function square-integrable. This is accomplished by replacing the Hamiltonian H by

$$H(\eta) = H - i \cdot \eta \cdot W, \quad (1)$$

where η is a real, non-negative number referred to as CAP strength parameter. W is a local, positive semi-definite one-particle operator. The matrix representation of $H(\eta)$ is complex symmetric (a real basis set is assumed), so that its spectrum is no longer real but consists of complex energies. By varying the CAP strength η it is possible to identify resonances in a straightforward manner (see Ref. [27] for details) and determine their complex Siegert energies $E_{\text{res}} = E_R - i \cdot \Gamma/2$. E_R is the real part of the resonance energy, Γ the decay width. The lifetime τ of a non-stationary state follows immediately, $\tau = \hbar/\Gamma$.

One of the major advantages of the CAP method, besides its simplicity, is the fact that it can be easily used in connection with electronic correlation methods: a one-particle potential, i.e., the CAP, is simply added to the matrix obtained by a chosen, problem specific, quantum chemistry method. The resulting complex symmetric matrix is then diagonalized, for example by means of an appropriately adapted Lanczos procedure [28–30]. We use here a recently developed method called CAP/CI [7,31], which combines the addition of a complex absorbing potential with the multi-reference configuration-interaction [32,33] approach.

Several successful applications of CAP/CI have

already been presented in the literature. Sommerfeld et al. investigated the $^2\Pi_g$ resonance as well as long-lived states of N_2^- [31,34] and predicted the existence of the metastable dianion C_2^{2-} [35,36]. Ingr et al. calculated the potential energy curve of the $X^2\Sigma_u^+$ resonance state of F_2^- [37]. We studied ICD in the HF dimer [7], and recently we discovered that molecular anions undergo electronic decay following inner-valence ionization [38].

3.3. Decay widths of inner-valence excited $(HF)_3^+$

Employing the correlation consistent basis sets [39,40] aug-cc-pVDZ on the hydrogen atoms and aug-cc-pVTZ on the fluorine sites, we made use of the ab initio program package MOLCAS [41] to calculate closed-shell molecular orbitals, i.e., Hartree–Fock one-particle states, of $(HF)_3$. The molecular point group reflecting the symmetry of the equilibrium geometry of $(HF)_3$ is C_{3h} . The Abelian subgroup of relevance for the ab initio calculation is C_s . Those nine configuration state vectors that correspond to a single hole in each valence orbital of A' symmetry (C_s) as well as all single excitations of these references — in the frozen-core approximation — were employed to describe the cationic many-electron configuration space. This procedure leads to size-consistent results, which is an important ingredient when studying clusters.

The CAP/CI results we obtained for the three energetically lowest cationic inner-valence states of $(HF)_3$ are presented in Table 1. The doubly degenerate states arising at an ionization potential of 40.1 eV are of E' symmetry in the language of the group C_{3h} . The state at 40.6 eV is totally symmetric. The ICD

Table 1

Ionization energies of $(HF)_3$, at which the three energetically lowest inner-valence states of $(HF)_3^+$ are formed, their corresponding decay widths and their lifetimes^a

| Resonance | E_{ion}/eV | Γ/meV | τ/fs |
|----------------------|----------------------------|---------------------|------------------|
| 1st and 2nd (E') | 40.1 | 67 | 9.8 |
| 3rd (A') | 40.6 | 130 | 5.2 |

^a Results were obtained by means of the complex-absorbing-potential method implemented at the multi-reference configuration-interaction level (CAP/CI) [7,31].

lifetimes of these states are found to be below 10 fs, corresponding to decay widths of about 100 meV. This happens to be of the same order of magnitude as the extremely short lifetimes usually associated with Auger decay (see Ref. [42], for example). Our calculations clearly demonstrate the high efficiency of the intermolecular energy transfer process responsible for ICD.

It is of interest to compare the ICD lifetimes of inner-valence excited $(\text{HF})_3^+$ with the corresponding lifetimes in the hydrogen fluoride dimer [7]. Decay in the trimer is faster approximately by a factor of 4, resulting from the larger number of decay channels. We expect this trend of decreasing ICD lifetimes to continue until the first coordination shell, consisting of next neighbors surrounding the monomer that carries the initial inner-valence vacancy, is filled. Further coordination shells probably exert only a minor influence, but this remains to be studied. There is no similarly pronounced environment effect for Auger decay following core ionization of a weakly bound cluster.

In this paper we have concentrated on a hydrogen-bonded system. The ICD phenomenon is far more general, however. Before concluding we would like to mention that recently we investigated ICD in van der Waals clusters [43]. As a consequence of the much weaker chemical bond, longer ICD lifetimes in comparison to hydrogen-bonded systems were found. Furthermore, the influence of nuclear dynamics turned out to be of particular importance. Our studies have shown that the kinetic energy spectrum of the emitted ICD electron directly reflects the nuclear wavepacket on the cationic inner-valence surface due to a remarkable stretching and mapping effect. We are certain that further investigations will reveal additional exciting details of the intermolecular Coulombic decay process in clusters.

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