

Giant Intermolecular Decay and Fragmentation of Clusters

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In sharp contrast to molecules, electronic states of clusters with an excited intermediate-shell electron can efficiently decay via an intermolecular Coulombic mechanism. Explicit examples are presented using large scale *ab initio* propagator calculations. The mechanism is illustrated and its generality is stressed. [S0031-9007(97)04795-9]

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Quantum states of electronic systems typically decay by photon and/or electron emission. Energetically low lying states decay radiatively while highly excited levels involving the excitation of inner-shell electrons decay more efficiently by emitting an electron (Auger decay). It is only for very deep inner-shell electrons of heavy elements that x-ray emission constitutes the prominent decay channel [1]. States which can decay only radiatively, i.e., states with excited outer-shell electrons, exhibit an exceedingly long lifetime (\approx nanoseconds) compared to Auger-decaying states. For instance, a vacancy in the $1s$ shell of a fluorine atom has a lifetime of about 3.3 fs (0.20 eV linewidth) [2]. This lifetime depends only weakly on whether the fluorine atom is free or integrated in a molecular system. The total decay rate is essentially determined by the neighboring atomic electrons. Deeper electron vacancies typically decay faster. An excited or ionized state of the sulfur atom with a vacancy in the $1s$ shell, for example, lives for about 1.6 fs [3], and if the vacancy is in the $2p$ shell the lifetime extends to 66 fs [4].

As mentioned above, the environment of the atom influences only moderately the lifetime of the deep vacancy (e.g., of a $F1s$ vacancy). If at all, we can only expect interesting environmental effects on the total Auger decay rate to take place for vacancies in intermediate shells. However, a closer look at the energetics of the decay in typical molecules brings a problem to light. The ionization potential (IP) of a $F2s$ electron in, say, the HF molecule, is about 40 eV [5], but the release of these 40 eV is insufficient to ionize a second electron: the lowest double ionization potential (DIP) of HF is about 45 eV [6]. Similarly, the IP of an $O2s$ electron in H_2O is approximately 35 eV [7], again too small an energy to allow a second electron to leave the system. The lowest DIP of water is about 38 eV [8]. The situation changes substantially as we move to clusters. While the IP of intermediate shells differs only slightly from that of the monomer unit, some DIPs are lowered considerably in the cluster and the autoionization channel opens. More importantly, we shall also show in this Letter that the accessible decay becomes dramatically efficient in clusters.

Atomic and molecular clusters have been subject to continuous interest over many years [9–11]. Most of the interest has been devoted to the possible geometrical structures and properties of the clusters in their electronic ground state. Much less attention has been paid to excited electronic states and no attention to highly excited states involving intermediate shell electrons and their decay. Owing to the large density of electronic states in the corresponding energy range, these states are difficult to compute even for relatively small molecules [12] and even more so for clusters. In principle, there are several possibilities to calculate the Auger decay rates once these states have been computed. One approach is to calculate the rates using an *ab initio* scattering method, as is done for the decay of inner-shell vacancies of atoms and small molecules [13–15]. Another approach relies on the Hamiltonian continued into the complex energy plane [16,17]. The decaying states become resonances with complex energies, where the imaginary part is related to the inverse lifetime. Both approaches are beyond practicability for clusters because of the complexity and number of the states involved. Moreover, simplifying approximations made for inner-shell vacancies cannot be transferred to the much more complicated intermediate-shell ones.

We propose to use a different approach. The groups involved in the present study have acquired considerable experience in the *ab initio* computation of ionization [18] and of Auger [19] spectra using Green's function and propagator methods. Recently, the introduction of efficient block-Lanczos algorithms [20] have made these methods applicable to larger systems [21,22]. The correct scaling of the results with the number of particles (size consistency) is an indispensable ingredient of these methods when applied to clusters.

The ionization and Auger spectra of several monomers and clusters have been computed using the methods described in Refs. [19,21]. The ionization and Auger spectra are related to the imaginary part of the one-particle Green's function and the particle-particle propagator, respectively. The technical details of the computations will be given elsewhere [23]. We mention here that the basis sets used contain, in addition to the standard Gaussian

functions, functions with exponents describing emitted electrons with the appropriate kinetic energies [24].

Figure 1 shows the computed ionization spectrum of the HF molecule and of the $(\text{HF})_3$ trimer. The calculations have been performed at the respective ground state geometries [25]. The spectral intensity of the HF molecule has been computed before [26] and compared to experiment [5]. Ionization of the outermost 1π and 3σ orbitals, which have essentially $F2p$ character, gives rise to the first and second peaks in the spectrum, respectively. Ejection of an electron from the $F2s$ shell (2σ molecular orbital) leads to a split peak at about 40 eV binding energy. The computed spectrum of the trimer is new. It exhibits a similar peak pattern, with all peaks broadened and shifted to higher energies. The intensity ratio of the components of the $F2s$ derived peaks has altered considerably. These gross differences between the monomer and the trimer are interesting by themselves, but will not be further discussed here. Because of the cyclic symmetry of the trimer, the 1π level is split into four and the 3σ level into two components. The resulting energy splittings reflect the interactions between the monomer units in the trimer.

As already discussed in the introduction, the Auger decay of the $F2s$ levels is possible in the cluster and a closer

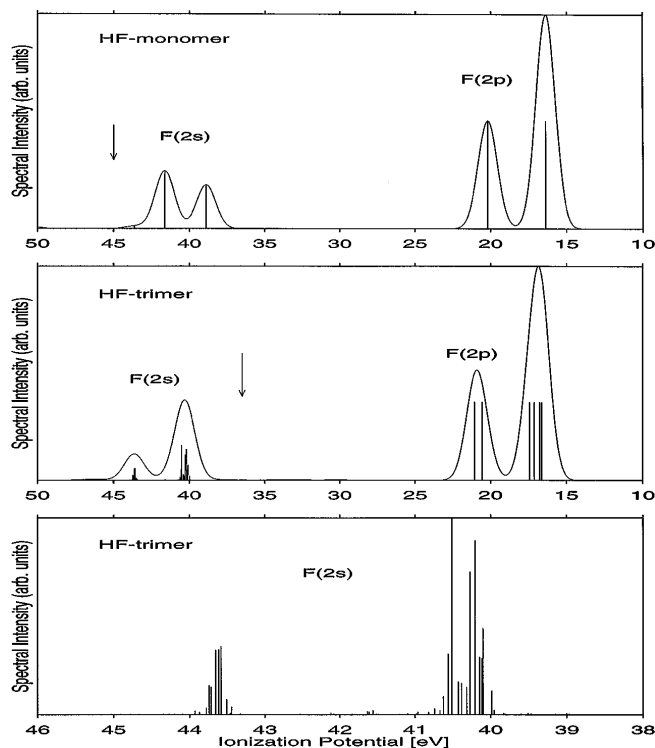


FIG. 1. Spectral intensity of singly ionized states of HF (upper panel) and $(\text{HF})_3$ trimer (central panel). The computed stick spectrum at the IPs is convoluted with Gaussian functions to simulate a finite experimental resolution. The lower panel shows on an expanded energy scale the high energy part of the stick spectrum (line bundles) of the trimer. The onset of double ionization is indicated by arrows.

look at the $F2s$ derived peaks in Fig. 1 reveals this decay. Instead of the two lines in the spectrum of HF a dense fine structure appears which is shown on an expanded scale in the lowest panel of Fig. 1. Its discreteness is due to the finite basis set we use. Because of this finite basis set bundles of line fine structures appear instead of continuous distributions reflecting the Auger decay of the two $F2s$ levels. The widths of these line bundles should be related to the corresponding lifetime broadening. Even a conservative estimate shows that the lifetime of the $F2s$ levels is shorter than that of the well-studied $F1s$ core level of molecules mentioned in the introduction.

According to the introduction, the $F2s$ levels in the HF molecule cannot autoionize because of the high DIP. We have also computed the DIPs of the trimer and found the lowest DIP to be 36.4 eV, i.e., about 9 eV lower than in the monomer. As seen in the central panel of Fig. 1, the value of the DIP separates in the trimer the $F2p$ and $F2s$ levels, allowing for the decay of the latter with maximum kinetic energies of the ejected electron of about 5 eV for the first and 10 eV for the second peak. The key for the decay in the cluster is highly interesting. Unlike the decay of core levels, which is intra-atomic in nature, the decay of the intermediate shell vacancy is intermolecular: a $F2p$ electron of the monomer carrying the initial $F2s$ vacancy drops into this vacancy and the excess energy is used to eject a $F2p$ electron from a neighboring monomer. Indeed, the small value of the trimer's lowest DIP is due to the two-site nature of the double vacancy. The values obtained for the one-site DIPs, where both $F2p$ vacancies are on the same monomer, are similar to those of the HF molecule.

The above findings are not specific to HF clusters. We have computed the ionization spectra of several clusters and obtained very similar qualitative results. Interestingly, similar decay mechanisms prevail also in *excited* and in *doubly ionized* states of clusters. For the sake of brevity we concentrate on the following in the latter. There are several experimental methods available to produce such states [27–29]. One of them is Auger spectroscopy itself. Figure 2 shows the computed Auger spectra of H_2O and $(\text{H}_2\text{O})_3$. The spectra show the doubly ionized states and their population resulting from $\text{O}1s$ Auger decay. The calculations have been performed at the ground state geometries [30]. The Auger spectrum of the water molecule has been measured [8] and analyzed [31] in the literature. Owing to the many more possibilities to create two vacancies than a single vacancy in a molecule, the Auger spectra are more complex than ionization spectra. For our purposes it suffices, however, to indicate that the first group of states in Fig. 2 are characterizable by two vacancies in the $\text{O}2p$ shell, the second group by one vacancy in the $\text{O}2p$ and one in the $\text{O}2s$ shell, and the last group possesses two vacancies in the $\text{O}2s$ shell.

Clearly, doubly ionized states can, in principle, decay by electron emission, just as singly ionized states do. The mechanism for the decay is Coulombic and for the sake of

brevity we shall also refer to this decay as Auger decay. If the decay channels are open, we rather expect the decay to be much fiercer than the usual Auger decay of single vacancies. If both vacancies are localized in the same region of space, the response of the outer shells to the vacancies should be approximately 4 times stronger than the response to a single vacancy [32].

By Auger decay a doubly ionized state gives rise to a manifold of triply ionized states. The lowest triple ionization potential (TIP) of the oxygen atom is 103.69 eV [33], and this value drops down to about 85 eV in the H_2O molecule [34]. Consequently, the doubly ionized states of H_2O depicted in Fig. 2 are not affected by a further Auger decay except those at the very high energy end of the spectrum. The situation is drastically different for the water clusters to be discussed in the following.

$(\text{H}_2\text{O})_3$ in its ground state has a cyclic structure [30]. The presence of two adjacent neighbor monomers enhances the number of effectively coupled decay channels and may amplify the decay of the double vacancy on each of the monomers. We would like to stress that, owing to the local character of Auger decay, those dicationic states are preferentially populated which have their two vacancies on the same monomer. The central panel of Fig. 2

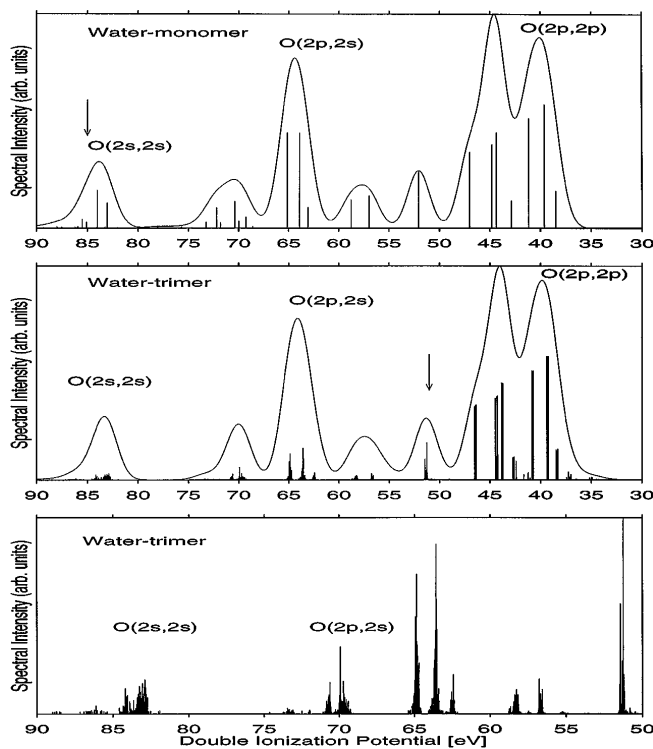


FIG. 2. Auger spectrum of H_2O (upper panel) and $(\text{H}_2\text{O})_3$ trimer (central panel). The computed stick spectrum at the DIPs is convoluted with Gaussian functions to simulate a finite experimental resolution. The lower panel shows on an expanded energy scale the high energy part of the stick spectrum (line bundles) of the trimer. The threshold for triple ionization is indicated by arrows.

shows the computed $\text{O}1s$ Auger spectrum of the $(\text{H}_2\text{O})_3$ cluster. Most of the intensity can be attributed to one-site double vacancy states and hence the overall appearance of the Auger spectrum of the trimer is astonishingly similar to that of the monomer shown in the upper panel of Fig. 2. Only some weak structures in the spectrum of $(\text{H}_2\text{O})_3$ remind one of the two-site vacancies, e.g., the low energy tail at 37 eV and below. Several two-site vacancy states are located at energies well below the one-site ones, but they acquire only little intensity in the Auger spectrum.

A close look at the H_2O and $(\text{H}_2\text{O})_3$ spectra shows that, while the two nearly agree in their spectral envelope, they strongly disagree in the line structure at the higher energy part ($\text{DIP} > 50$ eV). There, the trimer's spectrum exhibits bundles of line fine structures at the positions of the corresponding monomer peaks. This effect is due to the coupling of the one-site double vacancies on one monomer to higher excited configurations where one of the vacancies is on a neighboring monomer. Since triple ionization channels of $(\text{H}_2\text{O})_3$ are open for these peaks, the line bundles correspond to a decay width of the states which is clearly visible in the lower panel of Fig. 2. The corresponding states of H_2O are stable against Auger decay, but they decay in the trimer with an enormous width of up to 0.5 eV (1.3 fs) or even more. The relevant lowest TIP with an one-site double vacancy on one monomer and a single vacancy on a neighboring monomer is calculated to be about 51 eV. The lifetime of the states in the peak between 83 to 87 eV is shorter than that of the other states because here both vacancies are $\text{O}2s$ holes which can decay individually, in contrast to a single $\text{O}2p$ vacancy (see discussion of Fig. 1).

We have found beyond doubt that, in sharp contrast to molecules, states of clusters with an excited intermediate-shell electron (often called inner-valence electron) can efficiently decay by an intermolecular Coulombic mechanism. An outer-valence electron at the same monomer carrying the inner-valence vacancy drops into this vacancy, and the excess energy is used to eject one electron from a neighboring monomer. The decay results in a cluster with two monomers being positively charged. Since the monomers are usually weakly bound in molecular clusters, the repulsion of these charges eventually leads to a fragmentation of the cluster into smaller units at specific sites. This efficient fragmentation plays a role in connection with the abundance of clusters in stellar and interstellar media.

The intermolecular Coulombic decay is of a very general nature and should apply to a large variety of clusters and other weakly bound systems. It opens new possibilities to study intermolecular interactions in these systems. The limited resolution of state-of-the-art spectrometers may make the observation of the decay in the ionization and Auger spectra difficult. We propose to analyze the intermolecular decay by measuring the Auger electron in coincidence with the primary photoelectron

as a function of photon energy. Above some threshold coincidences should be observed for the clusters but not for the monomers.

Finally, we would like to briefly discuss why the new mechanism takes place and where its efficiency comes from. The electronic states with excited inner-valence electrons are usually highly correlated states. If we neglect this complexity, the leading term for the decay width according to the golden rule formula is proportional to

$$\left| \int k^*(\mathbf{r})v_i^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} v_f(\mathbf{r})v_f'(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \right|^2,$$

where $v_i(\mathbf{r})$ is the orbital of the initial inner-valence vacancy, $k(\mathbf{r})$ is the scattering wave function of the ejected electron, and $v_f(\mathbf{r})$, $v_f'(\mathbf{r})$ are the orbitals of the two resulting final vacancies. Since many pairs of final vacancies can result by the decay, one has to sum over all open channels. Apart from the strong correlation of all states involved and the large number of open channels, the relatively low kinetic energy of the ejected electron presents another complication in the accurate theoretical assessment of the decay width.

In normal Auger decay, the ejected electron's energy is large and the core orbital $v_i(\mathbf{r})$ is very localized at its nucleus, and hence the decay is only efficient if both final vacancies v_f and v_f' are also localized or at least possess localized components at the same nucleus. In the inter-molecular decay mechanism, on the other hand, it suffices that $v_i(\mathbf{r})$ and $v_f'(\mathbf{r})$ are on the same monomer and overlap. $v_f(\mathbf{r})$ can be on a neighboring monomer since the emitted electron has a fitting relatively long wave length, in contrast to the normal Auger electron which is fast and its wave function oscillates rapidly. The presence of several and even many open channels is, of course, helpful in establishing an efficient decay. As a trend, we expect the decay as well as the subsequent fragmentation to be more effective for monomers closer in space. However, if the monomers come very close they form rather a larger molecule than a weakly bound system, and this will raise the threshold energy for the decay and suppress it.

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