Highly excited electronic states of molecular clusters and their decay

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Highly excited electronic states of molecular clusters with intermediate-shell vacancies are calculated and analyzed using large scale ab initio Green’s function calculations. In sharp contrast to molecules, an intermolecular Coulombic mechanism has been found to lead to an ultrafast decay of singly and doubly ionized states with vacancies in the inner-valence region. Small hydrogen-bonded (HF)\(_n\) clusters (\(n = 2–4\)) have been selected as explicit examples to illustrate the proposed decay process, which does not occur in the HF monomer. The decay mechanism and the main factors that exercise an influence on it are discussed. The corresponding decay widths are estimated in selected cases, showing that the lifetimes of the states are of the order of few femtoseconds. © 1998 American Institute of Physics. [S0021-9606(98)30123-3]

I. INTRODUCTION

The study of clusters is a subject of rapidly growing interest. In particular, the class of weakly bound molecular clusters gave rise to many investigations in the last few years.\(^1\)–\(^3\) These systems are particularly important in the exploration of intermolecular interactions and can be considered as linking together the properties of molecular systems and the corresponding bulk states. The recent accumulation of progress in theory and experiment allows the study of even demanding systems like the hydrogen-bonded clusters, with their strong directional intermolecular bonds, with astonishing accuracy.\(^4,5\)

Up to now most of the investigations have been devoted to the properties of the clusters in their electronic ground state. This includes the determination of geometries, intermolecular potentials, vibrational properties and dynamics of formation and fragmentation.\(^1\)–\(^5\) Much less attention has been paid to excited electronic states\(^5\)–\(^15\) —especially to highly excited states involving intermediate-shell electrons—and their decay. The study of these highly excited states is very promising because it provides a deep insight into the electronic structure of clusters and allows an understanding and interpretation of phenomena based on excitation processes. Important spectroscopic techniques involving excited electronic states are, e.g., photoionization\(^7\)–\(^8\),\(^16,17\) and Auger spectroscopy.\(^18\) Some reasons for the deficit in experimental investigations on highly excited states of clusters have been removed in the last several years by developing sources of radiation with high intensity that are tunable in wide energy ranges (cyclotron radiation, lasers) in combination with new coincidence-detection techniques,\(^19\)–\(^22\) and also by the development of cluster beam apparatuses with largely improved size selectivity. Parallel to this experimental progress, the development of faster computers and efficient new quantum chemical methods permits the calculation of properties of even extended systems like clusters with remarkable accuracy.

Excited states have a finite lifetime. Therefore, one of the most relevant and challenging tasks concerning excited states is to analyze their decay properties. This is especially important when studying excited electronic states of weakly bound molecular clusters, where the electronic decay can easily lead to a subsequent fragmentation of the excited system into specific subunits. In principle, excited electronic states can decay by photon and/or electron emission. It is well known that energetically low lying states decay radiatively while highly excited states, involving excitation of inner-shell electrons, decay more efficiently by electron emission (Auger decay).\(^23\) These complementary types of decay processes are responsible for the largely different lifetimes of outer- and inner-shell vacancies. States which can decay only radiatively (excited outer-shell electrons) have long lifetimes compared to states which decay via electron emission (deeper electron vacancies). While the decay of outer-shell vacancies is strongly influenced by the chemical environment at the location of the primary excitations, the lifetime of inner-shell vacancies depends only weakly on the molecular environment (intra-atomic process). Therefore, interesting environmental effects in excited states that decay primarily via electron emission can only be expected to take place for vacancies in intermediate shells (excited inner-valence electrons). But in typical molecular systems the decay of intermediate-shell vacancies via Auger emission is impossible because of energetic reasons: The ionization potential (IP) of intermediate-shell electrons is too small for autoionization, i.e., smaller than the lowest double ionization potential (DIP). The same situation is found when starting with doubly ionized states involving intermediate-shell vacancies: Here the lowest triple ionization potential (TIP) is too high in energy to enable autoionization.

We have shown recently\(^24\) that this situation changes substantially in the case of weakly bound molecular clusters. The IPs in these systems are only slightly different compared to the monomer’s values whereas the energy onset of double
ionization in the clusters is lowered considerably because of the now possible spatial separation of the two vacancies on different monomer units. This leads to an opening of the autoionization channels for the intermediate-shell vacancies in the molecular clusters and makes their efficient decay possible. A very similar situation appears when starting with doubly ionized states that are localized at the same monomer unit, leading to a decay to triply ionized states with the three holes spatially distributed over at least two different monomer units. Based on these observations we have proposed a new efficient intermolecular Coulombic mechanism for the decay of the excited intermediate-shell electrons in the weakly bound clusters. This mechanism is in sharp contrast to the intra-atomic decay which is typical for highly excited electronic states of molecules.

In the present paper we discuss the decay of excited intermediate-shell electrons of small hydrogen fluoride clusters as explicit examples to illustrate the recently proposed intermolecular decay mechanism in more detail. Large scale ab initio Green’s function methods are used to calculate the ionization and double ionization spectra of the systems. These calculated spectra are then analyzed in order to observe signs for an electronic decay of the excited states that are populated in the spectroscopic transitions. We use the Green’s function approach to analyze the decay processes in a somewhat indirect way. The large number and high density of electronic states in the energy range of excited intermediate-shell electrons, and the importance of correlation effects for these electrons rule out the use of standard quantum chemical methods to calculate the decay rates directly. Methods such as ab initio scattering theory or the analytic continuation of the Hamiltonian into the complex energy plane are still beyond practicability for clusters, also because of the large number of possible decay channels. Simplifying approximations that work well for corelike vacancies break down in the much more complicated situation of intermediate-shell vacancies.

The paper is organized in the following way. In Sec. II we briefly describe the methods we use to calculate and analyze the singly and doubly ionized states of the clusters. In Sec. III we then present and discuss the results obtained for the decay of the singly and doubly ionized states of the (HF)$_n$ systems in comparison with the well-known results for the corresponding monomer HF. Finally, Sec. IV constitutes a summary of the crucial points.

II. METHODS AND COMPUTATIONAL DETAILS

A. Calculation of the excited states

The very many singly and doubly ionized states in the valence region of the ionization and double ionization spectra of the molecular clusters were computed using the Green’s function formalism. The algebraic diagrammatic construction scheme (ADC) to approximate the one-particle Green’s function and the particle-particle propagator has been used to calculate the ionization and double ionization spectra, respectively. The ADC scheme has been discussed in detail in the literature and we only want to briefly recall here some basic principles of the method. The ADC $(n)$ approximation for a given order $n$ of perturbation theory leads to a Hermitian eigenvalue problem in the configuration space of the cation or dication. The solution of this eigenvalue problem yields directly the ionization or double ionization potentials as eigenvalues and the corresponding spectroscopic factors are directly related to the eigenvectors. All computed quantities determined are size consistent, which is very relevant when discussing clusters.

In the calculation of the ionization spectra we have used the ADC(3) scheme which is also known as the extended two-particle-hole Tamm–Dancoff (2ph-TDA) approximation. The configuration space in this third-order scheme comprises all the one-hole (1h) and two-hole-one-particle (2h1p) configurations based on the Hartree–Fock orbitals of the neutral ground states of the systems (closed shell). Cationic states that are perturbatively derived from 1h configurations (main states) are described consistently through third-order perturbation theory. The states derived from 2h1p configurations are calculated only with first-order accuracy.

The double ionization spectra have been calculated with the second-order ADC(2) scheme. Here the configuration space comprises all two-hole (2h) and three-hole-one-particle (3h1p) configurations in relation to the Hartree–Fock ground state orbitals. Dicationic states which are perturbatively derived from 2h configurations (main states) are accurate through second order of perturbation theory. Similarly, the states with mainly 3h1p configuration contributions (satellite states) are accurate through first order of perturbation theory.

Besides the important property of size consistency these methods offer the advantage of a much more compact configuration space compared to equivalent configuration interaction calculations. These properties are of fundamental importance in the calculation of extended systems.

A crucial point in the calculation of the manifold of excited states for the clusters is the large dimension of the ADC matrices (typical dimensions between $10^4$ and $10^5$) in combination with the extremely high density of eigenstates needed especially in the inner-valence region of the spectra. The exact calculation of many dense lying roots of such large eigenvalue equations is very problematic and often hardly possible. But, on the other hand, owing to this high density of states, the spectrum can be well characterized via the accurate determination of the spectral envelope around the dense state distribution. This task can be accomplished very effectively by employing a moment preserving block-Lanczos diagonalization procedure to the main space of configurations only. This method provides an exponential convergence rate on the spectrum of main space components. The block-Lanczos procedure has been implemented in the ADC Green’s function computer programs and investigated in detail.

The calculated dicaticonic states have been further characterized according to the spatial distribution of the two-hole density using a two-hole population analysis. With this analysis one decomposes the 2h pole strength of the ADC eigenvectors into their localized atomic contributions. These contributions can be split in two principal parts: the sum of terms describing the localization of the two holes on single atomic centers (one-site terms) and the sum of terms describ-
ing the localization of the two holes on pairs of atoms, each of them carrying one hole (two-site terms). The dominance of one of these contributions over all the others for a given state indicates the spatial localization of the holes in this state.

All calculations on the excited states of the HF clusters have been performed at the equilibrium geometries of the neutral ground state systems. The orbital energies and Coulomb integrals resulting from Hartree–Fock calculations on this neutral ground state serves as input for the corresponding ADC calculations. For the Hartree–Fock calculations the GAMESS—UK program package has been used. The ADC programs used are described in Refs. 45, 46, 49. In the ADC computations the 1s core orbitals of the fluorine atoms as well as their highest lying corelike virtual counterparts have been excluded from the active configuration space after checking their negligible influence on the numerical results.

B. Description of the decay phenomena

A very characteristic property of the inner-valence region of the ionization and double ionization spectra is the high density of relevant excited states already present in relatively small molecular systems, and even more so for clusters. This high density is connected with strong mixing of quasidegenerate main and excited configurations leading to intensity redistributions and breakdown of the independent particle picture.

When the Auger decay of the inner-valence vacancies is possible, a further increase of the density of states occurs in the spectra. This increased density is accumulated in characteristic distinct dense line fine structures grouped around the decaying states. The line fine structures describe the decay of the excited states via coupling to the continuum states of higher ionizations. Because of the finite discrete basis set description, distinct line bundles appear instead of continuous intensity distributions. For example, in the case of a single initial vacancy, the decay is described through an enhanced coupling of the 1h configuration with 2h1p configurations where the excited electron models the outgoing Auger electron.

We have already mentioned that the calculation of excitation energies and spectroscopic factors through exact solution of the ADC eigenvalue problem is hardly possible for the inner-valence region of even moderate-size systems because of the large number and density of states. We have applied numerous modern diagonalization methods including, e.g., the block-Davidson algorithm, and all have failed. Therefore, approximate diagonalization methods have to be used. Now the question arises whether the use of approximate diagonalization methods affects at all the correct description of the Auger decay of the excited states which emerges in the spectra in the form of dense line fine structures.

In contrast to other approximate diagonalization methods, the iterative moment-preserving block-Lanczos algorithm we use for the approximate solution of the large ADC eigenvalue problem has an important property: it exhibits a convergence rate on the spectral envelope of the main space components which is exponential in the number of iterations and the line widths. This property allows us to describe the spectral envelope around the dense line structures in the inner-valence area correctly. It is essential to note here that, in fact, the spectral envelope around the dense line fine structures is the only physically meaningful quantity in the description of the decay: The discrete line structure we obtain in our finite discrete basis set calculations only mimics the continuous distribution to be expected in the limiting case of an infinite basis set description. By virtue of the block-Lanczos convergence properties, these distributions are described correctly even if the underlying discrete states are not fully converged individually. The accurate convergence of the spectral envelope is reached after performing much fewer iterations than one would need for the exact calculation of the eigensolutions.

Obviously, the number of block-Lanczos iterations necessary for convergence on the spectral envelope depends on the desired resolution of the spectrum. The envelope is constructed by convoluting each of the calculated discrete lines with a Gaussian or Lorentzian function of given full width at half-maximum (FWHM) and then adding up all contributions to determine the envelope. The smaller the selected FWHM, the higher the number of block-Lanczos iterations needed to converge on the spectral envelope. To simulate an ionization or double ionization spectrum with its limited experimental resolution and additional vibrational broadening effects, FWHMs of several electron volts are often sufficient. For such large values the typical number of block-Lanczos iterations is very small. In our case, in order to describe the continuous distribution around a dense line bundle describing a decay and, in particular, to estimate decay widths of the order of 0.1–0.01 eV, we need a higher degree of convergence. To illustrate this, we have plotted in Fig. 1 the calculated spectral envelopes of three of the dense line bundles describing the decay of inner-valence vacancies in the double ionization spectrum of the HF trimer for increasing numbers of block-Lanczos iterations with a FWHM of 0.05 eV. Converged spectral envelopes are obtained already after 300–400 iterations. After reaching convergence of the spectral envelope for a selected degree of accuracy (e.g., FWHM =0.05 eV) the decay width is estimated by fitting the spectral envelope around each group of densely clustered lines (representing a decaying state) by a Lorentzian function. Its position and width reflect the energetic position and inverse lifetime of the decaying state, respectively. This procedure will be further discussed in detail later on.

C. Basis sets

It is of great importance to consider the influence of the basis set used in the calculations of the decay phenomena. We have primarily used a correlation-consistent Dunning basis set of double-zeta quality including polarization functions and augmented by a set of diffuse functions on each of the fluorine centers (aug-cc-pVDZ). This basis set is a compromise between feasibility of calculations for the larger systems and accurate description of the decay phenomena. Additionally, we have also performed extensive basis set studies to investigate the influence of the basis functions on the quality of the description of the decay in the spectra.
From numerous calculations of valence ionization\(^{46,49}\) and double ionization spectra\(^{52,53}\) we know that standard Gaussian basis sets of double- or triple-zeta quality including at least one set of polarization functions allow the correct description of at least the principal features of the spectra for typical molecular systems. Because of the dominance of main configuration contributions (1h or 2h) in the outer-valence region of the spectra, the basis set dependence is less pronounced here than in the inner-valence region, where excited configurations (2h1p or 3h1p) including excitation of an additional electron into a virtual orbital are very important. To describe these excitations correctly, additional Rydberg or diffuse functions can be helpful.

Once electronic decay of the excited states becomes possible, the influence of the basis set on the description of the spectra has to be considered even more carefully. This influence is easily anticipated since we try to simulate a continuum of states with a finite discrete basis set. The energy region of the continuum we have to model depends on the possible energies of the outgoing Auger electron in the decay and, therefore, on the possible excess energies of the process. The strategy is now to include Gaussian functions with the appropriate exponents in the basis set so that they allow us to describe the discrete states that fall into this excess-energy region (typical values between 5 and 15 eV) in the continuum of possible decay channels of the clusters. The more, and therefore denser, we place there functions, the higher is the probability to hit all the relevant energy differences that correspond to possible decay channels. In the case that there are only a few decay channels available, this task is very difficult to accomplish. For the larger molecular clusters, however, where one finds dense lying decay channels, it is possible to describe the decay using fewer additional diffuse functions with an accuracy sufficient to estimate the decay widths: A single basis function can serve to describe the

FIG. 1. Convergence of the block-Lanczos pseudospectrum (spectral envelope) on the line bundle distributions describing the decay of selected inner-valence doubly ionized states of the (HF)\(_3\) cluster. Two separate energy regions are shown, corresponding to fluorine (2s, 2p) and (2s, 2s) ionizations. The spectral envelope results from the convolution of the computed stick spectrum with Gaussian functions of 0.05 eV FWHM. The calculated discrete states are plotted only for the highest number of block-Lanczos iterations, and indicate the computed F one-site 2h populations.

FIG. 2. Basis set dependence of the computed line bundles describing the decay of inner-valence vacancies in the double ionization spectrum of the (HF)\(_3\) cluster. Upper panels: cc-pVDZ basis set, central panel: aug-cc-pVDZ basis set with one additional set of diffuse functions (s, p, d on fluorine; s, p on hydrogen). Lower panels: cc-pVDZ basis set with three additional sets of diffuse functions on the fluorine centers constructed by the method of Kaufmann et al. (Ref. 54). The vertical bars indicate the individual computed transitions of height proportional to their F one-site 2h populations.

FIG. 3. Neutral ground state structures of the systems (HF)\(_n\) (n=1–4) resulting from experimental data and \textit{ab initio} calculations (Refs. 25–28). (Nuclear distances are given in angstrom, angles in degree.)
electron emitted in several decay channels. The additional Gaussian functions we introduce to model the continuum in a selected energy region can be constructed using the method of Kaufmann et al.\textsuperscript{54} In this method the exponents of a sequence of diffuse functions are constructed by maximizing their overlap with a series of Slater-type functions which constitute a basis for Laguerre–Slater functions. These functions then span low energy continuum solutions in a limited radial interval around the atomic center.

However, the potential to extend the basis sets in a systematic way is very limited. One reason for this limitation is due to linear dependencies arising when trying to place functions in a narrow energy region. Another is the fast growing demand on time and disk space resources with increasing number of basis functions. Fortunately, the continuum electrons with somewhat higher excess energies are already well described with the Gaussian functions that are included in the standard basis sets. This is, for example, the case for the double vacancies with mainly F(2s,2p) character in the HF trimer. Moreover, we have found that it suffices to use standard basis sets with one set of diffuse functions per atom, such as the aug-cc-pVQZ basis, in order to arrive at a qualitative description of the decay processes in the larger clusters, i.e., in HF trimer or larger. In our basis set studies we have seen that the inclusion of further diffuse basis functions does not change the decay widths appreciably. In most cases only the density and/or location of states within the distribution describing the decay is influenced.

To illustrate the influence of diffuse basis set functions on the computed line bundles describing the decay, we have reported in Fig. 2 the computed inner-valence region of the double ionization spectrum of the HF trimer. Traces of the line bundles can already be seen when the basis set cc-pVDZ\textsuperscript{51} is used, which does not contain diffuse functions. An eye-catching strong enhancement of the bundles is observed for the basis set aug-cc-pVQZ which contains one set of diffuse functions per atom. We further augmented this basis set by adding several sets of diffuse functions obtained via the above-mentioned method of Kaufmann et al. to the fluorine centers. A typical result is depicted in the lower panels of Fig. 2, where three additional sets of diffuse s, p, and d functions have been added to the cc-pVDZ basis set. It is seen that the decay width does not change substantially any more. The results reported in the forthcoming sections have been determined using the aug-cc-pVQZ basis set. In relevant cases we have checked the stability of the results by augmenting this basis set by diffuse functions as described above. In this way we hope to have arrived at reliable estimates for the spectral envelopes from both the points of view of block-Lanczos iterations and basis set convergence.

III. RESULTS AND DISCUSSION

In a recent investigation\textsuperscript{24} we have proposed an intermolecular Coulombic decay mechanism for highly excited electronic states of weakly bound systems like molecular clusters. This decay mechanism is in sharp contrast to the well-known Auger decay in molecules which is intra-atomic in nature. To further illustrate the decay of highly excited states of molecular clusters involving intermediate-shell vacancies, we have chosen the small \((\text{HF})_n\) clusters \((n=2–4)\) as a first example. In the last several years the neutral ground state structures of these hydrogen-bonded systems have been thoroughly investigated theoretically using large scale \textit{ab initio} computations\textsuperscript{25–28} and partly also experimentally with various spectroscopic techniques.\textsuperscript{55–60} Figure 3 shows the resulting neutral ground state structures of the \((\text{HF})_n\) systems \((n=1–4)\). To the best of our knowledge there are no investigations on highly excited electronic states of these systems available.

A. Singly Ionized states

In order to analyze the singly ionized states of the clusters and their decay, we have calculated the valence ionization spectra with the ADC(3) approximation scheme for the evaluation of the one-particle Green’s function.\textsuperscript{38} The block-Lanczos diagonalization algorithm has been used to approximately extract the eigenvalues and eigenvectors of the large ADC eigenvalue problem. The calculated ionization spectra for the systems \((\text{HF})_n\) \((n=1–4)\) are shown in Fig. 4.

The ionization spectrum of the HF molecule has already been calculated\textsuperscript{61} and compared to the available experimental data in the literature.\textsuperscript{62} The valence spectrum is well separated in two distinct regions: the low-energy part \((16–21\text{ eV})\) consists of two main peaks which result from ionization out of the outer-valence \(1\pi\) and \(3\sigma\) orbitals, respectively. These orbitals have essentially F 2p character and—as the two single lines in the spectrum indicate—the ionization in this energy region can be qualitatively well described in the independent-particle picture. The higher-energy region in the spectrum \((36–45\text{ eV})\) results from ionization out of the inner-valence \(2\sigma\) orbital with mainly F 2s character. The single line one would expect in the independent-particle picture is split in two ‘‘main peaks’’ at about 40 eV and a weak satellite structure at about 43 eV. The observed line splitting is due to a partial breakdown of the independent-particle picture in the inner-valence region. This well-known effect,\textsuperscript{50} which is typical for the inner-valence spectra of many molecular systems, is due to the quasidegeneracy of inner-valence single-hole configurations with higher excited configurations involving outer-valence electrons. These interactions lead to a redistribution of the contributions of the inner-valence single-hole configurations over several or even many states in the spectrum and destroys the simple picture of main lines corresponding to 1h configurations with a series of satellites corresponding to 2h1p configurations following at higher energies.

Despite the observed traces of the breakdown effect, the most important result is that we observe no sign of decay of any of the states which build up the valence ionization spectrum of the HF monomer. We shall now show in detail, discussing the results for the HF clusters, that the Auger decay of an excited state should be visible in the spectrum as a dense distribution of lines that cluster around the decaying state, simulating a continuous intensity distribution. This effect is due to the coupling of the configurations that represent the decaying state to higher excited configurations that lie already in the continuum. We begin with the very clear instance of this phenomenon observed in the calculated inner-
valence ionization spectrum of the HF trimer. The HF trimer has a cyclic $C_{3v}$ symmetric ground state structure with each of the HF units acting simultaneously as H donor and H acceptor in the hydrogen bonds (see Fig. 3). Because of the equivalence of the monomer units, the envelope of the calculated valence ionization spectrum of the HF trimer is very similar to the one of the HF monomer with broadened peaks that are shifted to higher energies. As seen in Fig. 4, the outer-valence region now contains six states: four which result from the splitting of the 1p levels, and two from the splitting of the 3s levels of the interacting monomer units. Since these splittings are small compared to the energy separation of the 1p and 3s levels of HF, the appearance of the outer-valence spectra of $\text{HF}_n$ and HF is similar. In contrast to these similarities, the line structure in the inner-valence region, resulting from F 2s derived states, has changed drastically. It no longer shows distinct main lines with some satellites, but dense bundles of lines which resemble continuous distributions and cluster around the positions of the corresponding monomer peaks shifted to higher IPs by about 1.5–2.0 eV. Let us now analyze in detail what is the origin of such a large and fundamental difference in the behavior of the HF monomer and trimer. Subsequently, we shall turn to the interpretation of the ionization spectra of the HF dimer, with its open-chain structure, and of the cyclic HF tetramer. The dimer will be seen to fit into the main picture of the process in a much more obvious way than it would do at this point of discussion (see Fig. 4).

In order to confirm the proposed interpretation of the appearance of dense line bundles in the inner-valence region of the ionization spectrum of the HF trimer as indications of the decay of the inner-valence vacancies, we have also calculated the manifold of dicationic states in the valence region of these systems. In general, only dicationic states with lower ionization potentials than the singly ionized states are possible final states of an Auger decay of the latter. In the case when there are no dicationic states with lower energy available, the decay is impossible; in other words, there are no open channels for autoionization. In Fig. 5 we have plotted the valence ionization spectra of the $\text{HF}_n$ systems ($n=1–4$) against the calculated double ionization spectra. The comparison of the energy positions of the cationic and dicationic states for the HF monomer shows clearly that no Auger decay is possible for the valence singly ionized states in this system for energetic reasons: The lowest dicationic state is much higher in energy (by 5 eV) than the highest cationic state. The channels for autoionization are closed. This situation is typical for the valence region of many molecules in general but changes drastically when going to the weakly bound molecular clusters. By inspection of the energy positions of the singly ionized versus doubly ionized states in the calculated spectra of the small $\text{HF}_n$ clusters ($n=2–4$) one can clearly observe the appearance of doubly ionized states which are drastically lowered in energy compared to the singly ionized states.

We can understand this general effect in the weakly bound clusters by analyzing the hole distribution of the dicationic states with a two-hole population analysis. Using this analysis we detect a strong localization of the holes in all the dicationic states of the clusters. In fact, the states can be
cleanly classified in two groups: those where both holes are localized at the same monomer unit (one-site states) and those with each of the two holes localized on a different monomer unit (two-site states). The one-site states are in general only very slightly shifted in energy compared to the monomer, where this is the only possible type of state. The shift is more pronounced in the dimer owing to the asymmetry of the two constituent units. We notice here a splitting of all monomer lines, arising from one-site localization of the two holes on the two differently behaving HF units (H donor, H acceptor). Two-site states, on the other hand, can only appear in the clusters, and exactly this kind of state is responsible for the dramatic lowering, by as much as 10 eV, of the double ionization threshold in the clusters compared to the HF monomer. Of course, this lowering results from the much reduced hole repulsion in the two-site states. The shifts of the two-site doubly ionized states to lower energies is so large that already for the HF dimer some of these states lie lower in energy than the inner-valence singly ionized states. This opens autoionization channels for the inner-valence singly ionized states. This opens autoionization channels for the inner-valence singly ionized states, whereas the outer-valence states are not affected at all. The major change in this general situation when going from the HF dimer to the larger clusters is the increase in number and density of open decay channels leading to doubly ionized states. The largest change is observed between (HF)$_2$ and (HF)$_3$. The number of neighboring HF units increases from one unit in the open-chain dimer to two units in the cyclic trimer structure. The increase in the density of states is smaller when going further to the HF tetramer, and the number of nearest neighbors stays the same for each of the monomer units. With this information in mind we can now return to the analysis of the cluster ionization spectra in Fig. 4.

Because of the asymmetric hydrogen bond in the HF dimer two different HF-monomer units result, and the calculated valence ionization spectrum shows a line splitting more pronounced than that found in the spectra of the trimer and tetramer. The degeneracy of the $\pi$ orbitals of the monomer units is lifted and, as expected in the independent-particle picture, the outer-valence region of the spectrum consists of six lines resulting from ionization out of the six orbitals with mainly F 2$p$ character. In the inner-valence region we observe four “main lines” resulting from a split of each of the two states in the monomer. But in contrast to the monomer spectrum, additional satellite structures appear, grouped around the four “main states” in a characteristic way. These
structures can be interpreted, in analogy to the results for the HF trimer, as weak signs of the decay of the inner-valence vacancies in the dimer. The effect is very weak here due to the small number of open decay channels in the dimer (see Fig. 5), which makes the description of the decay with a finite discrete basis set particularly inappropriate.

The calculated ionization spectrum of the cyclic HF tetramer with $C_{4v}$ symmetry is very similar to the spectrum of the cyclic HF trimer, as is seen by comparing the spectral envelopes, and this is easily explained on the basis of the similarity between the basic structures of the two systems (see Fig. 3). Both clusters are built up by a cyclic arrangement of rotationally equivalent molecular units, each acting as a H donor and H acceptor simultaneously. A closer look at the discrete line structure from which the spectral envelope is derived, however, reveals even more pronounced bundles of line structure in the inner-valence part of the tetramer’s spectrum, with higher density and larger widths than in the HF trimer. In addition, the centers of these distributions are clearly shifted to higher energies in the HF tetramer. These observations fit nicely into the global picture we arrived at by inspecting the doubly ionized states of the systems. The higher density of available open decay channels makes the decay in the tetramer even fiercer than in the trimer.

The crucial general consequence that we can draw from these results is that, in contrast to the monomer, the Coulombic decay of the inner-valence vacancies in the clusters is possible. Because of the existence of low-lying doubly ionized states with holes localized on different monomer units, the decay has to be intermolecular, leading to two-site final dicaticionic states. Like in the monomer itself, the intramolecular decay to one-site final dicaticionic states is energetically not possible.

Where does the large efficiency of the decay of the inner-valence vacancies come from? As we shall better appreciate later on, the decay widths are comparable to, or even larger than, those in normal Auger decay of core levels. This fact may be surprising at first, because we have just seen that the decay is energetically only possible if the final state vacancies are localized on different monomer units, while, for normal Auger decay, it is well known that the decay is efficient only for those final states that are localized at the same site as the initial core vacancy. This apparent contradiction can be removed by adopting a simple picture in which the leading term for the Coulombic decay rate is, according to the golden rule formula, proportional to

$$\left| \int k(r)v_{i}(r') \frac{1}{|r-r'|} v_j(r)v_j(r')drdr' \right|^2.$$  

Here, $v_i(r)$ is the orbital with the initial vacancy, $k(r)$ the scattering wave function of the ejected electron, and $v_j(r)$, $v_j'(r)$ are the orbitals with the final vacancies. Because of the manifold of possible final vacancies one has to sum over all energetically open decay channels. In normal Auger decay the orbital with the initial vacancy is a core orbital which is very localized at one atomic center. Because of the large energy gap between core and valence orbitals, the energy of the ejected electron is large (short wavelength). Therefore, the Coulomb matrix elements for the decay are large, i.e., the decay is efficient, only if both final valence vacancies $v_j(r)$ and $v_j'(r)$ are localized at the same atomic center where the initial core vacancy is situated (intra-atomic mechanism). The situation is different if the initial vacancy is in the inner-valence region. Now, the energy gap between initial and final vacancies is much smaller (typically 5–15 eV in the molecular clusters) and therefore the ejected electron is slower (longer wavelength) than in normal Auger decay. This fact, in combination with the less localized initial inner-valence vacancy, gives rise to acceptably large Coulomb matrix elements also in the case when one of the final vacancies $v_j'(r)$ is localized at the same center as the initial vacancy and the other vacancy $v_j(r)$ is localized on a neighboring monomer unit. This situation results in a manifold of possible decay channels for the molecular clusters.

The proposed intermolecular Coulombic decay mechanism for the inner-valence vacancies in the clusters can be summarized as shown schematically in Fig. 6: An outer-valence electron at the monomer unit with the inner-valence vacancy drops into this vacancy and the resulting excess energy of the process is used to eject one electron from the outer-valence shell of a neighboring monomer unit. This process can be viewed as an ultrafast energy transfer between the monomer units in the excited cluster. Since the process results in a weakly bound cluster with two positively charged monomer units, the Coulomb repulsion can be expected to

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**FIG. 6.** Schematic representation of the proposed intermolecular decay mechanism of the inner-valence vacancies of the molecular clusters (b) and the energetically forbidden decay of inner-valence vacancies in the corresponding isolated monomer molecule (a).
lead to a fragmentation of the system into specific fragmentation products.

In order to obtain a crude estimate of the typical decay widths and hence of the lifetimes of the inner-valence vacancies in the clusters, we have analyzed the dense line bundle distributions of the HF-trimer spectrum in more detail. To this end we have performed extensive basis set studies to ensure that we include all the essential contributions to the decay widths with our finite Gaussian basis set, as discussed in Sec. II C. Each of the two dense line distributions at about 40 and 44 eV in the trimer spectrum of Fig. 4 consists of two overlapping distributions that are due to $^2A'$ (at higher energy) and $^2E'$ states (at lower energy). The two line bundles at about 40–41 eV overlap to a lesser extent and can be quite accurately separated while, since the calculations of the spectra are performed in an Abelian subgroup and because of the incomplete convergence of the block-Lanczos diagonalization, it is practically impossible to distinguish between the two types of states in the distribution at higher energy (about 44 eV). Two Lorentzian functions have been used to fit the envelope of the discrete line distributions for the $E'$ and $A'$ states at about 40 eV. The two tightly overlapping distributions at higher energy are fitted with a single Lorentzian curve to simulate a continuous intensity distribution. The vertical bars indicate the individual computed transitions of height proportional to their pole strength.

B. Doubly ionized states

Doubly ionized states of molecular clusters can, in principle, decay via the intermolecular decay mechanism like the singly ionized states do. To illustrate this effect in a systematic way we have calculated the valence double ionization spectra of the small (HF)$_n$ clusters ($n = 2$–4) with the ADC(2) method and compared the results with the well-known Auger spectrum of the HF molecule.

As we have earlier discussed, a strong localization of the electron vacancies, typical for weakly bound systems, takes place in the dicatonic states of the HF clusters. The two-hole population method allows us to analyze the charge density of the computed states and thus, in this case, easily classify them as one-site states (having both holes essentially localized at the same monomer unit) and two-site states (where each hole resides on a different monomer unit). The usefulness of this analysis can hardly be overemphasized for the understanding of the nature, spectroscopic and dynamic properties of the dicatonic states which depend strongly on the hole distribution. We have shown how this method enabled us to explain the decay mechanism for the singly ionized states, revealing its intermolecular character dictated by the two-site nature of the charge distribution in the dicatonic states energetically reachable through decay.

For reasons of simplicity we have restricted our further studies to the decay of those doubly ionized states where both holes are strongly localized on the same monomer unit (one-site states). These are the states which are preferentially populated in the normal Auger decay of core ionized systems because of the intra-atomic nature of the decay mechanism for inner-shell vacancies. This fact offers the possibility to simulate the essential features of the intensity distribution in Auger spectra in a simple way, by plotting only the one-site component of the total 2h pole strength which is localized at the site of the initial core-hole. A double vacancy can itself undergo a decay similar to the Auger decay of a single vacancy provided that decay channels are energetically open. If the two vacancies are localized on the same monomer unit this decay is expected to be much stronger than the decay of a single vacancy. In a simple picture the response of the outer-valence orbitals to the two vacancies should be four times stronger than the response to a single vacancy.

Figure 8 shows the calculated fluorine one-site spectra of the (HF)$_n$ ($n = 1$–4) systems. Because of the single F center in the HF monomer, we can view the one-site spectrum as a direct estimate of the intensity distribution in the F(KLL) Auger spectrum of the HF molecule. The F(KLL) Auger spectrum of HF is well known experimentally and also theoretically. It consists of three distinct parts with the first peak structure between 40 and 60 eV consisting of six main lines which describe the double ionization out of F 2p orbitals and can thus be denoted as F(2p, 2p). The peak structure between 67 and 90 eV corresponds to doubly ionized states with essentially F(2s, 2p) character, i.e., one inner-valence F 2s and one outer-valence F 2p vacancy. It is built up by four main lines and some weak satellite structures at about 83 eV. The high energy part of the valence spectrum
shows a peak structure between 100 and 110 eV with one main line at about 100 eV and some weak satellite structures at higher energies. These lines correspond to doubly ionized states with mainly F$^{2+}$ contributions. The calculated spectrum of the HF molecule shows no sign of a further decay of the dicationic states. In analogy to the case of singly ionized states, the decay of doubly ionized states should be indicated in the spectrum by the appearance of dense line distributions simulating the width of the decaying states in the finite basis set representation. This finding has been confirmed in extensive basis set studies including large sets of diffuse functions to simulate the outgoing Auger electron in a possible decay process. The reason for the lack of decay channels in the HF dication becomes obvious when looking at the energetics of a possible decay. Using the ADC(2) method for the evaluation of the three-particle Green’s function$^6$ we have calculated the manifold of triply ionized states. These states are the potential final states for the decay of the dicationic states by electron emission. We found the lowest triple ionization potential (TIP) for HF to be about 100.1 eV. This value is too high to allow for autoionization.

The situation changes drastically when moving to the molecular clusters. The calculated spectra of the small (HF)$_n$ clusters are depicted in Fig. 8. As in the calculation of the ionization spectra of these systems, the neutral ground state structures have been used. The spectral envelope of the F one-site spectrum of the HF dimer divides the spectrum in three distinct regions. This envelope, and in particular the underlying discrete line structure, show important differences from the monomer. As already discussed in Sec. III A, the two monomer units have a different character: one unit acts as a H donor, the other as H acceptor in the intermolecular hydrogen bond. Due to the strong hole localization of all the dicationic states, the spectrum thus consists of two superposed distinct spectra. These two contributions, namely, the states with both holes localized on the H-donor unit and the states with both holes localized on the H-acceptor unit, are shifted against each other by about 5 eV.
the former states lying at lower energies. This shift persists for all states throughout the whole spectrum and is mainly due to electrostatic interactions. These interactions and their detailed impact on the appearance of the spectra are interesting by themselves but are not analyzed further here. What interests us now is the appearance of bundles of line fine structure around the main peak positions lying in the inner-valence region (DIP > 65 eV). This effect is due to the coupling of the F one-site double vacancies (2h configurations) on a monomer unit to excited configurations (3h1p) where one of the three vacancies is on a neighboring monomer unit. Because of the possible separation of the three holes on different units, the triply ionized states are substantially lowered in energy compared to the HF molecule. Thus, autoionization of the doubly ionized F one-site states to triply ionized F two-site states is now possible because there are TIPs of the cluster which are lower in energy than DIPs. The lowest TIP of the dimer with two holes on the same monomer unit and the third on a neighboring unit is estimated to be about 65 eV. This, and other multisite triple ionization channels, are open for the states in the spectrum which possess one or two inner-valence vacancies. The line bundles observed in the spectrum above 65 eV (see Fig. 8) simulate the continuous distributions of the decaying F(2s,2p) and F(2s,2s) states. In our finite basis sets the outgoing electron (continuum electron) is roughly represented in 3h1p configurations that include the excitation of an electron to diffuse orbitals. Interestingly, and in total agreement with the energy layout of the dimer’s doubly ionized states, we find somewhat more pronounced decay widths for the one-site states of the H-acceptor unit compared to those of the H-donor unit. This should be related to the larger number of energetically open decay channels available for the one-site states localized on the former unit.

Before continuing with the discussion of the spectra of the HF clusters we would like to briefly describe the mechanism governing the decay of the dicationic states, sketched in Fig. 9. The mechanism is, in principle, closely related to the one discussed for the singly ionized states in Fig. 6 but involves many more kinds of possible initial and final states. For reasons of simplicity we have restricted our presentation to initial states with one vacancy in the inner- and the other in the outer-valence region of the same monomer unit (one-site states). Other situations can easily be anticipated. The initial state can—in analogy to a single inner-valence vacancy—decay in the following way: An outer-valence electron at the doubly ionized monomer unit fills the inner-valence vacancy and the resulting excess energy of the process is used to eject an outer-valence electron from a neighboring monomer unit. The process leads to a triply charged cluster with two holes localized on the monomer unit of the initial vacancies and the other on a neighboring unit, and is approximately described in the ADC(2) calculations by two-site 3h1p configurations.

It is easy to see now that, starting with the trimers, there appear additional possibilities for the intermolecular decay. Two selected examples which can be expected to be particularly important are presented in Fig. 9. In both examples, the monomer unit with the initial vacancies interacts with two neighbors. In the first example this interaction leads to triply charged three-site states [described via three-site 3h1p configurations in the ADC(2) calculations]. In the second example the interaction leads—after simultaneous emission of two electrons—to quadruply charged three-site states. The latter process cannot be properly described by the second-order ADC scheme since the (three-site) 4h2p configurations which would be required to approximate the final states appear in fourth order. Because of their weak Coulomb repulsion, three-site triply ionized states appear at lower ionization potentials compared to the corresponding two-site states and could, on energy grounds, constitute an important decay channel. On the other hand, the corresponding decay matrix elements should be smaller for three-site than for two-site states, which reduces the efficiency of the decay in the first example. In the second example, the three-site quadruply ionized states appear at high energies and could play a detectable role only in the highest energy region of the inner-valence ionization.

The F one-site spectrum of the cyclic HF trimer shown in Fig. 8 exhibits a very similar envelope to that of the HF
monomer, with three distinct areas corresponding to states derived from \((2p,2p), (2s,2p)\) and \((2s,2s)\) double hole configurations with increasing energy. Inspecting the discrete state distribution, one observes well separated extremely strong and broad line bundles in the \((2s,2p)\) and \((2s,2s)\) regions of the spectrum. The widths of these distributions are much broader than the ones observed in the HF dimer. This effect can be attributed to more than one factor. First, like in the dimer, we have open decay channels leading to two-site \(3h\) states. These states are comparable in energy to those of the HF dimer with an estimated onset of TIPs of about 65 eV, but their number and density is much larger because of the larger number of neighboring atoms for each monomer unit. Second, as discussed above, a new type of final \(3h\) states is present in the trimer which greatly enhances the number of possible decay channels. In these \(3h\) states each of the holes is localized on a different monomer unit (three-site states). We estimate the onset of these decay channels to be at energies slightly higher than 60 eV. The coupling matrix elements of these states to the initial two-hole one-site states are expected to be smaller than for the three-hole two-site states. Nevertheless, since many of the three-site states are available, their presence may indeed noticeably shorten the lifetime of the decaying states. The \(F\) one-site double ionization spectrum for the cyclic HF tetramer is, as expected, very similar to the one of the HF trimer with somewhat broader line bundles. The major difference between the trimer and tetramer is the larger number and density of possible decay channels available in the latter because of the larger number of monomer units. For each monomer, however, the number of neighboring units and also, approximately, the relative energy positions of the two-site \(3h\) states remain unchanged.

The decay widths for the double vacancies of the HF trimer have been estimated in a similar way to that described above for the single vacancies. Again, by varying the basis set we were able to ensure that the major contributions to the decay widths are included. We have selected the states with \(A'\) and \(E'\) symmetry in the inner-valence region between 78 and 102 eV for further analysis. In this region we observe three distinct distributions of dense line bundles centered around 79, 82 and 100 eV, respectively (see Fig. 8). The two distributions at lower energies are due to the decay of double vacancies with mainly \(F(2s,2p)\) character; the high energy distribution corresponds to the decay of double vacancies with mainly \(F(2s,2s)\) character. The spectral envelope around the line distributions is converged as discussed in Sec. II B and shown in Fig. 1. To determine the individual decay widths, a Lorentzian function is used to describe the broadening of each decaying state, by fitting the converged bundle envelope.

Our analysis of the line bundle at 100 eV shows that this describes the decay of three quasidegenerate states with mainly \(F(2s,2s)\) character. These states correspond to double vacancies localized on the three monomer units. For each of the decaying states a Lorentzian curve with a FWHM of 0.20–0.25 eV (lifetime of about 2.6–3.3 fs) describes the distribution best. These fitted Lorentzian curves are plotted in Fig. 10. The corresponding distributions at lower energies for the \(F(2s,2p)\) derived states (at 79 and 82 eV) are best described with Lorentzian curves of about 0.18–0.20 eV FWHM (lifetime of about 3.3–3.6 fs). Because of the finite basis sets used and the high energies of the states, these values should be viewed only as crude estimates of the decay widths. As expected, the lifetimes of the double vacancy states is shorter than those of the single vacancy states discussed in Sec. III A. Furthermore, double vacancies in the \(2s\) shell tend to live shorter than those with one hole in the \(2s\) and one in the \(2p\) shell.

**IV. SUMMARY AND CONCLUSIONS**

In the present work we have clearly shown that—in sharp contrast to molecules—excited electronic states of molecular clusters with inner-valence vacancies can efficiently decay via the intermolecular Coulombic mechanism predicted in Ref. 24. This effect has been investigated by analyzing the ionization and double ionization spectra of several molecular clusters, calculated with large-scale \textit{ab initio} Green’s function methods. As explicit examples to illustrate the decay, we have selected here small HF clusters. In the proposed mechanism, an outer-valence electron at the monomer unit that carries the initial inner-valence vacancy drops into this vacancy and the resulting excess energy is transferred in an ultrafast process to a neighboring monomer unit where it is used to eject an outer-valence electron. The process leads to a cluster with increased number of charges, distributed over neighboring monomer units. A fragmentation of the cluster because of the resulting Coulomb repulsion is very likely.

The intermolecular decay of the inner-valence vacancies is possible in the clusters because of the substantial energy lowering of the final states of the decay relative to the initial states. This effect is due to the fact that low lying states of multiply charged weakly bound systems exist where the
electron vacancies are strongly localized on different constituent subunits. This leads to the opening of autoionization channels which are closed in the isolated monomer molecules.

The observed high efficiency of the decay, which results in decay widths that are comparable to, or even larger than, those typical for core vacancies, is due to two main factors. One factor is the non-negligible Coulombic decay matrix element expected for relatively small kinetic energies of the emitted electron and the final vacancies localized on neighboring monomer units. The other factor is the very large number of potentially available decay channels in the clusters because of the many possible ways to distribute the final vacancies in the systems.

We would like to mention that the proposed intermolecular decay mechanism is very general in nature. We have shown here that it is present in singly and doubly ionized states and we expect it to be active in neutral excited states as well. Furthermore, it should apply to all types of weakly bound systems. We have performed additional calculations on different systems that are not presented here and the results confirm the general picture of the decay. The systems studied include small H₂O clusters, mixed H₂O-HF clusters and also rare gas systems like Ar₃.

The theoretical description of the decay of highly excited states in clusters is not feasible with ab initio scattering methods. We have therefore analyzed the decay phenomena through a careful study of the efficiently calculated ionization and double ionization spectra. These spectra are themselves of interest, since very little is known on the ionization and Auger spectra of clusters and the corresponding cationic and dicationic states. For the experimental detection of the intermolecular decay methods other than ionization and Auger spectroscopy should be adopted. The limited resolution and other effects like vibrational broadening make the detection of the decay in the spectra difficult if not at all impossible. A more promising method to analyze the intermolecular decay experimentally would be, for instance, the coincidence measurement of the Auger electron and the primary photoelectron as a function of the photon energy. Above some threshold energy, coincidences should be detected for the molecular clusters but not for the monomers themselves.

The investigations we have presented so far are only suited to give a qualitatively correct description of the intermolecular decay process. In order to gain a deeper insight into the mechanism and its determining factors, further studies are necessary. For these, the existing methods have to be extended in order to enable a more detailed analysis of the states involved in the decay process. Also, the extension of the investigations to other types of highly excited states, e.g., neutral states, is desirable.

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