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Direct Observation of the Dynamics of Electronic Excitations in Molecules and Small Clusters

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Femtosecond time-resolved photoelectron spectroscopy is applied to study relaxation paths of excited states of mass-selected negatively charged clusters. As a first example, the lifetime of an excited state of the carbon trimer anion is measured directly. In addition, the mechanism of the decay, i.e., the configurations of the participating electronic states, is determined from the photoelectron spectra. In general, this method can be used to study all kinds of electronic excitation and relaxation processes in mass-selected nanoparticles.

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The development of femtosecond lasers has made it possible to study fast dynamical processes in atoms, molecules, and condensed matter [1,2]. A further step forward was the combination of femtosecond lasers with photoelectron spectroscopy [3–6], which allowed the direct observation of reorganization of the electronic structure after photoexcitation. In such an experiment, the pump pulse triggers dynamical processes such as single particle excitations or fragmentation, and with the UV-probe pulse a photoelectron spectrum is recorded at a given delay. The series of photoelectron spectra reveals the time evolution of the system with increasing pump/probe delay. The method has been successfully used to study fast processes in molecules [3,4] and solids [5,6]. In the present paper, we describe the application of this technique to study the decay of electronic excitations in mass-selected nanoparticles and clusters, where the time scales and decay mechanisms might be different from the bulk properties as a result of the finite size of the particles.

For small aggregates with a well-defined number of atoms (clusters), it is known that the properties may vary with each additional atom. Therefore, for experiments on clusters, mass separation is essential. One successful method used for the study of the ground state electronic structure of clusters is photoelectron spectroscopy of negatively charged ions [7–9]. The anions can easily be mass separated. To compensate for the low target density of the anion beams, an UV laser is used as an intense light source. Since photoelectron spectra contain information about the initial and final states, data about the electronic structure of negative and neutral clusters are obtained. Recently, this technique has been combined with femtosecond lasers to study fast fragmentation processes in molecules and clusters such as I_2^- [10], $I_2^-(Ar)_n$ [11], and Au_3^- [12].

In the present paper, we present the application of this technique to observe the time evolution of electronic excitations in mass-selected clusters. As a first example, we have studied the decay of an excited state of the carbon trimer anion C_3^-. This state had been detected first as resonance in the photodetachment cross section and it was assigned to a Feshbach resonance, which decays by electronic autodetachment [13]. Taking advantage of the new technique, we determined the lifetime of this excited state directly. In addition, the photoelectron spectra reveal the nature of the participating electronic states unambiguously. Especially, it was possible to directly determine the neutral "parent state" (see below) by detachment from the excited resonance proving the assignment to a Feshbach resonance. This example demonstrates the power of the method for studying electronic excitations in clusters and nanoparticles.

Details of the experimental setup have been described elsewhere [12,14,15]. The anions are generated directly in a pulsed arc cluster ion source and mass separated with a time-of-flight mass spectrometer. A selected bunch of anions is irradiated by the pump and probe laser pulses, and the kinetic energy of the detached electrons is measured using a "magnetic-bottle"-type time-of-flight electron spectrometer. The energy resolution is about 50 meV. The femtosecond laser pulses are generated by a mode-locked Ti-sapphire oscillator and amplified by a regenerative amplifier pumped by a 10 Hz Nd:YAG laser. The second harmonics of the output of the amplifier is used for the experiment with wavelengths between 390–402 nm (2.95–3.18 eV). The pulse is split into pump and probe pulse, which both have equal intensities ($\sim$1 mJ/cm^2) and pulse widths ($\sim$300 fs, measured by a single shot autocorrelator).

Figure 1 displays a comparison of two photoelectron spectra of C_3^- obtained with zero delay (trace 1) and with large delay (13 ps, trace 2) between pump and probe pulse. Both spectra have been obtained with a photon energy of $h\nu = 3.1$ eV. The spectra are normalized to the intensity of peak *A* located at a kinetic energy of 1.1 eV. Within the uncertainty of the experiment, this corresponds to the difference of the photon energy and the electron affinity of C_3^- (EA = 1.995 eV [16]) and peak *A* is assigned to direct detachment from the electronic ground state $^2\Pi_g$ of C_3^- with the configuration $3\sigma_u^2 1\pi_g^1$ [17] (only the uppermost occupied orbitals are given for simplification). The final state is the ground state $^1\Sigma_g^+$ of neutral C_3 with the

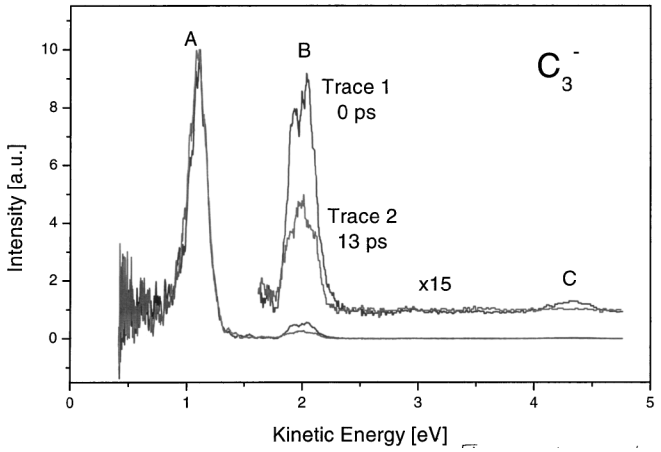

FIG. 1. Pump/probe photoelectron spectra of C_3^-, recorded at zero delay (trace 1) and at a delay of 13 ps (trace 2). The photon energy is 3.1 eV, the pulse widths of the pump and the probe laser pulses are 300 fs, and the intensities are about 1 mJ/cm^2. Peak *A* at 1.1 eV kinetic energy is assigned to the transition from the ground state $^3\Pi_u$ of C_3^- to the neutral ground state $^1\Sigma_g^+$ (processes I and II, see text and Fig. 2). Feature *B* at 2.0 eV is assigned to the transition from the $^2\Delta_u$ excited state of C_3^- to the $^3\Pi_u$ excited state of C_3 (process III). The weak feature *C* located at 4.3 eV is assigned to the transition from the $^2\Delta_u$ excited state of C_3^- to the $^1\Sigma_g^+$ ground state of C_3 (process IV).

configuration $3\sigma_u^2$ [17]. An identical peak has also been observed using nanosecond lasers [16].

Feature *B* is located at a kinetic energy of 2.0 eV and has not been observed previously. Its intensity with respect to the main feature *A* varies depending on the time delay between the two laser pulses. At zero delay, its intensity is about double compared to the case at large delay (>10 ps). This indicates that its origin might be due to a two-photon process. Then, the intensity should depend quadratically on the laser intensity. If both pulses are well separated, the intensity of peak *B* is the sum of contributions from both pulses: $I_{\mathrm{pump}}^2 + I_{\mathrm{probe}}^2 = 2I_0^2$ ($I_{\mathrm{pump}} = I_{\mathrm{probe}} = I_0$). For zero delay, in case of a two-photon process the intensity is double: $(I_{\mathrm{pump}} + I_{\mathrm{probe}})^2 = 4I_0^2$ in agreement with the experiment (Fig. 1). As a first idea, one would expect an increase of $h\nu = 3.1$ eV of the kinetic energy (corresponding to a kinetic energy of 4.3 eV) of an electron detached in a two-photon process. Such a peak is observed also, but with an extremely low intensity (peak *C* in Fig. 1) and will be discussed later. For the two-photon feature *B*, an increase of 0.9 ± 0.1 eV only is observed, and there are 2.2 eV of energy missing.

The photoelectron data can be understood if we assume the existence of an excited state of the anion located at an energy above the electron affinity. Such excited anionic states of atoms and molecules are well known as resonances in electron scattering experiments on neutrals [18,19]. There are two different types—shape resonances and Feshbach resonances [20,21]. For shape resonances, the electron is weakly bound in the potential of the neutral core by an angular momentum barrier and the decay occurs by tunneling through the barrier. The parent state is the state of the neutral atom (ground or excited state), and the decay of the shape resonance into this neutral state is energetically allowed. For Feshbach resonances, the electron is bound with a positive electron affinity to the neutral core, which must be in an excited electronic state (the parent state of the Feshbach resonance). Autodetachment occurs via electronic autodetachment, i.e., the neutral core relaxes into its ground state transferring the energy to the additional electron which is ejected [22]. In contrast to shape resonances, the decay occurs by concerted action of at least two electrons resulting in considerably longer lifetimes.

If, in the case of a Feshbach resonance, the excited anion is hit by a second photon, the additional electron is removed leaving the neutral in the excited parent state of the resonance. Since lifetimes of such resonances may be 1 ps or less, this two-photon process contributes significantly to the photoelectron yield only at very high photon intensities typically achieved using femtosecond lasers. This explains why feature *B* has not been observed in experiments using nanosecond lasers. The kinetic energy of such an electron is increased with respect to the electron from direct photodetachment by the energy of the second photon ($h\nu = 3.1$ eV) minus the excitation energy of the neutral parent state. Accordingly, the experiment allows the identification of the parent state from the positions of the two-photon peaks observed in the photoelectron spectra.

In our case, 2.2 eV (=3.1 eV − 0.9 eV) of energy are missing and should correspond to the excitation energy of the neutral parent state of the Feshbach resonance. Indeed, there is a known excited state of neutral C_3 with the proper energy: the first excited state $^3\Pi_u$ with an energy of 2.152 eV [16,17] and a configuration $3\sigma_u^1 1\pi_g^1$. We conclude that at zero delay electrons are detached from a Feshbach resonance of C_3^- with the parent state $^3\Pi_u$. Very likely, the additional electron of the Feshbach resonance occupies the uppermost bound single particle orbital (the $1\pi_g$ orbital), and we conclude that the configuration of the Feshbach resonance should be $3\sigma_u^1 1\pi_g^2$.

From photodetachment cross section measurements, several Feshbach resonances of C_3^- are already known [13]. Such a resonance is located at an excitation energy of 3.07 eV above the anion ground state. Since both this resonance and the photon energy of our femtosecond laser (= 3.1 eV) exhibit a considerable broadening, we identify this resonance to be the same as the one excited in our experiment. Based on calculations, this resonance of the detachment cross section has been assigned to the $^2\Delta_u$ excited state of C_3^-. This supports the analysis above based on our photoelectron data (Fig. 1).

The pump/probe photoelectron data reveal the full picture of the different processes induced by the laser radiation beyond the findings of the previous cross section measurements [13]. There are at least three processes

TABLE I. Energies and configurations of the electronic states of C_3^- and C_3 involved in the four different detachment processes [13,16,17]. The electron affinity of C_3 is 1.995 eV [16]. The energies of the excited states are given in eV with respect to the corresponding ground states.

Symbol States	Symmetry	Configuration	Energy (eV)
Anion			
C_3^-: ground state	$^3\Pi_u$	$4\sigma_g^2\,1\pi_u^4\,3\sigma_u^2\,1\pi_g^1$	0.00
C_3^{-*}: excited state (Feshb.[a])	$^2\Delta_u$	$4\sigma_g^2\,1\pi_u^4\,3\sigma_u^1\,1\pi_g^2$	3.07[c]
Neutral			
C_3: ground state	$^1\Sigma_g^+$	$4\sigma_g^2\,1\pi_u^4\,3\sigma_u^2$	0.00
C^*: excited state (parent[b])	$^3\Pi_u$	$4\sigma_g^2\,1\pi_u^4\,3\sigma_u^1\,1\pi_g^1$	2.152[d]

[a]The excited state $^2\Delta_u$ of C_3^- is a Feshbach resonance decaying by a two-electron autodetachment process into the neutral ground state.
[b]The $^3\Pi_u$ excited state of neutral C_3 is the parent state of the Feshbach resonance.
[c]From Ref. [13].
[d]From Ref. [16].

induced by the interaction with the laser beam (see also Table I and Fig. 2).

I. Direct detachment from the ground state (one-photon, peak *A*):

$$C_3^- + h\nu \rightarrow C_3 + e^- \qquad (E_{\rm kin} = 1.0\ {\rm eV}).$$

II. Resonant autodetachment (one-photon, peak *A*):

$$C_3^- + h\nu \rightarrow C_3^{-*} \rightarrow C_3 + e^- \qquad (E_{\rm kin} = 1.0\ {\rm eV}).$$

III. Direct detachment from the excited state (two-photon, peak *B*):

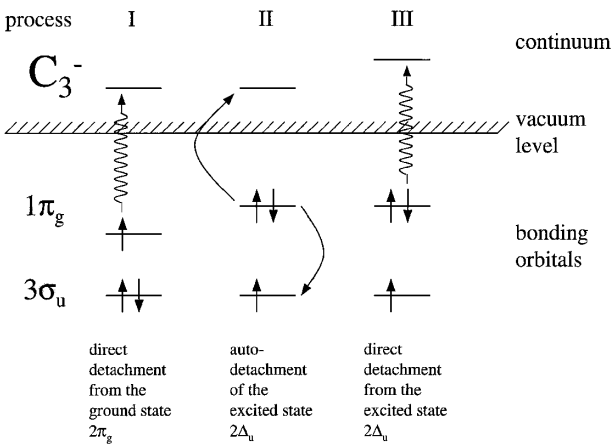

FIG. 2. Schematics of the three main detachment processes contributing to the photoelectron spectrum displayed in Fig. 1. In the one-photon process 1, the additional electron of the anion occupying the $1\pi_g$ single particle orbital is detached leaving the neutral C_3 in its ground state with the configuration $3\sigma_u^2$. In process II, a photon excites the $^2\Delta_u$ state of C_3^-, which decays by autodetachment in a two-electron process into the neutral ground state. In the two-photon process III, the pump photon excited the $^2\Delta_u$ state of C_3^- and the probe photon detaches one electron from the $1\pi_g$ single particle orbital leaving the neutral C_3 in the configuration $3\sigma_u^1\,1\pi_g^1$ corresponding to the $^3\Pi_u$ excited state.

$$C_3^- + h\nu_{\rm pump} \rightarrow C_3^{-*},$$

$$C_3^{-*} + h\nu_{\rm probe} \rightarrow C_3^* + e^- \qquad (E_{\rm kin} = 1.9\ {\rm eV}).$$

The kinetic energies of the detached electrons are given for photon energies of $h\nu = h\nu_{\rm pump} = h\nu_{\rm probe} = 3.1$ eV. Processes I and II yield identical features in the electron spectra (peak *A* in Fig. 1), because the initial and the final state are the same for both one-photon channels (Fig. 2). The two-photon process III results in the appearance of feature *B*.

By direct electron detachment of C_3^{-*} with the configuration $3\sigma_u^1\,1\pi_g^2$ only the neutral excited state ($3\sigma_u^1\,1\pi_g^1$) is accessible, but not the neutral ground state with the configuration $3\sigma_u^2$ (Table I). The ground state can be attained only if the detachment is accompanied by simultaneous deexcitation of the second electron occupying the $1\pi_g$ orbital into the $3\sigma_u$ orbital. Such a two electron "shakedown" process is rather unlikely. However, at the kinetic energy corresponding to the appearance of electrons from such a shakedown process, a very weak signal is observed (feature *C* in Fig. 1). We conclude that a fourth process contributes to the photoelectron spectrum:

IV. Shakedown detachment from the excited state (two-photon, peak *C*):

$$C_3^- + h\nu_{\rm pump} \rightarrow C_3^{-*},$$

$$C_3^{-*} + h\nu_{\rm probe} \rightarrow C_3 + e^- \qquad (E_{\rm kin} = 4.2\ {\rm eV}).$$

The difference between processes III and IV is the final state of the neutral C_3, which is the ground state in the case of process IV.

In a pump/probe experiment, the lifetime of an excited state can be measured directly. Figure 3 displays the dependence of the intensity of peak *B* in Fig. 1 on the delay between the pump and the probe laser pulses. According to process III, this dependence is directly related to the lifetime of the Feshbach resonance (noted C_3^{-*}). From an exponential fit (Fig. 3) the lifetime τ of the Feshbach resonance $^2\Delta_u$ of C_3^- is determined to be

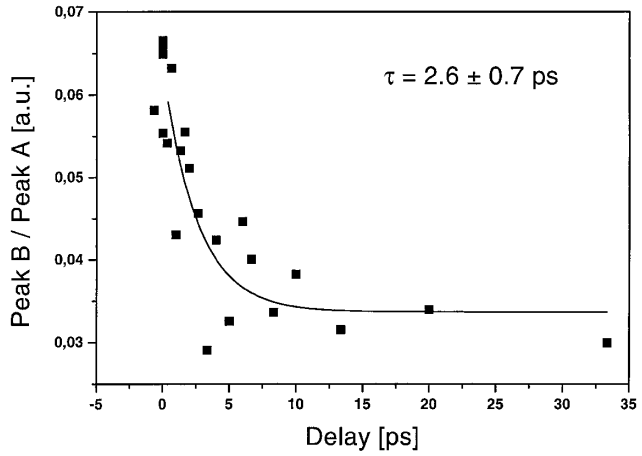

FIG. 3. The change of the relative intensity of peak *B* with increasing pump/probe delay. The intensity is measured with respect to the one of peak *A*. An exponential fit is also shown corresponding to a lifetime of 2.6 ± 0.7 ps.

$$\tau(^2\Delta_u) = 2.6 \pm 0.7 \text{ ps}.$$

This agrees with the findings of Tulej *et al.*, who estimated the lifetime of this resonance to be shorter than 5 ps based on theoretical considerations [13].

In conclusion, we present results of the application of time-resolved photoelectron spectroscopy to study the decay of an excited electronic state in mass-selected cluster anions. As a first example, we studied the electronic autodetaching process of a Feshbach resonance of C_3^- and could distinguish four different channels contributing to the photoelectron signal. The electronic states involved into the excitation and decay of the resonance are extracted from the data. Especially, with our experimental method the parent state of the resonance can be identified unambiguously. Finally, by taking advantage of the extreme time resolution of the femtosecond lasers, we measured the lifetime of the excited state directly. Our analysis is supported by the results of recent photodetachment cross section measurements [13] proving the validity of our analysis. We demonstrated that time-resolved photoelectron spectroscopy of cluster anions reveals the decay channels of electronic excitations and their lifetimes. The use of charged particles allows for an accurate mass separation, and in the future the method will be applied to study various electronic excitation in clusters and nanoparticles.

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