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Real-time study of the femtosecond harpooning reaction in $Ba\cdots FCH_3$

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A real-time observation of an ultrafast intracluster harpooning reaction in an electronically excited metal atom-molecule complex is reported. Using the laser pump-probe technique the intracluster bimolecular reaction $Ba\cdots FCH_3 \rightarrow BaF+CH_3$ has been investigated both in the real-time and frequency domains. The directly measured reaction time of 250 fs is in very good agreement with the decay time obtained by inverse Fourier transformation of the photodepletion spectrum of the parent $Ba\cdots FCH_3$ cluster. [S1050-2947(99)50103-0]

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INTRODUCTION

The alkali-metal plus halide reactions constitute a classical system of gas phase reactions involving harpooning [1], which was thoroughly studied in the alkali-metal age of molecular beams by Herschbach's [2], Bernstein's [3], and other groups' [4,5]. It is perhaps one of the best studied families and has become a venerable example in the molecular reaction dynamics field as a prototype of a fast, direct mechanism, with an ionic intermediate (transition state) lasting in the subpicosecond regime.

Early studies of these gas phase electron transfer reactions included diffusion flames [6,7] and molecular-beam experiments in which both total and differential reaction cross sections were determined [8–10]. To elucidate the nature of the reactive transition states in these molecular-beam studies the effect of systematic variation of pre- and postcollision variables, e.g., reactant and product quantum-state specification, was examined.

For bimolecular reactions (full collisions) a number of techniques have been developed in the last ten years to observe transition states during individual collisional events. Well-known examples of this new transition state spectroscopy (TSS) involve observation of intermediate states in emission [11] and absorption [12]. One of the most interesting approaches recently developed consists of ''complexing'' the reagent on a specific range of precursor geometries prior to reaction. In this approach one uses a van der Waals complex in which a laser pulse photoinitiates the chemical reaction on the excited potential-energy surface. This type of study was pioneered by Soep and co-workers [13–15] using the $Hg\cdots Cl_2$ and the $Ca\cdots HX$ (X=halogen) complexes and by Wittig and co-workers [16,17], who studied intracluster reactions; for example, in the $H\cdots OCO$ complex. The first study of an alkali-metal atom harpooning reaction using this approach was recently made by Polanyi and co-workers [18,19] on $Na\cdots XR$ (XR=organic halide) van der Waals complexes, and recently the $Ba\cdots FCH_3$ complex photodissociation has been studied by González Ureña and co-workers [20], providing basic spectroscopic and dynamical information about this electron transfer reaction.

From the time domain approach, in pioneering studies, Zewail and co-workers [21–23] have applied femtosecond lasers to make a real-time observation of bimolecular collisions. These experiments succeeded in measuring lifetimes for product formation by abstraction and exchange reactions such as $H+CO_2 \rightarrow OH+CO$ and $Br+I_2 \rightarrow BrI+I$. Furthermore, the femtosecond dynamics of electron transfer reactions involving an ionic transition state in molecule-molecule complexes, e.g., in benzene-I_2, has been analyzed by this group [24]. These reactions are based on the harpooning mechanism in the generalized sense, while the harpooning reaction as introduced and originally studied is related to the electron transfer from an alkali-metal or alkaline-earth-metal atom to a molecule. To the best of our knowledge no femtosecond real-time experiment has been reported for a harpooning reaction in a metal atom-molecule complex. In addition, a combined and simultaneous study of the spectroscopy and dynamics using both frequency and time domain data is still not available for this well-known type of reaction in such complexes.

In the present work we describe what we believe to be the first experimental real-time probe of a harpooning reaction in a metal atom-molecule complex as well as a highly elucidating example in which both frequency and time domain spectroscopic data are reported and discussed for the reaction in such a complex. To this end, the pump and probe technique has been applied to the intracluster reaction:

$$Ba\cdots FCH_3 + h\nu \rightarrow BaF + CH_3,$$

using two experiments that have in common the same cluster formation source and the same reagent and product detection, i.e., the measurement of the complex depletion and the product formation, but using different, though complementary, experimental approaches. Thus while in the work of Gonzalez Ureña and co-workers the measurements were carried out using nanosecond laser pulses and the spectra were taken in the frequency domain, in the work of Radloff and co-workers femtosecond laser pulses were used to measure in real time the same complex depletion and product formation. The advantages of carrying out this type of interrelated investigations are obvious, as they should, in principle, pro-

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vide a more complete and complementary picture of the underlying dynamics for the harpooning reaction.

EXPERIMENT

A detailed description of the experimental apparatus employed by Gonzalez Ureña and co-workers has been reported elsewhere [20] and only a brief description will be given here. The weakly bound complex $Ba\cdots FCH_3$ was produced by laser desorbing barium into a helium carrier gas that contained CH_3F (~10%). The mixture was then expanded through a supersonic nozzle and the pulsed jet was skimmed with a 1.0-mm skimmer before entering the detection chamber. The molecular beam formed by the skimmer was probed inside the acceleration region of a linear time-of-flight mass spectrometer. In order to take action spectra, i.e., to monitor the appearance of the species due to the photoinduced reaction as the laser wavelength was changed, the second-harmonic output of a neodymium-doped yttrium aluminum garnet (Nd-YAG) laser was split into two beams. One was doubled to give 266 nm and used to ionize the species of interest and the other pumped a dye laser (0.08-cm^{-1} bandwidth), which was used to induce the chemical reaction within the weakly bound complex. The tunable dye laser is responsible for the decrease in concentration of the complex and the uv light monitors the production of the BaF product. As in our previous work [20] the dye laser arrived 10 ns earlier than the uv laser to the beam-laser interaction zone. The reader is referred to Ref. [20] for further information about the experimental technique and spectroscopic method.

With respect to the experiment of Radloff and co-workers the same laser vaporization source was used to produce the $Ba\cdots FCH_3$ complex. The molecular beam is crossed by two weakly focused copropagation laser beams in the interaction region of a time-of-flight mass spectrometer. The laser system used is a commercial Ti:sapphire laser and amplifier system (Clark MXR) tuned to 800 nm, which is combined with a commercial optical parametric amplifier (OPA) system (Clark I-GOR-SHG). The second harmonic of the OPA signal wave is tuned to the resonance of the $Ba\cdots FCH_3$ complex at 618 nm and is used to pump the clusters. The third harmonic of the Ti:sapphire laser at 267 nm is applied to probe the excited clusters by ionization. The full width at half maximum (FWHM) of the laser pulses is about 130 fs. Typical values of the laser fluences are about 0.5 mJ/cm^2 for the pump as well as the probe beam. At these fluences the optimum signal-to-background ratio is obtained for the parent and the product ions. Nevertheless, the ion signals have to be averaged over a large number of laser pulses. Variations of the laser intensities are strongly restricted. The enhancement of the pump laser intensity causes a strong reduction of the signal-to-background ratios, especially the background signal of BaF^+, which is due to BaF formation during the interaction of the vaporization laser with the metallic barium and the solvent increases for larger intensities. Hence, quantitative measurements of the intensity dependence of the different signals are not possible at the present time. We have probed only qualitatively the intensity dependence of the ion signals in order to reveal rough information about the single- or two-photon absorption in the ionization process.

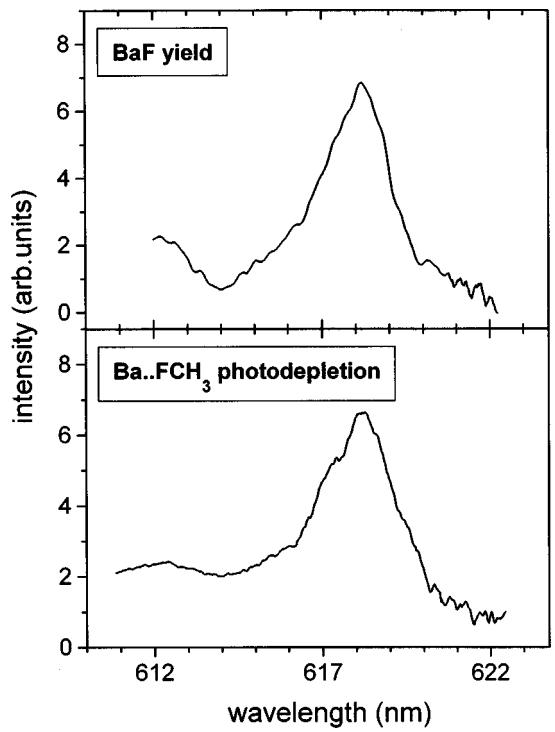

FIG. 1. (Top) BaF action spectrum obtained from the photoinitiated $Ba\cdots FCH_3 + h\nu \rightarrow BaF + CH_3$ reaction. The BaF^+-ion signal is shown as a function of the photodepletion wavelength. (Bottom) Photodepletion action spectrum for the parent $Ba\cdots FCH_3$ cluster over the same wavelength range. The spectrum was taken from Ref. [20] for a better comparison with that of BaF. See text for comments.

A standard delay line is used to scan the time delay between the pump and probe pulses. Similarly to the frequency domain experiment the ion signal is detected by a microchannel plate detector in the time-of-flight mass spectrometer, digitized by a fast digital oscilloscope (Tektronix TDS 520 A) and stored and processed by a personal computer. In the experiments the repetition rate is restricted by the vaporization laser to 10 Hz, the mass spectra are accumulated typically for 30 laser pulses at each delay time τ, and averaged over 70 up- and down-scans of the delay line.

RESULTS AND DISCUSSION

The top of Fig. 1 displays the action spectrum of the BaF reaction channel, i.e., it represents the BaF^+-ion signal obtained by the 266-nm ionization wavelength as a function of the dye laser wavelength used for photodepletion. The closer resemblance of the BaF and the $Ba\cdots FCH_3$ photodepletion signals is clearly manifested. The latter spectrum was taken from Ref. [20] for a better comparison. Notice the clear resonance at 618.2 nm in which both photodepletion and BaF signals show their maximum values.

In Fig. 2 the ion signals for the parent cluster $Ba\cdots FCH_3$ and the two species BaF and Ba are shown as a function of the delay time between the femtosecond pump pulse at $\lambda_1 = 618$ nm and the femtosecond probe pulse at $\lambda_2 = 266$ nm. Discussing at first the Ba^+ ion signal we observed a relatively strong peak that is due to the nonresonant absorption of one pump and one probe photon by the Ba atoms in the beam and hence reflects the cross correlation signal of the

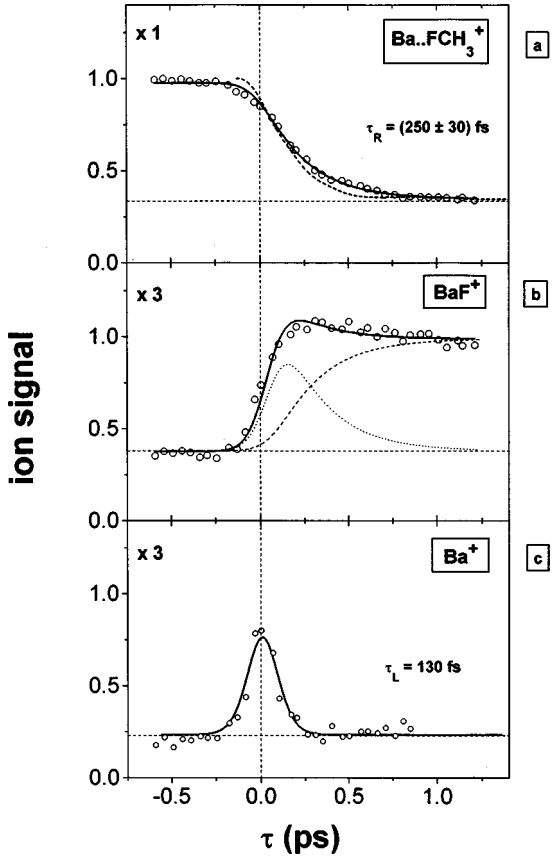

FIG. 2. Ion signals for (a) Ba···FCH_3, (b) BaF, and (c) Ba as a function of the delay time τ between pump pulse at 618 nm and probe pulse at 266 nm. The solid lines represent the theoretical fits discussed in the text. In (a) the dashed line represents the autocorrelation function obtained by the Fourier transformation of the photodepletion spectrum shown in the lower part of Fig. 1. In (b) the dashed and dotted lines denote different contributions to the signal (see text). The numbers in the upper left corner are the magnification factors for the different ion signals.

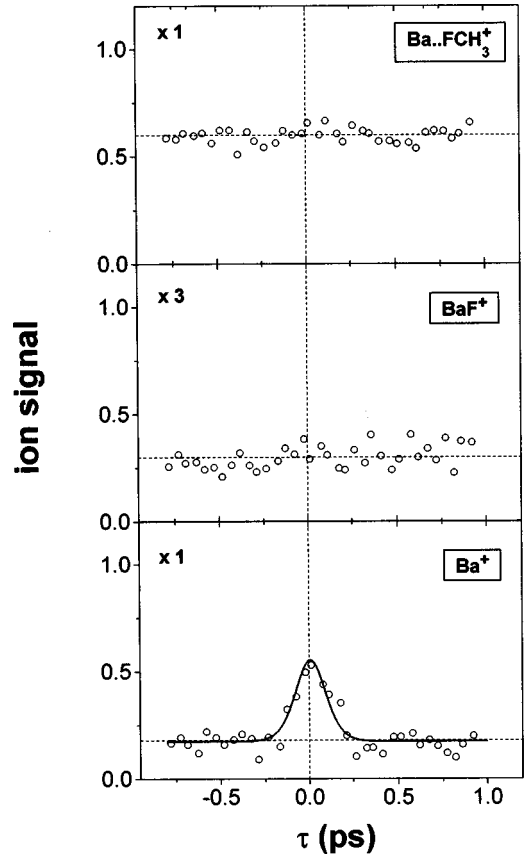

FIG. 3. Ion signals for Ba···FCH_3, BaF, and Ba versus delay time τ between pump pulse at 630 nm and probe pulse at 266 nm. Except for the different pump wavelength the experimental conditions are identical to Fig. 2.

laser pulses with a defined zero delay time. The theoretical fit corresponds to the cross correlation curve of the laser pulses with a $\mathrm{sech}^2(t)$ shape and a width of $\tau_L = 130$ fs. The background signal is caused by the absorption of two photons with the wavelength λ_2, which are necessary to ionize the Ba atoms (ionization potential IP=5.21 eV). Accordingly the peak-to-background ratio has been enlarged by reduction of the probe laser fluence. A possible contribution to the Ba^+-ion signal for $\tau > 0$ resulting from fragmentation of the parent molecule in the excited or ionized state was not observed because the cluster concentration is much smaller than the number of neutral Ba atoms in the molecular beam.

The parent cluster with the ionization potential of 4.5 eV [20] will be ionized by only one probe photon of 4.66 eV energy. The ion signal decreases strongly during and after interaction with the resonant pump laser pulse at $\lambda_1 = 618$ nm (see Fig. 2), whereas under identical conditions, except for the irradiation with a nonresonant pulse at $\lambda_1 = 630$ nm, no signal variation has been observed as displayed in Fig. 3. The time constant of the decay channel is $\tau_R = 250$ fs. This quantity is obtained by fitting the experimental points with a theoretical model that describes the resonant coherent interaction with the pump pulse by optical Bloch equations with a single-exponential decay of the excited state. The laser parameters used for convolution are identical with those derived from the fit of the Ba^+ signal.

It is very interesting to point out the excellent agreement between the time evolution of the Ba···FCH_3 measured in the present femtosecond pump and probe investigation and that obtained by inverse Fourier transformation of the photodepletion spectrum, which is described by the dashed line in Fig. 2 (top). It is remarkable that both pieces of data, i.e., the frequency domain and the time-resolved spectrum provide an unique and consistent picture of the dynamics underlying the Ba···FCH_3 photodissociation.

The product BaF^+ ions are characterized by a relatively large background signal (at $\tau < 0$), which is due to absorption of the $2h\nu_2$ photons as well as the $1h\nu_2$ and $1h\nu_1$ photon. The background signal varies strongly with the fluence of the probe laser but remarkably also with the pump laser fluence. The ionization potential IP$\sim$4.85 eV for BaF[20] requires the absorption of two photons for ionization from the ground state. The BaF^+ signal increases very fast by resonant excitation of the parent cluster at $\lambda_1 = 618$ nm. In contrast, by irradiation of the parent cluster with a nonresonant pump pulse at $\lambda_1 = 630$ nm no BaF formation can be detected (cf. Fig. 3).

The fitting curve for the time-dependent BaF^+ signal [full line in Fig. 2(b)] is obtained by the superposition of two contributions: The main part represents the formation of BaF with the time constant $\tau_R = 250$ fs due to the harpooning

reaction within the excited parent complex $(Ba\cdots FCH_3)^*$. The time evolution of the product [broken line in Fig. 2(b)] is complementary to the decay of the parent ion signal with the identical time constant [cf. Fig. 2(a)]. The second contribution arises from the partial fragmentation of the excited $(Ba\cdots FCH_3)^+$ ion formed by absorption of the probe pulse by the excited $(Ba\cdots FCH_3)^*$ complex. The time evolution of this part [dotted line in Fig. 2(b)] follows the depletion of the excited parent state with the time constant $\tau_R = 250$ fs, as given above.

Thus, the surprisingly fast rise of the BaF^+ signal can be explained, despite a significantly longer reaction time. The details of the electron transfer process can be elucidated by further real-time experiments and by molecular-dynamical simulations on the basis of *ab initio* calculated potential surfaces. Work is now in progress in both directions and will be the subject of a future publication.

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