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Spectroscopy and dynamics of the Ba··FCH$_3$ complex excited in the 728–760 nm wavelength region

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Abstract. The laser-induced intracluster Ba··FCH$_3$+ $h\nu \rightarrow$ Ba* + CH$_3$F photofragmentation has been investigated in the 13158–13736 cm^{-1} energy range, corresponding to the electronic $\tilde{\mathrm{A}}'$-state of the Ba··FCH$_3$ molecule. The major photofragmentation path was found to be the non-reactive Ba* + CH$_3$F channel. The photodepletion action spectrum of the Ba··FCH$_3$ was measured using nanosecond pump and probe technique, showing a broad feature with a maximum photodepletion cross-section of 8 Å^2. The action spectrum of the non-reactive Ba photofragmentation channel was also measured. The results are discussed in the light of a proposed mechanism for the harpooning reaction leading to BaF when the complex is excited to the $\tilde{\mathrm{A}}$ electronic state.

PACS. 36.40.Jn Reactivity of clusters – 36.40.Qv Stability and fragmentation of clusters – 34.50.Rk Laser-modified scattering and reactions

1 Introduction

The investigation on intermediate species between reactives and products, namely, the transition state region [1], constitutes one of the most exciting and expanding research fields in molecular reaction dynamics and laser spectroscopy [1–16]. Zewail's group has probed the transition states of reactions in real time using femtosecond lasers [5]. Another approach developed for this type of study consists of complexing the reagent in a specific range of precursor geometries prior to reaction. A good example of the latter category is the Ba··FCH$_3$ weakly bound complex whose spectroscopy and photofragmentation dynamics have been studied by our group using nanosecond laser techniques. The photodepletion spectrum of the excited Ba··FCH$_3$ has been measured in the 545–630 nm region, displaying two distinct regions that were interpreted as two different electronic states named $\tilde{\mathrm{A}}$ and $\tilde{\mathrm{B}}$ with well defined resonances at the wavelength 618.2 and 550 nm, respectively. In both electronic states, we observed two open photofragmentation channels: a reactive one, giving BaF + CH$_3$ via a harpooning reaction, and a non-reactive one, giving Ba + FCH$_3$ [17]. We found a fast photo-depletion reaction was taking place in about 270 fs when exciting the complex to its electronic $\tilde{\mathrm{A}}$-state (see also Ref. [4] for further details). This result was confirmed by femtosecond time-resolved observation of the intracluster harpooning reaction in the Ba··FCH$_3$ complex with the finding of a lifetime of 270±30 fs for the excited $\tilde{\mathrm{A}}$-state [18,19].

Recently, a mechanism for the ultrafast Ba··FCH$_3$ + $h\nu \rightarrow$ Ba··FCH$_3$($\tilde{\mathrm{A}}$) $\rightarrow$ *products* reaction was suggested [22] which involves the existence of a new Ba··FCH$_3$($\tilde{\mathrm{A}}'$) state, that lies below the $\tilde{\mathrm{A}}$-state and correlates with the asymptotic Ba(^{1}D) + CH$_3$F products. The proposed mechanism was based upon ab initio calculations and further experimental identification of the $\tilde{\mathrm{A}}'$-state by two-colour two-photon ionisation using 130 fs pulses [21,23].

As the intracluster reaction involves the electron transfer from the excited Ba to the F atom, an energy barrier should be expected for the reactive channel due to the negative electron affinity of the FCH$_3$ [21]. According to spectroscopic measurements from this laboratory [4] as well as from ab initio studies [21] the resonant excitation of these studies (λ = 618 nm) corresponds to the transition from the vibronic ground state ($v'' = 0$) to the lowest vibrational level ($v' = 0$) of the excited $\tilde{\mathrm{A}}$-state of the Ba··FCH$_3$. As a result, the necessary vibrational energy for the C–F stretch is not available and can only be obtained by internal conversion from the $\tilde{\mathrm{A}}$-state to the lower-lying excited electronic $\tilde{\mathrm{A}}'$-state. Thus, the energy transfer gained by this non-adiabatic coupling promotes the C–F stretch and, consequently, the electron transfer reaction. Strong support to this mechanism has been provided not only by ab initio calculations [21], but, especially, by pump and probe time-resolved photoelectron spectroscopy of both Ba··FCH$_3$$^+$ and BaF$^+$ ions [22].

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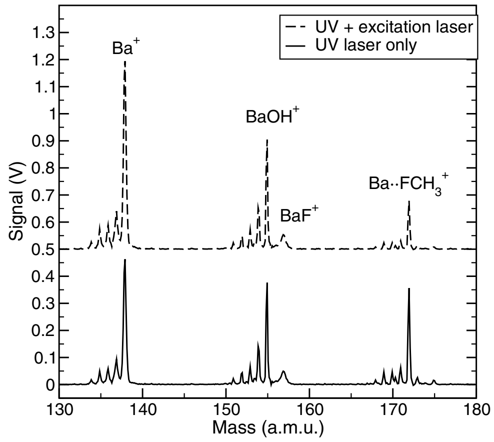

Fig. 1. Time of flight mass spectra of the Ba + CH_3F system. The lower spectrum was measured with the 266 nm radiation only for ionisation, while for the upper spectrum the excitation laser was also used, tuned to 745 nm.

The present letter is aimed at to investigate the spectroscopy and dynamics of the Ba··FCH_3 complex in this $\tilde{A}'$-state. To this end both Ba··FCH_3 photodepletion and product action spectra were measured using nanosecond laser excitation over the 728–760 nm region.

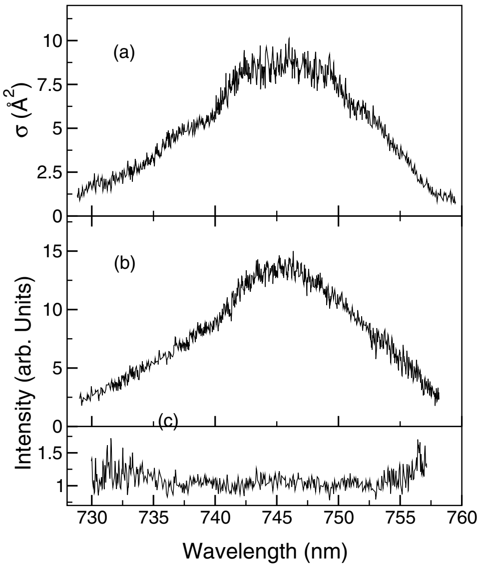

Fig. 2. (a) Photodepletion cross-section, σ, of the Ba··FCH_3 weakly bound complex, corresponding to the electronic $\tilde{A}'$-state. (b) Product action spectrum for the Ba non-reactive channel of the Ba··FCH_3 photofragmentation. The signal is normalised with the excitation laser energy. (c) Reaction probability of the Ba channel as a function of the excitation laser wavelength.

2 Experimental

The experimental apparatus employed in this work has been described elsewhere [4]. Basically, the Ba··FCH_3 weakly bound complex is produced in a laser vaporisation source followed by supersonic expansion. The molecular beam is then probed inside the acceleration region of a linear time of flight mass spectrometer, using the fourth harmonic output of a Nd–YAG laser for ionisation.

Two different lasers have been used for the excitation of the complex: in the 728–740 nm range a tunable dye laser with a bandwidth of 0.08 cm^{-1} has been employed, while in the 740–760 nm range the idler output of a OPO laser (Coherent Infinity) with a bandwidth of about 5 cm^{-1} has been used.

The ionisation laser is delayed by about 10 ns with respect to the excitation laser. Wavelength calibration was achieved using a standard hollow-cathode spectral lamp (Sn/Ne, Cathodeon).

Care was taken to keep the excitation laser energy within a regime where the Beer-Lambert law can be applied, as shown in reference [4]. A key feature of the experimental technique is the simultaneous measurement of both the complex photodepletion and the product action spectra. See references [24,25] for further details.

3 Results and discussion

The time of flight (TOF) mass spectra of the Ba + CH_3F system shown in Figure 1 reveal the behaviour of the weakly bound complex when excited at 745 nm (dashed line): clearly, the Ba··$FCH_3{}^+$ signal decreases compared to the signal obtained with the ionisation laser only (solid line), which indicates that a photofragmentation process is taking place. The Ba^+ signal increases, while the BaF^+ signal remains constant, indicating only a non-reactive open photofragmentation channel [17].

The most intense peaks appearing in the spectra correspond to species containing the ^{138}Ba isotope with the other four most abundant isotopes appearing at shorter flight times. The Ba^+ and BaF^+ signals observed in the spectrum with the UV laser only are due to Ba and BaF contained in the molecular beam, originating from the laser vaporisation source, and the BaOH present in the molecular beam is produced through the reaction of the laser-evaporated Ba with water vapor present in the gas line [4].

The decrease of the Ba··$FCH_3{}^+$ signal was then measured as a function of the excitation laser wavelength in the 728–760 nm range, thus obtaining the photodepletion spectrum of the weakly bound complex in its electronic $\tilde{A}'$-state. The simultaneous measurement of the excitation laser energy, together with the determination of the Ba··$FCH_3{}^+$ signal with the UV laser only, allowed us to determine the absolute photodepletion cross-section, σ, as a function of the excitation energy [15,16]. The resulting spectrum is shown in Figure 2a. It represents the average of 20 runs in conditions where the Beer-Lambert law can be applied. The spectrum shows a broad and diffuse structure. The maximum photodepletion cross-section is about 8 Å^2. Notice how the excitation energy corresponding to this maximum is $\nu_1 = 13422.8\,cm^{-1}$ ($\lambda_1 = 745$ nm), which confirms the energy value for the vertical transition from

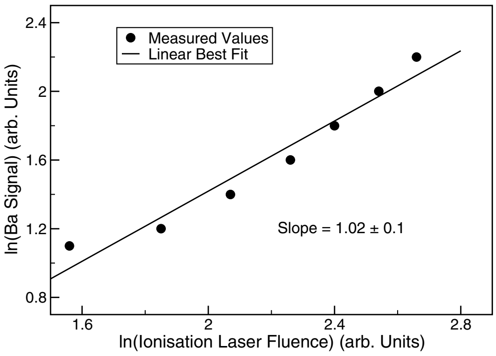

Fig. 3. Ba$^+$ signal from the Ba··FCH$_3$ photofragmentation vs. ionisation laser fluence. The parent complex was excited at 745 nm.

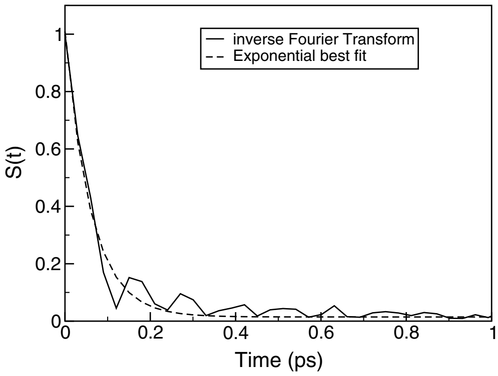

Fig. 4. Solid line: autocorrelation function $S(t)$ corresponding to the photodepletion spectrum shown in Figure 2a. Dashed Line: best-fit exponential decay ($\tau \simeq 60$ fs). This data have been normalised to 1 at $t=0$.

the ground state to the electronically excited Ã′-state of the complex as obtained from ab initio calculations [21].

Given the almost structureless, broad feature of the spectrum, it can be concluded that the difference in bandwidth of the two lasers employed for the excitation of the complex (dye laser and OPO), has no effect on the final result.

The time of flight mass spectra (Fig. 1) reveal that the decrease of the complex signal is accompanied by an increment of the Ba$^+$ signal, which suggests at least one open, non reactive, photofragmentation channel (no depletion was observed for other species present in the beam over this wavelength region). Thus we measured this increment along with the photodepletion of the parent complex as a function of the excitation laser energy. The result is shown in Figure 2b, where the Ba$^+$ signal is normalised with the excitation laser energy.

The spectrum shows a structure and shape very similar to that of the photodepletion spectrum of the parent molecule. This suggest that the breaking of the van der Waals bond is the major open channel for the photofragmentation of the Ba··FCH$_3$ complex after excitation to its electronic Ã′-state.

The signal of the Ba product was also measured as a function of the ionisation laser fluence, exciting the parent molecule at 745 nm. Figure 3 shows clearly that the ionisation of the Ba product is a single-photon process. This suggests that the Ba is produced in its ^{1}D state, given the Ba ionisation potential of 5.21 eV [26] and the ionisation laser energy of 4.66 eV (the ^{1}P state is energetically not accessible).

The mass spectra (Fig. 1) already suggested that no BaF was formed from the photofragmentation of Ba··FCH$_3$. In fact, no signal of BaF$^+$ originating from the photodepletion was found despite the relatively low BaF ionisation potential of 4.8 eV [27], ionising with 266 nm ($h\nu$ = 4.66 eV). That means that only if the BaF was produced in the electronic ground state, and with few excited vibrational states, one photon would not suffice for ionisation. Considering that after laser excitation of the Ba··FCH$_3$ complex to its Ã′-state the total energy available for ground state (BaF + CH$_3$) products is about 2.89 eV [21], the specific yield of BaF in its lower vibrational states seems very unlikely. Apparently, the reactive channel is not open for the photofragmentation of Ba··FCH$_3$ when excited to its electronic Ã′-state, while both Ba and BaF products from the reactive and the non-reactive photofragmentation channels were found in the electronic Ã-state [17]. The absence of a BaF$^+$ signal confirms previous findings from femtosecond pump and probe experiments (see for example Fig. 9 of Ref. [28])

As shown in a previous work [25], the reaction probability P_R^i for the i photodissociation channel can be determined by the ratio of the i channel action spectrum over the total photofragmentation spectrum. This method cancels out the spectroscopic factors, and only the dynamic part remains. Thus, we can estimate the energy dependence of the relative reaction probability for the non-reactive product action channel of the Ba··FCH$_3$ photodepletion using the measured photodepletion intensity and product signal spectra. The result is shown Figure 2c. It shows basically a flat line, apart from some experimental noise. This is another indication that there are no competing photofragmentation channels.

It has been shown that the autocorrelation function of the excited state wavefunction, $S(t)$, is obtained by inverse Fourier Transform of the measured spectrum [29,30], providing a means to estimate the lifetime of the system in the excited state from measurements in the frequency domain. Despite its limitations, this method has already shown to be valid for the excited Ã-state [25], and also in the present case there is a very good agreement between the lifetime estimated from our measurements and the results from measurements in the time domain: The time constant of the best-fit exponential decay to the inverse Fourier Transform of the measured spectrum is about 60 fs (Fig. 4), while the lifetime of the complex measured by Radloff and co-workers in a real-time experiment was 50±10 fs [23].

According to the ab initio calculations reported in reference [21] there is an electronic state of Ba··FCH$_3$ below the electronic Ã-state, which was denominated Ã′-state. The maximum of absorption is expected to be found at 745 nm. The potential energy curve along the Ba··C axis

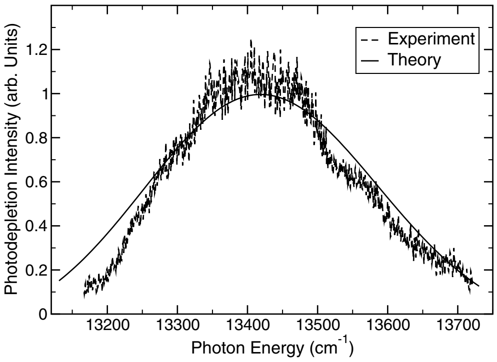

Fig. 5. Dashed line: photodepletion spectrum of Ba··FCH$_3$ corresponding to the $\tilde{A}'$–$\tilde{X}$ transition, measured in the present work. Solid line: calculated absorption spectrum of Ba··FCH$_3$ from the ground vibronic state to the repulsive part of the $\tilde{A}'$-state, for a laser spectral width of 7 nm (from Fig. 5 in Ref. [21]).

for this state is repulsive for the $\tilde{X}$ and $\tilde{A}$ equilibrium geometries. The vertical $\tilde{A}$–$\tilde{A}'$ energy gap for the $\tilde{A}$ equilibrium geometry is of the order of the degenerate C–H stretch mode [21].

Our measurements of the photodepletion action spectrum of the Ba··FCH$_3$ in its $\tilde{A}'$-state show a maximum at 745 nm, which is in perfect agreement with the ab initio calculations. Figure 5, which displays our experimental result and the calculated curve from Figure 5 in reference [21], shows that also the shape of the measured spectrum is in agreement with the calculations, considering that in the theoretical curve a laser linewidth of 7 nm has been taken into account. The measurement of the product channels reveals that only the non-reactive photofragmentation channel is open. No BaF product was found from the $\tilde{A}'$-state photofragmentation. This result is confirmed by the estimation of the energy dependence of the relative reaction probability for the Ba product shown in Figure 2c. The ionisation of the Ba product emerging from the Ba··FCH$_3$ photofragmentation is a single photon process, suggesting that the $\tilde{A}'$-state correlates with the ^{1}D state of the Ba atom.

A simple process should thus conduce to the photofragmentation of the $\tilde{A}'$-state: a photon with an energy of about 13420 cm^{-1} excites the molecule directly to the $\tilde{A}'$-state. There is no vibrational energy available whatsoever to increase the F–C distance, and thus no charge transfer reaction is taking place. The repulsive potential energy curve leads to a fast fragmentation of the complex.

One can now confirm the suggested mechanism for the charge transfer in the $\tilde{A}$-state: after excitation of the Ba··FCH$_3$ complex to its electronic $\tilde{A}$-state, at time 0, an internal conversion takes place from the $\tilde{A}$-state to the energetically lower-lying $\tilde{A}'$-state. The excess energy goes into the degenerate C–H stretching mode. This internal conversion takes about 250 fs. The C–H stretching mode is probably strongly coupled to the C–F vibration, so that the energy barrier for the BaF formation can be overcome fast. It has to be fast because the Ba–C distance rapidly increases due to the repulsive character of the $\tilde{A}'$-potential, and for increasing Ba–C distance the barrier for the harpooning reaction becomes higher. So the total reaction time is about 300 fs [4,18]. In this view, the reaction is not possible in the $\tilde{A}$-state, although there is enough total energy, because there is no vibration. On the other hand, we know that the reaction is taking place. The energetic difference between the $\tilde{A}$- and the $\tilde{A}'$-state is very similar to the energy of the degenerate C–F stretching mode. The $\tilde{A}'$-state correlates to the Ba ^{1}D state, which means that the Ba 5d electron is oriented along the symmetry axis of the complex, which in turn gives rise to a weak bonding state with a probably large Ba–C equilibrium distance. Thus the potential of this state is likely to be repulsive for the $\tilde{X}$ and $\tilde{A}$ equilibrium geometries, which is consistent with our findings, and with the ab initio calculations. Also the lifetime of the $\tilde{A}'$-state has to be very short, because we know that the total lifetime of the $\tilde{A}$-state is about 300 fs, and the internal conversion may easily require a few hundred of femtoseconds. So the estimated lifetime of 50 fs, and also the fact that there is no coupling to other bound states, is consistent with the proposed reaction mechanism.

The present results indicate that after excitation of the Ba··FCH$_3$ complex into its $\tilde{A}'$-state, the weak Ba–F van der Waals bond of the complex breaks faster than the nearest neighbour strong F–C bond. This is somewhat the opposite to the result found when the Ba··FCH$_3$ complex is excited to the $\tilde{A}$-state. In this case significant BaF yield was observed, showing an even faster reaction time than that of the non-reactive (Ba + FCH$_3$) photodissociation channel, indicating that in the excited $\tilde{A}$-state the strong F–C bond breaks faster than the weak Ba–F bond.

Clearly the main difference supporting this opposite dynamical behaviour is the distinct nature of the excited potential energy curves along the reaction coordinate. While in the $\tilde{A}$-state this potential shows a vdW well supporting several vibrational modes, in the $\tilde{A}'$-state the potential is purely repulsive. The fast recoil dynamics supported by this repulsive potential with a decay time of the order of 50 fs, as deduced from the present investigation, does not facilitate any coupling with the strong C–F bond. This is consistent with the present finding of only one (non-reactive) channel in the Ba··FCH$_3$($\tilde{A}'$) photofragmentation. The time dynamics of the excited complex in its $\tilde{A}'$-state is so fast that the overall process constitutes a good example of *band-selective chemistry*, i.e. direct excitation of the $\tilde{A}'$-state, into the Ba··FCH$_3$ coordinate, leads to the breaking of the Ba–F bond. Even when exciting the vibrational CH$_3$ mode prior to the 745 nm excitation, the fast photodissociation dynamics does not allow for a dramatic change in breaking the strong C–F bond: indeed, using combined IR + VIS femtosecond pulse excitation results in 12±7 % increase of the BaF$^+$ signal [28].

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