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Excitation laser fluence effects on the $Ba\cdots FCH_3 + h\nu \rightarrow BaF + CH_3$ intracluster reaction

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Abstract

In this work, results on the $Ba\cdots FCH_3 + h\nu \rightarrow BaF\ (Ba^*) + CH_3\ (CH_3F)$ reaction obtained under high laser field conditions are reported. We have found that the two-photodissociation channel yields, i.e. the reactive BaF and non-reactive Ba^* products, exhibited opposite behaviour depending upon the laser fluence. Whereas the BaF yield rises as the laser fluence is increased, the Ba^* yield decreases over the same laser fluence range. In other words, the product $(Ba^*)/(BaF)$ branching ratio changes significantly from low to high laser fluence in such a way that the (photoinitiated) $Ba\cdots FCH_3 \rightarrow BaF + CH_3$ reaction may be controlled by changing the intensity of the excitation laser field.

1. Introduction

Laser control of chemical reactions is currently attracting a considerable attention from both theoretical and experimental point of view [1–3]. Among several schemes to implement the control of a chemical reaction one of the most promising is based on quantum interference control mostly applied to unimolecular reactions. For this type of processes, in which a single reactant molecule is transformed to several product molecules, two types of control have been applied. Namely, the 'two-beam interference control' [4–6] and the 'two-pulse time delay control' [3,7,8]. While in the former case control is achieved by quantum interference between different reaction pathways relating the same initial and final states, the latter method uses a variable time delay between two extremely short light pulses.

In the present work, we report on the control of the (photoinitiated) $Ba\cdots FCH_3 + h\nu \rightarrow BaF + CH_3$ intracluster reaction achieved by changing the fluence of the excitation laser. Pioneering work on photofragmentation of $Fe(H_2O)_n^+$ clusters ($n = 1$–9) as a function of the laser fluence at different wavelengths was carried out by Mest-

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dagh and co-workers [9]. Linear dependence of cross-sections (0.05 $Å^2$) was always found even at fluences up to 100 mJ/cm^2. Here the two photofragmentation channels i.e., reactive BaF and non-reactive Ba^*, yields exhibited opposite behaviour depending upon the laser fluence. Indeed, whereas the BaF yield increases with increasing laser fluence, the Ba^* yield decreases over the same laser fluence range. In other words, the product $[Ba^*]/[BaF]$ branching ratio changes significantly from low to high laser fluence conditions. It is emphasised that we used nanosecond laser pulses being the excitation laser fluence the only adjustable variable. The simplicity of this scheme could also be of interest for practical applications.

2. Experimental

A detailed description of the molecular beam apparatus is given elsewhere [10,11] and only a brief description will be presented here. The weakly bound complex $Ba\cdots FCH_3$ is produced in a laser vapourisation source followed by supersonic expansion, using a gas mixture of He with a 10% of CH_3F. The molecular beam is then probed in a different chamber using a laser ionisation coupled with a linear time-of-flight mass spectrometer.

Two lasers are used for the probing of the molecular beam. A tunable laser induces the reaction in the $Ba\cdots FCH_3$ weakly bound complex while a second laser ionises the complex and the $Ba\cdots FCH_3$ photofragmentation products. An infinity-XPO laser with a bandwidth of typical 5 cm^{-1} and a pulse duration of 3.5 ns is used for excitation of the complex, while the fourth harmonic of a Continuum NY80 Nd:YAG laser (266 nm, pulse duration 7 ns) is used for ionisation. The excitation laser arrives about 7–10 ns earlier to the beam-laser interaction region than the ionisation laser. This is achieved using an electronic delay generator provided by the infinity-XPO laser.

The pump and probe scheme used in the present experiment is the following:

$$\mathrm{Ba}\cdots\mathrm{FCH_3} + h\nu_{\mathrm{pump}} \rightarrow (\lambda = 617.7\ \mathrm{nm}) \begin{cases} \nearrow \mathrm{BaF} + \mathrm{CH_3} \\ \searrow \mathrm{Ba^*} + \mathrm{CH_3F} \end{cases}$$

$$\mathrm{BaF} + h\nu_{\mathrm{probe}}\ (\lambda = 266\ \mathrm{nm}) \rightarrow \mathrm{BaF^+}$$

$$\mathrm{Ba^*} + h\nu_{\mathrm{probe}}\ (\lambda = 266\ \mathrm{nm}) \rightarrow \mathrm{Ba^+}$$

The BaF^+ signal is produced by direct one photon ionisation of BaF product absorption of the 266 nm photon, as demonstrated in previous work (see for example Fig. 2 of [12]). With respect to the Ba^* product, direct one photon ionisation of

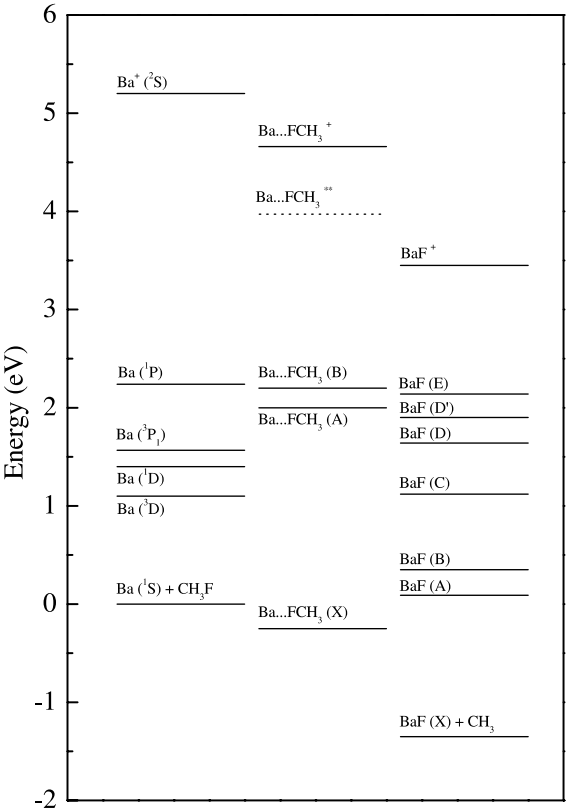

Fig. 1. Energy level diagram of the $Ba + CH_3F$ system. The left column shows the Ba electronic energy levels and the right one the BaF energy levels. The centre column displays an approximate location of the $Ba\cdots FCH_3$ electronic states including the hypothetical $(Ba\cdots FCH_3)^{**}$ Rydberg state. See text for comments.

Ba ground state is not possible at 266 nm, so only metastable Ba^* product can be ionised. See Fig. 1 for an energy diagram of the system here investigated. Under the present experimental conditions the 266 nm probing laser intensity was always kept at a very low intensity to guarantee that two-photon absorption process was, if any, a very minor effect. It should be recalled that the pumping laser wavelength excites the $A \leftarrow X$ electronic transition of the $Ba \cdots FCH_3$ complex only, i.e., it does not affect the free Ba atoms present in the beam expansion at all (see [11] for details).

The experiment consisted of measuring simultaneously the BaF^+ and Ba^+ signals at two different conditions: (a) using UV photons ($\lambda = 266$ nm) and (b) using first a pump XPO laser ($\lambda = 617.7$ nm) and then, 10 ns later, the UV ($\lambda = 266$ nm) laser. The BaF and Ba^* action signals were estimated from their, (b) minus (a) signals, respectively. This procedure was then repeated at different XPO laser fluences. The latter was modified by using a high energy variable attenuator (Newport mod. 935-5-OPT). This procedure ensured that the focus and optical features of the laser beam remained unchanged.

3. Results and discussion

Fig. 2 (solid line) shows a time-of-flight mass spectrum of the $Ba + FCH_3$ system when the fundamental output of the Nd:YAG is used for vapourisation and the species in the beam are ionised with the 266-nm radiation. A significant depletion of the monomer signal is observed when the excitation OPO laser is tuned to 617.7 nm and allowed to enter into the detection chamber (dashed line). It should be indicated that no depletion is observed for other species contained in the beam, indicating that these should probably absorb at different wavelengths. Furthermore the enhancement of both Ba and BaF signals is clearly noticed due to complex photofragmentation (see [12,13] for further details).

As for the Ba^* signal, it should be emphasised that no Ba^* ion signal was observed with the pump laser only, even though higher fluences were employed. Thus, taking into consideration the energetic diagram, one can conclude that the non-reactive photofragmentation channel here investigated, with the $\lambda = 266$ nm probing, corresponds to metastable $Ba(^1D_1, ^3P)$ states.

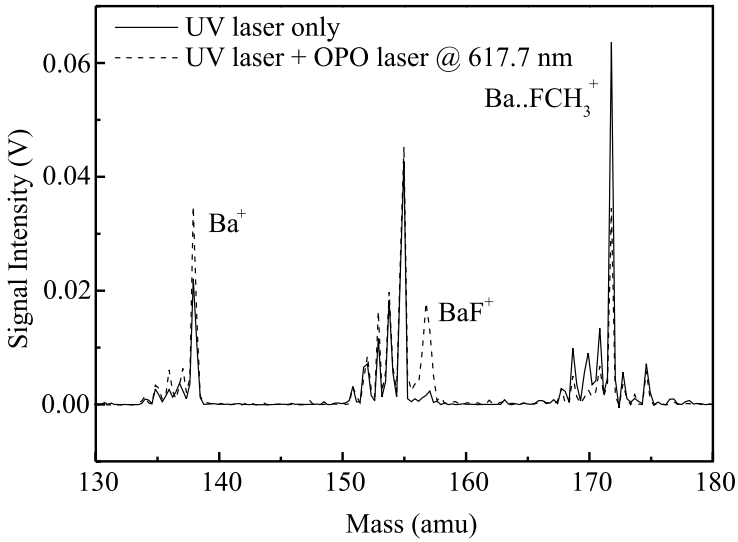

Fig. 2. Solid line: time-of-flight mass spectra of the $Ba + CH_3F$ system. Strong depletion of the $Ba \cdots FCH_3$ complex is observed when the OPO laser is tuned to 617.7 nm. The enhancement of both Ba and BaF signals is also clearly noticed as a result of the complex photofragmentation.

The individual photofragmentation channel yields are displayed on Figs. 3 and 4 as a function of the laser fluence. Both ΔBa^* and ΔBaF signals were obtained using the same procedure. The ΔBa^* was calculated by subtracting the Ba^* (UV) signal from the Ba^* (UV + VIS). Here UV and VIS stand for the signal measured when the UV ($\lambda = 266$ nm) and XPO ($\lambda = 617.7$ nm) laser were employed, respectively. The most interesting feature is the laser fluence dependence of both reactive, ΔBaF, and non-reactive, ΔBa^*, yields. While ΔBa^* increases reaching a maximum around 1.9 mJ/cm^2 with a subsequent decline beyond this fluence value, the ΔBaF always increases over the studied laser fluence range. Clearly, the $[Ba^*]/[BaF]$ branching ratio as depicted in Fig. 5 is not con-

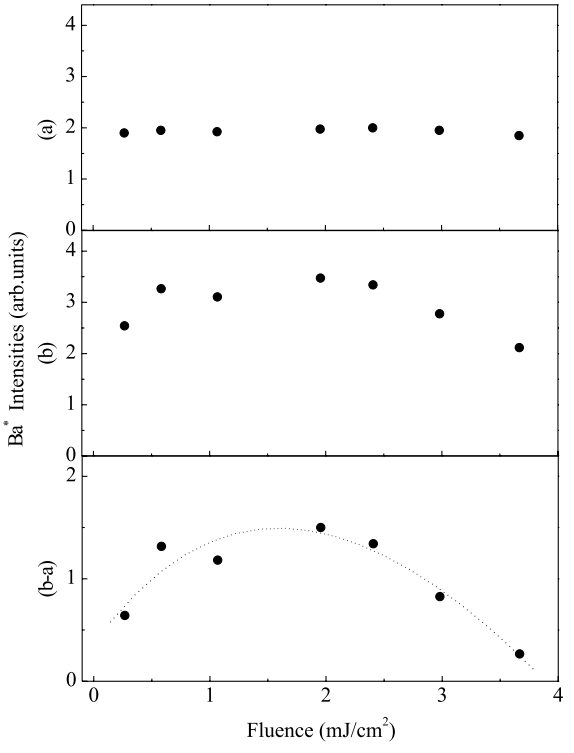

Fig. 3. Ba^* photofragmentation yield ratios as a function of the laser fluence. (a) Ba^* signal with the UV laser, (b) Ba^* signal when VIS pump laser operated 10 ns before the probe UV laser arrives to the ionisation region. ΔBa^* signal obtained by subtracting (a) from (b) signal. In all cases the same relative units are used.

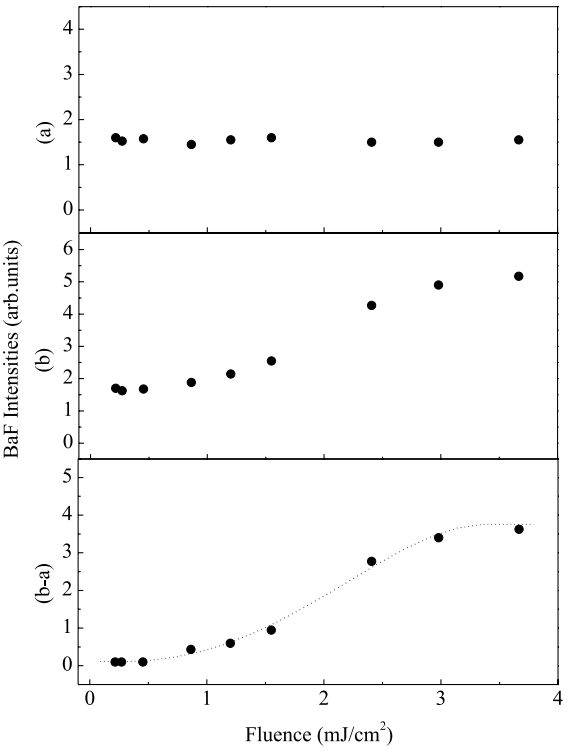

Fig. 4. Same presentation as in Fig. 3, but now for the BaF channel. Notice the opposite behaviour of the present BaF channel when compared with previous Ba^* data, in particular for laser fluences beyond ~2 mJ/cm^2.

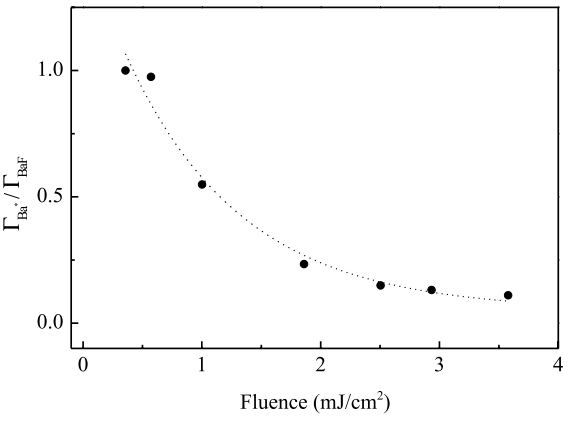

Fig. 5. Laser fluence dependence of the $[Ba^*]/[BaF]$ branching ratio. Points: present experimental results; dotted line is just a guide to the eye.

stant but depends of the laser field employed to induce the reaction.

For an understanding of the present results it should be remarked that as the complex is irradiated with more and more photons a coherent superposition of both ground and excited states is created. In addition, the $Ba\cdots FCH_3$ decomposes via two channels, e.g.

$$Ba^* + FCH_3 \xleftarrow{2} (Ba\cdots FCH_3)^* \xrightarrow{1} BaF + CH_3$$

and consequently the lifetime of the excited $(Ba\cdots FCH_3)^*$ may be influenced not only by the two channel photofragmentation dynamics but also by the intense laser field conditions. In this view, the actual $(Ba\cdots FCH_3)^*$ concentration is not longer constant but follows a periodical time dependent functionality controlled by the Rabi frequency and so by the laser fluence F. Indeed $[Ba\cdots FCH_3^*]$ will vary as $\sim\sin^2(\Omega/2)t$, in which the Rabi frequency, Ω, is proportional to $\sim F^{1/2}$ (hereafter we will write $\Omega = aF^{1/2}$, a being a laser fluence independent parameter). The coherent superposition of complex excited and ground states leads to a shortening of its lifetime which may favour the faster photodissociation channels as F, and so Ω, increases. As a result, photofragmentation products could be selectively formed as long as the reaction time is comparable with the Rabi period $1/\Omega$. It is out of the scope of the present Letter to describe the calculation of the transition moment and the Rabi frequency for the studied transition as a function of the laser fluence. However, as it will be published elsewhere [14], the Rabi period lies about the picosecond time domain over the low laser fluence range used in the present experiment, reaching the sub-picosecond regime at high fluences [14]. To the best of our knowledge there is no experimental information about the reaction time associated to the non-reactive channel yielding Ba^* products. However, the reaction time for the BaF channel has been measured to be about 270 fs by the femtosecond pump and probe technique [15,16]. Thus one can assume that the reaction time for the non-reactive channel could well be of the order of picoseconds as it is the (usual) case in photodissociation dynamics of van der Waals molecules. Bearing all this in mind, it seems that the employed laser conditions are probably suitable to achieve the control of the intracluster reaction by changing the laser fluence.

One of the crucial questions concerning the interpretation of present results is whether or not a multiphoton process is controlling the fluence dependence of the different reaction channels, because if such a process was present it could open new routes to turn on the reaction and produce the BaF. In this view, the enhancement of the BaF yield, as the laser fluence increases, would reflect the predominance of this new route rather than the (favoured) faster photofragmentation channel due to the shortening of the (excited complex) lifetime as the Rabi frequency increases. This alternative is further discussed below.

Let us consider for example the absorption of two-photon by the $Ba\cdots FCH_3$ complex. A two-photon mechanism would put 36.283 cm^{-1} into the system. As can be seen in the energetic diagram of Fig. 1 this would form a $Ba^+\cdots CH_3F$ ion surrounded by the Rydberg electron in a different orbital. In principle this state might evolve to form $BaF^+\cdots CH_3$ underneath the Rydberg state and subsequently $BaF^* + CH_3$. Thus, this BaF^* could then be easily excited by the probe ($\lambda = 266$ nm) photon.

The $Ba\cdots FCH_3$ absorption at 618 nm was studied in [16] (see, for example, its Section 3.1), monitoring the strong peak of the $Ba\cdots FCH_3^+$ signal caused by the simultaneous absorption of the one pump photon ($\lambda = 618$ nm) and one probe photon ($\lambda = 400$ m). Typical values of the (120 fs) pump and probe laser fluences were 0.5 and 1 mJ/cm^2, respectively. For the pump laser the used fluence of 0.5 mJ/cm^2 and 120 fs pulse duration gave a laser intensity of ca. 4×10^9 W/cm^2. As reported in [16] a linear dependence was always found for each photon over a range of 4 in laser fluence.

Obviously, the comparison between the possible two-photon regime induced in the present nanosecond experiment and previous [16] femtosecond experiment must integrate the pulse duration. Taking the latter into account one can show that the two-photon absorption process would therefore be much less probable in the present experiment than in the previously reported femtosecond study [16].

On the other hand, the possibility that such $(Ba\cdots FCH_3)^{**}$ Rydberg state leads into $BaF + CH_3$ through $Ba^+\cdots FCH_3 \rightarrow BaF^+ + CH_3$ reaction underneath of the Rydberg electron seems very unlikely. The $(Ba\cdots FCH_3)^+$ seems to be a very stable ion. When the $Ba\cdots FCH_3$ ionisation potential (see Fig. 4 in [11]) was measured, the $Ba\cdots FCH_3^+$ signal increased smoothly with the laser ionisation energy even though the $BaF^+ + CH_3$ channel was energetically opened (see energetic diagram), which can only be interpreted as that the $Ba\cdots FCH_3^+$ fragmentation into $BaF^+ + CH_3$ should be a very minor channel, at least at present excitation energies.

In summary, taking all the above considerations into account we conclude that multiphoton processes can be ruled out under the present experimental conditions.

4. Concluding remarks

The most interesting finding of the present work is that the $(Ba\cdots FCH)^*$ two-photodissociation channel yields, i.e. the reactive BaF and non-reactive Ba^* products, exhibited opposite behaviour depending upon the laser fluence. The BaF yield rises as the laser fluence is increased. However, the Ba^* yield reached a maximum at low fluences with a subsequent decline over the high laser fluence range. This opposite behaviour was attributed to a different reaction times associated to each individual photofragmentation channel of the $Ba\cdots FCH_3$. In this picture, the faster channel, the BaF product, would be favoured with respect to the slower one, the Ba^* product, as the excited complex lifetime becomes shorter as the Rabi frequency increases. This would justify the observation that the product $(Ba^*)/(BaF)$ branching ratio changes significantly from low to high laser fluence in such a way that the (photoinitiated) $Ba\cdots FCH_3 + h\nu \rightarrow BaF + CH_3$ reaction could be controlled.

A key feature of the present investigation is the use of nanosecond laser pulses with the excitation laser fluence as the only adjustable parameter to achieve the control of the photoinitiated reaction. Furthermore the application to a bimolecular reaction by clustering the reactants in a van der Waals should also be remarked. The simplicity of this scheme could be of interest when one considers its potentiality for practical applications.

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References

[1] R.N. Zare, Science 279 (1998) 1875.
[2] S.A. Rice, Nature 409 (2000) 422.
[3] A. Assion, T. Baumert, M. Bergt, T. Brixner, B. Kiefer, V. Seyfried, M. Strehle, G. Gerber, Science 282 (1998) 919.
[4] M. Shapiro, P.J. Brumer, J. Chem. Phys. 84 (1986) 4103.
[5] M. Shapiro, P.J. Brumer, J. Chem. Phys. 97 (1992) 6259.
[6] L.-C. Zhu, V. Kleiman, X.-N. Li, S.P. Lu, K. Trentelman, R.J. Gordon, Science 270 (1995) 77.
[7] D. Tannor, S.A. Rice, J. Chem. Phys. 83 (1985) 5013.
[8] T. Baumert, M. Grosser, R. Thalweiser, G. Gerber, Phys. Rev. Lett. 67 (1991) 3753.
[9] L. Dukan, L. del Fabbro, P. Pradel, O. Sublemontier, J.M. Mestdagh, J.P. Visticot, Eur. Phys. J. D 3 (1998) 257.
[10] S. Skowronek, R. Pereira, A. González Ureña, J. Chem. Phys. 107 (1997) 1668.
[11] S. Skowronek, R. Pereira, A. González Ureña, J. Phys. Chem. 101 (1997) 7468 (Special issue on Stereodynamics).
[12] S. Skowronek, A. González Ureña, in: R. Campargue (Ed.), Atomic and Molecular Beams: The State of the Art, Springer, Berlin, 2000, p. 353.
[13] S. Skowronek, A. González Ureña, Prog. React. Kinet. Mech. 24 (1999) 101.
[14] A. González Ureña et al., in preparation.
[15] V. Stert, P. Farmanara, W. Radloff, F. Noack, S. Skowronek, J. Jimenez, A. González Ureña, Phys. Rev. A 59 (3) (1999) 1727.
[16] P. Farmanara, V. Stert, W. Radloff, S. Skowronek, A. González Ureña, Chem. Phys. Lett. 304 (1999) 127.