# Transition State Spectroscopy of the Photoinduced Ca + $CH_3F$ Reaction. 1. A Cluster Isolated Chemical Reaction Study

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The "cluster isolated chemical reactions" technique is used to examine the dynamics of the photoinduced reaction producing electronically excited CaF when 1:1 Ca•$CH_3F$ complexes are deposited at the surface of large argon clusters. This technique ensures quantitatively that 1:1 complexes are actually at the origin of the observed signals. The reaction is monitored by observing the CaF chemiluminescence while scanning the photoexcitation laser. The resulting action spectrum contains information about the absorption bands of the complex, filtered by the dynamics of the reaction. The observations suggest a profound alteration of the calcium electronic structure and a control of the reaction by the CF stretch in $CH_3F$.

## 1. Introduction

From the early days of chemical physics, it has been known that chemical reactions are controlled by the passage through the transition state region of the reaction.[1] Many strategies have been developed to unravel the dynamics of reactive systems in this region, especially in the case of electron-transfer reactions (see ref 2 and references therein for a review). One of them is to perform the spectroscopy of the transition state: the reaction is photoinduced close to the transition state region and is monitored as a function of the wavelength of the photoinduction laser. Essentially four routes have been followed to conduct such experiments. They differ by the way reactants are put together and the way the reaction is photoinduced. The reaction is either (i) induced by electronic excitation in a 1:1 van der Waals complex of two reactants (the prereactive complex)[3], or (ii) it is turned on by photodetachment in a molecular anions,[4] or (iii) it is photoinduced in reactants ordered at clean surfaces,[5] or finally (iv) it is photoinduced in a van der Waals complex that results from the association between reactants predeposited at the surface of large argon clusters. This is the so-called cluster isolated chemical reaction (CICR) technique developed in our laboratory.[6,7]

The argon cluster plays three successive roles in a CICR experiment that end up with an interesting flexibility for the production of well characterized prereactive complexes. The first role is that of a nest to collect independently each reactant of the future prereactive complex. The second role is that of a low temperature thermostat that allows the reactants to associate and form the prereactive complex. The third role is to serve as a reaction medium that is active dynamically mostly in the exit channel of the reaction. This has been exemplified recently when studying the reaction of excited calcium with HBr.[8,7]

The CICR technique is used here to unravel the reaction of excited Ca with methyl fluoride, $CH_3F$. The ground-state reaction is

$$\mathrm{Ca} + \mathrm{CH_3F} \rightarrow \mathrm{CaF} + \mathrm{CH_3} \qquad \Delta H = -79.9\ \mathrm{kJ/mol} = -0.83\ \mathrm{eV} \quad (1)$$

with the energetics taken from refs 9 and 10. Its mechanism can be viewed as a harpoon reaction going through an electron transfer from Ca to $CH_3F$. However, no bound state for an additional electron exists at the equilibrium geometry of the molecular reactant, and the halogen bond has to be stretched for the molecule to attach efficiently the extra electron.[11] This creates a barrier in the entrance channel of reaction 1, and although the latter is exothermic, Ca···$CH_3F$ complexes can be stabilized at the surface of large argon clusters. The reaction is turned on by electronic excitation of the complex. The aim is to document a situation where the electron transfer that is only partial in the ground state of the Ca···$CH_3F$ complex is transformed by the electronic excitation into a full electron transfer that promotes reaction 1.

Situations that are apparently similar, have been examined in free complex experiments by Polanyi and co-workers on 1:1 Li···$CH_3F$[12] and by Ureña, Radloff, and co-workers on Ba···$FCH_3$.[13−28] We shall see the that dynamics of the present Ca···$CH_3F$ system is significantly different from the latter dynamics. Finally, the reaction dynamics of metastable states of calcium with $CH_3F$ has also been explored in full collision.[29,30]

## 2. Experimental Section

**2.1. Principle.** The principle of the experiment is to generate a beam of argon clusters, at the surface of which Ca atoms and $CH_3F$ molecules are deposited by the pick-up technique. The average number of each per cluster is strictly controlled and the observed signal are assigned to 1:1 Ca···$CH_3F$ complexes deposited at the surface of the argon clusters. A CW laser is scanned while monitoring the fluorescence of the electronically excited species CaF.

**2.2. Experimental Setup.** The experimental setup used in this experiment has been fully described.[6,31,32]

Briefly, the argon clusters are grown by homogeneous condensation in a continuous supersonic expansion from a Campargue source[33] with a 20 bar stagnation pressure at room temperature and a 0.2 mm nozzle diameter. These expansion conditions yield argon clusters having an average size of 2000.[34] After extraction from the free jet by a 1 mm skimmer, the cluster beam passes through a differentially pumped chamber and a 3 mm collimator before entering the main chamber where the

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reactants are successively deposited on clusters. This is performed by collisional capture, i.e., the well-known pick-up technique.[35] First, argon clusters capture calcium atoms by flying through a 30 mm long cell, which is heated at about 450 °C to maintain a low-pressure calcium vapor along the beam path inside the cell. Then, after 17 mm, clusters undergo the second pick-up by passing through $CH_3F$ vapor effusing from a capillary tube.

The reactants, Ca and $CH_3F$, are deposited at the surface of the cluster by the pick-up. It has been shown spectroscopically that calcium stays on the surface.[36] Once on the cluster surface, reactants are free to migrate, to collide with each other, and either to react when a barrierless exothermic reactive channel is available or to associate when the binding energy between the two reactants is significant compared to the temperature of the argon clusters (about 35 K[37]).

After the main chamber, the cluster beam passes through chambers that house mass spectrometer analyzers. First, a time-of-flight mass spectrometer allows us to measure the mass distribution of the argon clusters and hence to inform on their average size. Second, a quadrupole mass spectrometer allows us to perform partial pressure measurements. These two diagnostics are used to determine the average number of $CH_3F$ molecules deposited per cluster in the second pick-up zone.

The second pick-up zone is also the illumination zone where the laser turns on the reaction and the observation zone of the chemiluminescence. The laser light is the doubled output of a cw tunable single frequency titanium–sapphire laser (Coherent 899-21). It is scanned between 361.7 and 423.7 nm accross the calcium resonance line ($^1P_1 \rightarrow$ThinSpace $^1S_0$) at 422.7 nm (in the air). The laser light is transported into the chamber by an optical fiber (0.6 mm core). It is refocused at the exit of the fiber as a slightly converging beam that crosses the cluster beam at right angles. It serves to photoinduce the reaction within the complexes present on the clusters. It serves also to characterize spectroscopically the average number of Ca atoms deposited per cluster.

Most (90%) of the fluorescence collected by an optical system from the observation zone, is focused on the entrance slit of a scanning grating monochromator and dispersed before detection by a cooled photomultiplier tube (RCA 31034). Ten percent of the fluorescence is extracted before the monochromator and directed on a second photomultiplier in order to monitor the total fluorescence. The photon counting technique is used for detection. After fast amplification and discrimination, signals from both photomultipliers are accumulated on multiscaler cards in a microcomputer.

The data acquisition system has been designed to extract the relevant signal due to photoinduced processes occurring on the argon clusters. Undesired signals are due mainly to blackbody radiation of the heated calcium cell and to "off-cluster" processes which could occur between gas-phase calcium and gas-phase $CH_3F$ effusing respectively from the cell and the capillary tube. A flag in front of the nozzle allows to turn the cluster beam alternatively on and off at a 1 Hz frequency in synchronization with the channel advance of the acquisition cards. This allows to record simultaneously spectra with and without the cluster beam. Laser on and laser off experiments have been performed also. Hence simple subtractions allow us to extract the desired signal.

**2.3. The Quantitative CICR Technique.** An important advantage of the CICR technique is the strict control of the average number $\langle m \rangle$ of reactants deposited per cluster. This makes possible to obtain quantitative results and, in particular,

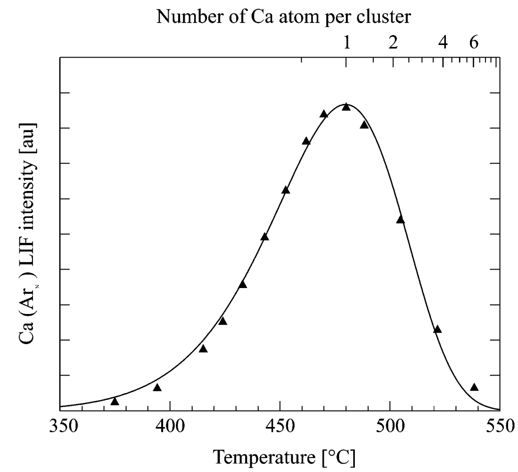


**Figure 1.** Measuring the calcium abundance on clusters by recording calcium laser-induced fluorescence vs the temperature of the calcium cell.

to find out the stoichiometry of the studied process. Indeed, the pick-up of reactants is a collisional process, that follows Poisson statistics. Therefore, the probability distribution $P_k(\langle m \rangle)$ of finding exactly $k$ reactants on a cluster follows a Poisson law of order $k$:

$$P_k(\langle m \rangle) = \frac{\langle m \rangle^k}{k!} \exp - \langle m \rangle \tag{2}$$

which depends on the single parameter $\langle m \rangle$. During an experiment, $\langle m \rangle$ is varied by changing the pick-up pressure, while recording the reactant or product signal. A fit of the corresponding curve by the Poisson distributions $P_k$ allows one to determine the best value of $k$, hence informing one on which number of reactants are involved in the process under study. Conversely, when $k$ is known, the method allows one to scale the variation of $\langle m \rangle$.

This method is at play in Figure 1 in order to determine the average number of calcium atoms deposited on the argon clusters in the absence of $CH_3F$ molecule picked-up on the cluster. For this purpose, the intensity of the laser-induced fluorescence of calcium is recorded as a function of the temperature of the calcium pick-up cell. Since the laser excites calcium atoms selectively and not dimers or trimers, the signal is expected to vary as the Poisson distribution of first order, $P_1$.[38] The latter is maximum when $\langle m_{Ca} \rangle = 1$. This property is used to scale the horizontal axis of Figure 1 so that the curve matches the Poisson distribution $P_1(\langle m_{Ca} \rangle)$, yielding an accurate calibration of the average number of calcium atoms per cluster as a function of the temperature of the calcium cell.

## 3. Experimental Results

Figure 2 displays the fluorescence observed when illuminating the clusters at 410 nm in an experiment where the clusters carry both Ca and $CH_3F$. The main band at 606 nm corresponds to the emission of free CaF($A^2\Pi \rightarrow X^2\Sigma^+$) with no change of the vibrational quantum number $\upsilon$. Its has two satellites on each side corresponding respectively to $\Delta\upsilon = \pm 1$, suggesting that the emitter has a significant internal excitation. The small band at 530 nm is assigned to the emission of CaF in the B $^2\Sigma^+$ state. The small feature at 657.5 nm is the calcium 4s4p $^3P \rightarrow 4s^2\ ^1S$ atomic line.

The chemiluminescence observed here is much more intense for emission from CaF(A) than from CaF(B) (see Figure 2). This contrasts with the full collision experiment reported in ref

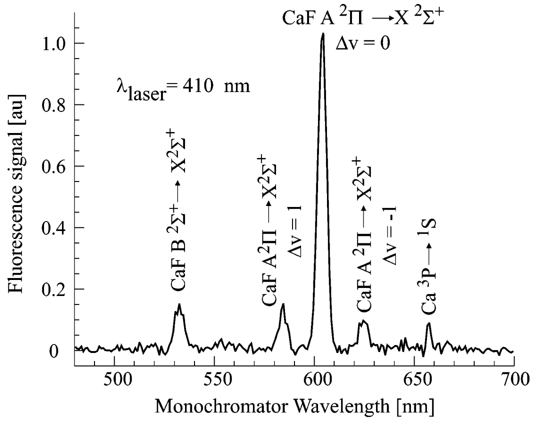


**Figure 2.** Fluorescence recorded when illuminating clusters carrying Ca and $CH_3F$ at 410 nm. The intensity of fluorescence is plotted as a function of the monochromator wavelength.

29 where the branching ratio CaF(A)/CaF(B) is estimated to $0.18 \pm 0.08$. The fact that the electronic level of calcium is 4s3d $^1D_2$ in ref 29, whereas it corresponds to an excitation to the blue of the 4s4p $^1P_1$ level in the present experiment plays necessarily a role in changing the CaF(A)/CaF(B) branching ratio. However, we do not believe that this is the sole explanation. Indeed, a similar change in the branching ratio between chemiluminescent products has already been observed when comparing our previous CICR experiment on the Ca + HBr reaction to a full collision experiment involving the same electronic excitation. It was concluded that the presence of the argon cluster is likely to quench partially the electronic excitation of chemiluminescent reaction products in the exit channel of the reaction.[7]

The quantitative CICR technique recalled above is used now to determine which of these signals results from the photoexcitation of 1:1 Ca$\cdots$$CH_3F$ complexes. From this analysis, it appears that the calcium emission at 657.5 nm is due to the photodissociation of the $Ca_2$ dimers that has been studied in our previous work.[38]

In contrast, the CaF emission is due to a photoinduced reaction that involves both calcium and $CH_3F$. The dependence of the corresponding signal with the average number of Ca atoms per cluster $\langle m_{Ca}\rangle$ is shown in the top of Figure 3. It is adequately fitted by the first-order Poisson distribution $P_1(\langle m_{Ca}\rangle)$ that is proportional to the number of clusters carrying a single Ca atom. The quality of the fit clearly indicates that the reactive signal originates from these clusters only. A complication arises when considering the dependence of the reactive signal as a function of $\langle m_{CH_3F}\rangle$, the average number of $CH_3F$ molecules per cluster. It is shown in the bottom of Figure 3. No single Poisson distribution adequately fits this signal over the full range explored experimentally. A reliable fit can be performed only when $\langle m_{CH_3F}\rangle$ is smaller than 1.3 using $[1 - P_0(\langle m_{CH_3F}\rangle)]$ as the fit function. The latter describes clusters carrying at least one $CH_3F$ molecule. The resulting fit, which is excellent up to $\langle m_{CH_3F}\rangle = 1.3$ only, indicates that beside complexes carrying one $CH_3F$ molecule, complexes carrying more than one molecule also participate to the chemiluminescence signal but with a lesser efficiency (for instance, because of the quenching of excited CaF by the other $CH_3F$ molecule).

The present purpose is to document 1:1 Ca$\cdots$$CH_3F$ complexes, the experimental conditions are thus adjusted for having $\langle m_{CH_3F}\rangle = 0.5$. This ensures that at least 77% of the observed chemiluminescence originates from cluster carrying a single $CH_3F$. Since it originates also from cluster carrying a single Ca

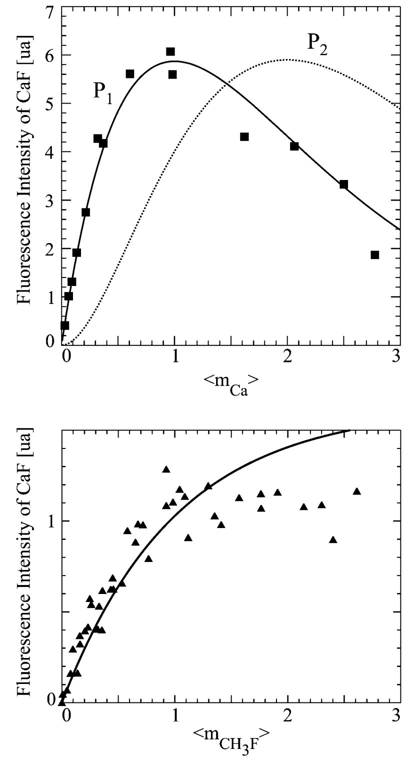


**Figure 3.** Fluorescence of electronically excited CaF as a function of the average number of Ca atom $\langle m_{Ca}\rangle$ (top) and of $CH_3F$ molecule $\langle m_{CH_3F}\rangle$ (bottom) per cluster. The solid line passing through the experimental points in the top figure is a fit by the first-order Poisson distribution $P_1(\langle m_{Ca}\rangle)$. The Poisson distribution $P_2(\langle m_{Ca}\rangle)$ is shown for comparison in the same figure. In the bottom figure, the solid line is a fit of the experimental points by $1 - P_0(\langle m_{CH_3F}\rangle)$ where $P_0$ is the Poisson distribution of zero order. See section 3 for details.

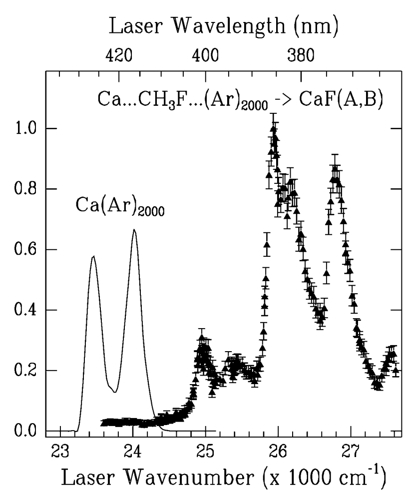


**Figure 4.** Action spectrum for the formation of the excited CaF product (experimental points). For comparison, the solid curve shows the excitation spectrum of the Ca(4s4p $^1P$)$Ar_{2000}$ fluorescence when no $CH_3F$ molecule is present on the argon cluster.

atom, this fraction of the signal is actually due to the 1:1 (Ca, $CH_3F$) system deposited on the same argon cluster. However, we do not know yet if it is associated as a Ca$\cdots$$CH_3F$ complex. The answer to this question appears in the discussion when observing the action spectrum.

The action spectrum obtained under these experimental conditions is shown in Figure 4: it was obtained by recording the CaF fluorescence intensity as a function of the excitation laser frequency. Action spectra were recorded independently whether CaF is in the excited states $A^2\Pi$ or $B^2\Sigma^+$. No difference

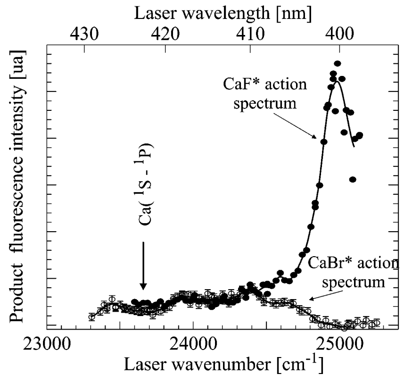


**Figure 5.** Zoom showing the red part of the action spectrum reported in Figure 4(dots labeled CaF* action spectrum). For comparison, the experimental points labeled CaBr* action spectrum recall the action spectrum of ref 7 for the formation of CaBr from a Ca···HBr complex deposited on an argon cluster.

appears between the two spectra. The experimental points in Figure 4 is thus the summation of the two spectra. The spectrum of Figure 4 extends over the full range observed experimentally, between 23600 and 27600 $cm^{-1}$. The tail between 23600 and 24400 $cm^{-1}$ is a significantly nonzero signal. It is enlarged in Figure 5. Between 24400 and 27600 $cm^{-1}$, the action spectrum exhibits a complicated structure with three main bands centered at about 25000, 25900, and 26800 $cm^{-1}$.

## 4. Discussion

The solid curve of Figure 4 recalls the excitation spectrum of the calcium fluorescence that has been recorded and analyzed in ref 36 in an experiment where only Ca is present on the cluster. Clearly, the two spectra shown in Figure 4 are very different. Hence, in the present Ca, $CH_3F(Ar)_{2000}$ experiment, Ca is not excited on the argon cluster prior to its association with $CH_3F$ for reacting afterward. Instead, the excited product CaF results from the photoexcitation of a Ca···$CH_3F$ complex, already formed on the argon cluster.

A series of works performed in this laboratory need to be recalled before starting the discussion of the action spectrum shown in Figure 4. They concern an apparently similar system, Ca···HBr, that turns out to be very different from the present Ca···$CH_3F$. These works address, experimentally and theoretically, the dynamics of the photoinduced reaction forming electronically excited CaBr, the prereactive complex, Ca···HBr, being either free[39,40,41] or deposited at the surface of large argon clusters (i.e., a CICR experiment as in the present work).[8,7]

The CICR work on the Ca···HBr system reports an action spectrum that extends in the range 23300−25000 $cm^{-1}$, on both sides of the calcium resonance line.[8,7] Smooth structures are observed. The overall shape of the spectrum mimics the much more structured action spectrum of the free Ca···HBr complex.[39,40] In both experiments, CICR and free complex, the action spectrum is interpreted as a local excitation of calcium, suggesting that HBr does not affect dramatically the electronic structure of Ca. Simply, it lifts the degeneracy of the 4s4p $^1P$ level of Ca, one of the resulting states being of A″ symmetry. The latter is T-shaped in its equilibrium geometry with the $4p\pi$ orbital aligned out of the (Ca,H,Br) plane. The dynamics of the reacting free complex in the A″ state is well described by wave packet calculations. The picture that emerges is that the complex has bending oscillations on either side of a funnel leading to the reaction with a high efficiency.[41] The presence of the argon cluster in the CICR experiment does not affect substantially the electronic structure of the complex, nor its geometry, nor its dynamics. This stems from a small shift of the action spectrum, only 90 $cm^{-1}$, whether the complex is free or deposited on an argon cluster. The argon cluster simply hinders and does not inhibit the oscillations of the complex that turn on the reaction.[8,7]

The intensity and location of the structures observed in the action spectrum of Figure 4 indicate an entirely different situation. A reminiscence of the behavior that has just been recalled for the Ca···HBr system actually exists but it is limited to the red part of the action spectrum between in 23600 and 24500 $cm^{-1}$. This appears in Figure 5, a zoom where the action spectrum of Figure 4 is compared to that of the Ca···HBr system. As seen in this figure, the action spectrum of the Ca···HBr experiment vanishes above 25000 $cm^{-1}$ where the dominant series of bands of the Ca···$CH_3F$ experiment appears. Something new happens in the latter system that does not seem relevant of the local excitation that prevails in the Ca···HBr experiment. This is very unexpected not only because of the present comparison with the Ca···HBr system but also because local excitation of the metal moiety prevails in all the apparently similar complexes that were investigated so far: complexes between an alkali atom and halogen containing molecules[12,42,49,] or a complex between barium and $CH_3F$.[15,19,23,25] Local excitation has also been found in many excited metal ion complexes such as $Mg^+CH_3I$ described in ref 50.

The series of intense bands observed in the action spectrum of Figure 4 cover the spectral range 24800−27600 $cm^{-1}$. They do not overlap transitions of free calcium and are located between the allowed transition to the 4s4p $^1P$ level at 23652 $cm^{-1}$ and the forbidden transition to the 4s5s $^1S$ at 33317 $cm^{-1}$. This reveals a profound alteration of the calcium electronic structure where the action spectrum of Figure 4 can be interpreted tentatively as due to one or two electronic transitions superimposed with a vibrational progression. Indeed, the series of intense features that are almost equally spaced at about 25000, 25900, and 26800 $cm^{-1}$ can be viewed as a vibrational progression. The corresponding vibrational constant, ca. 950 ± 50 $cm^{-1}$, cannot be associated with the weak van der Waals modes describing the movements of Ca within the complex. Instead, it is likely assigned to a deformation of the rigid $CH_3F$ molecule. The lowest vibrational mode of free $CH_3F$ has a 1049 $cm^{-1}$ constant. It is associated with the CF stretch,[51] and is tentatively assigned now to the vibrational progression in Figure 4. Hence, the CF stretch would appear as an important parameter that controls the reaction and the relative intensity of the series of peaks at 25000, 25900, and 26800 $cm^{-1}$ would reflect a compromise between an optimum Franck−Condon factor for the vibronic excitation and a good branching to the chemiluminescence channel.

The nature of the electronic transition that serves for the excitation of the complex is quite puzzling, since it is quite far from the electronic states of free calcium. Several possibilities can be invoked to account for the apparently non local excitation of the Ca···$CH_3F$ complex. The first one is a substantial mixing between the 4p and 5s orbitals of calcium and the antibonding $\sigma^*_{CF}$ orbital of $CH_3F$. This would result into a substantial electron transfer from Ca to $CH_3F$ in the excited state of the complex. Another possibility is the promotion of the 5s orbital to a diffuse Rydberg orbital that, stabilized by the large electric dipole of $CH_3F$ (1.86 D[52]), interacts strongly with the 4p orbital.

Alternatively given the apparently large role played by the C−F stretch, it is also conceivable that the progression observed in Figure 4 does not start at the origin of the electronic transition. If it starts at the $v = 1$ or 2 vibrational level of this deformation mode, the origin of the transition would be transported down, from 25000 to 24100 or 23200 cm$^{-1}$, i.e., in the latter case, to the red of the resonance transition of Ca. In that case, the picture of the electronic excitation would be that of a fairly local electronic excitation of the metal atom in resemblance with the situation encountered with Li$-$CH$_3$F[12] and Ba$-$CH$_3$F[23] systems. Nevertheless, the present situation is still very different since, in contrast with the Li$-$CH$_3$F and Ba$-$CH$_3$F systems, a substantial kick has to be given to the C$-$F stretch of CH$_3$F to turn on the Ca + CH$_3$F reaction. Then, the very small reaction signal observed below 24700 cm$^{-1}$ could correspond to the head of this excitation band when the kick to the C$-$F stretch is not large enough. The preliminary results of an ab initio calculation that will appear in a forthcoming paper tend to support this picture. In particular, it predicts a vibrational constant to the CF stretch in the electronically excited states of the Ca$\cdots$CH$_3$F complex that agree with the present observation of 950 $\pm$ 50 cm$^{-1}$.

## 5. Conclusion

A charge-transfer reaction forming excited CaF has been photoinduced in a 1:1 Ca$\cdots$CH$_3$F complex deposited at the surface of a large argon cluster of average size 2000. The experiment provides a fairly structured action spectrum for this reaction that extends between 24800 and 27600 cm$^{-1}$, a region that overlaps no transition of free calcium. This suggests at a first glance that the electronic structure of calcium is strongly affected by the interaction with methyl fluoride: either excitation to charge transfer states of the complex or the promotion of a valence electron of calcium to a diffuse Rydberg orbital. The structure of action spectrum also suggests a vibrational progression that is tentatively assigned to the CF stretch of CH$_3$F. It is conceivable that the action spectrum does not start at the origin of the electronic transition because it is filtered by the dynamics of the reaction, very small when the CF excitation is small.

The virtue of the present experiment is to allow for the assignment of the action spectrum to the 1:1 Ca$\cdots$CH$_3$F, a conclusion that is sometimes hard to achieve when the experiment is conducted on the free complexes formed in a supersonic expansion. In turn running such experiment gives a deeper insight into the dynamics of the reaction since the observed action spectra are more structured. Hence, a free complex experiment is currently under progress in our laboratory. Finally, to answer the issues about the nature of the excited state, ab initio calculations will be presented in a separate paper where the shape and location of the excited potential surfaces correlating to the excited 4s4p $^1$P and 4s5s $^1$S levels of calcium at large separations between Ca and CH$_3$F are calculated.

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