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Transition state spectroscopy of the photoinduced $\text{Ca} + \text{CH}_3\text{F}$ reaction II. Experimental and ab-initio studies of the free $\text{Ca} \cdots \text{FCH}_3$ complex.

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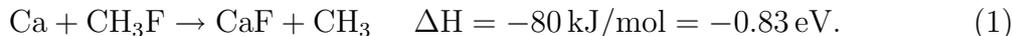
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Abstract

The $\text{Ca}^* + \text{CH}_3\text{F} \rightarrow \text{CaF}^* + \text{CH}_3$ reaction was photoinduced in 1:1 $\text{Ca} \cdots \text{CH}_3\text{F}$ complexes formed in a supersonic expansion. The transition state of the reaction was explored by monitoring the electronically excited product, CaF , while scanning the laser that turns on the reaction. Moreover, the electronic structure of the $\text{Ca} \cdots \text{FCH}_3$ system was studied using *ab-initio* methods by associating a pseudopotential description of the $[\text{Ca}^{2+}]$ and $[\text{F}^{7+}]$ cores, a core polarization operator on calcium, an extensive Gaussian basis and a treatment of the electronic problem at the CCSD(T) (ground state) and RSPT2 (excited states) level. In this contribution we present experimental results for the free complex and a comparison with the results of a previous experiment where the $\text{Ca} \cdots \text{CH}_3\text{F}$ complexes are deposited at the surface of large argon clusters. The *ab-initio* calculations allowed an interpretation of the experimental data in terms of two reaction mechanisms, one involving a partial charge transfer state, the other involving the excitation of the C-F stretch in the CH_3F moiety prior to charge transfer.

1 Introduction

The present paper is the second of a series [1] concerning the reaction



The energetics are taken from Ref. [2, 3]. Since the bonding in CaF is ionic, the mechanism of the reaction could be considered as a simple harpoon reaction where a low ionization energy atom, Ca, transfers one of its valence electron to an electron accepting molecule, CH₃F. However, a complication arises due to the internal degrees of freedom of CH₃F that has motivated our interest to this system. Methyl fluoride is representative of molecules that require deformation to become an electron attractor. No bound state of an additional electron exists at the equilibrium geometry of this molecule and the C-F bond has to be stretched, for the molecule to attach an extra electron [4] and become reactive. Hence, the dynamics of the reaction are expected to be more complex than suggested by the simple harpoon model. In particular, the transition state for a reaction to occur in excited electronic states may involve a geometrically wider range of the potential energy surfaces (PES's) than the point like crossing picture usually invoked in the standard harpooning mechanism. Moreover, as in the related Li + CH₃F reaction [5], a barrier is expected to block the ground state reaction 1, although it is exothermic. Evidence of this property has already been shown experimentally in the ground state since a 1:1 non reactive Ca ··· CH₃F complex could be stabilized on a large argon cluster (see paper I of this series [1]).

This class of electron transfer reactions where the molecular reactant needs deformation to attach an extra electron is generally encountered in reactions of alkali and alkaline earth atoms with methyl halide and hydrogen halide molecules. Some of the available literature, both experimental and theoretical is reviewed below. It mostly concerns alkali-hydrogen halides systems.

Experimentally, the dynamics of these reactions has been explored both in bimolecular collisions [6, 7, 8] and in van der Waals complexes by analyzing action spectra when

turning on the reaction with lasers and monitoring one of the reaction products. The Na/HF [9], Li, Na/HF, CH₃F [10, 11, 5], Na₂/CH₃Cl [12], Ca/HX [13, 14, 15, 16] and Ba/CH₃F [17, 18, 19, 20, 21, 22] systems were explored using the latter technique. Real-time studies have also been performed on the Ba/CH₃F system [23, 24, 25, 26, 27]. For all the studies appearing in the literature the observed branching to reaction is quite complex. For example, the Na/HF study reveals that exciting the H-F stretch promotes the electron transfer step prior to reaction [9] and the Ba/CH₃F studies indicate that the reaction proceeds only after the initial electronic excitation has been transferred to a lower electronic state.

Potential and dynamical calculations are also available, essentially for alkali/hydrogen halide systems [9, 28, 29, 30, 31, 32, 33, 34, 35, 36]. In particular the Na/HF system has benefited of extensive *ab initio* energetics and transition dipole moment calculations that yielded an action spectrum in good agreement with the experimental data [35, 36]. Concerning systems that contain an alkaline earth atom, besides the pioneering work of Isaacson and Muckerman on Ca+HCl [37], an extensive exploration of the ground state PES is available for Be/HF [38] as well as information on excited PES and the corresponding excited state dynamics for Ca/HCl [39, 40, 41, 42] and Ca, Ba/CH₃F [40, 24]. The work on Ca/CH₃F [40] is a semiclassical treatment of the dynamics, based on multipolar expansion of the electrostatic interaction between Ca and CH₃F. It is aimed at unraveling steric effects in the bimolecular collision between Ca(4s3d ¹D) and CH₃F, spatially oriented.

Process 1 is particularly attractive, given the results published in the first paper of this series, a Cluster Isolated Chemical Reaction (CICR) study where the van der Waals complex Ca...CH₃F is deposited at the surface of a large argon cluster [1]. When scanning the laser to turn the reaction on, a broad structured action spectrum was found. It appears quite blue-shifted, from the 4s4p ¹P ← 4s² ¹S calcium resonance transition at 422.8 nm, extending from 360 and 420 nm where no transition of calcium is expected. In that work it was concluded that a local excitation of the sole calcium

atom could not account for such a band. Two explanations were proposed, based either on purely electronic or on purely dynamical arguments. The first one implies a significant alteration of the calcium electronic structure that brings a level of calcium within the excitation region. This can be due either to a substantial electron transfer between Ca and CH₃F in the excited state, or to the promotion of the excited electron to a Rydberg orbital, stabilized by the interaction with CH₃F. The second tentative explanation was invoked due to the observation of structures in the action spectrum, an observation that makes the present Ca/CH₃F system very different from the apparently similar Ba/CH₃F system (Ca and Ba are both alkaline earth atoms) studied in the groups of Ureña [17, 18, 19, 20, 21, 22] and Radloff [23, 24, 25, 26, 27]. The structures observed in the Ca/CH₃F system were tentatively assigned to the C-F stretch in the CH₃F molecule, suggesting that this stretch plays an important role in the dynamics of turning on the reaction. Depositing one (or more) quantum on this vibration would lead to a substantial blue shift of the action spectrum with respect to the calcium resonance line, in agreement with the experiment.

The present work aims at clarifying the issues mentioned above on the nature of the electronic transitions that promote the reaction and on the influence of the dynamics in the observed action spectrum. In particular we would like to know whether the laser excitation directly turns on a charge transfer reaction mechanism. For this purpose, an experimental investigation was achieved, where the Ca \cdots CH₃F complex is "free" instead of being deposited on an argon cluster as in CICR experiments. Our expectation is that the solvation of a charge transfer intermediate by the argon environment of CICR experiments may redshift the corresponding part of the action spectrum. Comparing action spectra from CICR and free cluster experiments would then help to disentangle charge transfer from other reaction paths.

In parallel with the experimental investigation, we have carried out detailed *ab-initio* calculations of the PES's of Ca + CH₃F in the entrance channel, considering all the excited states of calcium up to Ca*(4s5s¹S). The electronic problem was treated

within a CASPT2 type scheme within a pseudopotential description of Ca and F. Moreover, since, as mentioned, charge transfer is expected to play a crucial role, we have also determined the dipole moments of various states along the entrance channel of the reaction.

2 Experiment

A full report of the experimental technique will appear in paper III of this series. Briefly, a He/CH₃F/Ca mixture is expanded into vacuum to generate a supersonic beam containing the Ca \cdots CH₃F complex. Laser evaporation is used to produce Ca in the gas phase. In addition to the desired complex, the beam contains other compounds: free Ca, CH₃F and CaF that were generated by the laser ablation of the Ca rod in the He/CH₃F mixture. The beam also carries clusters of these compounds.

The Ca \cdots CH₃F complex is excited selectively by a pulsed laser (the pump) with a nanosecond pulse width, tuned to absorption bands of the complex. Depending on the wavelength domain, the same laser or a second one (the probe) ionizes the desired compounds resulting from the laser driven reaction (and undesired compounds also present in the beam). The photo-ions are detected using time of flight mass spectrometry. In the present work, the CaF⁺ ion signal is monitored as a function of the pump wavelength. As always, in laser ablation experiments, the choice of expansion conditions, pulse energy and focusing of the ablation laser is quite difficult in order to get a signal originating reliably from reactions within the desired complex. The fluence of the pump laser (and probe laser when two lasers are used) is also of importance in this respect.

The pump laser is tuned over two spectral ranges, 535-421 nm and 415-353 nm, on each side of the Ca(4s4p ¹P \leftarrow 4s² ¹S) resonant transition at 422.8 nm. The latter spectral range includes the band already reported in our previous CICR experiment [1].

In the red range, the photon energy is not sufficient to allow both for the excitation of the complex and the ionization of the reaction compounds. Ionization is thus

performed using a second laser, the probe laser, operating at 354.7 nm and delayed by 5 ns with respect to the pump laser in order to ascertain that the probe operates on an excited neutral. Energetically, the probe pulses allow us to ionize CaF when excited in the $B^2\Sigma^+$ state. Recording the corresponding signal while scanning the pump laser provides the so-called action spectra of the reaction forming $\text{CaF}(\geq B^2\Sigma^+)$. As it will appear in paper III of this series, in contrast to signals measured in the blue range (see below), signals measured in the present red range could not be normalized to the concentration of the $\text{Ca}\cdots\text{CH}_3\text{F}$ complex. For this reason, only the overall location and extension of the band observed in this spectral region will be considered below, not its shape and detailed structure.

In the blue range, the photon energy is sufficient to, at once, turn on the reaction in the complex with one photon and further ionize the electronically excited products of the reaction with one or two additional photons. Given the ionization energy of CaF, the ionization can proceed either from a resonant two photon process on $\text{CaF}(A^2\Pi$ or $B^2\Sigma^+)$ with a low vibrational energy or from a single photon process on the same electronic states of CaF but with a substantial vibrational excitation. In both cases, the CaF^+ signal observed while scanning the laser documents the action spectrum, i. e. the reactive yield of $\text{CaF}(A,B)$ from excited complex. The ion signals measured here could be normalized to the concentration of the complex since a signal proportional to this concentration was available. Hence, a detailed analysis of structures in the measured spectrum is meaningful. Nevertheless, the shape of the spectrum is not corrected for variations of the ionization efficiency as a function of the CaF internal energy. Potentially this affects the relative intensities of the structures that appear in the spectrum since the internal excitation of CaF may vary from one end of the spectrum to the other. However, this does not affect the localization of the structures, the only question to be addressed in the present paper (a fully corrected spectrum will appear and will be discussed in paper III of this series).

3 Calculations

The calculations have been conducted using the MOLPRO *ab initio* package [43]. They aim to describe the ground and electronic states of the Ca/CH₃F system as Ca approaches CH₃F. A limited exploration of the corresponding PES's along the C-F coordinate is also performed as well as a rough exploration of the topology of the ground state surface.

3.1 Geometrical considerations

In the context of the bimolecular reaction 1 the approach between Ca and CH₃F corresponds to the entrance channel of the reaction. We anticipate earlier in the Introduction that, although the ground state reaction forming CaF+CH₃ is exothermic, it is blocked by a barrier. The experimental part of the present work took advantage of this property and indirectly confirmed the existence of such a barrier since it was possible to form a non reactive Ca \cdots CH₃F complex from which the reaction is turned on by photoexcitation. This was observed also in paper I of this series [1]. Hence, a local van der Waals well is expected to exist in the entrance channel of the ground state reaction that defines the equilibrium geometry of the complex. Its location was investigated in the present work, using a geometry optimization at the CCSD(T) level, corrected for the basis set superposition error (BSSE) with respect to the dissociation channel Ca + CH₃F.

The approach between Ca and CH₃F is described in Figure 1 by the distance between Ca and a dummy point x . Point x is located along the C-F bond at 1.2 Å from C. For the potential curve calculations, Ca approaches x along a line defined by the C- x -Ca angle set to 170°. The values 1.2 Å and 170° are somewhat arbitrary. They were chosen since the corresponding "Ca trajectory" is believed to be representative of an approach towards the F end of the CH₃F molecule.

3.2 The electronic problem

As already mentioned, the present calculations aim at predicting the excited PES's of $\text{Ca}\cdots\text{CH}_3\text{F}$. This implies in particular that the asymptotic energies at large separations between Ca and CH_3F are well predicted, *i.e.* a correct description of the transition energies of calcium are needed here up to 33000 cm^{-1} . For this purpose, we used the technique successfully applied in Ref. [44] where the core electrons of calcium are described by a $[\text{Ca}^{2+}]$ effective potential, complemented by a core-polarization operator to account for the significant electric dipole polarizability of $[\text{Ca}^{2+}]$ ($\alpha = 3.171\text{ a}_0^3$). The cut-off function used here to calculate the corresponding correction is that of Ref. [45], with the cut-off parameter set to 0.365 a.u. . An extensive uncontracted $[12\text{s},8\text{p},8\text{d},4\text{f}]$ valence Gaussian basis set was used to describe calcium. We shall see below that these choices provide a reliable prediction of the calcium energy levels, up to the $4\text{s}5\text{s }^1\text{S}$ levels.

An effective core potential was also used to describe the inner electrons of fluorine ($[\text{F}^{7+}]$) [46] whereas all the electrons of C and H were considered. This actually provides an inequivalent treatment of C and F. Nevertheless, the fact of including explicitly or not the 1s electrons should be of little importance on the present results given that these electrons are anyway kept inactive in the CI treatment (see below). A $(7\text{s},7\text{p},4\text{d})$ contracted into $[6\text{s},6\text{p},3\text{d}]$ basis set was used for F. The $6\text{-}311++\text{G}(2\text{d},2\text{p})$ and aug-cc-pvTZ basis sets of Ref. [47] are used for H and C respectively. One diffuse d and one diffuse f orbital on C were found necessary to get a reliable C-F distance when optimizing the CH_3F geometry at large $\text{Ca}\cdots\text{CH}_3\text{F}$ distances.

3.3 Types of calculations

Several types of calculations were completed: *a)* geometry optimization for the ground state of the complex; *b)* an extensive exploration of the energy variations in the ground and excited states of the complex along the Ca- x approach distance. *c)* a limited exploration of the PES's when varying the C-F distance in CH_3F while keeping the

Ca- x distance and the C- x -Ca angle fixed. More details are given now for each of these calculations.

a) The geometry optimization is performed at the CCSD(T) level for the ground state of the system. It includes the Ca- x distance, the C- x -Ca bending angle, the C-H and C-F distances and the umbrella angle of CH₃. However, it considers CH₃F as a regular tetrahedron, with two H-atoms off the C- x -Ca plane by +60° and -60° and the third one in the C- x -Ca plane. The C- x -Ca angle is defined as shown in Figure 1, with respect to the H-atoms. The optimization completed included a correction for the basis set superposition error as explained in section 5.1.

b) The energy variations for the excited states of the complex were explored as a function of the approach distance Ca- x , the C- x -Ca bending angle being set to 170°. The other coordinates defining the geometry of the system where excited states are to be calculated (*i.e.* the C-H and C-F distances and the umbrella angle of CH₃) are optimized for the ground state at each Ca- x distance with the C- x -Ca angle set to 170°. As above the ground state calculation is performed at the CCSD(T) level. In addition to providing geometries for the excited state calculation, this also provides the variation of the CCSD(T) potential energy along the Ca- x coordinate. A state-averaged MCSCF calculation, followed by RSPT2 (precisely the RS2C option of the MOLPRO package [48, 49]), was performed. The average includes the ten lowest singlet states that correlate adiabatically to the 4s² ¹S, 4s4p ¹P, 4s3d ¹D, and 4s5s ¹S levels of calcium at large Ca – CH₃F distances ¹. The active space consists of two electrons in 13 orbitals (asymptotically the orbitals 4s, 4p, 3d, 5s and 5p of Ca). The relevance of the RSPT2 calculation to describe the atomic excited states can be seen in table 1 where the asymptotic energies at large separation between Ca and CH₃F are compared with the experimental excited energies of free Ca. Since the orbitals are obtained from a state-averaged MCSCF calculation, we do not expect that the weakly bound ground state of the complex, even at the RSPT2 level to be accurate as the

¹Only singlet states are relevant for the comparison with the experimental action spectra since transitions to the triplet states from the singlet ground state are forbidden.

CCSD(T) calculations mentioned above which have been used to provide information on the ground state.

c) The exploration of the PES's along the C-F coordinates was limited to the vicinity of their minima in the entrance channel, the main goal being to be able to estimate vibrational properties along the C-F coordinate.

4 Experimental results

The action spectrum observed in the present experiment while monitoring CaF is shown in Figure 2. It reveals two bands labeled A and B in the figure. Only the spectral region corresponding to band B could be documented in our former CICR experiment due to the limited range achievable using a *cw* laser to excite the complex [1]. With the purpose of the present paper, the discussion below concentrates on the comparison between band B of the present action spectrum (free complex) and the band measured in the CICR experiment. Figure 3 present this comparison. A full discussion of the A and B bands of the free complex action spectrum in Figure 2 is beyond the scope of the present paper. It will appear in paper III of this series.

The similarity between band B and the CICR spectrum presented in Figure 3 is striking, but qualitative. The main features of the CICR spectrum serve as a guideline to examine the similarities and differences between the two spectra. First, the CICR spectrum is structured with three features at 24960, 25910, 26780 cm^{-1} respectively. These resolved bands appear blue shifted by 200 cm^{-1} with respect to corresponding features of the free complex spectrum as indicated by the dashed vertical lines in Figure 3. Additional structures exist in the CICR spectrum, one of which appears as an intense broad shoulder in the blue wing of the central peak near 26100 cm^{-1} . For reasons that will appear in the discussion, we tentatively assign this shoulder in the CICR spectrum to be a red shifted reminiscence of the very structured blue wing of the free complex spectrum. This correspondence is indicated in the figure by dot-dashed Gaussian shaped peaks. The peaks were drawn with the same width, 460 cm^{-1} , in

both experiments but the CICR peak was red shifted by 650 cm^{-1} with respect to the corresponding peak in the free complex experiment. Note the width chosen is somewhat arbitrary as it is dependent on the intensity of the peak. However the important point is that the corresponding peak is redshifted when the complex is solvated on argon whereas the other features are blue shifted.

5 Calculation results

5.1 Optimum geometry in the ground state

As already mentioned, the optimization is performed at the CCSD(T) level. It is corrected as it will appear below for the basis set superposition error (BSSE correction). The optimum geometry corresponds to the Ca atom located near the F atom of the CH_3F molecule in a bent Ca-F-C geometry. It is defined by the distances $\text{Ca}-x = 2.67\text{ \AA}$, $\text{C}-\text{F} = 1.43\text{ \AA}$ and $\text{C}-\text{H} = 1.09\text{ \AA}$, and by the values 220° and 107° for the bending angle $\text{C}-x-\text{Ca}$ and the pyramidalization angle of the CH_3 group, respectively. This optimum geometry is stabilized by 850 cm^{-1} with respect to the $\text{Ca} + \text{CH}_3\text{F}$ asymptote.²

Of course when the CH_3 group is let free to rotate about the C-F axis, there is an almost isoergic path corresponding to a circular groove about the axis. In the planar cut to the ground state PES that is defined in Figure 1, the groove appears simply as two quasi degenerate minima at $\text{C}-x-\text{Ca}$ angles of 140 and 220° . They appear in Figure 4, a cut of the ground state PES along the bending angle $\text{C}-x-\text{Ca}$ when Ca moves in the plane defined in Figure 1. The squares (fitted by the dashed curve) in the figure were provided by a CCSD(T) calculation where all the coordinate but the $\text{C}-x-\text{Ca}$ angle were adjusted to minimize the potential energy. Then a BSSE correction is performed using the counterpoise method of Boys and Bernardi for the fragments

²In preliminary calculations, we have identified a much deeper well on the ground state PES, which corresponds to an inserted structure FCaCH_3 connected without any barrier to the $\text{CaF} + \text{CH}_3$ asymptote. We can provide an estimate of the dissociation energy, 2.4 eV with respect to $\text{CaF} + \text{CH}_3$, *i.e.* 3.2 eV below the $\text{Ca} + \text{CH}_3\text{F}$ asymptote. It is separated from the present well by a very high barrier that cannot be overcome under the present experimental conditions. Such a deep insertion well has been identified in a CCSD(T) type investigation of the entire ground state PES of a similar system, Ca/HF [38].

Ca and CH₃F [50]. As observed in the figure, the BSSE correction reduces the depth of the two minima by more than a factor two (745 versus 1677 cm⁻¹)³ but does not affect their location. The region of the wells, between 120 and 240°, is indeed the region where the complex is the most compact, hence maximizing the effect of the ghost orbitals.

The two minima that appear in the figure are part of a broad well of ≈ 745 cm⁻¹. Comparatively, the 220 cm⁻¹ barrier between the two minima is significant.

Figure 5 reports ground state potential energy as a function of the approach distance Ca-*x*. The bending angle C-*x*-Ca is set to 220° in this calculation, which is the CCSD(T) calculation described in section 3.3b. Again, two results are shown in the figure, whether the BSSE correction is included (solid line and triangles) or not (dashed line and squares). A well depth of 850 cm⁻¹ is found along the BSSE corrected curve, corresponding to the equilibrium geometry of the Ca \cdots CH₃F complex. The BSSE correction reduces the well depth by a factor 2 (850 versus 1677 cm⁻¹) but as mentioned in the footnote above it also affects the equilibrium distance (Ca-*x* = 2.67 Å along the BSSE corrected curve, versus 2.52 Å without BSSE).

5.2 Excited potentials along the Ca-*x* distance

The excited potentials shown in Figure 6 correlate to the 4s3d ¹D, 4s4p ¹P and 4s5s ¹S of Ca. They are labeled with their asymptotic correlation as in C_{∞v} since the symmetry lowering due to the non linearity of the Ca-F-C assembly and that due to the presence of the H atoms is weak. Nevertheless the state labeling is put between quotation marks to stress on the approximate character of the symmetry. The curves labeled "Π" and "Δ" appear doubly degenerated on the scale of the figure whereas they are not rigorously identical in the calculation. The three "Σ" curves exhibit severe anti-crossings. In contrast, the two "Π" are almost parallel.

The overall shape of curves correlating to 4s4p ¹P is akin to the potential curves

³The value of 745 cm⁻¹ is smaller than the stabilization energy of the optimum geometry, 850 cm⁻¹, because the BSSE correction change slightly the Ca-*x* equilibrium from 2.52 Å where the present calculation is performed to 2.67 Å at the equilibrium geometry.

correlating to $\text{Li}(2p^2P) + \text{CH}_3\text{F}$ that appear in Ref. [5], including the anti-crossing that the upper curve undergoes with a higher Σ -like curve. In the present case, the $4s4p^1P$ $^1\Pi$ curve is stabilized by 2000 cm^{-1} with respect to the $4s4p^1P$ asymptote. The well depths of the curves that correlate adiabatically with the $4s3d^1D$ asymptote are 1530 cm^{-1} , 1940 cm^{-1} and 2910 cm^{-1} , respectively.

To help the discussion on the nature, either valence, Rydberg or charge transfer, of the electronic excited states in the $\text{Ca}\cdots\text{CH}_3\text{F}$ complex, permanent dipole moments were also calculated at the RSPT2 level as a function of the $\text{Ca}-x$ distance. Those associated with the molecular states $4s^2^1S$ $^1\Sigma$, $4s4p^1P$ $^1\Pi$, $4s4p^1P$ $^1\Sigma$ and $4s5s^1S$ $^1\Sigma$ are shown in Figure 7. The left panel of the figure shows the projection of these dipole moments along the C-F axis. The positive direction is from F to C, hence the positive dipole values at large $\text{Ca}-x$ distance corresponds to $\text{F}^{-\delta}\text{C}^{+\delta}$. The right panel shows the module of these dipoles. Interestingly, the left panel of the figure shows that the projection of the permanent dipole associated with the $4s4p^1P$ $^1\Sigma$ molecular state changes sign and becomes negative at short $\text{Ca}-x$ distances.

5.3 Potentials along the F-C coordinate

To estimate roughly the vibrational constant for the C-F stretch in both the ground state and excited states, a limited exploration of the PES's was performed as a function of the C-F distance. Figure 8 shows the results for states that are relevant for the discussion, *i.e.* the ground state and the states correlating adiabatically to $\text{Ca}(4s4p^1P_1)$. Only the F and CH_3 moieties are considered to calculate the reduced mass of the oscillator and get vibrational constants from these curves. This is very approximate, but sufficient for the present purpose given that the C-F bond is much stronger than the $\text{Ca}-\text{CH}_3\text{F}$ one. The resulting ω_e values is 960 cm^{-1} for the ground state, and 1065 and 770 cm^{-1} respectively for the $4s4p^1P_1$ $^1\Pi$ and $4s4p^1P_1$ $^1\Sigma$ curves.

6 Discussion

6.1 Electronic structure and geometry of the ground state complex

The ground state PES cut along Ca- x and BSSE corrected is shown in Figure 5 (solid curve and triangles). As already said, the well of 850 cm^{-1} that appears at a 2.67 \AA Ca- x distance, corresponds to a relative minimum of the ground state PES in the entrance channel of the reaction. The actual well depth is probably larger than 850 cm^{-1} since the counterpoise BSSE correction may be overestimated. Such a deep well depth is consistent with the experimental observation that $\text{Ca}\cdots\text{CH}_3\text{F}$ complexes are easier to form than $\text{Ca}\cdots\text{Ar}$ van der Waals complexes. Finally, the calculated well depth is also consistent with observations that will be reported in Paper III of this series where the well depth is bracketed in the range $900\text{-}1600\text{ cm}^{-1}$ from threshold considerations on the complex dissociation.

The equilibrium geometry of the ground state complex at the bottom of the 850 cm^{-1} well corresponds to a C-F bond length of 1.43 \AA . This value is longer than the 1.39 \AA value calculated for the free CH_3F molecule. Notice that the latter value for CH_3F is quite close to the experimental value of 1.382 \AA [51] and to that of a comparable calculation (1.395 \AA [23]). The lengthening of the C-F bond in the complex may be considered as due to some charge transfer from Ca to CH_3F , enhancing the negative charge carried by F. However, if not fully excluded, this effect is very small. A simple dipole-induced dipole approximation of the $\text{Ca}\cdots\text{CH}_3\text{F}$ interaction was made indeed, assuming a 1.85 Debye permanent dipole in CH_3F as in the free molecule and a 25 \AA^3 polarizability on Ca as in the free atom [51]. This interaction was used to provide the attractive part of a 6-12 Lennard-Jones potential, the repulsive part being adjusted to reproduce the 2.67 \AA equilibrium distance of the complex. As observed in Figure 5 the resulting potential curve (dot dashed curve) is between the BSSE corrected and uncorrected CCSD(T) calculation. Moreover the same dipole-induced dipole model was used in order to estimate the dipole of the complex. It is shown as a dashed curve

in Figure 5 and compares well with the *ab-initio* dipole shown in Figure 7.

When running the free complex experiment, the $\text{Ca} \cdots \text{CH}_3\text{F}$ complex is electronically excited from its ground state equilibrium geometry, a simple consequence of the Franck-Condon principle. Accordingly, in the geometry that is relevant to the free complex experiment, the Ca atom rotates almost freely in a cone of 35° around the F end of the CH_3F molecule. When turning to the CICR experiment where the complex is deposited on an argon cluster, we do not expect that the complex geometry is changed dramatically, except for the C-*x*-Ca bending angle that is probably fairly blocked inside this cone by the argon environment. This can be anticipated since the Ca-Ar (87 cm^{-1} [44]) and of CH_3F -Ar (estimated to 200 cm^{-1}) interaction energies are fairly small compared with the Ca- CH_3F binding energy (850 cm^{-1}). This expectation is consistent moreover with the qualitative similarity between the two action spectra shown Figure 3.

6.2 Assignment of bands A and B in the action spectrum

The first step in the interpretation is to assign bands A and B of the present action spectrum to specific molecular states of the complex. For this purpose, the action spectrum of Figure 2 is drawn in Figure 9 together with the potential curves of Figures 5 and 6. Doing so, the action spectrum was shifted by 850 cm^{-1} with respect to that of Figure 2 to account for the energy origin that was chosen to draw the theoretical curves. Of course, this does not take into account the zero point energy in the ground state. This is reasonable however because the zero point energy is due mostly to the CH_3 group and is unchanged by the electronic excitation.

Band A of the action spectrum is considered first. With the energy origin of Figure 9, it covers the range $18400\text{-}21600 \text{ cm}^{-1}$. The Frank-Condon region corresponding to the Ca-*x* distance of 2.67 \AA is shown as a vertical line. It crosses the excited potential curves of this energy region at 18830 , 19930 and 20484 cm^{-1} . According to the Frank-Condon picture, these values should correspond to maxima in the absorption of the complex. If no dynamical effect forces an additional internal excitation of the

complex to turn on the reaction, these values should correspond also to maxima in the action spectrum and the two extreme values should determine the range where band A is expected. In fact, the predicted band is located within band A of the action spectrum and is narrower by almost a factor two than that observed experimentally. A part of the discrepancy is probably related to inaccuracies in the calculations that could be in the order of 200 to 400 cm^{-1} . Since experimental uncertainties are also possible as mentioned in section 2 regarding the detailed structure of band A, the dynamics of the reaction associated with the excitation to this band is not discussed further.

Band B of the action spectrum is examined now. It is structured and covers the range 23800-26800 cm^{-1} with the energy origin of Figure 9. It overlaps a region crossed by the potential curves $4s4p^1P^{\prime}\Sigma^{\prime}$ and $4s4p^1P^{\prime}\Pi^{\prime}$. Very simply, we assign band B of the action spectrum to transitions towards these molecular states. As already noticed in the result section, these two potential branches show an analogy with those responsible for the LiF action spectrum in the $\text{Li}\cdots\text{CH}_3\text{F}$ work of Polanyi and coworkers (compare Figure 7 of Ref. [5] to the present Figure 9). However, the detailed comparison between the two action spectra and more specifically the relative location of their most intense features with respect to the relevant potential branches suggests very substantial differences in the dynamics of the two reactions. Hence the question in the present $\text{Ca}\cdots\text{CH}_3\text{F}$ study, is to relate electronic excitations and reactional processes.

6.3 Reaction mechanisms subsequent to excitation towards band B

6.3.1 Partial charge transfer mechanism

The excitation of the complex in band B corresponds to the Frank-Condon region towards the curves that correlate to $\text{Ca}(4s4p^1P)$. It is indicated on the vertical line in Figure 9. This suggests two absorption maxima, one at 21520 cm^{-1} for the intercept with the almost degenerated Π -like curves and the other at 25500 cm^{-1} for the intercept with the Σ -like curve.

The bluer of these maxima, at 25500 cm^{-1} , falls close to the maximum that marks

the blue edge of band B in the action spectrum (25700 cm^{-1}). This suggests that the blue part of band B is due to the excitation of the complex towards the " Σ " molecular state correlating *adiabatically* to $\text{Ca}(4s4p^1\text{P})$. To unravel the corresponding reaction mechanism we need to examine the electronic configuration of this state and its properties in terms of electron localization and dipole moment.

The region of interest along the $4s4p^1\text{P}, \Sigma$ curve is the suspended well at $R_e \approx 2.3\text{ \AA}$, the origin of which is better viewed in Figure 6. It is due to an anti-crossing between this curve and the upper $4s5s^1\text{S}''\Sigma''$ curve. The two curves exchange their electronic character at the anti-crossing that is located when $\text{Ca}-x \approx 3\text{ \AA}$. Hence, the reaction is due to an excitation that promotes the complex towards a state correlating *adiabatically* to $\text{Ca}(4s4p^1\text{P})$ and *diabatically* to $\text{Ca}(4s5s^1\text{S})$. The diabatic correlation indicates a large stabilization, likely related to a substantial electron transfer from excited Ca to CH_3F . This is substantiated below from general considerations on the permanent electric dipoles shown in Figure 7.

We recall that the value of $+2.1$ Debye calculated at large $\text{Ca}-x$ separation corresponds to a permanent dipole with CH_3F polarized as $\text{F}^{-\delta}\text{C}^{+\delta}\text{H}_3$. Two situations can occur when approaching calcium. The first one presumes no electron transfer from Ca to FCH_3 and at long distances calcium is simply polarized by the electric field due to the permanent dipole of FCH_3 . Hence, an additional dipole is centered on calcium, providing the following charge distribution $^{-\delta'}\text{Ca}^{+\delta'} \dots \text{F}^{-\delta}\text{C}^{+\delta}\text{H}_3$ and the dipole moment of the complex increases as the $\text{Ca}-x$ separation is decreased. Of course, the importance of the effect depends on the polarizability of the state of calcium under consideration, which is obviously larger for Rydberg states. However at short distance, in this latter case, the situation is complicated by the fact that one tends towards a complex with an inner CaCH_3F^+ core surrounded by the diffuse electron. The dipole is then essentially determined by the shape of the excited electron orbital. The second situation is expected in case of electronic excitation whenever the upper state becomes a charge-transfer state. In this case, the electron distribution may become $\text{Ca}^+\text{F}^-\text{CH}_3$

and the dipole moment negative.

Both situations can be observed in Figure 7. Not surprisingly, the transfer-less one is encountered when calcium is in the ground state (curve labeled $4s^2\ ^1\Sigma''$). The dipole moment of state $4s4p\ ^1\Pi''$ also appears as transfer-less. Starting from separation, the dipole increases slowly and smoothly for the two states indicating that their electron configuration does not change significantly when Ca approaches CH_3F . In contrast, the dipole moments of states $4s4p\ ^1\Sigma''$ and $4s5s\ ^1\Sigma''$ do not have a regular behavior. We start with the upper state $4s5s\ ^1\Sigma''$. At large Ca- x distances the corresponding dipole is positive, +5 Debye and more, consistent with the Rydberg character and large polarizability associated with $\text{Ca}(4s5s\ ^1\text{S})$. When $\text{Ca-}x \leq 6\ \text{\AA}$ the dipole along $4s5s\ ^1\Sigma''$ loses the asymptotic character and begins to decrease. This is due to an adiabatic mixing with a charge transfer configuration which becomes dominant at shorter distance. In addition, a further change occurs around $3\ \text{\AA}$, the present state undergoes an anti-crossing with state $4s4p\ ^1\Sigma''$. Hence, the decrease of the dipole moment must be followed (diabatically) on the inner part of latter curve. The dipole goes down to less than -5 Debye indicating a substantial charge transfer character to this state where the system resemble $\text{Ca}^+\text{F}^-\text{CH}_3$. We now discuss the $^1\Sigma''$ state dissociating into $4s4p\ ^1\Pi$. From the long distance range its dipole moment remains moderately positive, increasing from +2.1 to +3 Debye. Below the anti-crossing region, one may consider that the diabatic extension of the state which is actually the inner part of the $4s5s\ ^1\Sigma''$ state. The dipole goes up to +17 Debye and corresponds to a distorted diffuse 5s electron in the field of the $\text{Ca}^+\text{CH}_3\text{F}$ core.

Returning to the reaction mechanism corresponding to excitation towards the suspended well on the adiabatic $4s4p\ ^1\Pi''$ molecular state. From the above discussion, we know that this molecular state has a significant charge transfer character in the excitation region. Hence, we infer that the corresponding reaction mechanism implies an electron transfer as the initial step. Since the maximum of the action spectrum and that predicted for excitation of the charge transfer state are close together, we

anticipate that no additional barrier or only a quite weak one has to be overcome when the reaction is initiated by this excitation. However, this does not mean that a direct pathway exists to the reaction. The amount of electron transfer in the excited state may indeed not be sufficient for the system to evolve along a repulsive $\text{CH}_3 - \text{F}^-$ coordinate as in a standard harpoon picture. Instead, Figure 8 suggests that the excited system is formed close to a well along the C-F coordinate, implying that a barrier prevents the reaction in this PES. Hence, the barrierless character of the reaction suggests that it proceeds as explained in Ref. [23] for the excited $\text{Ba} \cdots \text{CH}_3\text{F}$ reaction, by an internal conversion to a lower electronic state. This mechanism is named the *partial charge transfer mechanism* hereafter to make the point that it does not reduce to a simple harpoon picture. A full analysis of this mechanism cannot be done without the simultaneous analysis of the dissociation of the complex as $\text{Ca} + \text{CH}_3\text{F}$. The two processes, reaction and dissociation are indeed competing. Such an analysis is beyond the scope of the present paper and will appear in paper III of this series. The point here is simply the charge transfer character of the excitation.

The *partial charge transfer mechanism* is actually one of those proposed in ref. [1] to account for the action spectrum in the CICR experiment. With the present discussion it accounts for the blue part of band B in the action spectrum of the free complex and has yet to be disentangled from other contributions. This is performed now as announced in the introduction. Since the excited molecular state involved by this mechanism has a charge transfer character that does not exist in the ground state complex, the corresponding feature in the CICR action spectrum is expected to be red shifted with respect to the corresponding one in the free complex experiment. The analysis suggested by the dot-dashed Gaussian peak in Figure 3 supports this idea: the Gaussian peak defines the blue side of band B in the free complex experiment and with the same width and a red shift of 650 cm^{-1} , it matches the shoulder that appears in the central peak of the CICR spectrum.

6.3.2 C-F stretch reaction mechanism

At this point, the *partial charge transfer mechanism* accounts for the blue side of band B in the action spectrum of the free cluster experiment and for a shoulder in the central peak of the CICR experiment. The rest of the two action spectra is thus related to another mechanism, the signature of which is the series of three peaks that appear both in the free complex and the CICR spectra. They are marked by dashed lines in Figure 3, at 24760, 25710 and 26580 cm^{-1} in the free complex spectrum and blue shifted by 200 cm^{-1} in the CICR spectrum. The almost equal spacing between the dashed lines suggests a vibrational progression. It was assigned tentatively in Ref. [1] to the C-F stretch.

Inspection of Figure 9 reveals a series of three peaks at 23910, 24860 and 25730 cm^{-1} respectively. The first band appears between the Π -like and the Σ -like potential curves correlating adiabatically to $\text{Ca}(4s4p^1P)$. Hence, extending the suggestion made in Ref. [1], we assign this series of peaks to the C-F vibrational progression originating in the well of the " Π " curve. The latter was calculated to be located at 21515 cm^{-1} and the C-F vibrational frequency to be 1065 cm^{-1} . In that case, the series of peaks would correspond to the excitation of the levels $v=2,3,4$ of this progression. With this in mind, "experimental" values defining this well can be deduced when fitting the positions of the peaks in the figure. Values of 21300 cm^{-1} $\omega_e = 1120\text{cm}^{-1}$ and $\omega_e x_e = 60\text{cm}^{-1}$ were found for the well depth, the vibrational constant and the anharmonicity parameter respectively. These values are very close to the calculation, confirming the assignment.

This second reaction mechanisms goes through the direct excitation of the C-F stretch within an electronic excited state that has no electron transfer character, even less than in the ground state of the complex since the dipole moment associated with state $4s4p^1S''\Pi''$ has a smaller absolute value than that associated with $4s^2^1S''\Sigma''$ (see right panel of Figure 7). This suggests that solvation by the argon environment should more effectively stabilize the ground state of the complex than the excited $4s4p^1S''\Pi''$ state. Hence the action spectrum is expected to blue shift in the argon environment

as observed experimentally in Figure 3.

7 Conclusion

The present paper is both experimental and theoretical. It is the second of series devoted to the photoinduced reaction forming CaF in a 1:1 Ca \cdots CH₃F complex. Paper I of this series is a Cluster Isolated Experiment (CICR) where the complex was formed at the surface of a large argon cluster and the reaction turned on by scanning a laser in the vicinity of the calcium resonance line. In the present paper, the complex 1:1 Ca \cdots CH₃F complexes were formed in the pulsed supersonic expansion of a He/Ca/CH₃F mixture. They are free in the gas phase, *i.e.* they are not supported by a cluster. As in the CICR experiment, the reaction is turned on by a laser, but over a wide range on both sides of the calcium resonance line. This provided the action spectrum of the photoinduced reaction that gives information on the access to the transition state of the photochemical reaction. Two broad structured bands (named A and B hereafter) were found. They are extending quite far on each side of the calcium resonance line.

The experiment is complemented by CCSD(T) and RSPT2 *ab-initio* calculations which provided cuts through the ground and excited singlet PES's of the Ca \cdots FCH₃ system along a Ca - CH₃F separation coordinate. When exploring these surfaces, the ground state of the system was continuously optimized. The ground state PES also benefits of a BSSE correction with respect to the Ca+CH₃F dissociation. The potential curves that are provided accordingly document directly the vertical excitation energies of the complex. A limited exploration of the PES's was performed also along the C-F coordinate, again with an optimization of the other coordinates in the ground state.

The first output of the calculation is a structural information on the ground state of the Ca \cdots CH₃F complex. The latter is slightly bent, with calcium close to the F end of CH₃F.

The comparison between the experimental action spectrum and the calculated

molecular curves helped to assign band A of the action spectrum to the excitation of molecular states that correlate to $4s3d^1D$ at large separation between Ca and FCH_3 , whereas band B is associated with the molecular states correlating to $4s4p^1P$. Two reaction mechanisms could be discussed for band B. The first one involves a partial electron transfer from Ca to CH_3F . However it cannot be reduced to a simple harpooning process since the excited complex is not expected to dissociate directly as $CaF + CH_3$. Instead, an internal conversion is likely to occur prior to reaction. In this respect, the Ca/ CH_3F system is akin to the Ba/ CH_3F studied in the group of Radloff and that of Ureña. No such electron transfer is implied in the second reaction mechanism that involves the deposition of two or more vibrational quanta in the C-F stretch in addition to the electronic excitation. The electron transfer that eventually promotes the reaction likely proceeds in a later step of the reaction, through an intermediate not directly accessible by vertical excitation from the ground state of the complex.

The above analysis provides a partial understanding of the excited Ca + CH_3F reaction but further works are needed to get a full picture of the excited state dynamics of this system. We already mentioned that paper III of this series is going to examine the competition between the present reaction channel and the Ca + CH_3F dissociation channel of the complex. A real time experiment that probes the exit channel of the reaction, far from the Franck Condon region of the reaction is also planned in order to get information on the apparently late charge transfer step that promotes the reaction. Finally, thorough PES's calculations are currently underway to allow for wavepacket propagation, a challenge at the moment, given the number of PES's coupled and the number of degrees of freedom expected to play a role in the dynamics.

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Ca level	Present calculation	Experiment [52]	Calculation of Ref. [53]
$4s4p\ ^3P$	14626	15263	15121
$4s3d\ ^3D$	20328	20356	20620
$4s3d\ ^1D$	21547	21849	21965
$4s4p\ ^1P$	23440	23652	23434
$4s5s\ ^3S$	31541	31539	
$4s5s\ ^1S$	33281	33317	

Table 1: Atomic term energies for Ca (in cm^{-1}). The experimental values are j -averaged.

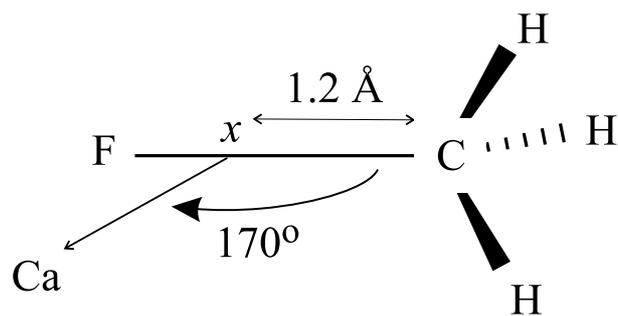


Figure 1: Geometry of the $\text{Ca} \cdots \text{CH}_3\text{F}$ complex used for the potential energy calculations reported in Figures 5 and 6.

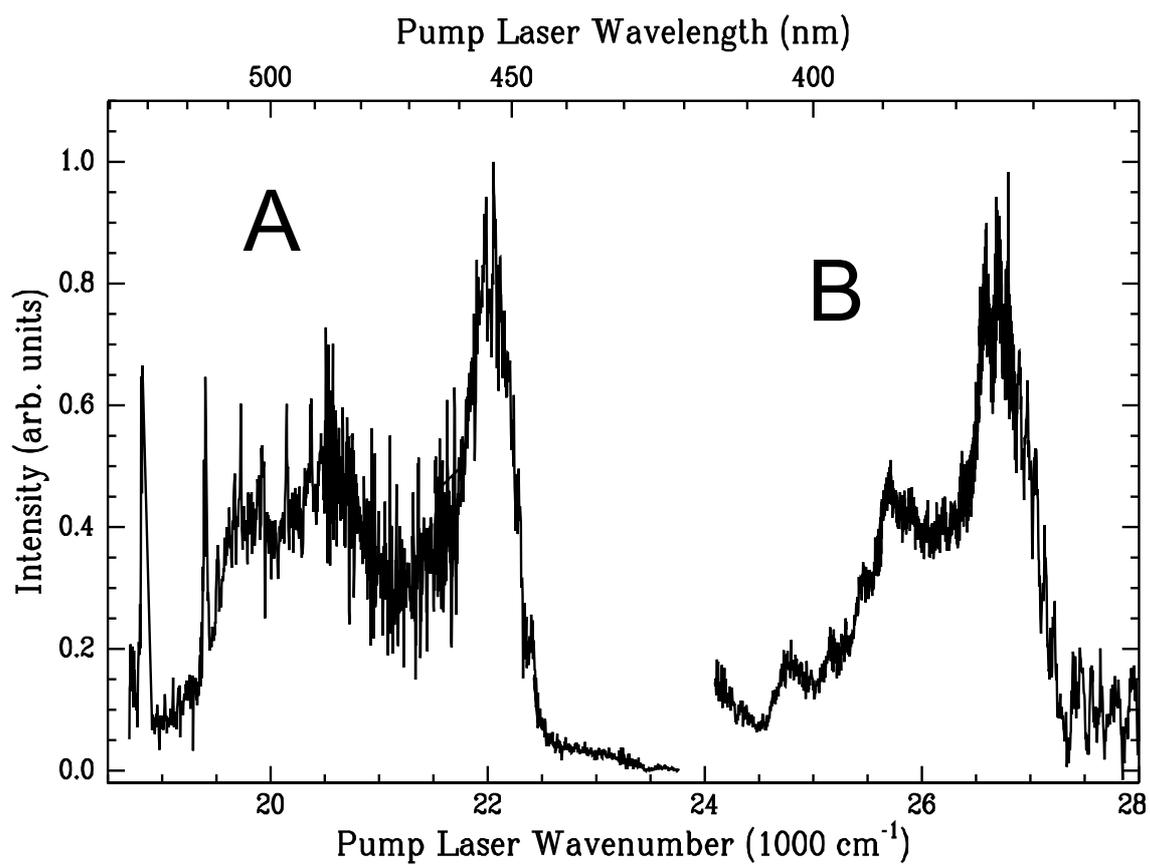


Figure 2: Action spectrum for producing electronically excited CaF in a 1:1 Ca...CH₃F complex.

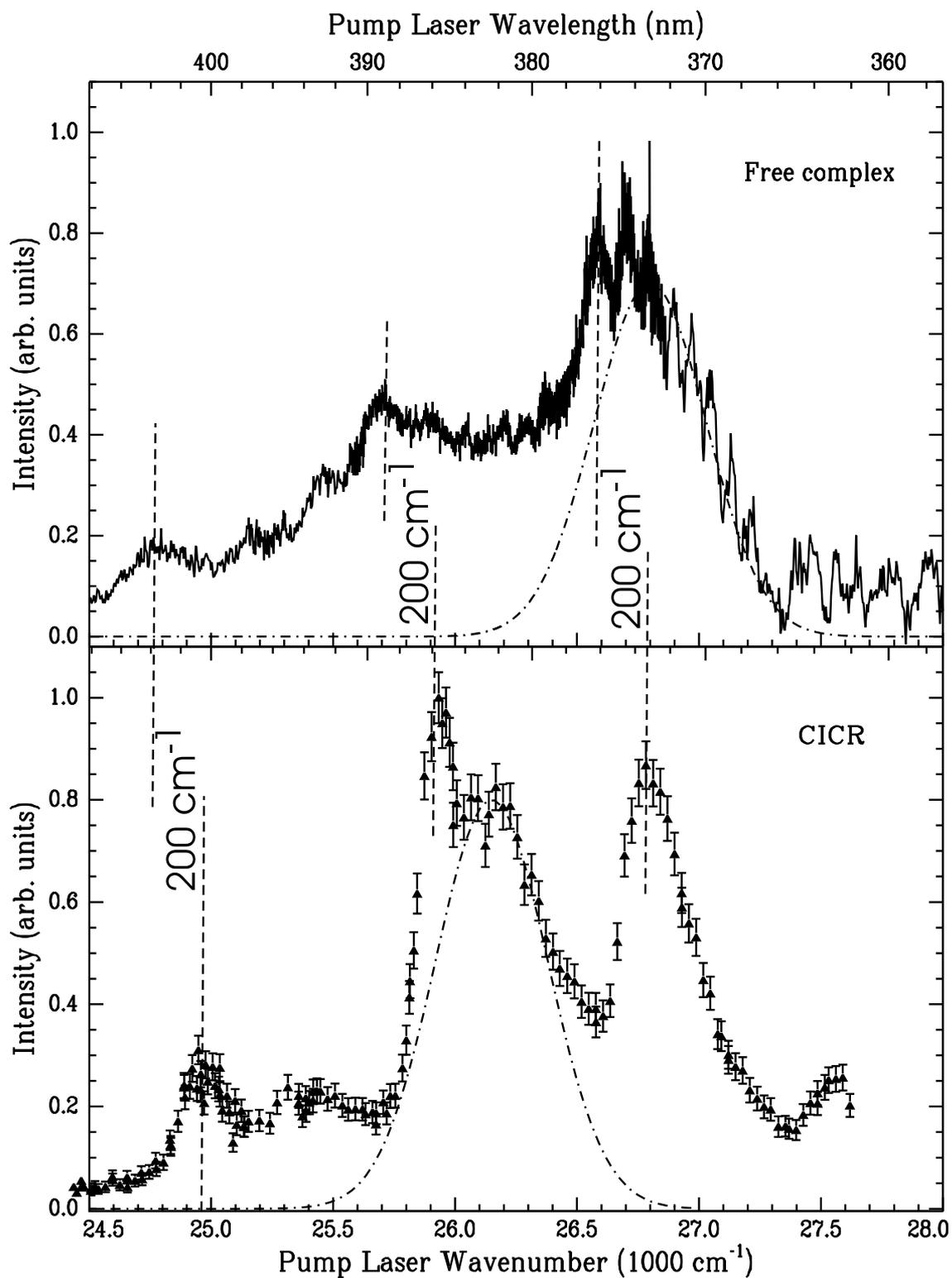


Figure 3: Band B of the action spectrum shown in Figure 2 (top panel). The bottom panel recalls the action spectrum measured in a previous CICR experiment where the $\text{Ca} \cdots \text{CH}_3\text{F}$ complex is deposited at the surface of a large argon cluster and CaF(A,B) monitored by its fluorescence [1]. The dotted dashed Gaussian curves are plotted to help the discussion.

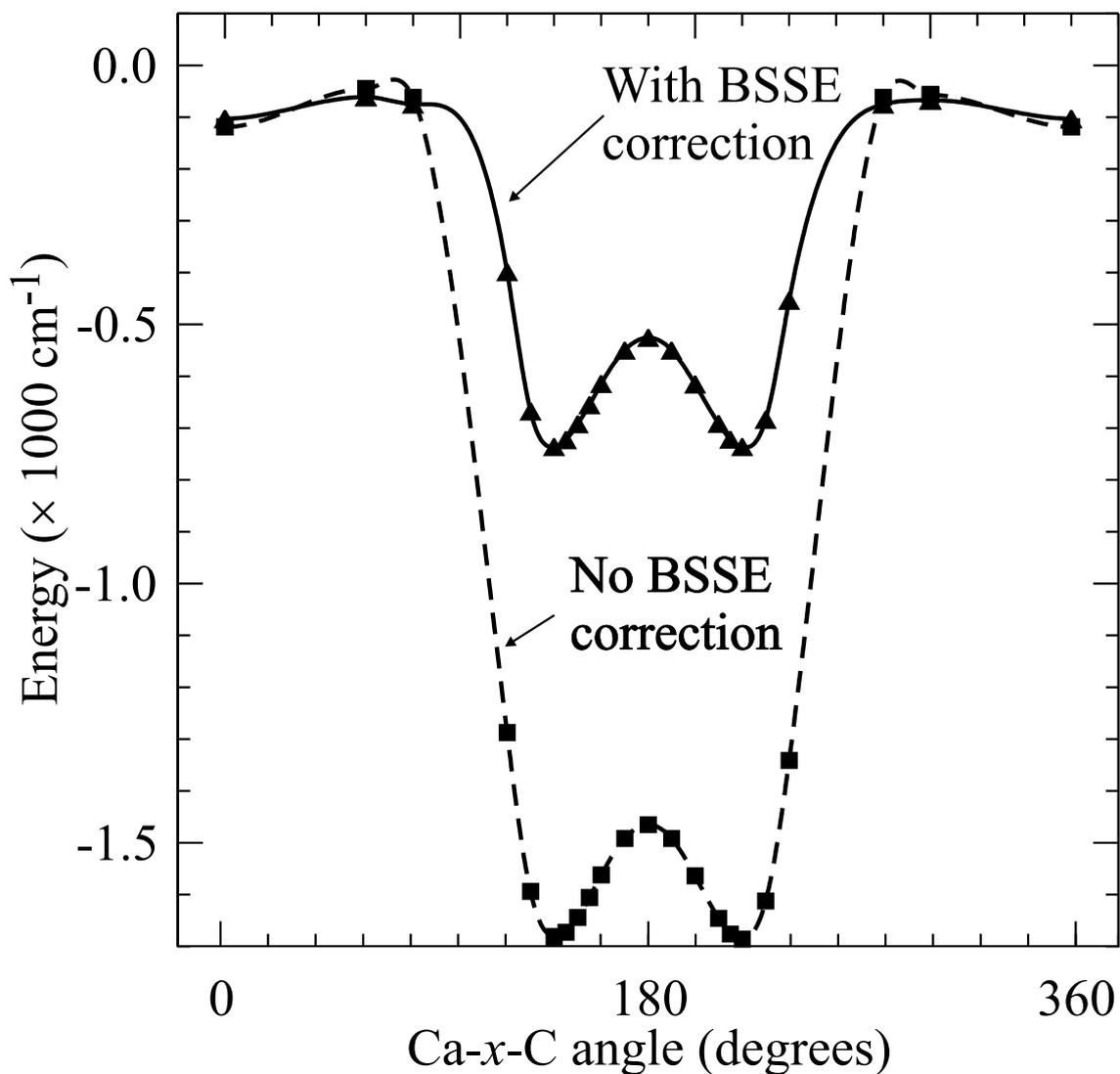


Figure 4: Calculation of the $\text{Ca}\cdots\text{CH}_3\text{F}$ ground state at the CCSD(T) level with the geometry optimization described in the text. The ground state energy (full triangles and solid line) is shown as a function of the bending angle C- x -Ca after correction for the BSSE (see the text). The dashed curve (and squares) shows the BSSE uncorrected curve. The origin of the energies corresponds to the dissociation of the complex as $\text{Ca}(4s^2\ ^1S_0) + \text{CH}_3\text{F}$.

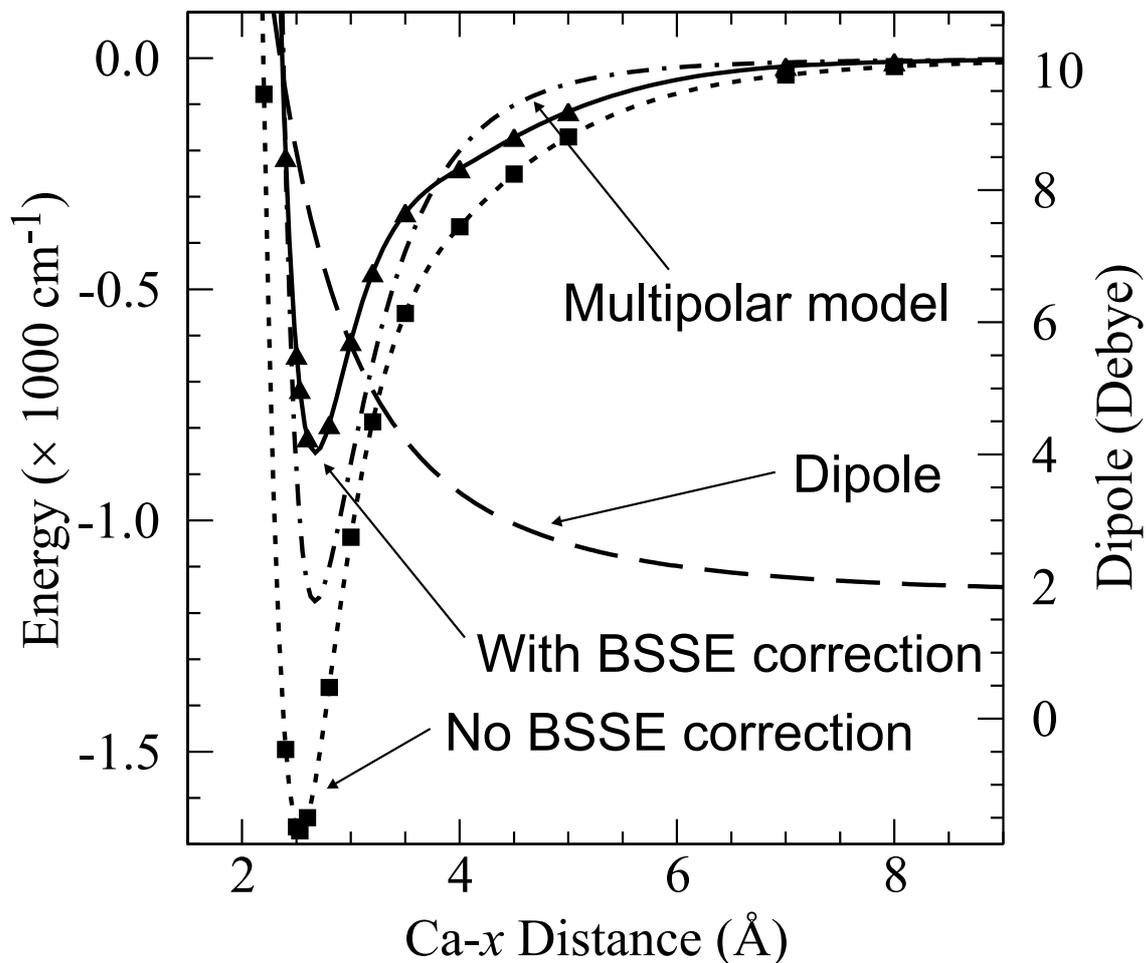


Figure 5: Same as Figure 4 but the ground state energy is shown as a function of the Ca- x distance. The full curve and triangles correspond to BSSE corrected potential energies, whereas the dashed curve and squares show uncorrected energies. The dotted-dashed and dashed lines refer respectively to the energy and dipole calculations in the multipolar interaction model discussed in section 6.

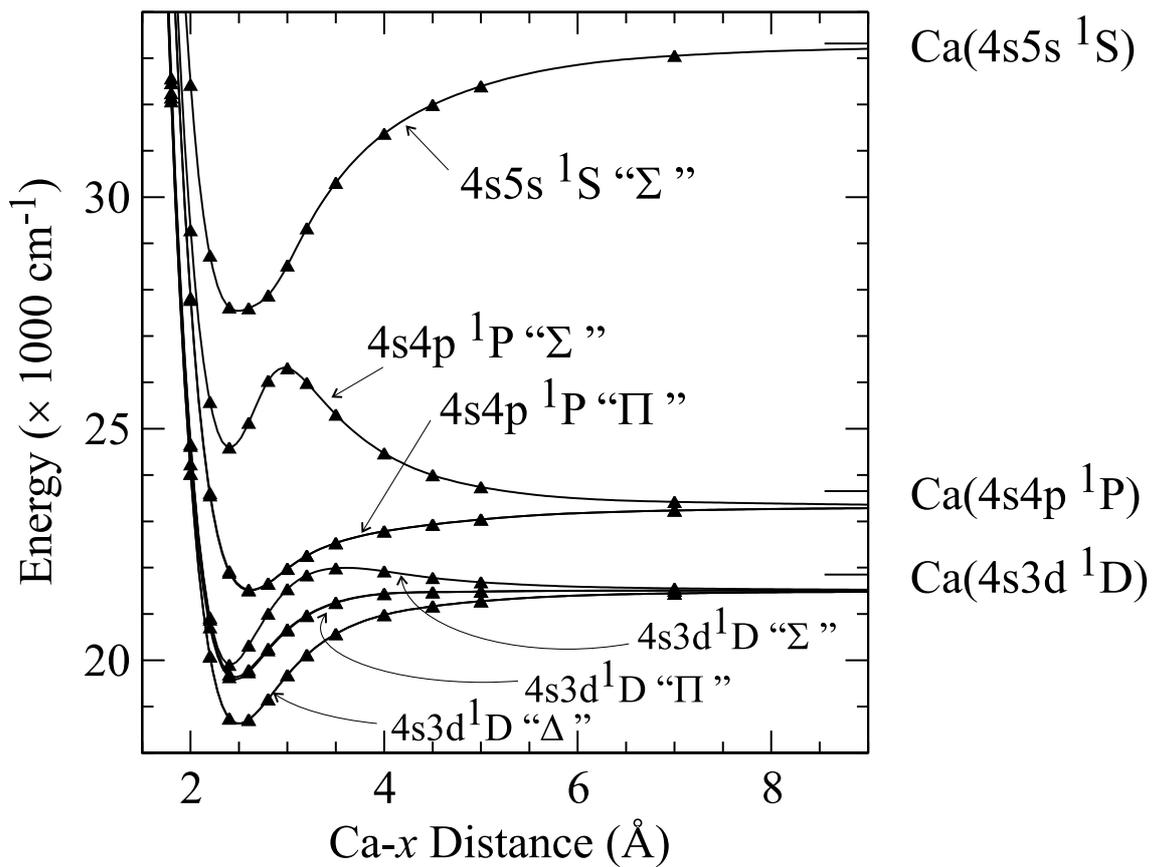


Figure 6: Same as Figure 5 for the excited singlet state calculation at the RSPT2 level as a function of the Ca- x distance. The labels giving asymptotic energy levels are placed at their experimental values.

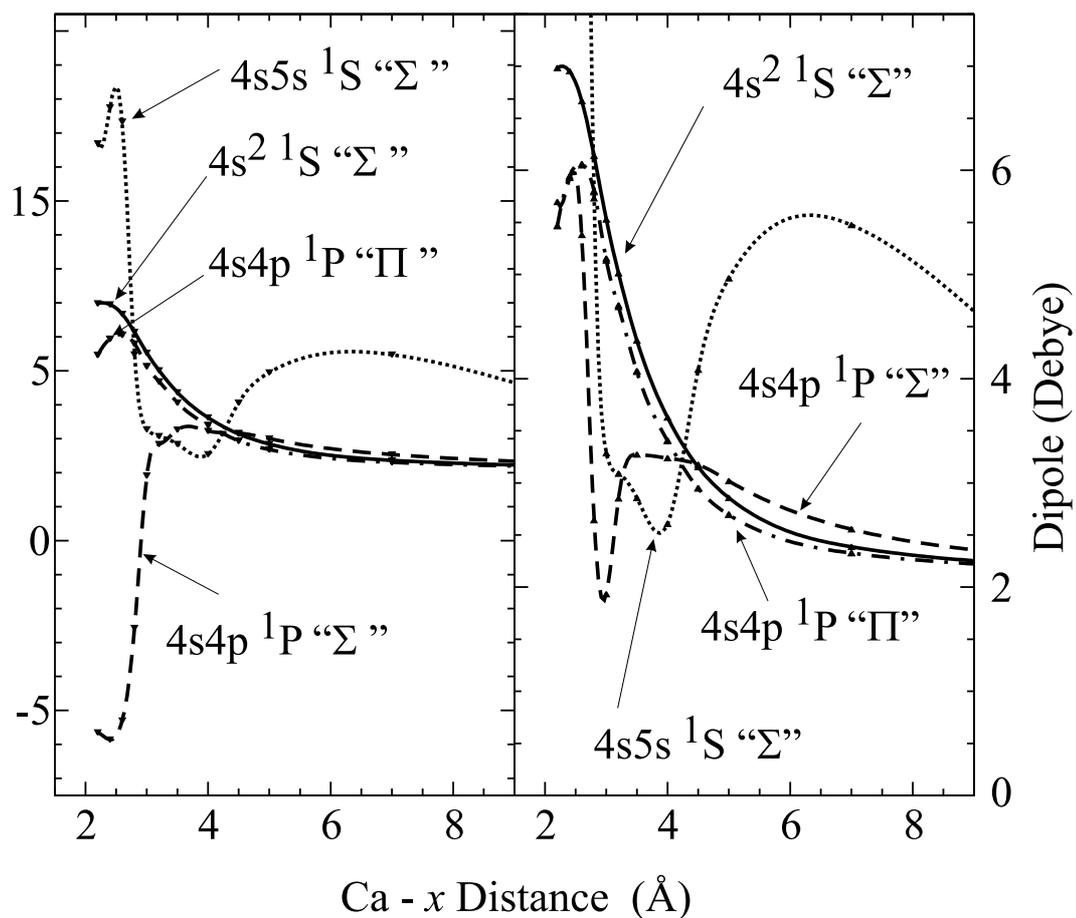


Figure 7: Permanent dipole moment of various electronic states of the $\text{Ca}\cdots\text{CH}_3\text{F}$ complex (as labeled in the figure) as a function of the $\text{Ca}-x$ distance. The left panel shows the projection of the dipoles along the F-C axis, the positive direction being from F to C. The right panel show the module of the dipole.

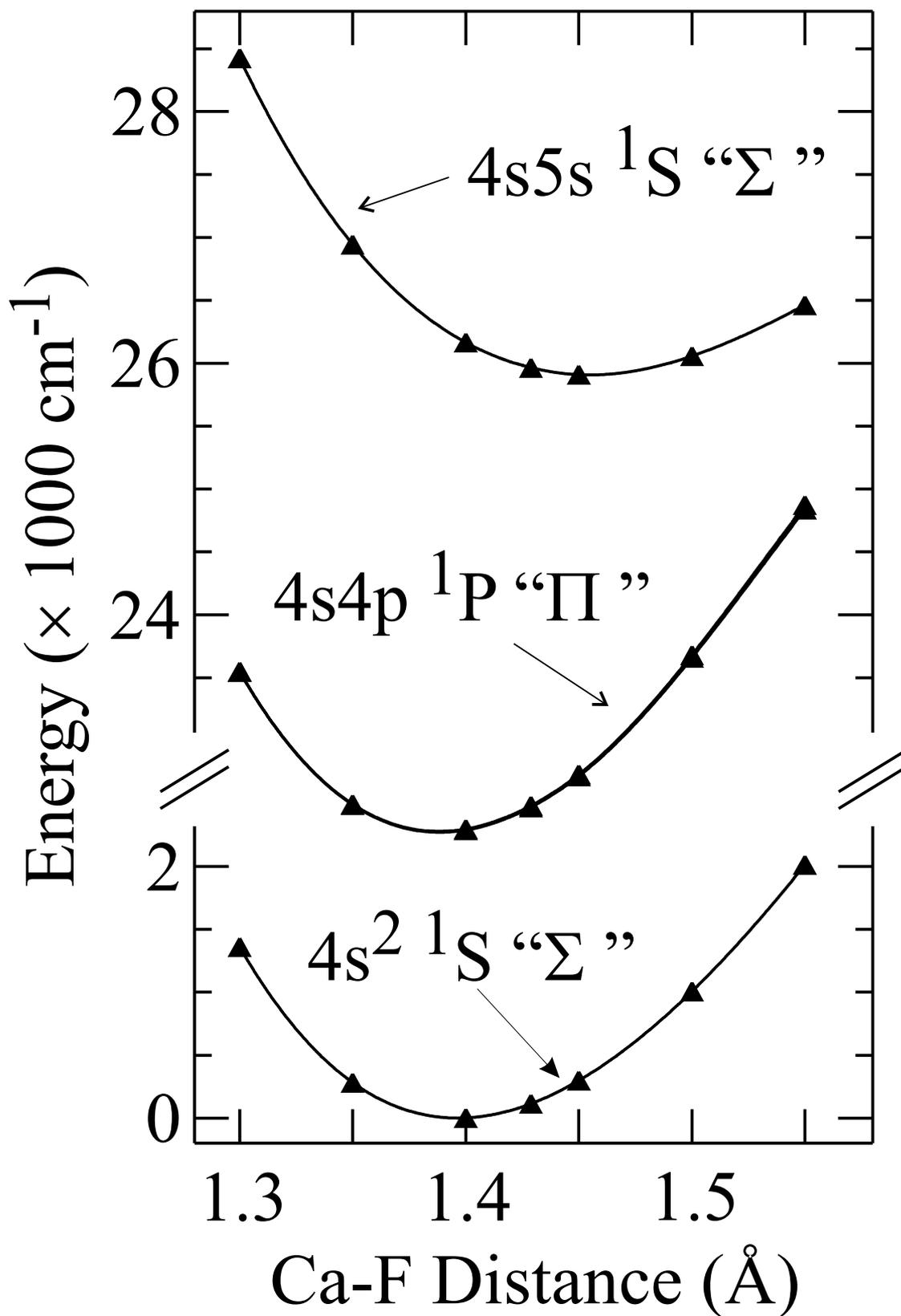


Figure 8: Potential energies at the MCSCF level as a function of the C-F distance for various electronic states of the Ca...CH₃F complex (as labeled in the figure).

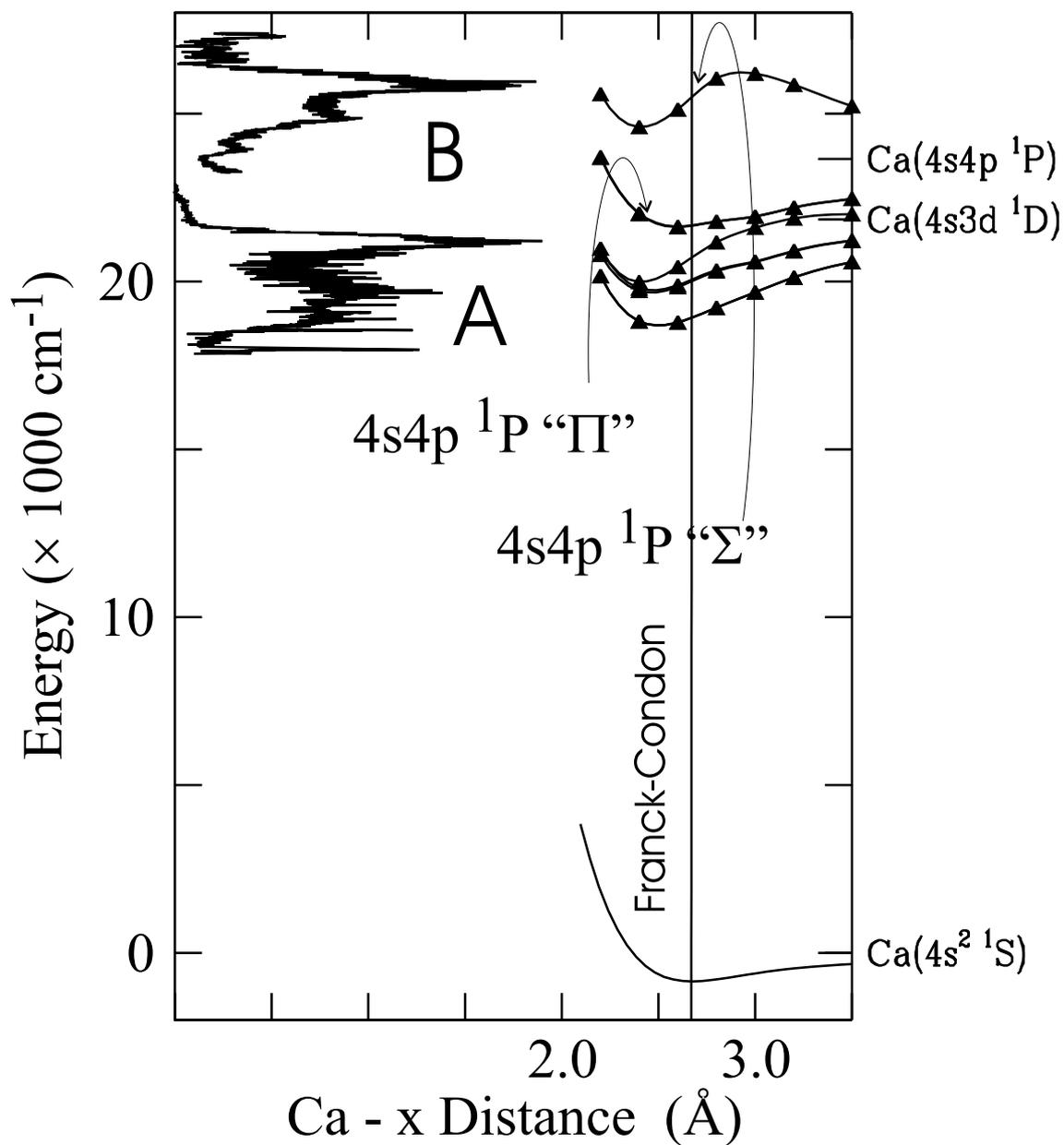


Figure 9: Compilation of the experimental results of Figures 2 with the theoretical potentials of Figures 5 (BSSE corrected) and 6. The energy origin is that of Figures 5 and 6 and the experimental spectrum is shifted accordingly (see text).