Laser Induced Fluorescence Spectroscopy of the Ca Dimer Deposited on Helium and Mixed Helium/Argon Clusters

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Abstract. We study the laser induced fluorescence spectroscopy of the calcium dimer deposited on helium and mixed helium/argon clusters. In the wavelength range between 365 and 385 nm, the Ca dimer is excited from its ground state up to two excited electronic states leading to its photodissociation in $Ca(^1P)+Ca(^1S)$: this process is monitored by recording the $Ca(^1P)$ fluorescence about 422.7 nm. These electronic excited states of Ca_2 are respectively a diexcited one correlating to the $Ca(4s\ 4p\ ^3P) + Ca(4s\ 3d\ ^3D)$ and a repulsive one correlating diabatically to the $Ca(4s\ 4p\ ^1P) + Ca(4s^2\ ^1S)$ asymptote, accounting for the dissociation of Ca_2 and the observation of the subsequent $Ca(^1P)$ emission. On pure helium clusters, the fluorescence consists of the calcium atomic resonance line $Ca\ (^1S \leftarrow ^1P)$ at 422.7 nm ($23652\ cm^{-1}$) assigned to ejected calcium, and a narrow red sided band corresponding to calcium that remains solvated on the helium cluster. Interestingly, the branching ratio to the ejection of $Ca(^1P)$ increases along with the wavelength of the excitation photon, *i.e.* when its energy decreases. This is contrary to what is intuitively expected and to what is really found on pure argon clusters. On mixed helium/argon clusters, a new spectral band appears on the red side of the calcium resonance line; the intensity and the red shift of this component increase along with the argon quantity deposited on the helium cluster: it is assigned to the emission of $Ca(^1P)$ associated with the small argon aggregate embedded inside the helium cluster.

Keywords: helium cluster; mixed helium/argon cluster; supersonic free jet; pick-up; laser induced fluorescence; photodissociation; calcium; calcium dimer
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INTRODUCTION

The CICR (Cluster Isolated Chemical Reactions) technique [1,2] was developed in our laboratory to study at a microscopic level, chemical reactions between reactants deposited on van der Waals clusters and to determine the effect of an environment on the dynamics of these reactions [3]. The CICR method makes also possible to study the spectroscopy of atoms or molecules deposited at the surface of the clusters. For example, we have investigated the spectroscopy of alkaline earth metals as barium[4] or calcium[5], deposited on large van der Waals clusters as argon or neon. An advantage of the CICR method is its flexibility, since it is an efficient way to form by successive pick-up[6] of their constituting moieties, species that are difficult to stabilize otherwise. Gas phase species such as the calcium dimer Ca_2 [7] has been studied accordingly. At the same period, the HENDI (HElium Nano Droplet Isolation) technique, initially developed in the group of Scoles[8] for similar purposes, has been used in many groups (see for example reviews [9,10]), especially because an helium droplet is a superfluid quantum medium of very low temperature (0.37K), interacting softly with reactants deposited at its surface or inside.

In 2005, we have modified the Campargue beam source[11] of our CICR experiment in a helium cluster beam source [12], hence extending the CICR technique to HENDI measurements. In recent works, we have studied the photodissociation at *ca* 380 nm of a Ca_2 molecule deposited on pure argon and on pure helium clusters [13,14]. A simple picture has emerged, showing that, two electronic excited states (shown in figure 3, right panel) participate to the photodissociation process in this wavelength region, the electronic excitation to each of them corresponding to the two components of the excitation spectrum (shown figure 3, top left panel): the excitation of the diexcited electronic state correlating to the $Ca(^3D)+Ca(^3P)$ asymptote is associated with the small band in the blue of the excitation spectrum, whereas excitation to the repulsive state, which correlates diabatically to the $Ca(^1S)+ Ca(^1P)$

asymptote, is associated with the main band of the excitation spectrum. The dissociation proceeds when the system has transferred to this state (dashed line arrow in figure 3), thus leading to the formation of $Ca(^1P)$, whose fluorescence emission is observed. The present paper revisits this process in pure helium clusters, with a higher resolution of the fluorescence emission, revealing an unexpected channel where $Ca(^1P)$ stays solvated in the helium cluster. The photodissociation of Ca_2 on mixed helium/argon clusters is studied also in the same excitation wavelength range.

EXPERIMENTAL SETUP

The experimental set-up features a helium cluster beam source, the expansion chamber, a differentially pumped chamber, the main chamber where the spectroscopic measurements are performed, and finally the mass spectrometer chambers: it is schemed in Figure 1. Helium clusters are grown in a supersonic expansion from a modified Campargue beam source [11]: with the help of a Sumitomo double stage cryocooler, temperature as low as 9K can be reached in the reservoir, allowing the formation of helium clusters inside the jet [12]. A cluster beam is extracted from the jet by a 1 mm skimmer into the second chamber, before entering the main chamber through a 3 mm collimator. Calcium atoms are deposited on clusters by collisional capture, *i.e.* the pick-up technique[6] : at the entrance of the main chamber, the cluster beam flies through a heated cell containing a low calcium vapor pressure (10^{-4} to 10^{-3} mbar). In this work, the temperature of the calcium cell is maintained at *ca* 500°C, which maximizes the proportion of calcium dimers deposited on the clusters.

Downstream the pick-up cell, the cluster beam reaches the interaction region, which is illuminated by the light of the cw laser. The near UV light is produced by frequency doubling the output of a cw Titane Sapphire laser (Coherent 899-21) in an extra-cavity doubler Wavetrain. The laser light is transported into the experimental chamber by an optical fiber (0.6 mm core) and refocused at the exit of the fiber into a slightly converging beam that crosses
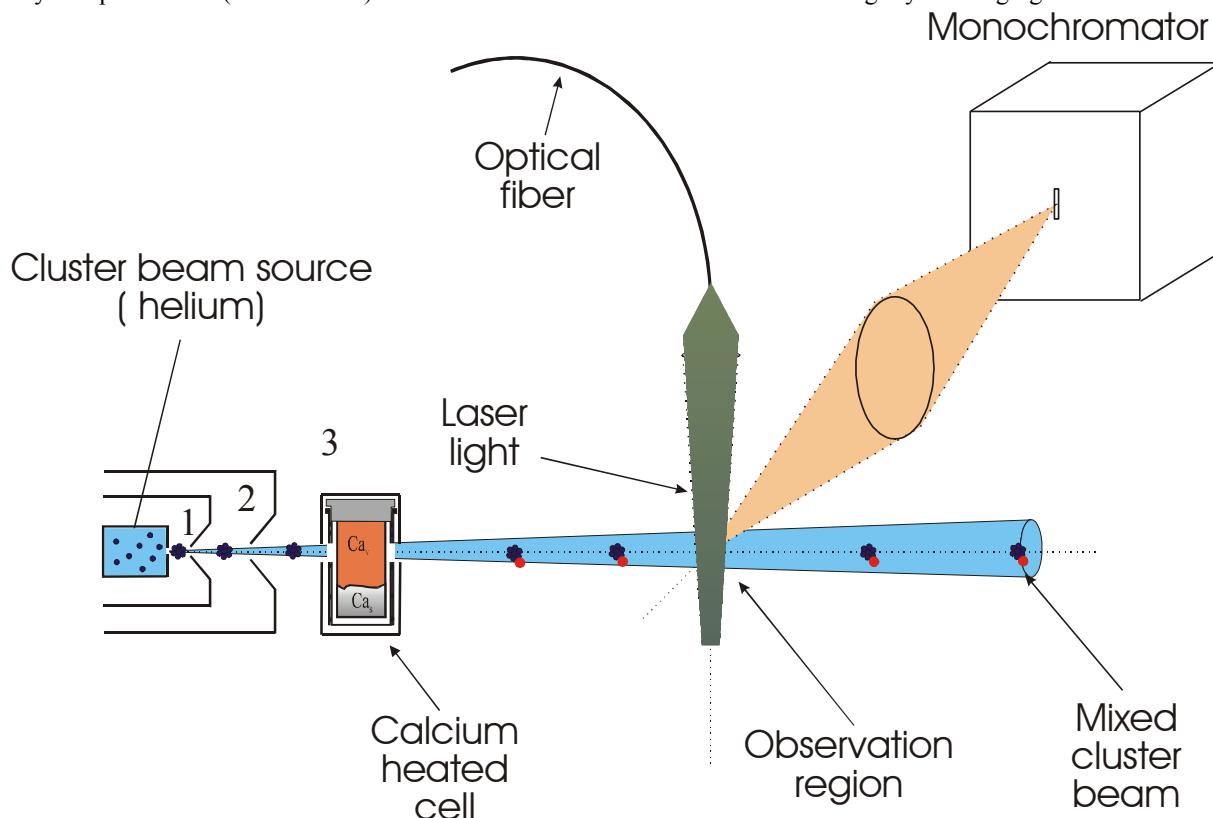

FIGURE 1. Scheme of the experimental set-up with Ca_2 deposited on pure helium clusters. In case of mixed helium/argon clusters, argon is introduced in the chamber 2, before entering the main chamber and crossing the calcium pick-up cell.

the cluster beam at right angle. The interaction region is also the observation zone, from which the fluorescence

emission is collected, dispersed by a grating scanning monochromator, and detected by a cooled photomultiplier tube RCA 31034 (PMT). The PMT signal is processed using the photon counting technique and recorded by a multiscaler card implemented in a microcomputer.

Both emission and excitation spectra are recorded. The emission spectrum is obtained by tuning the excitation laser at a fixed wavelength, the dispersed fluorescence being recorded, while scanning the wavelength of the monochromator. The excitation spectrum consists in recording the fluorescence at a fixed wavelength of the monochromator when the frequency of the excitation laser is varied. As the doubler cavity has to be exactly resonant with the output wavelength of the Titane Sapphire working in the free single frequency mode, the scan of the excitation laser frequency cannot be performed continuously and need to be done step by step. At each step, the laser is optimized at the desired frequency, and the emission spectrum is recorded. Hence, excitation spectra are constructed from the different emission spectra by integrating each of them on the desired wavelength range after normalization by the excitation laser intensity (such normalization is justified since the photodissociation process, which is observed, is induced by a single photon). A lot of the background signal is due to the blackbody radiation of the heated calcium cell. It is eliminated by a simple difference, when flagging the cluster beam alternatively on and off.

Helium clusters are formed from the following stagnation conditions: $P_0 = 9$ bars; $T_0 = 10$ K; $D^* = 5$ microns. With these conditions, the average size of the helium clusters can be estimated to a few thousands[10]. Mixed helium/argon clusters are formed by introducing a small quantity of argon in the second differentially pumped chamber by means of a capillary (see figure 1): hence, argon atoms are captured by pick-up and their average number per helium cluster increases along with the argon pressure.

EXPERIMENTAL RESULTS

Photodissociation of the Ca dimer deposited on pure helium clusters

Figure 2 shows the emission spectrum recorded with the monochromator resolution set to ca 0.2 nm, and a photo excitation at 377.6 nm (26483 cm^{-1}) of Ca_2 deposited on the helium clusters. As explained in the introduction, this emission is due to calcium excited in the ^1P state after photodissociation of Ca_2 as $Ca(6s6p\ ^1P)+Ca(6s^2\ ^1S)$ [13,14].
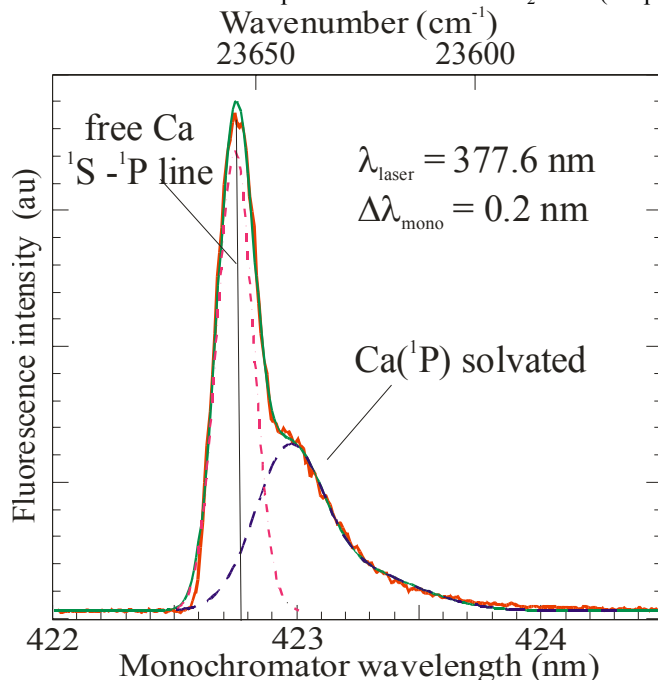

FIGURE 2. Emission spectrum after excitation of Ca_2 on pure helium clusters at 337.6 nm. The resolution of the monochromator is 0.2 nm.

Clearly, the emission spectrum of Figure 2 has two components, which can be interpreted as a line peaking at

422.7 nm superimposed to a broader band peaking at 423 nm. The former emission is adequately fitted by a single Gaussian shaped peak with a full width at half maximum (FWHM) of 0.18 nm. In contrast, the broad emission cannot be fitted so simply. Two Gaussians peaks are needed, centered at 423 and 423.2 nm with a FWHM of 0.32 and 0.6 nm, respectively. The width of the emission line is equal to the monochromator resolution and the corresponding emission wavelength is that of the resonance line $Ca(^1S \leftarrow ^1P)$ of free atomic calcium (422.7 nm; 23652 cm^{-1}). This emission is therefore assigned to that of free $Ca(6s6p\ ^1P)$. The other emission, *i.e.* the band peaking at 423 nm, is similar to the $Ca(^1P)$ emission in the bulk liquid helium [15]. It peaks at the same wavelength although its width is about three times smaller than in the bulk experiment. Likely, this band can be assigned to excited calcium atoms that remain solvated on the helium cluster after the photodissociation. Accordingly, a competition exists between solvation and ejection of the $Ca(^1P)$ fragment out of the helium cluster. Note that the solvation channel was not observed in the former works of this laboratory because of the lower resolution (2 nm) of the monochromator. Its observation here is actually very surprising.
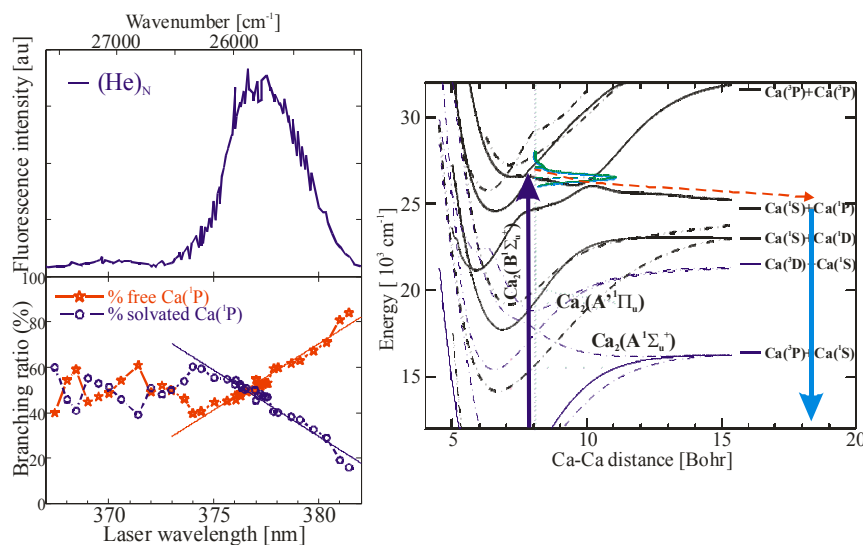

FIGURE 3. Left panel - excitation spectrum for Ca_2 deposited on helium clusters: total $Ca(^1P)$ fluorescence vs laser wavelength (top); percentage of free $Ca(^1P)$ emission (solid line, stars) and solvated $Ca(^1P)$ emission (dashed line, empty circles). Right panel -- calculated potential curves for the calcium dimer: comparison with the excitation spectrum.

The bottom left panel of Figure 3 presents the evolution of the branching ratio to free $Ca(^1P)$ emission (solid line – stars) and solvated $Ca(^1P)$ emission (dashed line – empty circles) as a function of the excitation laser wavelength (sum of both is 100%). Between 366 and 374 nm, the ratios can be considered as constant except perhaps some oscillations, which are close to the experimental noise in this region. Above 374 nm, the branching ratio to free $Ca(^1P)$ increases almost linearly from 42 to 82 percent, while the branching ratio to solvated $Ca(^1P)$ decreases accordingly. This result is unexpected since the contrary was observed on argon clusters [14] and it is opposite to the simple energetic consideration that less electronic energy in the system would result into a larger branching to solvation. The excitation spectrum of the overall $Ca(^1P)$ fluorescence for Ca_2 carried on helium clusters is displayed on the top left panel of Figure 3. It features a fairly large band peaking at 26520 cm^{-1} with a FWHM of 330 cm^{-1} plus a small side component blue shifted by 550 cm^{-1} [14]. It is remarkable to observe that the former band corresponds to the wavelength range where the branching ratio to ejection of Ca increases linearly.

Photodissociation of the Ca dimer deposited on mixed helium/argon clusters: a preliminary exploration

For the preparation of mixed helium/argon clusters, argon atoms are deposited on the helium clusters by pick-up in the second chamber: so, prior to the capture of calcium atoms, when several argon atoms are present on the same helium cluster, they have time to migrate, to collide each other and to aggregate. Figure 4 displays the emission spectra recorded for different foreline pressures of the argon pick-up capillary. Upon addition of argon atoms to the helium clusters, a new fluorescence band appears on the red side of the calcium resonance line. The red shift of this

band as well as its width increases with the amount of argon added to the helium cluster. At low argon deposition, it peaks at 423.8 nm with a width of less than 1 nm; at larger concentration, the wavelength of the maximum tends to 426.5 nm with a width of 1.8 nm. This emission is very similar to the fluorescence of $Ca(^1P)$ solvated on pure argon clusters[5,14], even if the latter one is more red shifted by 3 nm at 429 nm and has a larger width of 3.2 nm.
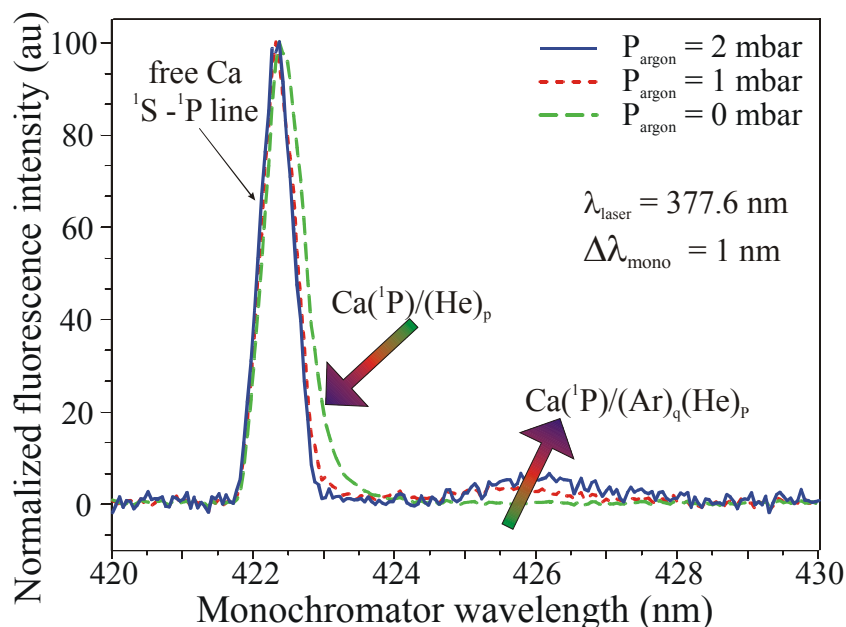

FIGURE 4. Emission spectra for various foreline argon pick-up pressures for a laser wavelength of 377.6 nm. A monochromator resolution of 1 nm was as a compromise to distinguish simultaneously the evolution of the different spectral components.

So, this new spectral band can be assigned to the emission of $Ca(^1P)$ interacting with an aggregate of argon atoms embedded inside the helium cluster. Simultaneously, with an increasing quantity of argon deposited on the helium cluster, the spectral component associated with the emission of $Ca(^1P)$ solvated in pure helium cluster decreases dramatically, as indicated by the fast disappearance of the spectral shoulder on the red side of the free calcium resonance line in figure 4.

DISCUSSION AND CONCLUSION

We have investigated the photo excitation and subsequent dissociation of Ca_2 deposited on pure helium and mixed helium/argon clusters according to $Ca_2 + h\nu \rightarrow Ca_2^* \rightarrow Ca(^1S) + Ca(^1P)$, where Ca_2^* corresponds to 2 different excited states: a diexcited state correlating to the $Ca(^3D)+Ca(^3P)$ asymptote and an excited repulsive state correlating diabatically to the $Ca(^1S)+ Ca(^1P)$ asymptote, leading to the dissociation and the observation of the $Ca(^1P)$ fluorescence.

On pure helium clusters, the structure of fluorescence spectrum at high resolution (0.2 nm) is the fingerprint of a competition between ejection and solvation of $Ca(^1P)$ following the dissociation of excited Ca_2 on the cluster; indeed, the fluorescence spectrum presents two components: *i*) the free atomic calcium resonance line $Ca(^1S \leftarrow ^1P)$ of the ejected $Ca(^1P)$; *ii*) a spectral red shoulder corresponding to the emission of the $Ca(^1P)$ solvated in the helium cluster. The behaviour of the branching ratios to ejection and solvation of $Ca(^1P)$ following the photo excitation of Ca_2 around 380 nm is also very different on helium and argon clusters. On argon clusters, the branching ratio to free excited calcium increases along with the photon energy *i.e.* as its wavelength decreases [14]. On the contrary, on pure helium clusters, at wavelengths above 374 nm, the branching ratio to free excited calcium decreases along with the photon energy *i.e.* as its wavelength decreases, while below 374 nm, both branching ratios to free and solvated $Ca(^1P)$ oscillates between 40 and 60 percents. This result means that the dissociation path is somehow different on helium clusters from what it is on argon clusters. This contrasts with the excitation channel since the excitation spectra have the same shape on helium and argon clusters, except the blue shift of 120 cm^{-1} on helium[14], which

likely means that the excited electronic states of Ca_2 are the same in both cases but are less stabilised by the helium cluster than by the argon one. So, it seems that the nature of the cluster has mainly an influence on the dissociation channel of photoexcited Ca_2; on argon clusters, the two excited electronic states are not differentiated in the exit channel; the argon cluster acts as a dissipative medium and slow down the calcium atom in its way out of the cluster: the more the photon excitation energy, the more the branching ratio to ejection of $Ca(^1P)$. By contrast, on helium clusters, the excitation of these states results in dramatically different behaviour in the exit channel: excitation of the higher state yields nearly equiprobability between ejection and solvation of $Ca(^1P)$; whereas excitation to the other curve stimulates ejection. Examination of the right panel in Figure 3 shows indeed that the vertical excitation from the ground state ends up near the anticrossing between the singly excited and the doubly excited curve. Hence, shifting the excitation wavelength to the red, still staying on the curve with a large oscillator strength (the singly excited curve), transfers the system to the repulsive part of the curve, and stimulates a rapid dissociation. Given the large energy release along this curve, compared to the expected solvation energy of $Ca(^1P)$ within the helium cluster, $Ca(^1P)$ likely moves out of the cluster. When comparing argon clusters to helium clusters, it seems that the dissociation is dominated by the slow-down effect of the cluster in the former case, whereas the details of the coupling between the excited electronic states are dominant in the latter case.

Addition of argon atoms to the helium clusters results in a dramatic change of the emission spectrum, with the appearance of a new band that can be assigned to solvated $Ca(^1P)$ interacting with a small argon aggregate embedded in the helium cluster, and a rapid decrease of the $Ca(^1P)$ solvated in pure helium. It is very likely that argon atoms form a small aggregate embedded in the helium clusters for interaction energy reasons and that solvated excited calcium will interact with this argon aggregate and remain at the interface between argon and helium. So in mixed helium/argon clusters, argon has a strong effect on the exit channel of $Ca(^1P)$ following the dissociation of Ca_2^*. Work is actually in progress to record the excitation spectrum of the $Ca(^1P)$ emission in order to determine the influence of argon on the photo excitation process of Ca_2 in mixed argon/helium clusters

ACKNOWLEDGMENTS

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