Eur. Phys. J. D **11**, 227–231 (2000)

The European Physical Journal D
EDP Sciences

Observation of the first vibrations of the newly born Cs–CH_3CN complex

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Received 27 October 1999

Abstract. The femtosecond photodissociation of CsI in the CsI–CH_3CN complex has been studied. Recurrences are observed in the detection of the Cs^+–CH_3CN ion complex. They are assigned to the first vibrations of the Cs–$NCCH_3$ bond formed after the CsI dissociation. This result is in good agreement with calculations on the similar NaI–CH_3CN system which predict a linear structure for the ground state complex.

PACS. 34.20.-b Interatomic and intermolecular potentials and forces, potential energy surfaces for collisions – 82.30.Eh Molecule-molecule reactions

1 Introduction

The use of van der Waals complexes for studying the reactive dynamics has been now widely developed since our first work in 1982 [1]. Two approaches have been developed: the first one was to study excited states reactions preparing directly the intermediate state of the reaction [2] and the second one proposed by Wittig's group [3] was to induce the photodissociation within the ground state complex to mimic the collision in a well defined geometry and therefore impact parameter.

In both approaches the initial geometry of the reaction is defined by the geometry of the cold ground state complex. Moreover the time $t = 0$ of the reaction is determined by the absorption of the first photon allowing to study the reaction dynamic in real time as shown by Scherer [4] in the HI–CO_2 complex. In this experiment the HI molecule is dissociated in the complex to study the H + CO_2 reaction. However, due to the mass ratio between iodine and hydrogen atoms, iodine is still very close to the H–CO_2 reactive pair and may affect the reaction dynamics.

In the process of studying the charge separation of an ion pair molecule induced by polar solvent molecules, we have worked on the photodissociation dynamics of alkali-halide salts embedded in polar clusters. At the moment, a few solvents have been studied (CH_3CN, H_2O, NH_3) as well as a few salts (NaI, CsI). The short time dynamics of NaI–$(H_2O)_n$ and NaI–(NH_3) does not exhibit any recurrence in the signal [5].

The CsI molecule is a convenient system for studying the collision induced reaction in a van der Waals complex for the following reasons. The two atoms are heavy, and therefore the dynamics will be relatively slow and can be followed with femtosecond lasers having reasonable widths (100 fs). The two atoms have comparable masses (127 and 133 a.m.u.) and therefore the kinetic energy released in the dissociation process is split nearly equally between the two atoms. This also implies that, if one atom is reacting, the other is leaving quite quickly and will not perturb so much the reactive process, at least the perturbation will be less critical than with H–X. The dissociation dynamics of the bare molecule is simple. The avoided crossing between the ground ionic state Cs^+–I^- and the excited covalent state correlating to the ground state atoms Cs+I occurs at a CsI internuclear distance of 17 Å [6]. The coupling is then very weak (≈ 0.07 cm^{-1}) [6] and the dissociation proceeds only on the diabatic curve in contrast with the NaI case where the coupling leads to the formation of an adiabatic bound state where recurrences are observed [7,8]. Since the ground state molecule has a strong ionic character (the ground state dipole moment is large $11.69D$ [6]), the van der Waals complex ground state structure with a polar molecule will be quite well defined due to strong electrostatic interactions.

We report here the femtosecond dynamics of the CsI dissociation within the CsI–CH_3CN complex. The formation of a Cs–CH_3CN molecule is monitored in time by detecting the Cs^+–CH_3CN ion and the recurrences observed can be assigned to the first vibrations of the newly formed Cs–N bond.

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† Our Colleague and friend D. Solgadi died the 10th of February 2000.

2 Experimental setup

The experimental setup is the same as previously described [7]. It consists in a supersonic beam coupled with a dual photoion photoelectron time-of-flight spectrometer and a femtosecond pump-probe laser.

Briefly, the pump λ_1(266 nm) is obtained by frequency tripling a Ti-sapphire regenerative amplifier, the probe wavelength λ_2 (800 nm) being the fundamental of the Ti-sapphire. The pump pulse energy is typically of the order of 5 μJ and the temporal width is in the 100 fs range. The probe at 800 nm is typically 70 fs broad and its energy in the order of 1 mJ. The cross correlation between the 266 nm and 800 nm laser beams has been measured on the multiphoton atomic ionization of Xe atoms leading to a 100 fs (FWHM) width assuming a Gaussian pulse shape.

The lasers are delayed in time by scanning a delay line with 33 fs steps. Both lasers are mildly focused onto the beam between the grids of the spectrometer by 1 m lenses. A typical time evolution is obtained by summing 10 to 20 scans with an average of 25 laser shots per scan step.

The most difficult part of the experiment has been to design a pulsed valve with a small oven downstream, heated at 500 °C, which allows to evaporate the CsI salt and to cool down the jet efficiently enough to produce stable clusters. The buffer gas (He at 3/8 atmospheres seeded with CH_3CN kept at around 50 °C in order to provide enough vapor pressure) is expanded from the pulsed valve into the small oven. The clusters formed enter, through a skimmer, the second chamber where the laser beams cross perpendicularly the molecular jet and the axis of the dual spectrometer.

3 Results

As mentioned in previous studies [9], we have never detected any CsI^+–CH_3CN ion in the time-of-flight mass spectrometer, even when the two lasers are not delayed in time. It seems thus that CsI^+–CH_3CN ions, which should be formed at time $t = 0$, undergo fragmentation and are detected as Cs^+–CH_3CN ions.

Although we were mostly interested in small clusters in this experiment, we tried to detect larger clusters also and we were not able to detect efficiently CsI–CH_3CN_n clusters with n bigger than 10. This is similar to what has been observed in the case of NaI–$(CH_3CN)_n$ where no cluster larger than $n = 8$ was detected [9]. The absence of large clusters has been interpreted as the signature of the charge separation within the solvent cluster from this critical size. This interpretation has been recently deep-rooted by calculations which show that in the NaI–$(CH_3CN)_n$ case, from 9 solvent molecules, the clusters where Na^+ and I^- are separated by 7 Å with two acetonitrile molecules shared between the ions are more stable than the ones where the two ions are in contact [10]. It seems then that the charge separation occurs in CsI–$(CH_3CN)_n$ for a critical size slightly larger than for NaI.

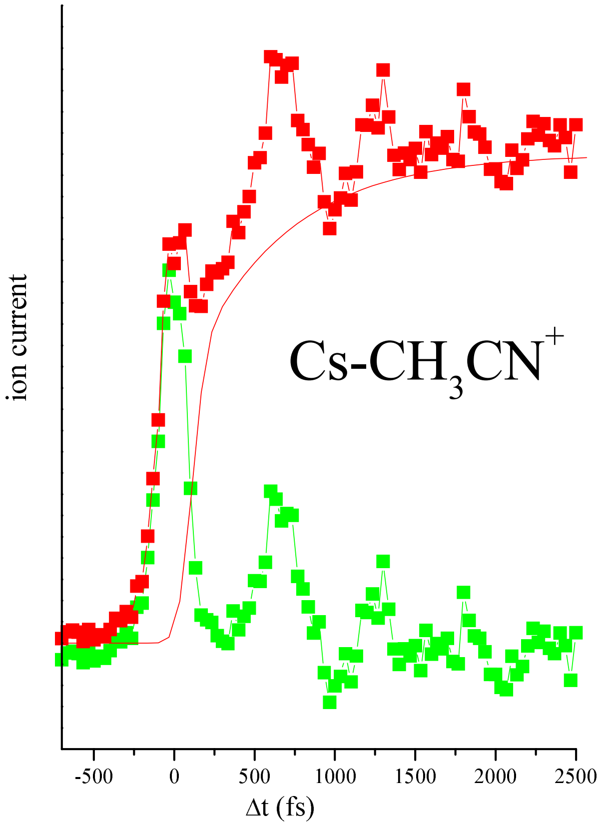

Fig. 1. Time evolution of the excited CsI–CH_3CN complex recorded on the Cs–CH_3CN^+ ion in dark light gray squares as a function of the delay between the pump (266 nm) and the probe (800 nm) lasers. On the vertical axis the relative intensity of the integrated ion peak. To enhance the recurrences a smooth biexponential growth has been subtracted (thin line). The resulting time evolution is given in light gray squares.

The time evolution observed when detecting the Cs–CH_3CN^+ ion is presented in Figure 1. In addition to the fast signal rise, a few oscillations with a period of about 700 fs are observed. At longer times the signal remains constant, which implies that the Cs–CH_3CN complex population remains stable.

4 Interpretation

In the bare CsI molecule, no recurrences are observed since the curve crossing between the ionic ground state and the covalent excited state occurs at too long a distance. Neither are these oscillations seen in (NaI, CsI)–(H_2O, NH_3) clusters [5]. The key point comes from the recent structure calculations we have carried out for the NaI–CH_3CN system [10]. Indeed, due to the strong dipole moment of both NaI and CH_3CN molecules, the expected complex ground state structure would *a priori* be a head to tail geometry. However, our calculations show that the equilibrium geometry corresponds to a quasi linear structure where the Na atom interacts strongly with the nitrogen atom of the cyano group. A similar structure is then expected for the CsI–CH_3CN complex.

One can understand the observed recurrences using simple classical dynamics calculations assuming the collinear complex as starting point.

Crude description:

- the first photon is absorbed and the Cs–I bond breaks;
- I goes away while Cs bumps in the rigid $NCCH_3$ molecule and pushes it ahead while the Cs–N bond is being formed;
- CsI–$NCCH_3$ (around $t = 0$) or Cs–$NCCH_3$ are ionized by the probe laser.

4.1 Potentials

We have used simple potentials and made some crude approximations.

The CH_3CN molecule is modeled as a simple N–X diatomic molecule, with one atom having the N mass (14 a.m.u.) and the second particle X having the CCH_3 mass (27 a.m.u.). These two particles are bound by a Morse potential, $D_e = 5$ eV and $\omega_e = 2000$ cm^{-1} [11]. The equilibrium distance, 2.46 Å, of this diatomic molecule has been adjusted to obtain the same moment of inertia as the acetonitrile molecule.

The CsI ground state is considered as a Morse potential with an equilibrium distance of 2.5 Å and the excited state is considered as a purely repulsive potential, such that the excess Franck Condon energy is about 5000 cm^{-1}. The CsI^+ ionic state is also modeled as a Morse potential with a binding energy of 0.4 eV and the same equilibrium distance as the ground state.

The Cs^+–CH_3CN Morse potential has been taken with a binding energy of 7000 cm^{-1} and an equilibrium distance of 3.1 Å [12].

The potential of the Cs($6s$)–N van der Waals complex is taken as a Morse potential with a frequency of 100 cm^{-1} and a binding energy of 1500 cm^{-1}, which leads to an ionization potential similar to that measured by the group of Fuke [13]. The equilibrium distance has been increased by 0.25 Å with respect to the ionic state internuclear distance as in the case of Na–CH_3CN [14].

The Π state Cs($5d$)–N is taken as a Morse potential with a frequency of 150 cm^{-1} and a binding energy of 3600 cm^{-1}. At infinite Cs...N distance, the Cs($6s$) $0^{1/2} \rightarrow$ Cs($5d$) $1^{1/2}$ transition lies at 14500 cm^{-1} [15].

The Σ state Cs($6p$)–N is taken as a repulsive interaction. The Cs($6s$) $0^{1/2} \rightarrow$ Cs($6p$) $1^{1/2}$ transition lies at 11700 cm^{-1} [15]. The Π state Cs($6p$)–N is expected to be lower in energy and thus can not be excited with one probe photon.

All the other interactions are taken as purely repulsive.

All the parameters given above have been varied and obviously the fine details of the dynamics are sensitive to these values, but the overall picture stays the same.

4.2 Detection scheme

Two ionization processes must be considered.

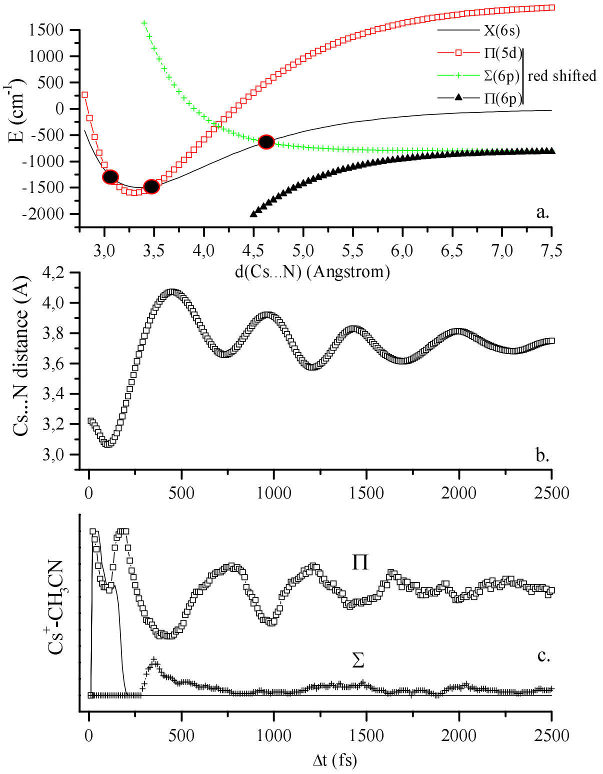

Fig. 2. (a) Cs–CH_3CN potential energy curves of ground state X (line), the $\Pi(5d)$ (open square), $\Pi(6p)$ (full triangle) and Σ (cross) states being red shifted by the energy of a probe photon, along the Cs–N coordinate. The Franck Condon points (full circle) define the region of the potential where the resonant condition is obtained. (b) Averaged Cs...N distance (Å) as a function of the time delay between the two lasers. (c) Decomposition of the calculated signal according the three different ionization processes: the direct ionization (straight line) occurs only at the beginning of the dynamics for less than 200 fs. The contribution of the resonant ionization through the Σ state (cross). The resonant ionization through the Π state (open square) reproduces the recurrence pattern as well as the loss of coherence in time.

4.2.1 Direct ionization

Two 800 nm photons (3.1 eV) cannot ionize Cs (ionization potential of Cs = 3.89 eV). The ionization potential of Cs–CH_3CN (3.2 eV) has been measured in the Fuke group [13] and is close but slightly higher than our probe energy. As a matter of fact, the two-photon ionization of the complex should be energetically allowed only if the Cs–N internuclear distance is shorter than the neutral equilibrium distance (3.35 Å), which allows to reach lower part of the ion potential energy curve and then decreases the appearance potential of the complex.

Furthermore, at the beginning of the dynamics, the iodine atom interacts with the cesium atom, and the ionization potential of the CsI–CH_3CN complex is then lowered by the Cs–I^+ binding energy will should insure an efficient ionization of the complex at time $t = 0$.

4.2.2 Resonant ionization

In Figure 2a, we have drawn the potential energy curves of the Cs–NCCH$_3$ complex as a function of the Cs...N internuclear distance. The origin of the energy is taken as the dissociation limit of the ground electronic state. The Π and Σ state potential curves have been red-shifted by the energy of one probe photon, *i.e.* 12500 cm^{-1}. In this dressed representation of the potential energy curves, the crossing points between the ground and excited states define very accurately the regions of the ground potential where the absorption of the probe pulse is efficient, *i.e.* the Franck Condon point. Taking into account the conservation of the kinetic energy, these points correspond to the Franck Condon distances where $E_{\text{excited state}} - E_{\text{ground state}} = h\nu$. As it was mentioned above, the Π state Cs(6p)–N cannot be reached from the ground X state with one probe photon and thus does not contribute to the signal. The Π state Cs(5d)–N can be reached twice per period, at 3 and 3.5 Å, while the Σ state can only be reached at 4.5 Å. As it was mentioned in the case of direct ionization, the energy of two probe photons does not allow to ionize directly the complex as soon as the Cs–N distance is longer than the equilibrium distance of the ground state, estimated here at 3.35 Å. Nevertheless, we can assume that an ionization process through Rydberg states occurs, and that Cs$^+$–CH$_3$CN ions will be produced at the Franck Condon points.

The ionization cross-section of the complex should then strongly depend on the Cs–N internuclear distance which will be underlined by the observation of maxima and minima in the Cs$^+$–CH$_3$CN ion product detection as a function of the time delay between the two lasers. As explained above, different ionization processes are considered and since their relative efficiency is unknown, each ionization pathway has been considered independently of the other.

To simulate the signal the following procedure is followed.

A trajectory is initiated in the ground state and periodically the system is switched to the excited surface where the CsI dissociates. The time evolution of the system is followed for 3 ps, and periodically (every 10 fs) one tests if

(1) the energetic difference between the ion and ground state potentials is smaller than the two-photon energy (non-resonant two-photon ionization),
(2) the energetic difference between the ground and the excited state potentials along the Cs–N coordinate is equal to a probe photon energy ±200 cm^{-1} (resonant condition).

After 3ps, the system returns on the ground state trajectory for 200 fs before next jumps to the excited surface. It should be noticed that a small random angle, within 1°, between the axis of the acetonitrile and CsI molecules is introduced in the ground state structure in order to break the collinear geometry.

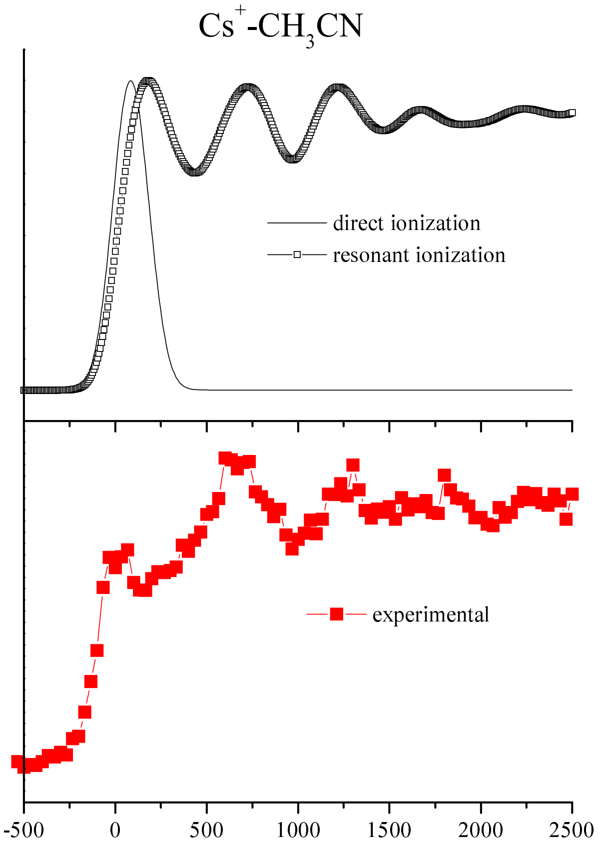

Fig. 3. Comparison between the experimental signal (bottom trace) and the calculated signals (upper traces) convoluted by a Gaussian-like function of 100 fs width, as a function of the time delay in fs. With the above potentials, a nice agreement is found except that the signal simulated is maximum at 200 fs and not at 700 fs.

The Cs...N distance and the calculated signal, averaged on 100 trajectories, have been reported in Figures 2b and 2c respectively.

The direct ionization (line graph) only occurs at the beginning of the dynamics for less than 200 fs. The non resonant ionization is energetically allowed only if the iodine atom is still in the vicinity of the cesium atom which is also very close to the acetonitrile molecule.

The resonant ionization through the Σ state (cross graph) appears after 300–350 fs, which corresponds to the average time necessary to reach the long range region of the ground state potential, around 4.5 Å. Since the Cs...N distance does not extend on a long range after the first period, the contribution of this process is then quite small.

The resonant ionization through the Π state (open square graph) exhibits recurrences which reproduce quite well, with the above assumptions, the observed Cs$^+$–CH$_3$CN ion signal.

The dynamics observed thus corresponds to the Cs–N elongation coordinate. After the first impact of the Cs atom on the N atom, the Cs–CH$_3$CN bond is stabilized but the amplitude of the vibrational motion along the Cs–N coordinate is still very large, as can be seen in Figure 2b.

In Figure 3, the Cs^+–CH_3CN experimental signal is compared with the calculated one convoluted by a Gaussian-like function of 100 fs width in order to simulate the temporal width of the laser. The initial coherence is quickly lost due to energy transfer to the N–CCH_3 coordinate and to the Cs–N–CCH_3 bending. The vibrational period is obviously strongly dependent on the potentials, mainly on the CsI initial excess energy and the Cs–N vibrational frequency. But even though the period of the recurrences is sensitive to the potentials, the presence of recurrences is preserved as long as the linear geometry is retained. Thus the observation of these recurrences is induced by the initial geometry: these vibrations are observed only because the complex is nearly collinear inducing a front collision, and if the CH_3CN molecule is set head to tail to CsI, such recurrences cannot be observed. As a matter of fact, for the CsI–H_2O system, only a fast decay is observed, indicating that there is no stabilization of the Cs–H_2O complex. The calculations of Peslherbes *et al.* [16] on NaI–H_2O predict that the water is not along the NaI internuclear axis and a similar structure is expected for CsI–H_2O. Then, the first collision of the alkali atom on the water molecule will transfer a large amount of rotational energy to the solvent molecule which will induce the rapid dissociation of the cluster.

5 Conclusion

We have reported the pump-probe femtosecond photoionization of CsI–CH_3CN complex detected as Cs^+–CH_3CN ion. The observed recurrences are assigned to the first vibrations of the Cs–CH_3CN complex issued from the dissociation of the CsI molecule within the cluster. This result corroborates the collinear geometry of the ground state complex previously proposed. More experiments on larger clusters as well as on similar systems such as RbI–CH_3CN are in progress and will be published in a forthcoming paper. More refined theoretical simulations are also in progress in our laboratory [12].

We are pleased to thank P. Meynadier, M. Perdrix, S. Guizard and O. Gobert for the maintenance of the femtosecond laser source. Many thanks to V. Brenner, P. Millié, E. Charron and D. Stibbe for helpful discussions.

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