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# Molecular picture of excited states and fragmentation paths of the $Na_5F_4$ cluster

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**Abstract.** The stability against fragmentation and possible relaxation of the lowest excited states of the $Na_5F_4$ cluster (representative of cubic non stoechiometric clusters with an excess sodium atom, also called sodium-tail) is investigated by means of one-electron pseudopotential calculations with particular reference to photoabsorption processes from the ground state. Whereas the equilibrium configuration of the ground state has $C_{3v}$ symmetry, the doubly degenerate $1^2$E excited state is affected by a conical intersection and a Jahn-Teller effect associated with the rotation of the sodium tail around the $C_3$-axis. This yields a "Mexican hat" topology for the lowest sheet with three equivalent $C_s$ minima. Alternatively the $2^2A_1$ state has a minimum retaining the $C_{3v}$ symmetry. The dissociation paths of the cluster along the $C_3$-axis into respectively $Na_4F_4$ + Na and $Na_4F_3$ + NaF are also investigated. Among the former paths, the excited states are found adiabatically stable with respect to the products. However in the $A_1$ symmetry, fragmentation into NaF exhibits an interesting avoided crossing between configurations correlated respectively with $Na_4F_3^+$ + $NaF^-$ and $Na_4F_3$ + NaF. Such interaction, similar to the well-known charge exchange processes in elementary molecules might induce non adiabatic predissociation of the $2^2A_1$ state. This mechanism is invoked to explain the differences between R2PI and depletion spectra, correlated with the dissociation or relaxation of the excited states.

**PACS.** 36.40.Mr Spectroscopy and geometrical structure of clusters – 36.40.Qv Stability and fragmentation of clusters – 31.15.Ar Ab initio calculations

## 1 Introduction

Spectroscopy is a powerful tool to get some insight into the physics of clusters. Up to now, and together with the measurement of ionization potentials, optical spectra have provided a direct access to the electronic properties of clusters and hence an indirect access to their geometrical structure. For several types of small clusters where absorption spectra could be determined theoretically with sufficient accuracy, the spectra were used to discriminate among various possible isomers [1–6]. Excess electron alkali halide clusters (*e.g.* non stoechiometric clusters) provide a specially interesting case since the bonding of the excess electron(s) is directly related to its (their) localization at the surface of the cluster or close to a structural defect. At the moment, experimental data for this family of clusters were essentially obtained in nanosecond timescale, mainly with two types of experiments. The first one is resonant multi-photon photoionization, and particularly the two-photon case (R2PI) in which a first photon brings the cluster to an excited state and the second photon ionizes it for detection sake. Such a technique was initially used for small alkali metal trimers and in particular allowed for the resolution of pseudo-rotation features in those systems [7–9]. However, this technique requires a long enough lifetime in the excited state to allow ionization by the second photon. It thus cannot always provide useful information when the excited states are dissociative. Depletion spectroscopy offers an alternative and a complementary technique to multi-photon ionization. Indeed, in this latter case the ionizing photon depopulates the ground state frustrating the excitation process. Detection is made possible by this difference process and the bound/*versus* dissociative character of the excited state is not crucial [10–13]. Thus the comparison between the two types of results can be used to infer to some extent the character of the excited states. Obviously the experimental following of excited states relaxation can be achieved today using time-resolved femtosecond experiments. However except the pioneering work of Zewail *et al.* on the NaI molecule [14], this technique, already applied to metal clusters [15,16] has not yet been used in alkali halide clusters but only for diatomics [17] or solvated molecule [18].

Theoretical descriptions of excess electron alkali halide clusters have shown that a single excess electron can give rise to several localization patterns, the major ones being the so-called F-center (the electron replaces a missing halogen), localization on an alkali tail (the electron localizes on a pending excess alkali atom), surface electron (for specially compact structures corresponding to magic numbers, the electron is weakly localized at the

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surface of the cluster) or localization at a missing edge or at a general surface defect [4–6,19,20]. In our previous work on $Na_nF_{n-1}$ clusters [5,6,20], we have developped a pseudopotential model which consists of a Born-Mayer plus coulombic interaction for the $Na^+$ and $F^-$ core ions and a quantal description of the excess electron *via* electron–$Na^+$ and electron–$F^-$ pseudopotentials. Polarization of the ionic cores as well as electron-ion correlation was added perturbatively. This model was shown not only to reproduce the ground state isomers [5] given by standard valence pseudopotentials [4] for $n = 2$, 6 but also their excited electronic structure in the range 1–3 eV [6]: the vertical transition energies and the oscillator strengths were found to agree with *ab initio* valence calculations [4] (accuracy better than 0.2 eV for the transition energies and 10% for the oscillator strengths). This agreement also proved the adequacy of the model for the excited states *e.g.* the electronic structure in this energy range does not exhibit electronic excitations on fluorine. We have moreover achieved a finite temperature simulation of the absorption spectra [6] by integrating the oscillator strength of the transitions along a Monte Carlo trajectory on the ground state, building the spectra as histogram functions of the excitation energies. Those simulations were compared with recent experimental results on $Na_nF_{n-1}$ clusters [9,21]. The best agreement about the lines positions and widths was found to correspond to a simulation temperature of about $T = 300$ K, in good concordance with the experimental estimates [22].

An interesting feature was found to occur in the particular case of sodium tail clusters. For this structural family and within a pseudopotential model for sodium, the ground state wavefunction of the pending sodium electron resembles a nodeless (slightly deformed) *s* type orbital. The lowest absorbing states can be described as resulting from electron excitation into (distorted) *p* type orbitals also essentially localized on the pending sodium. Two of these orbitals are approximately perpendicular to the sodium tail axis and have transition energies around 1.4 eV in $Na_{11}F_{10}$ for instance. The third orbital is directed along the sodium tail axis and lies at slightly higher energy, with a transition around 1.8 eV. Weak absorption also involves higher states to which this one-electron picture can still be extended. Those excited states explain the main features of the experimental absorption spectra. However the peculiar feature is that for this family, only the 1.4 eV peak was observed in R2PI experiment, whereas the 1.8 eV peak could actually be observed using depletion technique (Fig. 1). This suggests a selective behavior of the various excited states *versus* relaxation and/or dissociation. Whereas our previous work was essentially concerned with the ground state properties and absorption spectroscopy close to the equilibrium geometry, we intend in the present work, to bring some insight in this selective fragmentation of the excited states. We thus examine the behaviour of the excited states Potential Energy Surfaces (PES) along some relevant fragmentation paths.

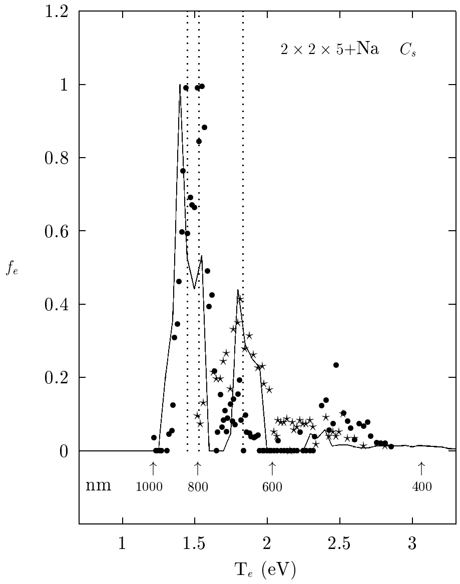

**Fig. 1.** Absorption spectra in $Na_{11}F_{10}$. Theory: Monte Carlo simulation at 300 K [6] (continuous line); experimental R2PI [9] (black circles); depleted spectrum [21] (stars). The dotted lines indicates the theoretical positions of the vertical transitions (in eV) at the ground state geometry. The arrows indicate the wavelengths in nanometers.

We have chosen to investigate the $Na_5F_4$ cluster. It consists of a pending sodium attached to a 2×2×2 cuboid along a $C_3$-axis and is the smallest sodium-tail cubic structure. Moreover its special symmetry will be shown below to be particularly interesting. The lowest dissociation channel of $Na_5F_4$ in the ground state was clearly found to be $Na_4F_4$ + Na ($D_e = 0.439$ eV [5]) which, as we will show below, is barrierless. This lowest channel was found to lie about 1.7 eV below $Na_4F_3$ + NaF ($D_e = 2.158$ eV [5]) close to two others channels, namely $Na_3F_3$ + $Na_2F$ ($D_e = 2.056$ eV) and $Na_3F_2$ + $Na_2F_2$ ($D_e = 2.096$ eV), not reported in [5]. Channel $Na_5F_3$ + F cannot be obtained within the present model since it involves a neutral fluorine. However in the standard valence calculations of Bonačić-Koutecký *et al.* [4] this dissociation channel was shown to be 7.9 eV higher than $Na_4F_4$ + Na. Those arguments show that in the ground state ($1^2A_1$), a marked energetical preference is found for $Na_4F_4$ + Na. The lowest excited states $1^2E$ (doubly degenerate) and $2^2A_1$ lie respectively 1.46 and 1.70 eV above the ground state equilibrium configuration, *e.g.* 0.6 eV and 0.4 eV below the three channels lying near 2.1 eV. One must however take into account the temperature ($T \approx 300$ K) and the kinetic energy excess which make dissociation towards those channel accessible in particular for state $2^2A_1$. The fragmentation mechanisms in excited states may follow indirect patterns because of non-adiabatic processes. Obviously the three channels are energetically accessible. Correlation of the initially populated excited states (in the compact cluster) with the dissociation fragments can yield or not to an electronic transfer. There is no strong expected rearrangement for the abstraction of Na. The same feature may be expected for the $Na_2F$ and $Na_3F_2$ products, provided that these fragments include the sodium-tail atom (which bears the excited electron). In both cases four NaF bonds must be broken and one expects significant barriers. We have probed the $Na_2F$ dissociation investigating the reaction path out of the $C_{3v}$ symmetry and we have found that the ground and the two lowest excited states exhibit no intercrossings and barriers around 2 eV, which makes direct fragmentation of the excited states rather unlikely. The same is expected for the $Na_3F_2$ channel. Oppositely the abstraction of the FNa tail fragment in the excited state involves an electron transfer and may be of particular interest. Indeed, because of the electron localisation on the pending sodium the cluster in an excited state $Na_5F_4^*$ is diabatically correlated with $Na_4F_3^+$ + $NaF^-$ and may undergo non adiabatic relaxation into $Na_4F_3$ + NaF through an interfragment electron-transfer ($Na_4F_3$ is an F-center cluster). As discussed above, the single fluorine atom abstraction, which cannot be treated with the present pseudopotentials, lies at too high an energy to be relevant even for fragmentation of the lowest excited states.

$Na_5F_4$ is a particularly convenient example of sodium-tail species, since it consists of a pending sodium attached to a 2×2×2 cuboid along the $C_3$-axis. It thus provides for fragmentation into $Na_4F_4$ a "natural" channel depending on the position of the extra Na along this axis. Moreover, for dissociation yielding NaF, the structural ground state of the fragment single excess electron cluster $Na_4F_3$ is a F-center cluster (also with $C_{3v}$ symmetry) described as the same 2×2×2 cuboid with a missing fluorine on the $C_3$-axis. Thus the $C_3$-axis is also a "natural"-axis for the abstraction of NaF.

In the present paper, we restrict ourself to the the discussion in terms of PES of the the fragmentation of $Na_5F_4$ into respectively $Na_4F_4$ + Na and $Na_4F_3$ + NaF following $C_3$ "collinear" dissociation through the study (i) of the stability of the concerned excited states and (ii) of the reaction path on the potential energy surfaces. This picture for cluster dissociation is in analogy with the study of molecular pre-dissociation in excited states and non-adiabatic transitions induced by potential curve crossings in simple diatomic molecules.

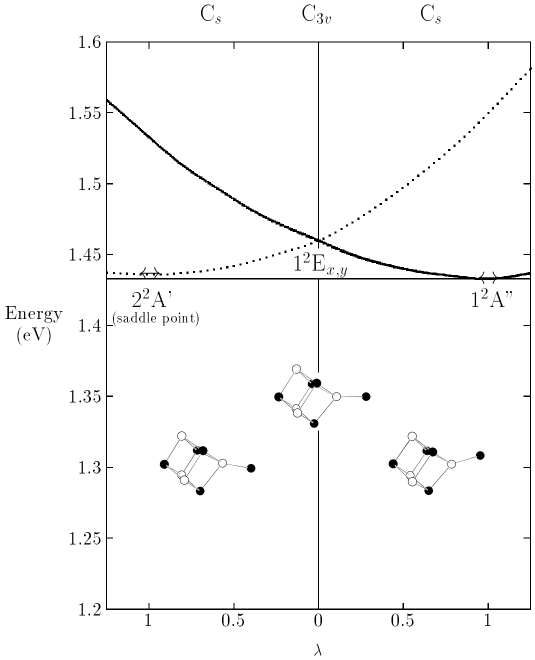

**Fig. 2.** Minimum energy path from $C_{3v}$ to $C_s$ symmetry for $Na_5F_4$. Let $q_{C_{3v}}$ and $q_{C_s}$ the coordinates of the singular structures, the coordinates $q(\lambda)$ of an intermediate structure are given by $q(\lambda) = \lambda q_{C_{3v}} + (1 - \lambda) q_{C_s}$.

## 2 Relaxation and quasi linear fragmentation paths

Prior to investigate dissociation, we examine the stability of the lowest excited species correlated with the doubly degenerate $1^2E$ states and with the non-degenerate $2^2A_1$ state in $C_{3v}$ symmetry. We have thus carried on optimizations in $C_s$ symmetry with relaxation of the $C_{3v}$ constraint starting from the ground state equilibrium geometry. The absolute minimum of the third excited potential energy surface (correlated with $2^2A_1$) is found to retain its $C_{3v}$ symmetry with very little relaxation with respect to the starting geometry. The situation is more complicated for the doubly degenerated state $1^2E$. In $C_{3v}$ there exists three $C_s$ equivalent symmetry plane and, for $Na_5F_4$, the sodium tail is along the $C_3$-axis common to the three $C_s$ planes. The $C_{3v}$ configuration actually appears as a conical intersection. Deviating from this symmetry, with the sodium tail remaining in one of the three $C_s$ planes, one obtains three equivalent $2^2A''$ absolute minima on the lowest sheet, essentially corresponding to a bending of the sodium tail (with an angle of 17° in the symmetry plane with respect to the former $C_3$-axis). These three minima (structure on the right in Fig. 2) are separated from each other by three equivalent $2^2A'$ saddle points characterized by a bending angle of −11° (left structure in the figure). This potential energy surface topology, which corresponds to the real rotation of the sodium tail around the symmetry axis, is analogous to that occuring in alkali or noble metal trimers and corresponding there to a pseudo-rotation. It is seen in the present case that the saddle points and the minima are energetically close (lying respectively 0.024 and 0.027 eV below the conical intersection), and that one may expect quasi-free rotation. The diagonalization of the Hessian matrix shows that in the ground state ($1^2A_1$), the softer vibrational mode is associated with the rotation of the sodium tail and characterized by a degenerate mode with an harmonic frequency of 12 $cm^{-1}$ (*e* symmetry). In the $2^2A_1$ electronic state, the softer frequency is again degenerate with the same symmetry *e* and a frequency of 49 $cm^{-1}$. In the $1^2A''$ (correlated with $1^2E$), the softer modes are no longer degenerate and have harmonic frequencies of 47 and 55 $cm^{-1}$. A special study of this rotational modes and their localization would be interesting with respect to future femtosecond experiments, but exceeds the scope of the present study. The Hessian calculation confirms here the discussion about the

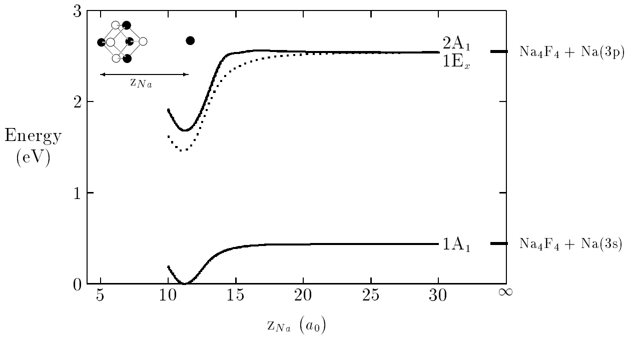

**Fig. 3.** Dissociation of $Na_5F_4$ into $Na_4F_4$ + Na. Each state is optimized along the $C_{3v}$-axis (distance of the leaving sodium atom to the opposite sodium atom of $Na_4F_4$). $^2A_1$ states: continuous lines; $^2E$ state: dashed line.

stability of the excited states, neither of them exhibiting strong relaxation nor adiabatically yielding to direct dissociation.

We now investigate the reaction paths. For dissociation into Na, the coordinate used is the distance $z_{Na}$ between the leaving sodium and the opposite one in the $Na_4F_4$ cluster. For fragmentation into NaF, the coordinate represents the distance $z_F$ between the fluorine atom of NaF and the opposite sodium atom in $Na_4F_3$. In the $C_{3v}$ symmetry, since the sodium atom always remains on the same side, the monitoring of the $z_F$ coordinate ensures the following of the NaF dissociation. In both cases, for each value of the dissociation coordinate, all other internal coordinates of the dissociation products ($Na_4F_4$, $Na_4F_3$ and NaF) were reoptimized in each excited state within a $C_{3v}$ constrained symmetry. This means that for each excited state, the potential curve represents the minimal adiabatic path (within the $C_{3v}$ symmetry group) reported here as a function of the dissociation coordinate. The avoided crossings between those PES allow to identify the existence and mechanisms of non-adiabatic transitions.

Dissociation into Na shows a very regular pattern (see Fig. 3). All states are bound at almost the same interfragment distance ($\approx 11.2a_0$) and have almost no barriers *versus* dissociation, except $2^2A_1$ which has a very small hump. There is no crossing and the dissociation energies of the excited states along this channel (1.08 eV and 0.86 eV for dissociation of $1^2E$ and $2^2A_1$ into Na($3p$)) are stronger than that of the ground state (0.45 eV). This barrierless endothermic fragmentation into $Na_4F_4$ + Na is quite consistent with the analysis of the electronic structure in the so-called Na-tail clusters [5] in which the excess electron localizes on the pending sodium ion, thus almost entirely screening the coulombic interaction with the rest of the cluster. In the same state, the situation results into a weaker bond and a longer bond length ($4.14a_0$ for the pending NaF bond in the ground state *versus* $3.8a_0$ for the free molecule $Na^+F^-$ ionic bond). In the excited state also, the removal of the pending sodium offers the lowest and easiest fragmentation path.

The PES corresponding to fragmentation into NaF are somewhat more complex and also brings some light on the electronic configurations of the ground and excited states of the cluster and their evolution with dissociation. We first examine the states with E symmetry. The first excited state $1^2E$ shows a regular barrierless adiabatic dissociation towards $Na_4F_3^*$ + NaF (dissociation energy of 1.75 eV, see Fig. 4). We have however investigated the nature of the wavefunctions by considering the Lőwdin population on the atoms of the NaF fragment. For all states of Figure 4, the fluorine atom bears a quite constant charge of −1 whatever the distance. Oppositely, the charge on the sodium atom of NaF for state $1^2E$ changes from 0.35 at $z_F < 9a_0$ to about 1 for $z_F > 12a_0$ as shown in Figure 5 (dashed line). This charge variation can be correlated with an avoided crossing between two states differing by charge exchange. The asymptotic adiabatic dissociation of $1^2E$ consists of neutral fragments $Na_4F_3(1^2E)$ + NaF (NaF being characterized by $Na^+F^-$). However, the short distance configuration with the electron on the pending sodium atom is analysed in term of subunits $(Na_4F_3{}^+)(FNa^-)$

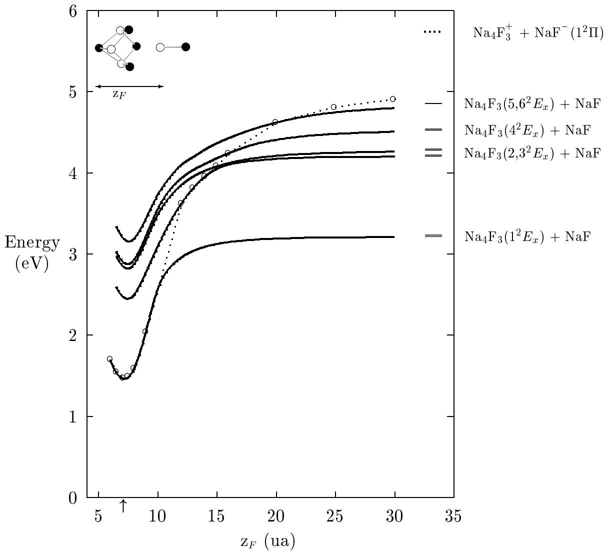

**Fig. 4.** Dissociation of $Na_5F_4$ into $Na_4F_3$ + NaF for $^2E$ states. Each state is optimized along the $C_{3v}$-axis (distance of the fluorine atom of NaF to the opposite sodium atom of $Na_4F_3$). The dashed line is a diabatic-like state corresponding to the $Na_4F_3{}^+ + NaF^-(1^2\mathit{\Pi})$ limit(see text). The arrow indicates the value of the $z_F$ coordinate in the ground state ($z_F = 7.07a_0$).

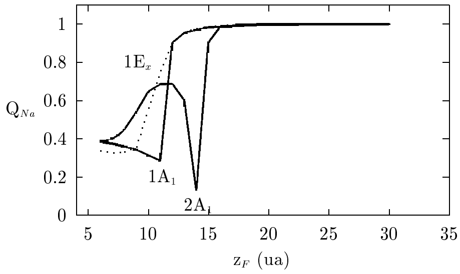

**Fig. 5.** Charges on the sodium atom of the leaving NaF in the dissociation of $Na_5F_4$ into $Na_4F_3$ + NaF for the ground state and the two first excited states. $^2A_1$ states: continuous lines; $^2E$ state: dashed line.

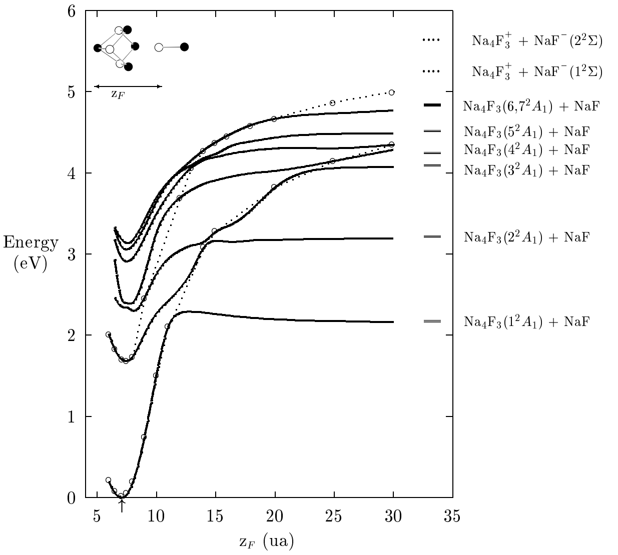

**Fig. 6.** Dissociation of $Na_5F_4$ into $Na_4F_3$ + NaF for $^2A_1$ states. Each state is optimized along the $C_{3v}$-axis (distance of the fluorine atom of NaF to the opposite sodium atom of $Na_4F_3$). The dashed lines are diabatic-like states corresponding to the $Na_4F_3{}^+$ + $NaF^-(1^2\Sigma$ and $2^2\Sigma)$ limits (see text). The arrow indicates the value of the $z_F$ coordinate in the ground state ($z_F = 7.07a_0$).

and correlated diabatically with a zwitterionic type product, namely $Na_4F_3{}^+(1^1A_1)$ + $NaF^-(1^2\Pi)$. This diabatic correlation is illustrated by the dashed line in Figure 4 which links the energy values corresponding to the wavefunction with the largest weight on the leaving sodium at each distance. At finite distance, this zwitterionic configuration is indeed dominated by an attractive coulombic behaviour and contributes strongly to the adiabatic state $1^2E$ for $z_F < 9a_0$. One notices that this state undergoes multiple avoided crossing with all the other excited states dissociating into neutral fragments.

We now examine the $A_1$ states for which the situation is significantly more complex (see Fig. 6). The potential energy curves of the two lowest states exhibit an avoided crossing around $z_F = 11a_0$. In the ground state, this avoided crossing results in a shallow barrier (0.13 eV) for the dissociation above $Na_4F_3$ + NaF. Again one can analyse the nature of $1^2A_1$ by following the charge on the atoms of the NaF fragment. The charge on the fluorine atom remains equal to −1. Alternatively, the charge on sodium jumps abruptly from a value close to +0.3 to +1.0 at $z_F = 11a_0$ (see Fig. 5). Thus at short distance, the analysis of the ground state wavefunction in terms of the fragments shows that it corresponds to $Na_4F_3{}^+$ + $NaF^-(1^2\Sigma)$ whereas it dissociates adiabatically towards $Na_4F_3$ + NaF. As for $^2E$ states, the interaction can thus be attributed to charge exchange. Figure 6 shows a diabatic-like potential curve (lowest dashed curve) obtained as for E states. For $z_F > 8a_0$ this curve is correlated with $Na_4F_3{}^+$ + $NaF^-(1^2\Sigma)$ and exhibits a regular $-1/R$ Coulombic behaviour. This configuration is responsible for the large stability of the ground state. A second

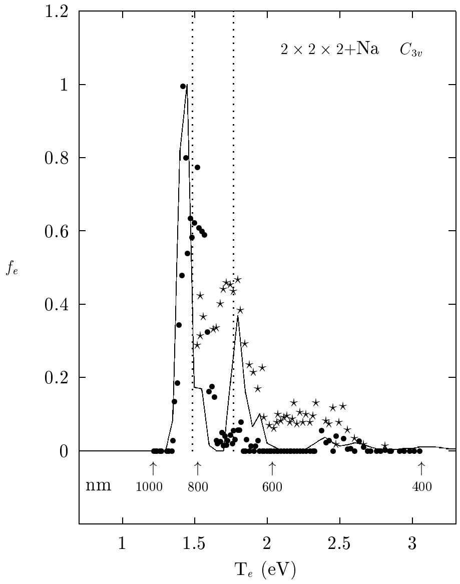

**Fig. 7.** Absorption spectra in $Na_5F_4$. Same legend as Figure 1.

zwitterionic configuration occurs in the same symmetry, involving a low excited state of $NaF^-$, namely $Na_4F_3{}^+$ + $NaF^-(2^2\Sigma)$. The associated diabatic-like curve (second dashed curve in Fig. 6) was obtained by linking the next states with largest electronic weight on the leaving sodium. This latter zwitterionic configuration contributes dominantly to state $2^2A_1$ at short distances.

In both $^2A_1$ and $^2E$ manifolds, one can thus observe patterns similar to ionic/covalent interaction in diatomic systems. This corresponds to the avoided crossing of repulsive "covalent" $Na_4F_3$ + NaF electronic configuration with an attractive "charge transfer" configuration. At longer distance, the latter exhibits cascade avoided crossings with the other excited states of same symmetry. Such pattern is well-known for instance in alkali diatomics [23] and alkali hydrides [24] or halogens [25]. The adiabatic dissociation energy of $1^2A_1$ towards $Na_4F_3(1^2A_1)$ + NaF is 2.17 eV and the adiabatic dissociation energy of $2^2A_1$ towards $Na_4F_3(2^2A_1)$ + NaF is 1.48 eV, the diabatic dissociation (*e.g.* the dissociation energies to the zwitterionic asymptotes) being 5.26 eV ($Na_4F_3{}^+$ + $NaF^-(1^2\Sigma)$) and 5.65 eV ($Na_4F_3{}^+$ + $NaF^-(2^2\Sigma)$).

## 3 Discussion and outlook

The experimental spectrum of $Na_5F_4$ is shown in Figure 7. It is seen that the R2PI spectrum (black dots) mainly has a single peak near 1.4 eV, which corresponds to excitation towards $1^2E$. The vertical excitation energy (geometry of the ground state) is 1.51 eV. In $C_{3v}$ symmetry, the minimum of the $1^2E$ state is found at almost the same $z_F$ as that of the ground state, corresponding to an adiabatic excitation energy of 1.46 eV. As already discussed, the excitation takes place in the vicinity of the conical intersection, close to the absolute minimum of the $1^2E$ surface, stable with respect to fragmentation into Na (by 1.08 eV) and also into NaF (by 1.6 eV). This stability *versus* fragmentation thus explains the observation of the $1^2$E state in R2PI experiments.

The situation is significantly different for the $2^2A_1$ state. As a matter of fact, this state has an adiabatic minimum at a geometry almost identical to that of the ground state. The vertical and adiabatic excitation energies are the same, namely 1.70 eV. The experimental R2PI spectrum shows an extremely weak signal in this range, whereas the depletion spectrum exhibits a marked peak near 1.7 eV. In the calculation, this minimum is located 0.84 eV below the adiabatic dissociation into $Na_4F_4(1^2A_1)$ + Na(3*p*) and 1.50 eV below the adiabatic dissociation into $Na_4F_3(2^2A_1)$ + NaF. The remarkable point is that it is located only 0.45 eV below the adiabatic dissociation products of the ground state, namely $Na_4F_3(1^2A_1)$ + NaF. Thus if the cluster is initially hot previous to excitation (ground state) it could be formed in the excited state with a certain amount of excess energy above its minimum. We have calculated the harmonic zero-point energies (ZPE) of $Na_5F_4$, which are 2363, 2476 and 2325 $cm^{-1}$ (0.29, 0.31 and 0.29 eV) for the $1^2A_1$, $2^2A_1$ and $1^2A''$ states respectively whereas the ZPE of $Na_4F_3$ are 1777 and 1698 $cm^{-1}$ (0.22 and 0.21 eV) in the $1^2A_1$ and $2^2A_1$ states respectively. The free NaF molecule frequency is $\omega_e = 569$ $cm^{-1}$ (ZPE of 0.035 eV). A vibrational temperature $T = 300$ K (resp. 600 K) would correspond to a kinetic energy of 0.27 (resp. 0.54) eV. The energy of the initial excited molecular species lies 0.14 (resp. 0.13) eV below (resp. above) the final dissociation products in their ground state (taking account of ZPE and vibrational temperature). One may thus infer that in the $2^2A_1$ state, $Na_5F_4$ is likely to undergo predissociation into $Na_4F_3(1^2A_1)$ + NaF through non-adiabatic coupling concerning the two lowest PES of $^2A_1$ symmetry in Figure 6. This may explain the quenching of the R2PI signal in the experiments.

## 4 Conclusion

Taking advantage of the $C_{3v}$ symmetry, we have achieved in the present work a molecular study of the stability and particular dissociative paths of the ground and excited states of $Na_5F_4$. We have shown that the rotation of the sodium tail might present interesting features and would deserve experimental femtosecond investigations. The possible influence of a non-adiabatic predissociation mechanism certainly extends to other $Na_nF_{n-1}$ sodium-tail clusters for which the abstraction of NaF should present the same pattern, *e.g.* an avoided crossing between ground and excited state characterizing charge exchange on the sodium atom. This would explain the similarity of the experimental spectra for all sodium tail clusters showing in depletion experiments a second peak around 1.7–1.8 eV which is absent from the R2PI signal. In this latter situation also, we think that real-time experiments would be helpful. From a theoretical aspect, the detailed study of the potential energy surfaces has been strongly facilitated by the use of the one-electron pseudopotential Hamiltonian. This partial PES study should be in principle complemented by further investigations to actually check the other degrees of freedom which have been discussed in the introduction. The determination of reaction paths involving simultaneously several excited sheets, numerous degrees of freedom and no symmetry is however not easy within a static picture. A more convenient way should be to achieve a non-adiabatic full three-dimensional dynamical study. One could consider non-adiabatic methods such as those used by Knospe *et al.* for charge exchange in atom-cluster collisions [26] which do not involve any explicitation of the PES (direct time-dependant methods). One may also couple the calculation of the various surfaces “on the fly” in the dynamics using hemiquantal [27] or surface hopping algorithms [28]. This would permit the determination of the reaction paths without *a priori.* It would moreover give access to the timescales of the competing processes. Advances have been recently published by Hartmann *et al.* [29] in the context of vibrational relaxation of $Na_2F$ or $Na_3F_2$ clusters in excited states.

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