

Vibrational relaxation of photoexcited Na₃F

V. Blanchet, J.M. L’Hermite, A. Le Padellec, B. Lamory, P. Labastie

Lab. Collisions Agrégats Réactivité, CNRS UMR 5589, IRSAMC-UPS, 118 route de Narbonne, 31062 Toulouse, FRANCE

Correspondence should be addressed to val@irsamc.ups-tlse.fr

We have investigated the vibrational relaxation of Na₃F by time-resolved photoionization at the threshold. Among the two isomers of Na₃F, we have studied the excited electronic states of the C_{2v} one. The pump–probe signal clearly shows damped oscillations, the period of which is fitted to 390±8 fs, close to twice the previously measured bending mode of Na₂F,¹ while the relaxation time is 1275±50 fs.

1. INTRODUCTION

Small Na_nF_{n-p} clusters can be considered as formed of n Na⁺ ions and $n-p$ F⁻ ions, which tend to form a rock-salt lattice, together with p excess electrons. The electronic arrangement, and hence the ionization potential, is thus very structure dependent, as indeed verified in Refs.[2,3,4,5,6,7,8,9]. In this respect, it may happen that different isomers of the same cluster present a significant difference between their ionization potential, allowing to monitor selectively the passage through one specific isomer in time-resolved experiments. Indeed, the ionization probability may become time-dependent, provided the probe pulse energy is low enough to photoionize only one isomer while the molecule is excited in such a way that it wanders through several structures. Na₃F is such a cluster, with two isomers: the lowest one with a quasi-planar C_{2v} structure and a vertical ionization energy of roughly 4.9 eV, while the second one with a 3D C_{3v} structure and a vertical ionization energy of 4.4 eV.[4,5] These structures are depicted on Fig. 1(a). Such a large difference in vertical ionization energies makes this cluster an ideal system to test the above ideas.

2. PHOTOPHYSIC OF Na₃F

The apparatus has been already described in Ref. [7]. The clusters are produced by laser vaporization of a sodium rod, with helium at about 5 bars as a carrier gas and a small amount of SF₆. The repetition rate is 10 Hz. In this configuration, the vibrational temperature of the formed clusters is roughly 400 K,[10] that gives 85% of C_{2v} geometry and 15% of C_{3v} for a Boltzman distribution. The laser beams are focused onto the cluster beam between the first two plates of an axial Wiley Mac-Laren Time-Of-Flight mass spectrometer with a reflectron. The photoionization efficiency curve as well as the photoabsorption spectrum determined by a photodepletion experiment are displayed on Fig. 1(b) and 1(c) respectively. The ionization threshold is at 4.3 eV, close to the 4.4 eV calculated for the C_{3v} isomer and 4.9 eV for the C_{2v} isomer (see the Fig. 1 (b)). The conclusion arising out of the photodepletion spectrum shown on Fig 1(c) and from *ab initio* calculations of the excited states, [5] is that the observed

spectrum is due to the C_{2v} isomer, and that the photoionization peak at 4.65 eV is a preionization resonance of this isomer (adiabatic ionization potential predicted at 4.26 eV). More information is available in Ref. [11].

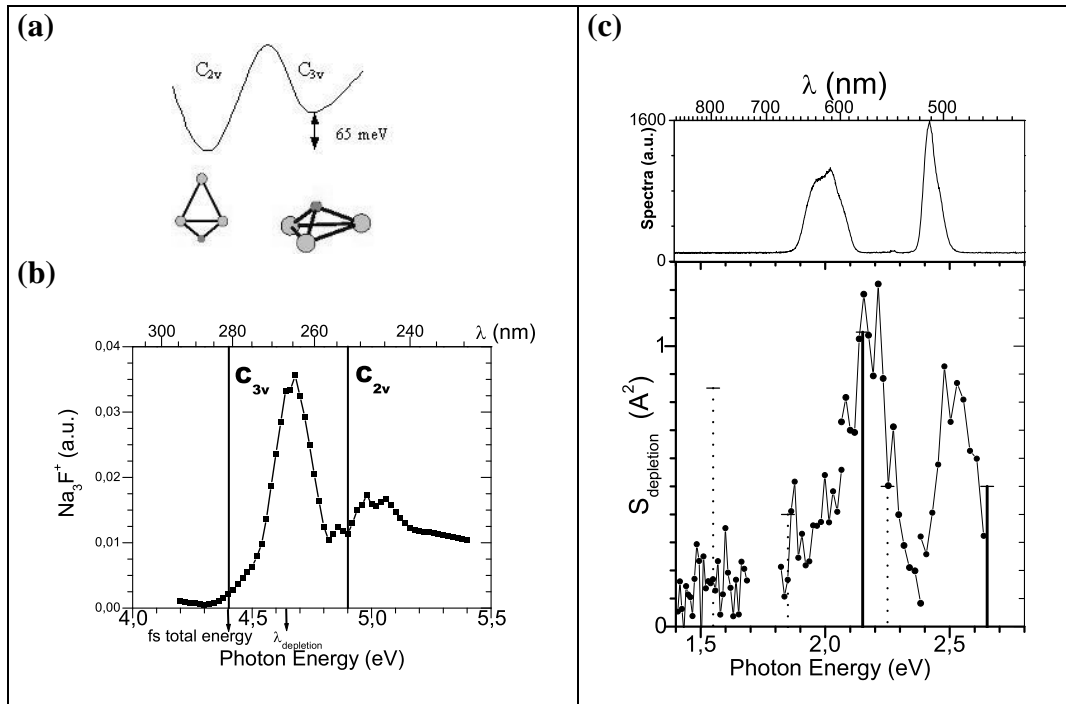


Figure 1 : (a) The two isomers of Na_3F . (b) Photoionization efficiency curve of Na_3F . *Ab initio* vertical ionization energies of the isomers are indicated by vertical lines. The UV probe photon energy used in the photodepletion experiment, as well as the femtosecond pump+probe total energy, is indicated by down arrows. (c) Photoabsorption spectrum of Na_3F determined by photodepletion spectroscopy. The calculated oscillator strengths for vertical excitations are indicated for both the C_{2v} and C_{3v} structures by straight and dotted lines respectively.[5] The spectra of the femtosecond pulses are also indicated.

3. TIME RESOLVED PHOTOIONIZATION

3.1. Excitation scheme

In order to study nuclear and relaxation dynamics in a pump-probe scheme by detecting ion signal, the total pump+probe energy should be just above the C_{3v} vertical ionization potential (4.4 eV), where the signal is likely to be most sensitive to a change of geometry. In order to simplify the dynamics, the vibrational energy in the excited state should be taken as low as possible, which lead us to a pump energy in the rising edge of the first band (~ 2.0 eV, the $1^1B_2+2^1A_1$ electronic state) or either the second band (~ 2.4 eV, the 1^1B_1 one) on the Fig. 1 (c). By selecting these two wavelength ranges, we reach as well the ionization threshold at 4.4 eV.

3.2. Experimental set-up

Each laser pulse is generated by a Non-collinear Optical Parametric Amplifier (NOPA).[12] The input of these devices is taken from the output of a 1kHz-1mJ chirped pulse amplification. One NOPA generates a 15nm-broadband pulse centered at 510 nm compressed with Brewster-cut fused silica prisms. The second NOPA generates a 40nm-broadband pulse centered at 620 nm compressed with chirped mirrors. On the top of the Fig. 1 (c), the

spectrum of the two pulses is shown. The cross-correlation signal, taking into account all the dispersive media on the beam paths, and recorded through a 20 μm -thick BBO crystal, has a full-width at half maximum of 180 ± 10 fs (Fig. 2). The linear chirps estimated are both in the range of $\phi''=800$ fs². Several studies have already pointed out the influence of a small linear chirp on the pump or either pulse relative to ultrafast dynamics.[13,14,15,16] Since we detect the ion signal and not a photoelectron spectrum,[17,18,19] the main consequence of a chirp on the pump pulse and probe pulse is to reduce the time-resolution. The poor pulse to pulse stability of the cluster beam is the main source of fluctuations. In order to get rid of spurious temporal variations, we normalize the pump-probe ion yield by the non-zero ion signal obtained with the 2.4 eV pulse alone, considered as proportional to the number of Na₃F clusters in the beam.

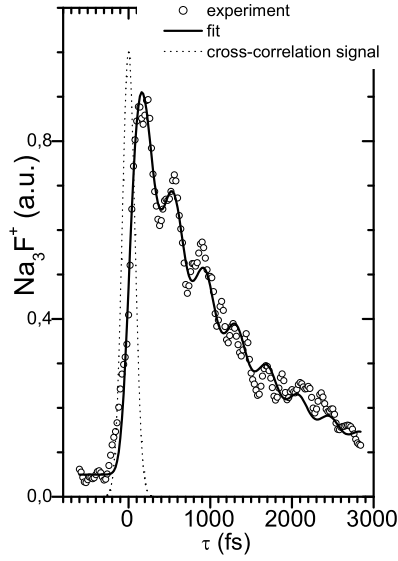


Figure 2: Fit (solid line) of the pump-probe signal (empty circle symbols) using Eqs. (1–3) with a cross-correlation signal of 180 fs FWHM (dot line).

3.3. Result and Discussion

Every Na_nF_p clusters absorb in the visible range.[11] However among all of them, only Na₃F shows a marked dependence on the time delay. Typical pump-probe signals are shown on Fig. 2. When 2.4 eV excites first Na₃F, the signal shows an oscillatory behavior together with an exponential decay. These oscillations are related to vibrational dynamics and the ability to observe them is fixed mainly by the strong geometry restriction on the ionization probability (only 4.4 eV as total energy). In order to extract the typical time constants of the wavepacket dynamics, the pump-probe signal is modeled by

$$S(\tau) = |g_{cc}(t) \otimes f(t)|^2 \quad (1)$$

where $g_{cc}(t)$ is linked to the cross-correlation signal with a FWHM $\tau_{cc} = 180$ fs by $g_{cc}(t) = e^{-2\ln 2 \times (t/\tau_{cc})^2}$. $f(t)$ models the population in the excited state that might be photoionized. In order to reproduce the main features observed on the Fig. 2, $f(t)$ is a decaying function with an oscillating part :

$$f(t) = e^{-t/2\tau_e} \times \left[(\cos(\Omega t) + \alpha \times \cos(\varphi - \Omega t)) + i(\sin(\Omega t) + \alpha \times \sin(\varphi - \Omega t)) \right] \quad (2)$$

where the pure decay part is homogeneous and characterized by τ_e , the period of the oscillations is 2Ω , α fixes the amplitude of the oscillations, and ϕ allows to introduce a shift T_s on the first maximum relative to the origin. The best fit parameters are $\tau_e = 1280 \pm 50$ fs, $\pi/\Omega = 390 \pm 10$ fs, $\phi = 3.47 \pm 0.50$ rad, $\alpha = 4.6 \times 10^{-2} \pm 2 \times 10^{-4}$. This results in a time-shift $T_s = 180 \pm 30$ fs, duration necessary to reach the geometry of highest ionization probability. The fit is shown on the Fig. 2.

The oscillations observed may be interpreted as a variation of the ionization potential induced by nuclear motion, or in other words a vibrational excitation in the excited state populated by the pump laser pulse. The overall time-dependant pump-probe signal vanishes with a decay time of about 1 ps that results from a drop of the Na_3F population open to ionization. Two alternative explanations may be given : either, the population of Na_3F^* decreases due to fragmentation or Na_3F^* evolves toward configurations in which it is no longer ionized. Ideally, the fragmentation hypothesis could be monitored through an increase of the Na_2F signal in the mass spectrum. Unfortunately, the background signal of Na_2F is huge which makes such a tiny variation undistinguishable. Wavepacket dynamics calculations are also performed to get a better insight.[20] Another surprising result from this time-resolved experiment is the absence of a clear time-dependency for negative delay. Indeed as mentioned above (see the figure 1 (c)), the 620 nm pulse might also excite the first band, later photoionized by the 510 nm pulse. As a matter of fact, the experimental curve has a small “bump” in this region that may be due to a “probe-pump” scheme with a very small decay time. A main explanation to the absence of visible signature at negative delay, may be easily explained by the strong requirement imposed on the ionization. Indeed a threshold ionization limits the number of geometries that might be probed.

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