IRSAMC

UNIVERSITE PAUL SABATIER — TOULOUSE III

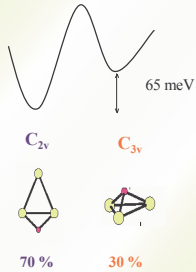CNRS — CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

Vibrational Relaxation of photoexcited Na$_3$F

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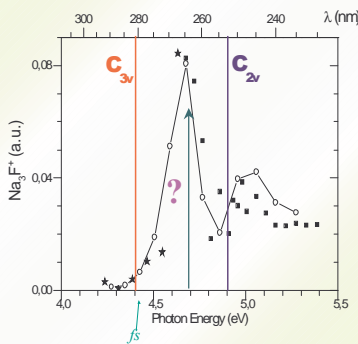## Na$_3$F ground electronic state : Two low-lying isomers

65 meV

C$_{2v}$ C$_{3v}$

70 %   30 %

• Na$_3$F : a two-excess electrons cluster
• strong correlation between the structure and the ionisation potential
• ionisation probability time-dependent for a probe pulse energy low enough to photoionise only one geometry
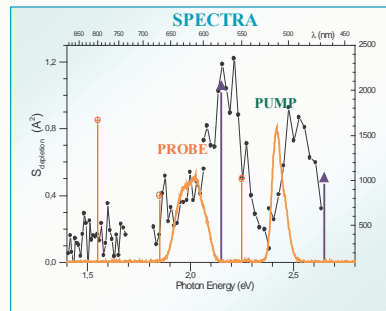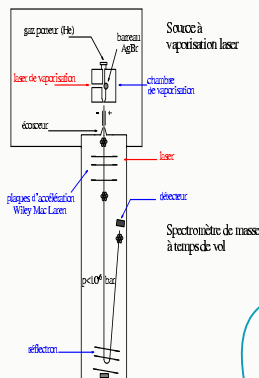
EXPERIMENT :
• Cluster detection : Wiley Mac-Laren TOFMS with reflectron (m/Δm= 4000)
• Average over 100 pulses.
• Femtosecond laser : 2 Non-collinear Optical Parametric Amplifiers - 1 kHz
PUMP : 510 nm (2.4 eV), Δλ = 15 nm , compressed with Brewster-cut fused silica prisms - 2.5 GW/cm^2
PROBE : 620 nm (2.0 eV)), Δλ = 40 nm , compressed with chirped mirrors - 20 GW/cm^2
• Cross-correlation signal through a 20 μm-thick BBO crystal.
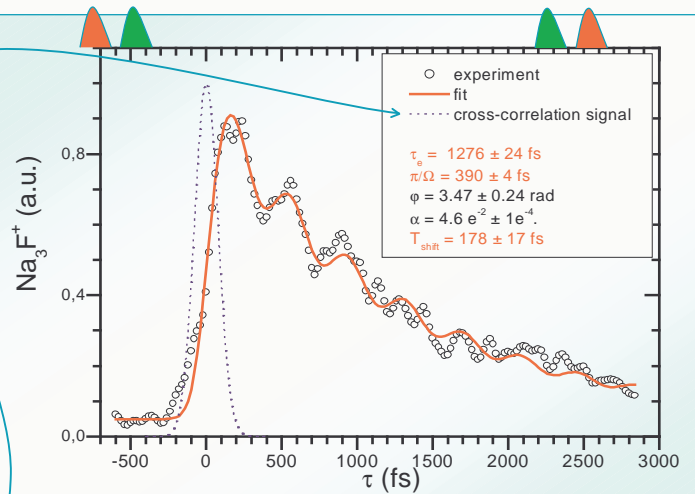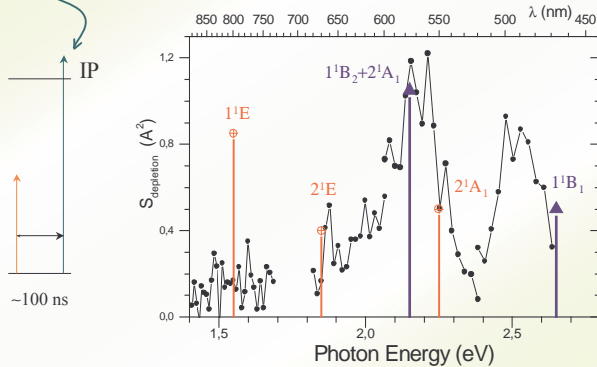• Estimated chirps φ''=800 fs^2. FWHM = 130 fs
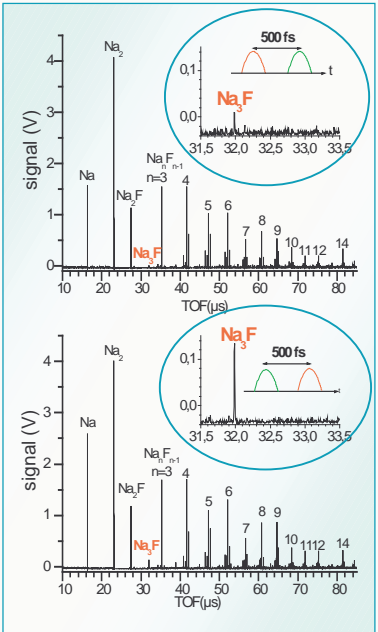
Photoionization Efficiency Curve

C$_{3v}$ C$_{2v}$
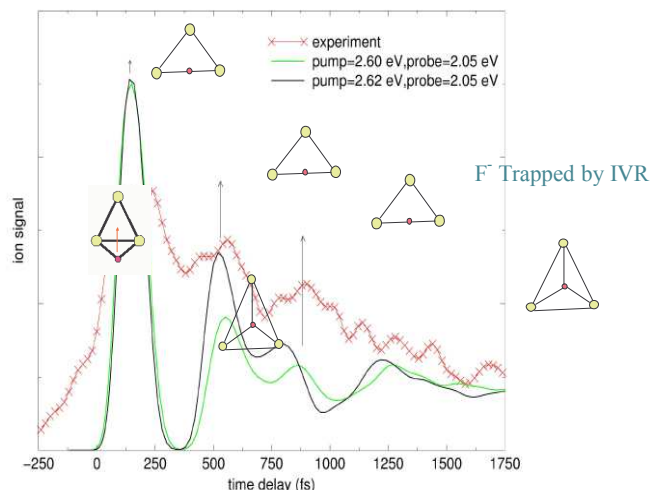
montage expérimental

SPECTRA

PROBE   PUMP

Spectroscopy of Na$_3$F : Photodepletion experiment

IP

~100 ns

1^{1}E
2^{1}E
1^{1}B$_2$+2^{1}A$_1$
2^{1}A$_1$
1^{1}B$_1$

τ_e = 1276 ± 24 fs
π/Ω = 390 ± 4 fs
φ = 3.47 ± 0.24 rad
α = 4.6 e^{-2} ± 1e^{-4}.
T$_{shift}$ = 178 ± 17 fs

○ experiment
— fit
····· cross-correlation signal

	C$_{2v}$			C$_{3v}$	
State	Abinit. eV	Exp. eV	State	Abinit. eV	Exp. eV
1^{1}B$_2$+ 2^{1}A$_1$	2.15	2.18	1^{1}E	1.55	-
1^{1}B$_1$	2.65	2.5	2^{1}E	1.85	-
			2^{1}A$_1$	2.25	-
1^{1}A$_1$ - ion	4.93 vertical	~4.8	1^{1}A$_1$ - ion	4.44 vertical	~4.4

Table : Excited states expected from abinitio calculations* and the ones observed through the photodepletion experiment. * V. Bonacic-Koutecky and J. Pittner, Chem. Phys., **225**, 173, (1997).

$$S(\tau) = \left| g_{cc}(t) \otimes f(t) \right|^2 \qquad g_{cc}(t) = e^{-2\ln 2 \times (t/\tau_{cc})^2}$$

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

WAVEPACKET SIMULATION (poster of M.C. Heitz et al.) :
Quantum Studies of the Excited States Dynamics of Small Alkali Halide Clusters

× experiment
— pump=2.60 eV,probe=2.05 eV
— pump=2.62 eV,probe=2.05 eV

F$^-$ Trapped by IVR