

**AUTOIONIZATION AND FRAGMENTATION OF Na<sub>2</sub>  
STUDIED BY FEMTOSECOND LASER PULSES**

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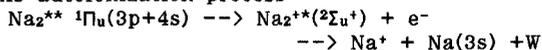
We report on first results obtained with femtosecond laser pulses applied to molecular beam studies of the dynamics and the pathways of ionization, autoionization and fragmentation of highly excited molecular states of Na<sub>2</sub>. Electronic autoionization of doubly excited molecular states and fragmentation of highly excited neutral and ionic states of Na<sub>2</sub> are hardly investigated and generally not well understood. This is mainly because (1) the final continuum states are usually not analyzed and (2) the dissociative ionization is not distinguished from neutral fragmentation with subsequent photoionization of excited fragments. To study the dynamics of multiphoton processes leading to excitation, autoionization and fragmentation we have applied ultrashort laser pulses to induce the transitions and Time-Of-Flight spectroscopy to determine the mass and initial kinetic energies of the fragments and the energy and angular distributions of ejected electrons. The experiments were carried out with "cold" molecular beams to ensure that only the lowest vibrational level  $v''=0$  in the molecule is predominantly populated.

Femtosecond pulses are generated in a home-built colliding-pulse-mode-locked ring dye laser (CPM) with 4 intracavity prisms to adjust for the group velocity dispersion. The emission peak has been shifted to 616.0 nm by adjusting the DODCI absorber concentration. The output of the CPM laser was amplified at a rate of 100 Hz in a Na<sub>2</sub>-laser pumped dye amplifier to produce pulses of 10 nJ energy and  $t=150$  fs time duration. The pulse length was measured using the autocorrelation by second harmonic generation (SHG) in a nonlinear crystal.

The TOF-spectrum in fig.1 clearly shows the observation of Na<sub>3</sub><sup>+</sup>, Na<sub>2</sub><sup>+</sup> and "slow" Na<sup>+</sup> as well as "fast" Na<sup>+</sup> fragment ions from sub-ps laser excitation with  $\lambda = 616.0$  nm. "Fast" and "slow" Na<sup>+</sup> ions originate from fragmentation processes occurring at small internuclear distances of Na<sub>2</sub>. Predissociation of Na<sub>2</sub><sup>\*</sup> and photoionization of Na<sup>\*</sup> as the origin of observed Na<sup>+</sup> ions can be ruled out considering the time duration of the 150 fs laser pulse. Based on this result, which is rather difficult to obtain from other experiments, and with the known molecular potential curves we completely determined for this model case the multiphoton excitation and -fragmentation pathways. With a pulsed tunable dye laser we observe in the wavelength dependent ionization spectra a very prominent peak at 616.08 nm in both the Na<sub>2</sub><sup>+</sup> and in the Na<sup>+</sup> channel. This is due to a resonance enhanced three-photon ionization of Na<sub>2</sub> which is shown in the potential energy diagram in fig.2. Dimer ions a preferentially formed in the  $v''=24,25$  and  $v''=14,15$  states of the electronic ground state X (<sup>2</sup> $\Sigma_g^+$ ) leading to electrons with kinetic energies of  $E=810\pm 10$  meV and  $E=940\pm 10$  meV which are actually observed in the electron spectrum. By absorption of one more photon from the fs-laser pulse the Na<sub>2</sub><sup>+</sup>-ion undergoes the bound-free transition  $\text{Na}_2^+(X, v'') + h\nu \rightarrow \text{Na}_2^{*+}({}^2\Sigma_u^+) \rightarrow \text{Na}^+ + \text{Na}(3s) + W$ . Taking into account the populated  $v''$ -levels and the known potential curves for the ionic ground and first excited states the corresponding bound-free transitions lead to recoil energies  $W$  between 10000 cm<sup>-1</sup> and 11000 cm<sup>-1</sup>. The energy  $W=10500 \pm 500$  cm<sup>-1</sup> obtained from the analysis of the TOF-spectrum perfectly agrees with that.

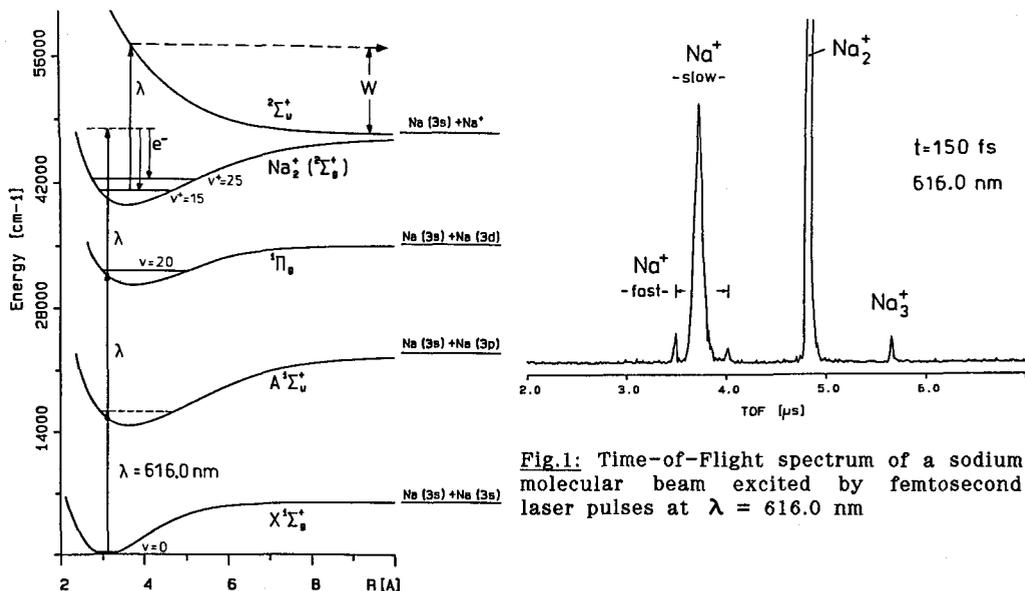
The observation of "slow" Na<sup>+</sup> ions however cannot be explained within this framework since photoionization of  $v''=20$  of the <sup>4</sup> $\Pi_g$  Rydberg state directly into the <sup>2</sup> $\Sigma_u^+$ -continuum is energetically forbidden for the applied laser wavelength. Based on the measured electron energy distribution and the recoil energy  $W=900\pm 500$  cm<sup>-1</sup>, obtained from the analysis of the "slow" Na<sup>+</sup> fragment ions, a consistent explanation is found by considering the excitation of doubly excited molecular states of Na<sub>2</sub>. The doubly

excited states  $\text{Na}_2^{**} (n'l, n'l')$  form a Rydberg series converging versus the  ${}^2\Pi_u$  state of  $\text{Na}_2^+$ , whose potential curve is known theoretically. Assuming that the shape of a  ${}^1\Pi_u$  state potential curve, correlated to  $\text{Na}(3p)+\text{Na}(4s)$ , is similar to the ionic  ${}^2\Pi_u$  curve and that it has a potential barrier at large internuclear distances like the  $B^1\Pi_u$  state from  $\text{Na}(3s)+\text{Na}(3p)$ , we believe that in the resonance enhanced three-photon process vibronic levels close to the dissociation limit of the doubly excited  ${}^1\Pi_u(3p+4s)$  state are excited. The wavefunctions of these vibronic levels extend from 3 Å to approximately 10 Å. These doubly excited levels may autoionize into the  $X^1\Sigma_g^+$  ground state of  $\text{Na}_2^+$  giving rise to electron energies between 260 meV and 500 meV which are actually observed. For internuclear distances greater than 6 Å the vibronic levels cross into the continuum of the repulsive  ${}^2\Sigma_u^+$  state of  $\text{Na}_2^+$ . Therefore for  $R \geq 6$  Å there is a second open autoionization channel which is responsible for the observed electrons having energies in the range from 0 meV to 160 meV. This autoionization process



of course simultaneously produces "slow"  $\text{Na}^+$ -ions whose kinetic energies depend on the internuclear distance  $R$  where the autoionization takes place.

In conclusion, this is the first reported experiment where a fs-laser has been used in combination with ion- and electron spectroscopy to clarify the ionization and fragmentation pathways of a multiphoton process investigated in a molecular beam experiment.



**Fig.1:** Time-of-Flight spectrum of a sodium molecular beam excited by femtosecond laser pulses at  $\lambda = 616.0$  nm

**Fig.2:** Potential energy diagram explaining the origin of "fast"  $\text{Na}^+$  ions