# AUTOIONIZATION AND FRAGMENTATION OF Na_2 STUDIED BY FEMTOSECOND LASER PULSES

T. Baumert, B. Bühler, R. Thalweiser and G. Gerber

Fakultät für Physik, Universität Freiburg, 7800 Freiburg, FRG

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_2. Electronic autoionization of doubly excited molecular states and fragmentation of highly excited neutral and ionic states of Na_2 are hardly investigated and generally not well understood. This is mainly because i) the final continuum states are usually not analyzed and ii) the dissociative ionization is not distinguished from neutral fragmentation with subsequent photoionization of excited fragments. Doubly excited states play a major role in the reaction dynamics of diatomic molecules, since these states directly couple the different continua of dissociation and ionization. Electronic autoionization and neutral dissociation are therefore competing processes, but information from both channels may be used to characterize the doubly excited molecular states.

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. Because of the strong cooling in supersonic expansions we predominantly produce Na_2 in the lowest vibrational state v"=0 and in very low J- states. The final continuum states can definitely be assigned from the measured electron- and ion-kinetic energy distributions.
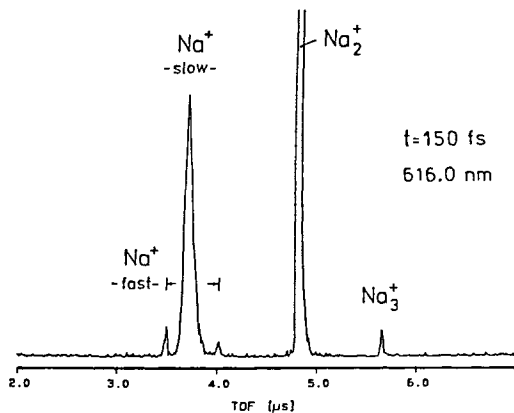
Fig.1: Time-Of-Flight spectrum of ions formed by the interaction of femtosecond laser pulses with a sodium molecular beam.

Application of femtosecond laser pulses considerably facilitates the interpretation of fragmentation processes, since the time duration of a laser pulse is much shorter than the fragmentation separation time. The terminal velocities of the separating fragments are typically 0.002 nm/fs for W=3000 cm^{-1} recoil energy. Therefore no further laser-induced excitation or ionization of the fragments can occur and all observed signals have to be related to processes which occur at small internuclear distances.

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 dye laser was amplified at a rate of 100 Hz in a N_2-laser pumped dye amplifier to produce pulses of 10 nJ energy and t=150 fs time duration. The pulse length was measured using the auto-correlation by second harmonic generation (SHG) in a nonlinear crystal.

The laser-molecular beam interaction region is placed between parallel plates and since the ions are extracted perpendicular to the beam with a low electric field, parent ions can be distinguished from fragment ions having initial kinetic energy. The released kinetic energy leads to a broadening or a double peak structure in the TOF spectrum due to fragments recoiling parallel and antiparallel to the extracting field. Therefore, from the observed difference in flight time the kinetic energy of the fragements can be inferred. The TOF-spectrum in fig.1 clearly shows the observation of Na_3^+, Na_2^+ and "slow" Na^+ as well as "fast" Na^+ fragment ions resulting from the fs-laser excitation at λ= 616.0 nm. "Fast" and "slow" Na^+ ions originate from fragmentation processes occuring at small internuclear distances of Na_2^*. Predissociation of Na_2^* and photoionization of Na^* as the origin of observed Na^+ ions can be ruled out considering the time duration of the 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.
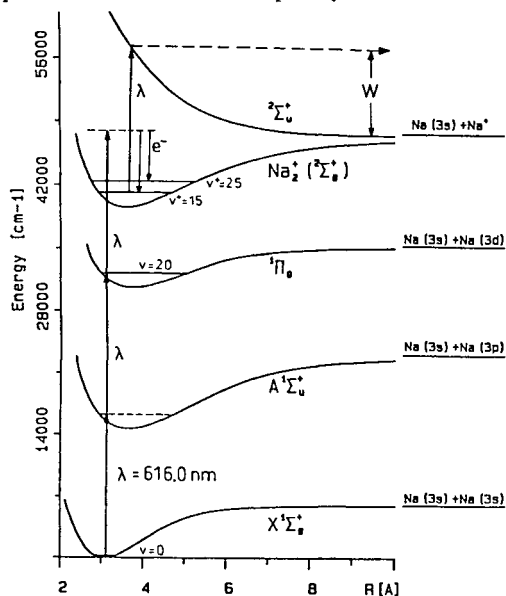
With a pulsed tunable dye laser we observed in the wavelength dependent ionization spectra between 610 nm and 620 nm a very prominent peak at 616.08 nm in both the Na_2^+ and the Na^+ channel. Based on the known spectroscopy of molecular Rydberg states of Na_2 it is evident that this peak in the Na_2^+ spectrum is due to a resonance enhanced three-photon ionization of Na_2 This process is shown in the potential energy diagram in fig.2. The ionization enhancing intermediate level $^1\Pi_g$ is populated by the two-photon process Na_2 (X $^1\Sigma_g^+$,v"=0) + 2hν --> Na_2 (Ryd $^1\Pi_g$,v*=20). The Rydberg-molecule is then photoionized by absorption of a third photon. The dimer ions are preferentially formed in the v*= 24,25 and v*= 14,15 vibrational states of the electronic ground state $X(^2\Sigma_g^+)$ due to favorable Franck-Condon factors. This direct ionization of the $^1\Pi_g$ Rydberg state leads to electrons having kinetic energies of E=810 +/- 10 meV and E=940 +/- 10 meV which are actually observed in the TOF-electron spectrum shown in fig.3. In addition to these strong peaks the electron spectrum shows less intense broad structures in the range

Fig.2: Potential energy diagram illustrating the origin of "fast" Na^+ ions.

between 300 meV and 500 meV and well below 200 meV extending to very low energies. The created dimer ions may now undergo a bound-free transition by absorption of one more photon from still the same fs-laser pulse:

$$Na_2^+ (X \; ^2\Sigma_g^+, v^+) + h\nu \longrightarrow Na_2^{+*} (^2\Sigma_u^+) \longrightarrow Na^+ + Na(3s) + W$$
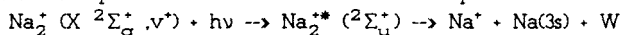
Taking into account the populated v^+-levels and the known potential curves for the ionic ground and first excited states the corresponding bound-free transitions lead to recoil energies W between 10000 cm^{-1} and 11000 cm^{-1}. The energy W=10500 +/- 500 cm^{-1} obtained from the analysis of the TOF-ion spectrum perfectly agrees with that. We therefore conclude that "fast" Na$^+$ ions are produced by the ionization and fragmentation process shown in fig.1.
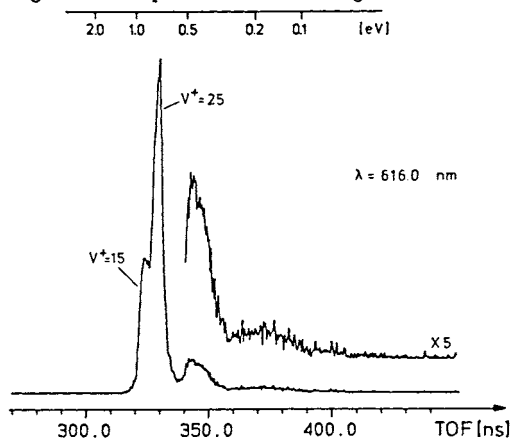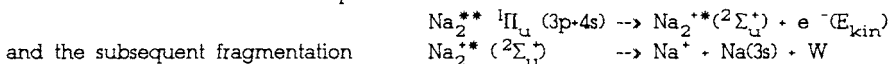

Fig.3: TOF-electron spectrum

The observation of "slow" Na$^+$ ions however cannot be explained within this framework since photoionization of the vibrational level v^*=20 of the $^1\Pi_g$ (3s + 3d) Rydberg state directly into the $^2\Sigma_u^+$ - continuum is energetically forbidden for the applied laser wavelength. Based on the measured electron energy distribution and the recoil energy W=900 +/- 500 cm^{-1}, obtained from the analysis of the "slow" Na$^+$ fragment ions, a consistent explanation is found by considering the excitation of doubly excited molecular states of Na$_2$ as it is shown in fig.4. The doubly excited states Na$_2^{**}$ (nl,n'l') form a Rydberg series converging versus the $^2\Pi_u$ state of Na$_2^+$, whose potential curve is known theoretically. Assuming that the shape of a $^1\Pi_u$ state potential curve, correlated to Na(3p)+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 Na(3s)+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 3Å to approximately 10Å. These doubly excited levels may autoionize into the $X(^2\Sigma_g^+)$ ground state of Na$_2^+$ giving rise to electron energies between 260 meV and 500 meV which are actually observed. For internuclear distances greater than 6Å the vibronic levels cross into the continuum of the repulsive $^2\Sigma_u^+$ state of Na$_2^+$. Therefore for R ≥ 6Å 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

and the subsequent fragmentation

$$Na_2^{**} \; ^1\Pi_u \; (3p+4s) \longrightarrow Na_2^{+*}(^2\Sigma_u^+) + e^- (E_{kin})$$
$$Na_2^{+*} (^2\Sigma_u^+) \longrightarrow Na^+ + Na(3s) + W$$

produce "slow" Na$^+$-ions whose kinetic energies depend on the internuclear distance R where the autoionization takes place.

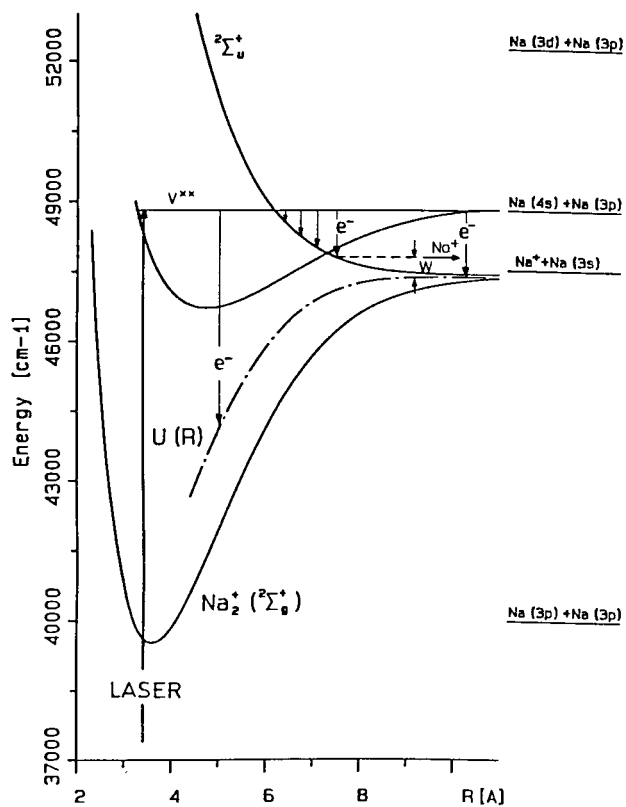**Fig.4:** Excitation and autoionization processes of doubly excited Na_2^{**}.

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