Molecular Photochemistry with Femtosecond Laser Pulses

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Abstract. Femtosecond laser pulses generated from an amplified colliding pulse modelocked ring dye laser have been employed in molecular beam experiments to study the dynamics and the pathways of multiphoton induced ionization, autoionization and fragmentation of Na_2. Energy distributions of photoelectrons arising from these processes and the mass and released kinetic energy of the corresponding fragment ions are measured by time-of-flight spectroscopy.

Alkali dimers and small clusters have recently been the subject of a number of ionization and fragmentation studies (1). In particular the sodium molecules Na_2 and Na_3 have received increasing attention. Because of their low ionization potentials two or three visible photons are sufficient for photoionization. With the intense lasers applied in most of the studies multiphoton processes are unavoidable. While purely nonresonant processes play only a minor role for the alkali systems, the dominant contribution to the ionization process is due to resonantly enhanced multiphoton ionization (REMPI). However, despite the numerous studies carried out with sodium, the ionization and fragmentation processes are in many cases not yet well known. This is mainly because i) the final continuum states are usually not analyzed and ii) dissociative ionization and neutral fragmentation with subsequent photoionization of excited fragments cannot be distinguished when using nanosecond or even picosecond laser pulses, since both processes lead to the same fragment ions.

Only recently have experiments been reported on sodium dimers with clearly identified fragmentation and ionization pathways: fragmentation of neutral Na_2 into two excited $Na^*(3p)$ atoms — the complementary process to laser-induced associative ionization — applying Doppler spectroscopy (2) and multiphoton ionization and dissociation of Na_2 via the double minimum state (2) $^1\Sigma_u^+$ and via Rydberg states using time-of-flight spectroscopy (3).

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We report on first results obtained with femtosecond laser pulses applied to molecular beam studies of the dynamics and the mechanisms of ionization, autoionization and fragmentation of highly excited molecular states of Na_2. In particular we have focussed our efforts on the understanding of the excitation and different decay processes of highly excited neutral states of Na_2 which are embedded in the molecular ion continua. Electronic autoionization of bound doubly excited molecular states Na_2^{**} (nl,n'l') and fragmentation of highly excited neutral and ionic states of Na_2 have hardly been investigated and are generally not well understood. The only two other studies of doubly excited molecular states we are aware of are concerned with the role of the repulsive $Q_1\ ^1\Sigma_g^+(2p\sigma_u)^2$ state in multiphoton ionization processes of H_2 (4) and with the determination of spectroscopic constants for the $^1\Sigma_g^-$ (4p+3d) state of K_2 (5). 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 (TOF) 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 a supersonic molecular beam. Because of the strong cooling in supersonic expansions we predominantly produce Na_2 in the lowest vibrational state $v''=0$ and in a very few low J states. The final continuum states can definitely be assigned from the measured electron and ion kinetic energy distributions. 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 fragment separation time. The terminal velocities of the separating fragments are typically 0.002 nm/fs for W=3000 cm^{-1} released kinetic 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 modelocked ring dye laser (CPM) with 4 intracavity prisms to adjust for the group velocity dispersion. The emission peak has been shifted to 616 nm by adjusting the DODCI absorber concentration. The output

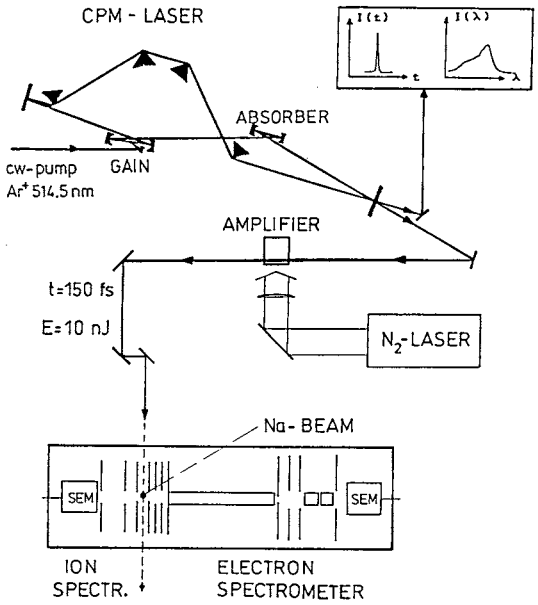

Fig.1. Femtosecond laser – molecular beam arrangement.

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 autocorrelation by second harmonic generation (SHG) in a nonlinear crystal. The laser pulse energy was intentionally kept at this low level in order to be able to investigate the basic physical processes.

The laser system and the schematic experimental arrangement of the ion and electron time-of-flight spectrometers are shown in fig. 1. The electron TOF-spectrometer had been calibrated by a series of REMPI measurements of atomic Na where electrons of definite kinetic energy are produced when using the two-photon-excited even states 3d, 4s, ... as ionization enhancing intermediate levels. 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 fragments can be inferred. This experimental technique is well known and has been used by several groups (6). The TOF spectrum in fig.2 clearly shows the observation of Na_3^+ , Na_2^+ and "slow" Na^+ as well as "fast" Na^+ fragment

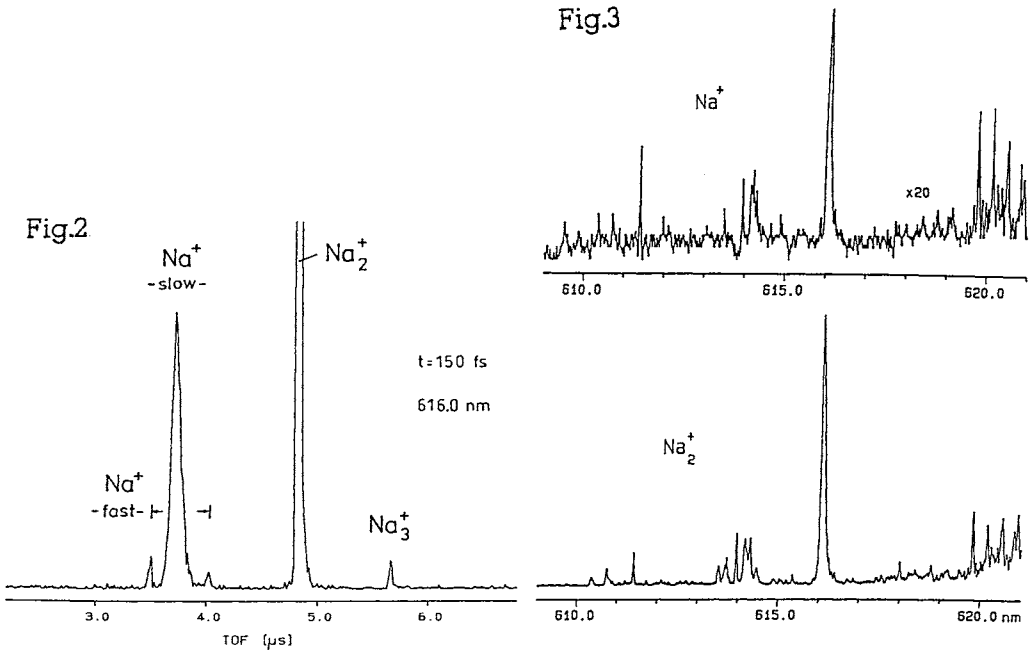

Fig.2. Time-of-flight spectrum of ions formed by the interaction of femtosecond laser pulses with a sodium molecular beam.

Fig.3. One color REMPI spectra of Na and Na_2

ions resulting from the fs-laser excitation at λ= 616 nm. "Fast" and "slow" Na^+ ions originate from fragmentation processes occurring 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 (τ=2.5 ns) we observed in the ionization spectra between 610 nm and 620 nm an isolated and very strong peak at 616.08 nm in both the Na_2^+ and the Na^+ channel. The wavelength dependent ionization spectra of atomic and molecular (Na_2) sodium are shown in fig.3. Based on the known spectroscopy of molecular Rydberg states of Na_2 (7) it is evident that this peak in the Na_2^+ spectrum is due to a resonance enhanced three-photon ionization of Na_2. This particular process is indicated in the Na_2 potential energy curve diagram given in fig. 4. The ionization enhancing intermediate electronic state

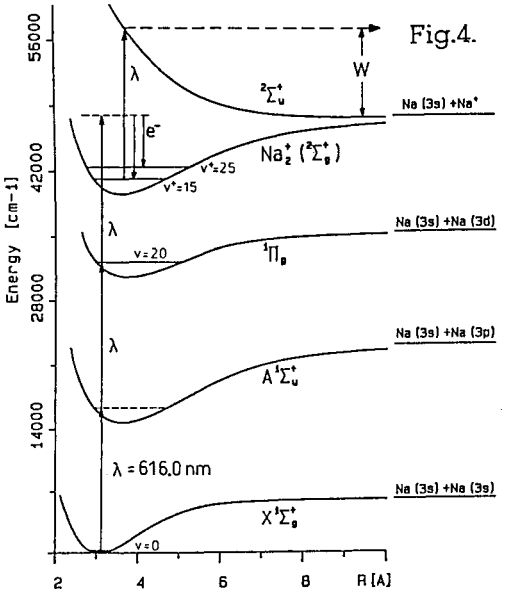

Fig.4. Potential energy diagram of Na_2 illustrating the process leading to "fast" Na^+ ions.

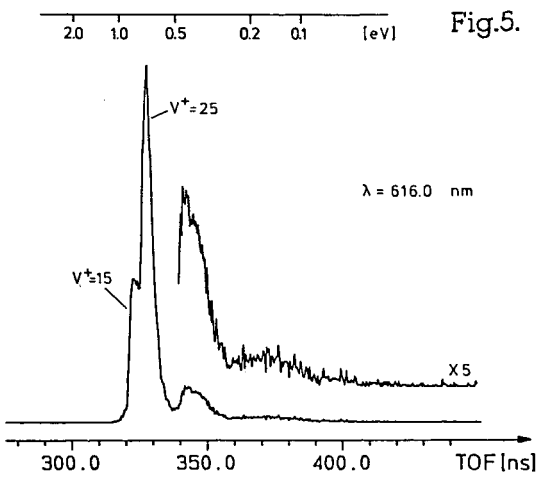

Fig.5. Time-of-flight electron spectrum.

$^1\Pi_g$ is populated by the two-photon process Na_2 ($X\ ^1\Sigma_g^+$,v"=0) + 2hν --> Na_2 (Ryd $^1\Pi_g$,v*=20). Because of the Na_2 molecules predominantly produced in the v"=0 level, the two-photon Franck-Condon factors and the upper $^1\Pi_g$ Rydberg state vibrational spacing ΔG, which is of the order of 100 cm^{-1}, approximately 90% of the excited Na_2 molecules are in the v*=20 level, despite the broad spectral distribution (≈150 cm^{-1}) of the femtosecond laser pulse. 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.5. In addition to these strong peaks the electron spectrum shows less intense broad structures in the range between 300 meV and 500 meV and around 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:

$$Na_2^+ (X\ ^2\Sigma_g^+, v^+) + h\nu \rightarrow Na_2^{+*} (^2\Sigma_u^+) \rightarrow Na^+ + Na(3s) + W$$

Taking into account the populated v^+-levels and the known potential curves for the ionic ground and first excited states (8) the corresponding bound-free transitions lead to recoil energies W between 9910 cm^{-1} and 11037 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.4.

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 is shown in fig.6. 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 (8). 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 built from Na(3s)+Na(3p), we conclude 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

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

and the subsequent fragmentation

$$Na_2^{+*} (^2\Sigma_u^+) \rightarrow Na^+ + Na(3s) + W$$

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

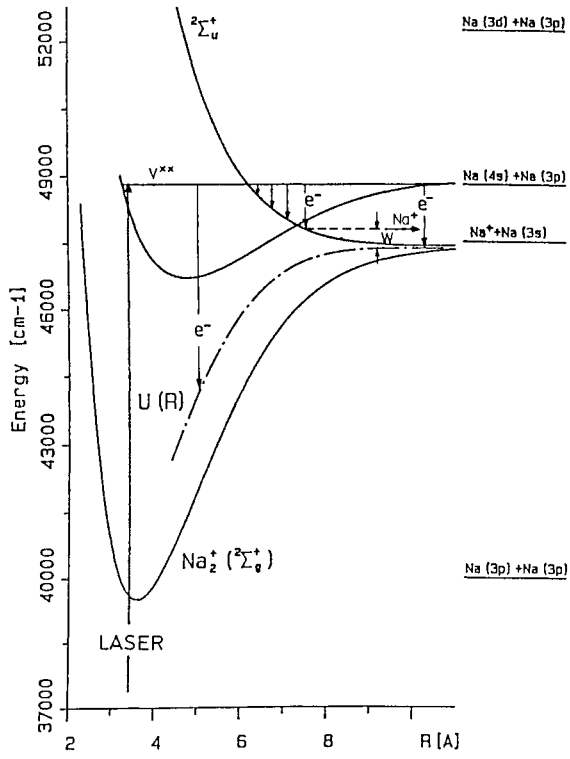

Fig.6. Excitation and autoionization processes of doubly excited Na_2^{**}

of the electron spectrum arising from bound-free transitions $^1\Pi_u(4s+3p) \longrightarrow {}^2\Sigma_u^+$, assuming a constant transition moment for the R-range under consideration, shows good agreement with the actually observed electron energy distribution.

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, autoionization and fragmentation mechanisms of molecules which are excited by multiphoton processes into an energy range of singly and doubly excited electronic states.

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