

Photofragmentation of Na_2^+ in Intense Femtosecond Laser Fields: From Photodissociation on Light-Induced Potentials to Field Ionization

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Photofragmentation of Na_2^+ molecules in well prepared vibrational levels has been studied employing intense (10^{11} – 10^{14} W/cm²) and ultrashort (80 fs) 790 nm laser fields. Four fragmentation channels with different released kinetic energies are observed. Depending on the applied laser intensity, the fragmentation of Na_2^+ is governed by photodissociation on light-induced potentials and field ionization followed by Coulomb explosion. Below 1×10^{12} W/cm², only photodissociation on light-induced potentials is seen. For intermediate laser intensities, field ionization at large internuclear distances competes with photodissociation, thus preventing the observation of above threshold dissociation. Field ionization at small internuclear distances dominates for the highest laser intensities used.

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Beyond the perturbative regime, the study of atoms and molecules in intense laser fields has long been a challenging task. The reward, however, has been the observation and study of a whole new set of physical phenomena. Even in small molecules, intense laser radiation may lead to complex photodissociation processes due to the strong coupling of the molecular electronic potentials with the intense electric field of the laser. Bond softening, vibrational population trapping in light-induced potentials, and above threshold dissociation (ATD) are signatures of this coupling [1–4]. All these processes can be understood within the picture of field-dressed state potentials.

Most of the recent work studying photodissociation in intense laser fields—both theoretically [4–6] and experimentally [3,7–9]—has concentrated on H_2^+ as the simplest model system. In addition to there being only two protons and one electron, the electronic eigenstates in H_2^+ are energetically well separated so that only the lowest lying states $^1\Sigma_g^+$ and $^1\Sigma_u^+$ can be coupled by an intense field thereby contributing to the dissociation.

In spite of these appealing features, the preparation of H_2^+ in a well defined initial state for experiments is difficult. Many experiments have been carried out by preparing the H_2^+ molecular ion starting from the electronic ground state of the neutral H_2 by the same laser pulse that is used to study the intense field effects. In general, it is difficult to distinguish the effects attributed to the ionization of the neutral molecule from the dissociation dynamics of the ionic molecule [5,10]. Several experiments tried to circumvent these difficulties by using very short (40 fs) laser pulses [11] or by studying an alternative system such as Ar_2^+ that can be produced directly out of a dc discharge [12]. Only recently this technique was extended to the generation of H_2^+ [13].

In this Letter we report on studies of the photodissociation dynamics of Na_2^+ in an intense laser field. The use of Na_2^+ as a model system has several fundamental advantages. First, well defined vibrational states in the

electronic ground state of Na_2^+ can be prepared via resonantly enhanced multiphoton ionization (REMPI) of Na_2 . Second, laser pulses much shorter than half of the vibrational period of Na_2^+ (150 fs) are readily available. Laser pulses much shorter in duration than half the vibrational period also ensure that the molecule cannot dissociate in the rising edge of the laser pulse—a phenomenon which has to be taken into account in the interpretation of experimental results [14]. A further incentive for using Na_2^+ to study photodissociation processes is that more than only the lowest electronic states have to be taken into account. The resulting coupling scheme, in connection with the relatively long vibrational period, opens up the possibility of studying and controlling the branching between different intense field dissociation channels [15]. Finally, within the intensity regime of our experiment, we should not only observe photodissociation on light-induced potentials but also field ionization followed by Coulomb explosion as predicted by theory [15–19].

The experimental setup is schematically shown in Fig. 1. A molecular beam of vibrationally cold Na_2 molecules in the $X^1\Sigma_g^+$ -electronic ground state was prepared by expanding pure sodium from an oven operated at 1000 K. In order to avoid space charge effects, an excitation scheme is employed which uses two separate interaction regions situated between the extraction plates of a linear time-of-flight (TOF) spectrometer. In the first interaction region, the Na_2 molecules were ionized by resonant two photon absorption using nanosecond dye laser pulses. Making use of the measured low vibrational temperature of the molecular beam and the known Franck-Condon factors for this REMPI process, specific vibrational levels of the electronic ground state of Na_2^+ are predominantly populated by tuning the wavelength of the dye laser into intermediate resonances. We chose a wavelength of 492.4 nm, resonant with the $B^1\Pi_u$ state of Na_2 to populate vibrational levels from $v^+ = 0$ to $v^+ = 5$ in the $X^2\Sigma_g^+$ -ionic ground state of Na_2^+ via a

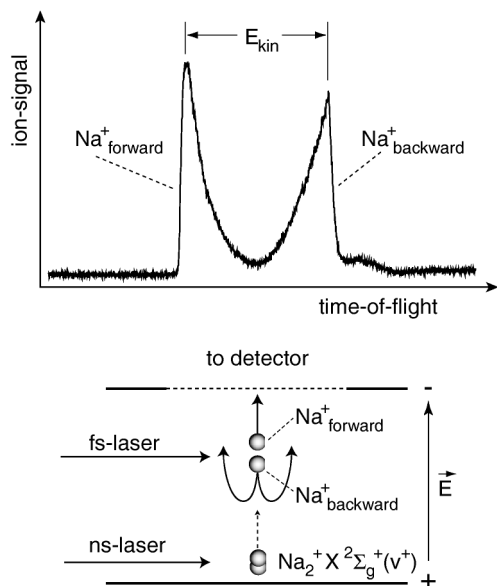


FIG. 1. The experimental setup is shown schematically with the two (ns- and fs-laser) interaction regions and with how the released kinetic energies of the fragments are measured. In the case of one interaction region and linearly polarized laser light (parallel to the TOF axis) fragments from a Σ - Σ transition of Na_2^+ are ejected towards and opposite to the detector. From the difference in arrival time the velocity and therefore the released kinetic energy of the fragments are determined. Note that if two interaction regions are used the molecules have an initial velocity towards the TOF axis and the distribution gets more asymmetric. The observed distribution in Fig. 2 is a sum of four different kinetic energies.

two photon process. With this excitation 80% of the total population is in the $v^+ = 0$ and $v^+ = 1$ levels [20]. After the preparation of the vibrational levels in the first interaction region, the Na_2^+ molecules were extracted from the molecular beam by a small static electric field and accelerated towards a second region spatially well separated from the molecular beam, as shown in Fig. 1. There the interaction with intense femtosecond laser pulses took place. The femtosecond laser pulses (80 fs, 800 μJ pulses at 790 nm) were focused by a 300 mm achromatic lens to reach peak intensities of up to $1 \times 10^{14} \text{ W/cm}^2$. Using a calibrated set of reflective attenuators we changed the applied laser intensity over 4 orders of magnitude. The polarization of the femtosecond laser was chosen parallel to the TOF axis. The Na^+ fragments were detected with the linear TOF spectrometer. The TOF spectrometer was calibrated using the known kinetic energy (1.53 eV) of Na^+ fragments produced by absorption of a third photon from the ns laser leading to photodissociation along the repulsive $^2\Sigma_u^+$ state of Na_2^+ .

With the second interaction region also placed between the parallel extraction plates of the time-of-flight spectrometer (see Fig. 1), fragment ions can be distinguished from parent ions having different kinetic energies and the released kinetic energies can be determined. This experimental technique is widely known [21,22].

The TOF spectra of Na^+ fragments formed in the second interaction region are shown in Fig. 2. From the shape of the spectra (minimum at 3.18 μs) one can infer that the fragmentation of the molecules takes place along the TOF axis. Such a fragment distribution along the laser polarization is attributed to the Σ - Σ transition coupling of the potential curves (Fig. 1) [4]. Similar observations have been described for H_2^+ [1,9,23]. The TOF spectrum obtained at $I_0 = 10^{14} \text{ W/cm}^2$ (Fig. 2) is a superposition of four different fragment distributions. From the calibration of the spectrometer we can determine the total kinetic energies of the different photofragments to be $0.5 \pm 0.1 \text{ eV}$ (A), $1.3 \pm 0.3 \text{ eV}$ (B), $2.9 \pm 0.5 \text{ eV}$ (C), and $4.7 \pm 1.0 \text{ eV}$ (D). It can be seen that the photofragments appear at different laser intensities. At laser intensities of up to $0.01I_0$ the spectra are dominated by fragmentation into channels A and B with the main contribution coming from channel B. At higher laser intensities photofragments from channel C start to emerge. The channel yielding photofragments with largest total kinetic energy release (D) appears at laser intensities above $1 \times 10^{13} \text{ W/cm}^2$.

The observed fragmentation processes cannot be understood from the field-free potential curves shown in Fig. 3. As explained in Refs. [2,4], the dressed state description is very helpful to obtain an overview over the electronic states contributing to the intense field dissociation processes. In Fig. 4 the dressed state potential curves of several electronic states of Na_2^+ are shown.

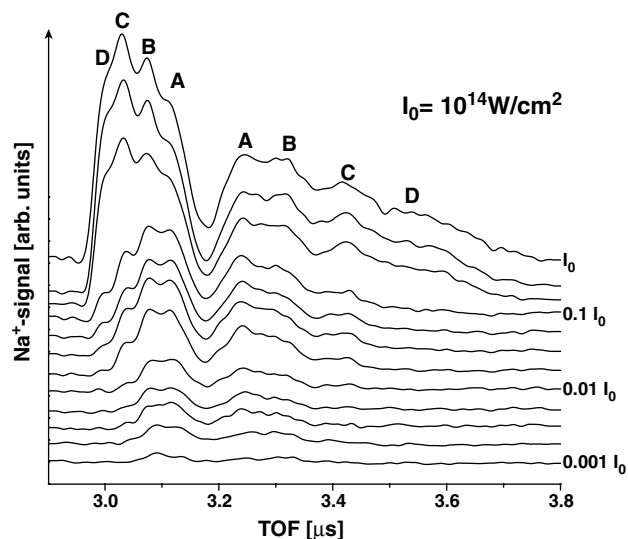


FIG. 2. Time-of-flight spectra of Na^+ fragments obtained from fragmentation of $\text{Na}_2^+ X^2\Sigma_g^+(v^+)$ in intense 790 nm, 80 fs laser fields at different laser intensities ranging from $1 \times 10^{11} \text{ W/cm}^2$ to $1 \times 10^{14} \text{ W/cm}^2$. The laser polarization was set parallel to the TOF axis. Four fragmentation channels with a released kinetic energy of 0.5 eV (A), 1.3 eV (B), 2.9 eV (C), and 4.7 eV (D) are observed. The observed total TOF distribution is a sum of four different fragment distributions with different kinetic energies.

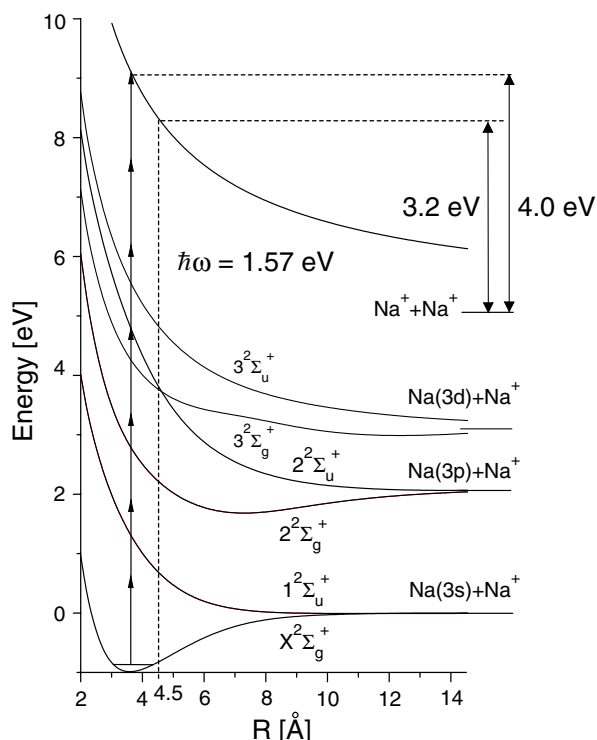


FIG. 3. Coulomb curve of $\text{Na}^+\text{-Na}^+$ and the field-free potential energy curves for electronic states of Na_2^+ . The Coulomb explosion at the equilibrium distance (solid line) leads to Na^+ fragments with a total fragment energy of 4.0 eV, whereas at a distance of 4.5 Å (dotted line) Na^+ fragments with a total fragment energy of 3.2 eV are formed. The vertical arrows indicate the photon energy of 1.57 eV for $\lambda = 790$ nm.

The dotted circles indicate the multicrossing points which become avoided crossings in the adiabatic dressed state picture. This can be understood in the context of calculations by Machholm and Suzor-Weiner [15] who showed that the repulsion of the adiabatic curves increases with the laser intensity. Therefore, the intensity of the laser pulse is the key parameter which determines whether a dissociation channel is open or closed. Taking into account that only the lowest vibrational levels of the $X^2\Sigma_g^+$ -electronic ground state of Na_2^+ are populated, only the first multicrossing region at 4.5 Å has to be considered for our excitation conditions. It is unlikely that the molecule propagates within the 80 fs pulse duration to the second and third multicrossing region. Therefore, we can expect three dissociation channels in which the Na_2^+ molecule can absorb one, two, or three photons from the intense laser field. The theoretically predicted total fragment energies for the one, two, and three photon absorption are 1.1 eV ($n = 1$ photon absorption), 0.5 eV ($n = 2$), and 2.1 eV ($n = 3$) [15]. Since the kinetic energies of the fragments from the $n = 2$ and $n = 3$ channels are well separated by the photon energy ($\hbar\omega$), the $n = 3$ channel is by definition ATD.

By comparison of the observed fragment kinetic energies with the theoretically predicted energies, we identify two photodissociation channels (Fig. 2). Within the

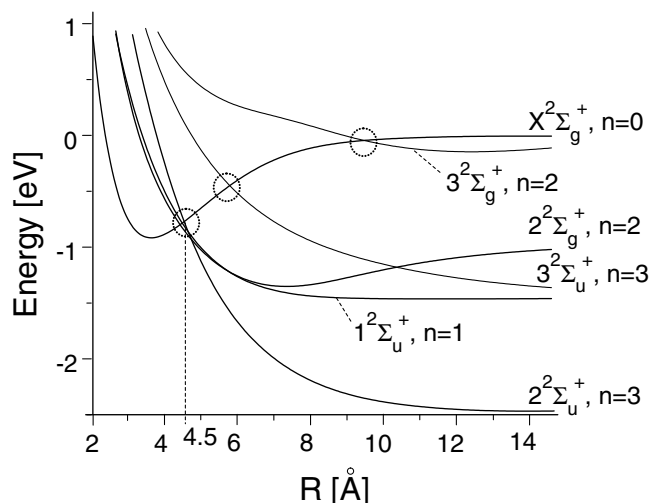


FIG. 4. Dressed state diabatic potential energy curves of electronic states of Na_2^+ . The dotted circles indicate the multicrossing regions. Only the first multicrossing region at around 4.5 Å plays a role. Photodissociation on light-induced adiabatic potentials leads according to [15] to fragments with released kinetic energies of 1.1 eV ($n = 1$, one-photon absorption channel), 0.5 eV ($n = 2$), and 2.1 eV ($n = 3$), respectively.

experimental errors the measured total kinetic energies of photofragments from channels A and B correspond to two and one photon absorption channels, respectively. The one photon absorption (channel B) couples the $X^2\Sigma_g^+$ -ground state to the $1^2\Sigma_u^+$ -potential curve and leads asymptotically to Na^+ and $\text{Na}(3s)$ fragments. Correspondingly, the two photon absorption (channel A) involves the $X^2\Sigma_g^+$ -ground state and the $2^2\Sigma_g^+$ -potential curve, leading asymptotically to fragments Na^+ and $\text{Na}^*(3p)$. At the lowest applied laser intensities ($I < 10^{12}$ W/cm²) primarily these two fragment channels are observed with channel B dominating the fragment distribution. This is also consistent with the theoretical results given in Ref. [15]. For lower laser intensities only these two channels are open and the lower order process ($n = 1$) is more probable. The calculations furthermore show that the threshold for the $n = 3$ channel—which couples the $X^2\Sigma_g^+$ -ground state with the $2^2\Sigma_u^+$ state by absorption of three photons—lies at 3×10^{12} W/cm². At this intensity the total dissociation yield should be strongly enhanced by the complete opening of the potential well [15]. Although an enhancement of the total yield is seen, no fragments with the expected energy (2.1 eV) for the ATD channel are observed. Instead of the expected 2.1 eV fragments a contribution with 2.9 ± 0.5 eV starts to emerge (channel C). Therefore the assignment of channel C to ATD is not justified. This difficulty can be solved by taking ionization into account. Calculations [19] showed that the ionization probability of Na_2^+ strongly depends on the internuclear separation and becomes large in the proximity of the crossing point. It reaches close to unity at around 4.5 Å for intensities above 3×10^{12} W/cm². Therefore, we attribute channel C to a dissociative ionization of the

molecular ion Na_2^+ . This process can be described in the following way: Initially the ionic molecule Na_2^+ dissociates along the “ $n = 3$ light-induced potential curve” towards larger internuclear separations. Then, still within the duration of the laser pulse, it reaches a distance in the proximity of 4.5 \AA where the ionization probability increases dramatically and field ionization resulting in Na_2^{++} takes place. From a Coulomb explosion at this internuclear distance Na^+ fragments with a released kinetic energy of 3.2 eV are expected (see Fig. 3). The actually measured kinetic energy of $2.9 \pm 0.5 \text{ eV}$ supports our conclusion. With this interpretation, the field-ionization process dominates and the ATD channel is suppressed. Note that in Ref. [15] such a competition between dissociation on light-induced potentials and field ionization was also pointed out.

For intensities above $1 \times 10^{13} \text{ W/cm}^2$, channel *D* shows the strongest contribution to the fragment distribution (Fig. 2). We interpret the origin of this fragmentation channel as field ionization followed by Coulomb explosion at the ground-state equilibrium distance of 3.6 \AA . From this process one estimates a released kinetic energy of 4.0 eV as indicated in Fig. 3. This agrees within our experimental errors with the measured kinetic energy release of $4.7 \pm 1.0 \text{ eV}$. Also the appearance intensity for this process supports our interpretation. Note that direct ionization from the inner or outer turning point of $\nu = 1$ (3.4 \AA ; 3.8 \AA) would lead to fragments with released kinetic energies of 4.2 eV and 3.8 eV , which is within our observed value of $4.7 \pm 1.0 \text{ eV}$.

For intensities above $1 \times 10^{13} \text{ W/cm}^2$ all four channels are observed. This is attributed to the spatial intensity distribution of the laser beam: At these high intensities, the fragments corresponding to channels *A* ($n = 2$) and *B* ($n = 1$) arise from the low intensity spatial wings of the femtosecond-laser beam.

In conclusion, we have studied the photodissociation of Na_2^+ in intense 790 nm laser fields using laser pulses much shorter than half of the vibrational period of the molecule. Starting from well defined vibrational levels we observed the interplay between two competing processes: dissociation on light-induced potentials and field ionization. The intensity dependence of the four fragmentation channels shows the interplay between these two processes. For low intensities, dissociation dominates. At the other extreme, above $1 \times 10^{13} \text{ W/cm}^2$, field ionization occurs at the ground-state equilibrium distance (channel *D*). The molecule has no time to dissociate along the light-induced potentials and Coulomb explosion occurs directly. Within this interpretation, channel *C* lies between dissociation and ionization. There the fragmentation process starts with dissociative motion on the light-induced potential but only until an internuclear separation is reached where the field-ionization probability is close to unity. In this way, the observation of the ATD channel is suppressed.

These results compare favorably with recent theoretical models [15,19].

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