Transient Photoelectron Spectrum of NaI During Photodissociation at 307 nm

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Alkali halides MX, where M stands for an alkali metal atom and X for a halogen atom, constitute a prototype of avoided covalent-ionic curve crossing and non-adiabatic transition problems. The ground state of diatomic M^+X^- is an ion pair state due to strong coulomb attraction between M^+ and X^- ions, while the asymptotic ground state of separate atoms are neutral fragments $M(^2S_{1/2}) + X(^2P_{3/2})$ that correlates with the lowest covalent excited states of the diatomic molecule around the ground state equilibrium bond length.[1] It takes more energy to separate the species into ions ($M^+ + X^-$) than into neutral fragments (M + X) due to the strong coulomb attraction between the ions. Thus, the ion pair curve crosses with that of neutral fragments at certain nuclear distance R_x. If R_x is sufficiently short and the interaction between the two states is strong, the crossing is an avoided one, resulting in two adiabatic curves with a trapping well in the excited state. On the other hand, when the crossing distance is large and the coupling is weak, the excited state becomes essentially a repulsive one. In the strong coupling regime, a NaI molecule excited to the upper well will exhibit oscillating motion in the well. The excited molecule will make non-adiabatic transition to the lower curve with a finite probability at the avoided crossing point. The relevant potential energy curves of NaI are presented in Figure 1.

A pioneering real-time study on photodissociation of NaI was done by Zewail's group by detecting the fluorescence of dissociation product Na in a gas cell,[2] which clearly showed the oscillation of nuclear wave packet in the excited state potential well as well as the non-adiabatic transition leading to dissociation. Later, the real-time excited state dynamics of NaI was refined in a molecular beam by a pump-probe transient photoionization study,[3] and details of the ionization process gave further understanding of the NaI photodissociation dynamics. Wave packet dynamics,[4] solvation,[5] and bimolecular reaction of NaI[6] were also studied by the same method of photoionization. In a series of effort to systematically study the dynamics of several alkali halides, the photodissociation of RbI was also studied.[7] However, pump-probe transients of photoelectrons only at a few selected energy ranges were reported in the previous study.[3] In this work, the full photoelectron spectrum of NaI is reported to reveal further details of the photodissociation dynamics of this prototypical alkali halide molecule.

This study was performed in CEA (Saclay, France) with the experimental setup described previously.[4] It consists of a supersonic molecular beam coupled with a dual photoion

photoelectron TOF spectrometer and a femtosecond laser system. Briefly, the pump wavelength at 307 nm was obtained by doubling the output of a continuum-seeded dye amplifier. The probe wavelength was the third harmonic (266 nm) of the Ti:sapphire regenerative amplifier. The pump pulse energy is typically of the order of 10 μJ and the temporal width is about 100 fs. The probe at 266 nm is 70 fs broad and its energy in the order of 10 μJ. The probe laser beam is delayed in time relative to the pump beam by scanning an optical delay line by 33 fs steps. Both laser beams are mildly focused by 1-m lenses between the grids of the spectrometer where the molecular beam of NaI crosses the laser beams. Typically, a pump-probe transient signal is obtained by summing 20 scans with an average of 25 laser shots at each scan step. Alkali halide molecules were evaporated at 500 °C in a small oven attached to the opening of a pulsed nozzle. The buffer gas (He at 0.5 atm) is expanded from the pulsed valve into the small oven, to cool down the molecular beam of NaI. The molecules enter the second chamber through a skimmer, where the laser beam crosses perpendicularly the molecular jet and the axis of the dual spectrometer. Both TOF spectrometer (electron and ion) have been described previously along with the calibration
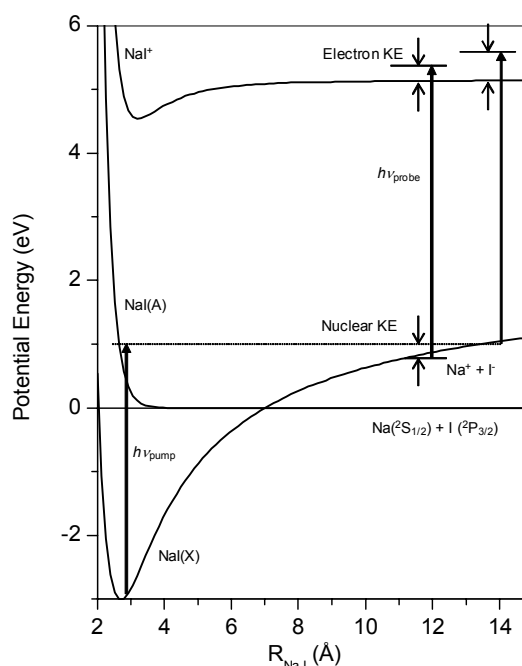
Figure 1. Potential energy curves of NaI.

(a)

(b)
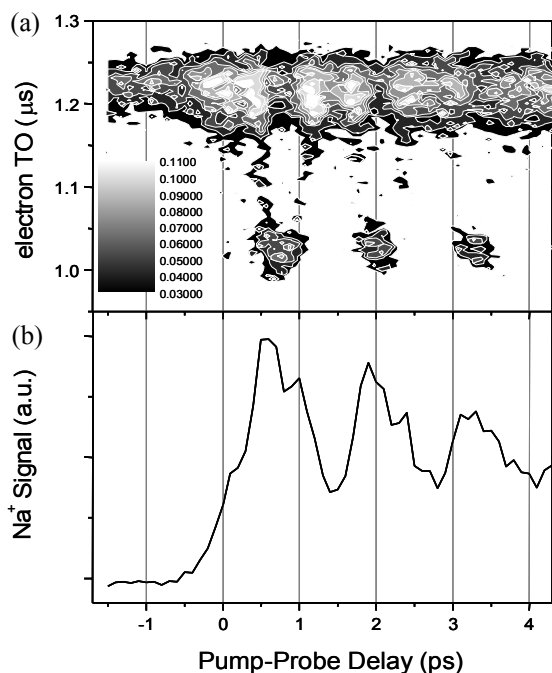
Figure 2. Transient ion and electron signal of NaI. Pump 307 nm, probe 266 nm (a) photoelectron spectrum, (b) photoion transient.

procedure for the electron kinetic energy measurement.[8]

Dissociation dynamics of NaI has already been investigated in the previous study by femtosecond pump-probe ionization, where the transients of high-energy and low-energy electron were obtained respectively.[3] However, a full photoelectron spectrum was obtained in this study as a function of pump-probe delay in order to get a detailed picture of the photoionization process. NaI was excited by an ultrafast 307 nm laser and the excited-state dynamics was probed by 266 nm. The full pump-probe photoelectron spectrum is presented as a 2-dimensional (2-D) map in Figure 2(a). The horizontal axis stands for the delay between the pump and the probe pulses, which corresponds to the reaction time after the photodissociation event. The vertical axis is the time-of-flight (TOF) of the electrons that were issued from the photoionization, which can be converted into the kinetic energy of the electrons. Longer electron TOF corresponds to lower electron kinetic energy (EKE), while shorter electron TOF stands for higher EKE. The intensity of the photoelectron at each delay time and each TOF is represented with different color, whose scale is shown as an insert in Figure 2(a).

In this 2-D map, one can clearly see that the kinetic energy and the intensity of the emitted photoelectrons vary as a function of the pump-probe delay. The EKE is low at time zero, but around 0.6 ps the EKE becomes higher. Then the EKE shows oscillating behavior superimposed on a decay, which is also seen in the ion signal of the Figure 2(b). As reported in the previous study,[3] Na$^+$ ion is produced by dissociative ionization at the outer turning point of excited state potential well, because the ionization cross section is ~ 200 times greater in the ionic (Na$^+$I$^-$) part of the potential curve

than in the covalent region. Thus the first peak of the Na$^+$ signal in Figure 2(b), which results from the dissociative ionization of NaI, is seen at half the recurrence time. However, because the photoelectron TOF spectrometer accelerates electrons by only a few volts, slower electrons are collected with higher efficiency while faster electrons fly away from the electron spectrometer axis. Therefore, the signal intensity is higher for low EKE, i.e. longer electron TOF, and the apparent temporal variation of intensity is out-of-phase with the ion signal.

The kinetic energy of the photoelectron is governed by conservation of total energy and kinetic energy for the nuclei, because the kinetic energy of heavy particles (i.e. nuclei) is preserved upon ionization. Therefore the photoelectron energy is the difference between the ionic NaI$^+$ potential and the sum of the excited A state potential and the probe photon energy, as illustrated in the equation below and Figure 1.

$$E_{photoelectron} = h\nu_{probe} + E(NaI(A)) - E(NaI^+)$$

At the outer turning point indicated with the arrow on the right in Figure 1, where the ion signal is at its maximum, photoelectron has its maximum energy because the kinetic energy of nuclei is lowest and the difference between ionic and excited states is smallest. Thus, the difference of the excited and the ionic state potential energy curves was mapped by the transient photoelectron spectrum.

In this study, the dissociation of NaI was studied by observing both ion and electron signal as a function of delay between the photodissociation laser and the probe laser. A more detailed study, e.g. using femtosecond stimulated Raman spectroscopy,[9] could be useful in revealing more details of transient geometry change during the photo-dissociation.

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