Observation of Predissociated Excited States in Mixed Alkali Trimer Clusters Na_2K and K_2Na: Time-Resolved Spectroscopy of Bound−Free Transitions

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For the first time, predissociated excited electronic states of mixed alkali trimers exhibiting vibrational structure in their time-resolved spectra were found. The one-color femtosecond pump and probe technique was employed to study the predissociated excited electronic states of Na_2K trimer located between 730 and 790 nm. States were populated with one photon of the probe pulse. Dynamics was monitored by ionization of the excited trimer with two photons of the probe pulse. In the case of Na_2K, excitation wavelength-dependent dissociation times between 2.5 and 6 ps were obtained. The ion signal of Na_2K^+ recorded at 770 nm revealed an oscillatory structure with a dominant period of 490 fs, while the transient spectrum of the NaK fragments exhibited oscillations with an estimated period of 440 fs, characteristic for the wave packet dynamics in the NaK $A^1\Sigma^+$ state. In the case of K_2Na, no wave packet dynamics was resolved for the trimer's short-living predissociated excited state ($\tau < 5$ ps) populated at 735 nm.

Introduction

Triatomic homogeneous metal clusters, such as Li_3, Na_3, and K_3, have been intensively studied in the past two decades by means of stationary[1−10] and transient[11−18] spectroscopic techniques. Bound excited states of triatomics were first observed by the resonant multiphoton ionization (REMPI) technique,[1−2,8] and the method of depletion spectroscopy made the detection of predissociated states possible.[3−7,9] The dispersed fluorescence technique was employed to study the predissociation of excited sodium and potassium trimers on helium nanodroplets.[10] Deep insight into the dynamics of bound−bound and bound−free electronic transitions can be obtained by employing ultrafast observation schemes.[11−18]

The ultrafast pump and probe experimental technique in the femtosecond time regime is a powerful tool to study the dynamics of bound−free transitions. The principle of the pump and probe experimental observation scheme used in this study is indicated in Figure 1: The clusters are electronically excited with the first ultrafast laser pulse (pump pulse) into a predissociated state, from which they dissociate directly or after a few oscillations. The temporal evolution of the predissociated excited state is monitored with the second ultrafast laser pulse (probe pulse), which ionizes by two photons the excited particles after a well-defined variable time delay Δt. Thus, the decay of the transient ion signal reflects the dissociation time of the predissociated state. Furthermore, provided oscillations take place before dissociaton, also the vibrational dynamics in the predissociated state can be monitored as well, if the ionization probability from the excited state depends on the reaction coordinate.

In C- and D-excited electronic states of the sodium trimer, the fragmentation takes place within a few picoseconds after optical excitation. The corresponding predissociation lifetimes were measured by different research groups.[13−15] A similar behavior of potassium trimer's excited state was observed as well.[17,18]

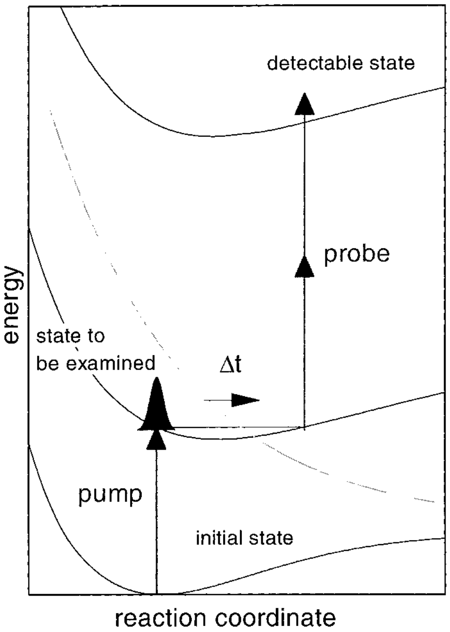

Figure 1. Pump and probe experimental observation scheme for a bound−free transition study.

Experimental Section

The scheme of our experimental setup is shown in Figure 2. The laser system consisted of a Spectra Physics model 3960 Tsunami titanium:sapphire laser pumped with a Spectra Physics model 2080 argon ion laser. The oscillator provided pulses of about 80 fs duration with a spectral width about 170 cm^{-1} fwhm tunable between 720 and 880 nm. The laser beam was split, and the probe pulse passed a linear translation delay stage enabling us to vary the time delay between the probe and pump pulses. The pump and probe beams were realigned collinearly in a Michelson-type arrangement.

The neutral alkali clusters were prepared by coexpansion of alkali metal vapor with argon as a carrier gas through a 70 μm

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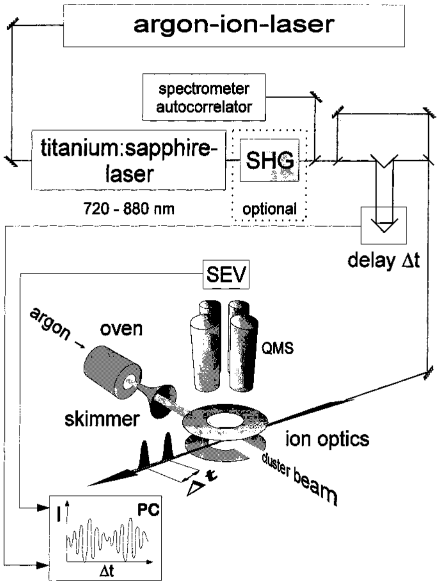

Figure 2. Scheme of the experimental setup.

nozzle into the vacuum. The oven was filled with pure alkali metals: the pure sodium (40%) was placed in the front part of the oven (near to the nozzle), while the pure potassium metal (60%) was located in the rear part of the oven. The oven was heated to an operating temperature of 800−900 K. To avoid clogging of the nozzle and to achieve sufficient partial vapor pressures of both metals, the temperature of the nozzle was kept higher by 80−100 K than the temperature of the oven. Argon pressure of 3−5 bar was used to produce a continuous beam of cold clusters. The oven chamber was pumped by a 3000 L/s Balzers diffusion oil pump, allowing to keep the pressure in the oven chamber below 10^{-3} mbar.

The molecular beam entered the second chamber (interaction chamber) through a 1 mm diameter skimmer. The interaction chamber was differentially pumped with a 2200 L/s Balzers turbo molecular pump, establishing 10^{-6}−10^{-5} mbar pressure. During the measurement, the intensity of the molecular beam in the interaction chamber was monitored by a Langmuir−Taylor detector (LTD).

The laser beams were focused on the molecular beam passing between the electrical lenses of a quadrupole mass filter (Balzers QMG 420 mass spectrometer, QMS). The cluster ions were mass-selected with a typical resolution $m/\Delta m$ higher than 200. The transmitted ion signal was measured by a secondary electron multiplier (SEV) and amplifier.

To obtain the real-time spectrum, the transient ion signal was recorded as a function of the delay time between the pump (excitation) and probe (ionization) pulse.

Results and Discussion

Predissociated excited states of the mixed sodium−potassium trimers undergoing ultrafast photodissociation were observed. The decay times characterizing the rate of photodissociation were obtained with a similar kinetic model as used for the sodium and potassium clusters.[14,18,19] Briefly, this model assumes a time-dependent ion signal proportional to the excited-state population and takes into account the population of the monitored dissociating trimer state with triatomic photofragments of larger clusters. The kinetic model is illustrated in Figure 3, and the excited-state population $N(t)$ after excitation with a δ-pulse can be described by the following equation.[19]

$$N(t) = N_0 \exp(-t/\tau_1) + \alpha[\exp(-t/\tau_m) - \exp(-t/\tau_2)] \quad (1)$$

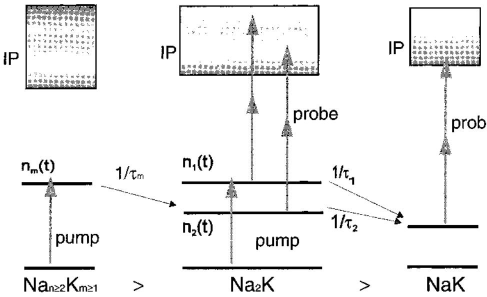

Figure 3. Fragmentation model used for computing the lifetime of the predissociated excited state.

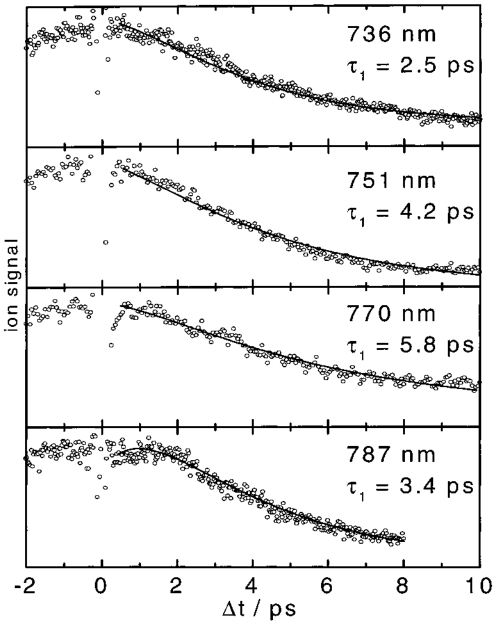

Figure 4. Temporal evolution of the three-photon signal of Na_2K for four different wavelengths. The calculated lifetime of the excited state is shown, too.

with initial population N_0 prepared by the pump pulse, τ_1 the predissociation lifetime of the initially prepared excited trimer, τ_m the time constant describing the population of the excited state via fragmentation of larger agregates, τ_2 the predissociation lifetime of the triatomic fragments, and α the τ_2-dependent preexponential factor. In data analysis, the width of the real pump pulse was considered using a deconvolution algorithm. In the case of the oscillatory signal, Fourier transform analysis was performed to reveal the frequencies characteristic of the excited-state vibrational dynamics.

Na_2K. Transient one-color three-photon ionization spectra of the Na_2K trimer were recorded over the wavelength region between 730 and 790 nm. The wavelength-dependent transient Na_2K ion signals indicative of a very fast dissociation are plotted in Figure 4, together with the corresponding decay time τ_1 (2.5−5.8 ps) of Na_2K^* which was obtained by applying eq 1 to the experimental data. Notice that only one decay time τ_1 can be extracted from the experimental data, and the contributions of τ_m and τ_2 are negligible. The decay time τ_1 exhibits a maximum at 770 nm excitation. The ion signal of the NaK fragments was monitored simultaneously in the experiment. The transient ion signals of the Na_2K trimer and the diatomic fragments NaK recorded at 770 nm are shown in Figure 5. The rise time of the NaK fragment signal is identical with the decay time τ_1 of the Na_2K trimer, which means that the dominant fragmentation channel of the Na_2K trimer is a loss of a sodium atom. No sodium dimer fragments were detected under given experimental

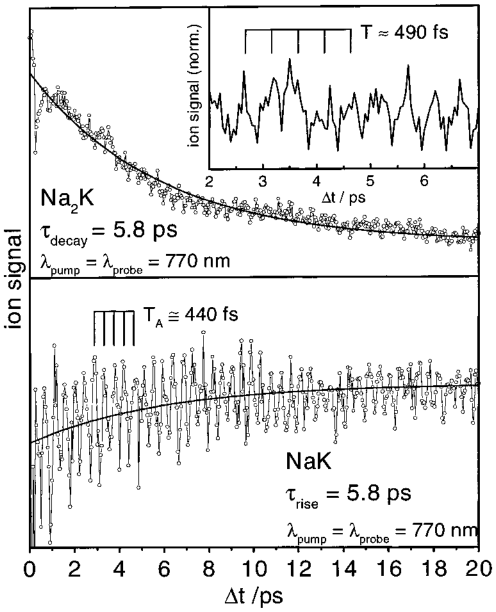

Figure 5. Time evolution of the Na_2K signal and the diatomic NaK fragment signal at 770 nm. The decay time of the Na_2K signal (5.8 ps) is the same as the rise time of the NaK signal. Clear oscillation with periods of 490 and 440 fs are visible for Na_2K and NaK, respectively. Inset: enlarged signal of Na_2K for clarity.

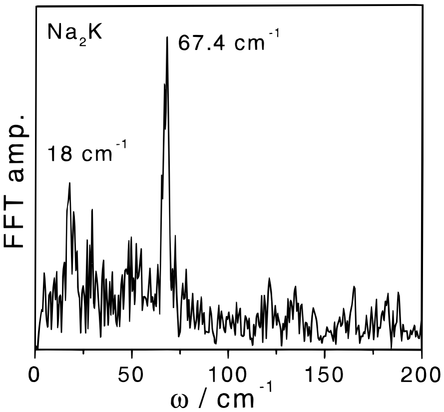

Figure 6. Fourier spectra of the transient Na_2K signal for an excitation wavelength 770 nm.

conditions. Moreover, both the Na_2K and NaK transient ion signals exhibited clear oscillations with dominating periods about 490 and 440 fs, respectively (see Figure 5). The 440 fs oscillation period seen on the NaK signal is identical with the oscillation period characteristic for the wave packet dynamics in the NaK $A^1\Sigma^+$ state.[20,21] The result of the Fourier analysis of the Na_2K real-time signal is shown in Figure 6 and reveals a 18 cm^{-1} and a 67.4 cm^{-1} frequency component. The assignment of the observed frequency components to normal modes in the mixed trimer Na_2K and the identification of the excited electronic state involved require accurate theoretical calculations.

K_2Na. The transient ion signal of the K_2Na trimer obtained at 735 nm excitation reveals a short-living predissociated state. The time-resolved K_2Na ion signal is shown in Figure 7. The cluster fragmentation is described with a decay time shorter than 5 ps. At this wavelength, no clear oscillations on the ion signal were resolved and the fragments were not identified.

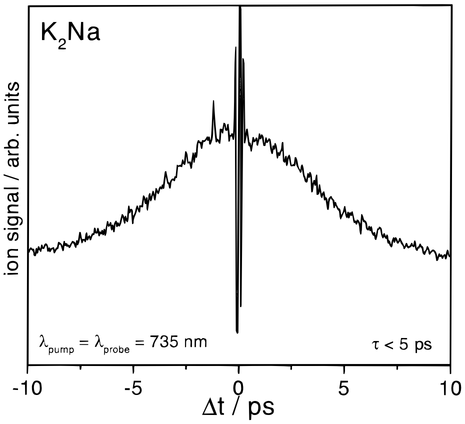

Figure 7. Transient signal of K_2Na excited at 735 nm. The calculated photofragmentation time is about 5 ps.

Summary

New predissociated excited states were observed in the mixed alkali metal timers Na_2K and K_2Na by employing femtosecond pump and probe spectroscopy. The lifetimes of the excited states were determined (2.5−6 ps for Na_2K, approximately 5 ps for K_2Na), and in the case of the Na_2K cluster the vibrational dynamics in the parent trimer (dominant oscillations with period T_{osc} = 490 fs) and in its fragment NaK (T_{osc} = 440 fs) was clearly resolved. The theoretical work needed for an assignment of the resolved frequency components in the transient spectrum of Na_2K and for an identification of the involved excited electronic states is in progress.[22]

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