Size-Selective Depletion Spectroscopy of Predissociated States of Na_3

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The Na_3 photodissociation spectrum is studied by depletion spectroscopy. For the first time a predissociated state is observed in Na_3 and detected both by depletion and by recording of the related photofragments. The method is promising for photodissociation studies in clusters.

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The electronic properties of small metal clusters are of great importance for the understanding of the fundamental mechanisms of catalysis and surface chemistry. The investigation of the electronic structure is primarily carried out through molecular spectroscopy. In recent years, it has been demonstrated[1-3] that the metal clusters can efficiently be produced in molecular beams. Moreover, the resonant two-photon ionization (TPI) spectroscopy is now well known as an efficient method to select transitions belonging to a given species in a molecular beam. However, despite intense activity in the cluster research area, no gas-phase spectra of homonuclear particles larger than dimers has been reported in the literature, with the exception of Na_3[4,5] and Cu_3.[6] This situation can be partially explained by radiationless fast relaxation of the excited states. The relaxation can occur either by predissociation if the corresponding channels are open, or by intramolecular vibronic relaxation, possibly leading to dissociation for states having energy larger than the dissociation threshold. Such fast-relaxation channels of alkaline-earth-cluster states located beyond the first ionization limit have been demonstrated,[7,8] for example, to be predominant compared to autoionizing transitions. In the case of Na_3, Gole *et al.*[9] have shown the importance of the photodissociation processes in the visible absorption spectrum. For transition-metal clusters, also, the excited states beyond the dissociation threshold have been found to be mainly dissociative.[10]

We report in this Letter the first observation by depletion spectroscopy of a predissociated excited state in Na_3, which was simultaneously recorded with the resulting Na_2^* photofragments. The principle of our method is illustrated in Fig. 1: A tunable laser $h\nu_1$ excites Na_3 to the predissociated state. Then the Na_3^* particles dissociate to $Na_2^* + Na$. A second photon of the same laser $h\nu_1$ ionizes the resulting Na_2^* fragments, and the $Na_2{}^+$-ion signal is recorded as a function of the irradiating laser wavelength. In order to confirm that the parent cluster of the observed transitions is Na_3, the molecular beam is simultaneously irradiated by a probe uv laser $h\nu_2$. This uv laser is capable of ionizing Na_3 directly from the ground state, and is used to monitor the Na_3 population in the molecular beam. Whenever a predissociating transition is excited by $h\nu_1$, a depletion of the $Na_3{}^+$ intensity is monitored by $h\nu_2$. The effect is most efficient when the predissociating transition is saturated. Smalley and coworkers[6] have performed a similar experiment on Cu_3, without, however, recording the related photofragments.

The basic part of the experimental setup is the seeded supersonic molecular beam which has been described in detail in the work of Delacrétaz and coworkers.[11] The metal vapor is expanded into the vacuum through a small orifice of typically 50 μm diameter with argon as a carrier gas. The argon pressure, which is mainly limited by the 1500-l/s diffusion pump, can reach up to 10 bars. The metal pressure ranges between 10 and 100 mbar. With this expansion system, very cold Na clusters can be generated. A hot-band analysis of the obtained spectra showed vibrational temperatures of Na_3 down to 30 K,[12] and rotational temperatures of Na_2 down to 7 K.[5] Neutral-

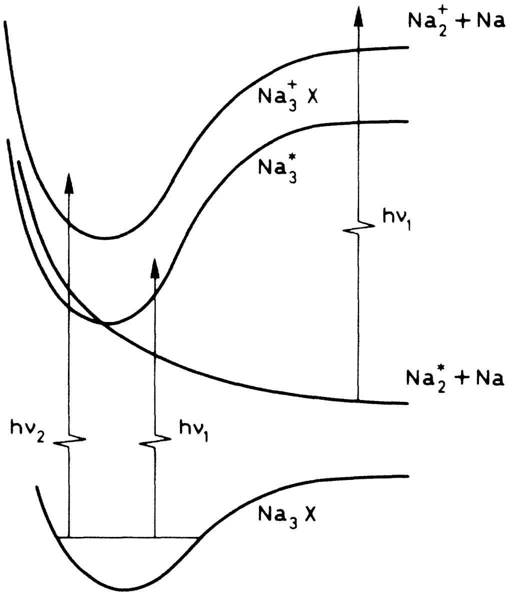

FIG. 1. Principle of the depletion experiment.

beam intensities are permanently monitored with a surface ionization detector. A stilbene-420 dye laser pumped by a pulsed Lambda Physik excimer laser is used to excite the Na_3 clusters ($h\nu_1$), and to ionize the resulting Na_2^* photofragments. A small portion (2%) of the excimer laser output, which operates at 308 nm, directly ionizes the remaining Na_3 particles. The two laser beams are collinear and irradiate the molecular beam at right angles. The entrance of a quadrupole mass spectrometer is perpendicular to the particle and the laser beams. The measurements are performed by setting the mass spectrometer on the Na_2^+- or Na_3^+-mass peak, while the ion signal is recorded as a function of the $h\nu_1$ wavelength.

Figure 2(a) shows the ion signal recorded on the Na_2^+ channel at moderate laser power (typically 0.2 mJ/pulse and 10 kW peak power). The spectrum exhibits a regular progression corresponding to vibrational levels of the excited state. In the same experimental conditions, no ion signal is detected on Na^+ and Na_3^+.

Despite the harmonic character of this progression, the observed excited state cannot be attributed to Na_2: All the Na_2 states in this region have been calculated by Jeung[13] to high precision ($\simeq 100$–$200\ cm^{-1}$) and none of them correspond with the experimental results. In fact, for Na_2, the energy of the laser ($\simeq 23\,000\ cm^{-1}$) would lead to an excitation close to the dissociation limit $Na(3p)+Na(3s)$, where the Franck-Condon factors are negligible[14] and the vibrational spacings very small ($<30\ cm^{-1}$). Moreover, the rather symmetric structure of each band [Fig. 2(b)] does not correspond to the usual rotational progression of a dimer.

As a consequence, the observed spectrum must be related to the predissociation of larger clusters. To find the parent cluster, we performed the depletion spectroscopy experiment. The power of the exciting laser ($h\nu_1$) (typically 5 mJ/pulse) was set to saturate the predissociating transition. The energy of the 308-nm probe laser was sufficient[1,7] to directly ionize odd clusters like Na_3, Na_5, etc., but not to reach the Na_2 ionization potential.[15] The power of this laser (typically 5 mJ/pulse) was set to avoid undesired multiphoton transitions, but sufficiently high to provide a good signal on Na_3^+ and Na_5^+.

Figure 3 (upper curve) shows the depletion signal obtained on Na_3^+ while the relating predissociation spectrum, recorded on the Na_2^+ fragment, is shown below. The perfect coincidence between the Na_3^+ depletion spectrum and the predissociation spectrum is striking and demonstrates that Na_3 is the parent cluster. The comparison of Figs. 2(a) and 3 (lower curve) shows the influence of the saturation on the relative intensities of various vibrational bands. Figure 4 compares the depletion signal observed for Na_3^+ (upper curve) and Na_5^+ (lower curve). Both curves show the relative depletions, which, in the case of Na_5, reaches 70%. For Na_5, however, no structure is observed. This confirms the importance of dissociation processes in the excited states of large clusters. The decrease in the dissociation yield beyond 420 nm is partially due to the profile intensity of the dye laser. From the dissociation yield and the laser power, we deduce that the

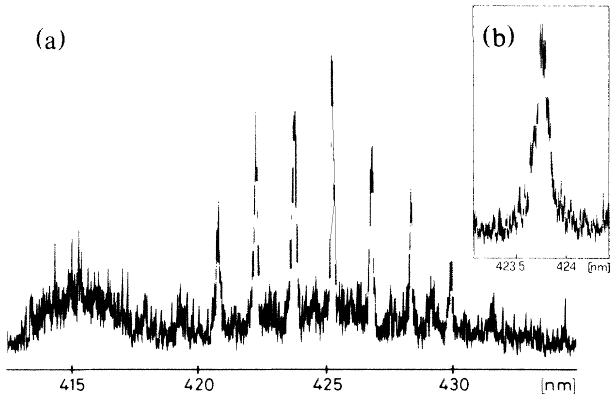

FIG. 2. Spectrum recorded on the Na_2^+ channel at moderate laser power. (a) The whole spectrum; (b) detailed structure of a vibrational band.

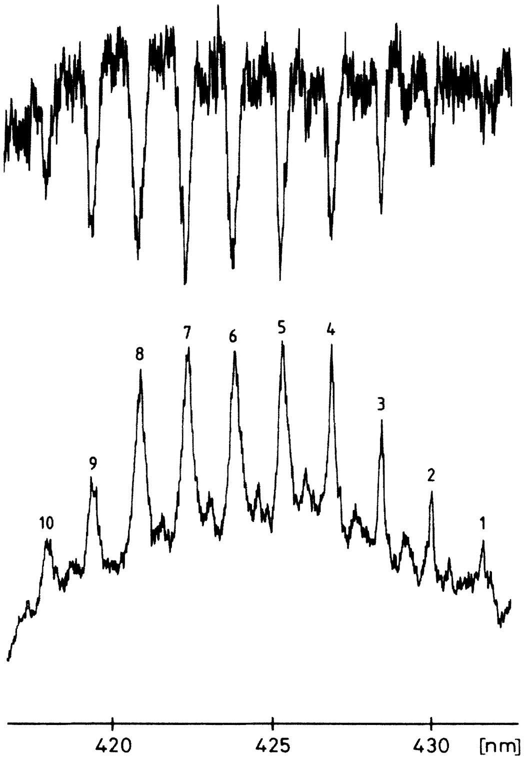

FIG. 3. Upper: depletion signal recorded on Na_3^+. Lower: TPI signal recorded on the Na_2^+ channel.

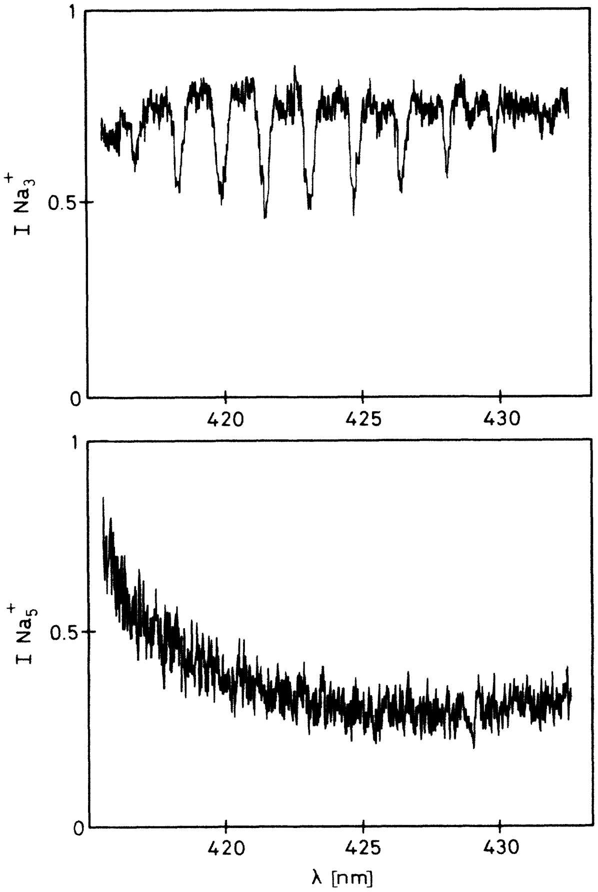

FIG. 4. Depletion signal recorded on Na_3^+ (upper curve) and Na_5^+ (lower curve).

photodissociation cross section can be estimated to be about 10^{-17} cm^2 which corresponds to a typical value for a strongly allowed transition.[16]

In the Na_2^+ spectrum [Fig. 2(a)], a continuous hump is observed in the 415-nm region. This continuous spectrum corresponds to a direct bound-free transition in Na_3, as confirmed by the fact that the continuous signal of the Na_3 depletion spectrum, which is superimposed on the vibrational progression, increases for wavelength shorter than 420 nm (Fig. 3, upper curve). No hump is observed in the Na_2^+ saturated spectrum of Fig. 3 (lower curve), because of a nonresonant TPI background from unexcited Na_2. The continuous dissociation spectrum probably corresponds to the absorption by the dissociative state which is also responsible for predissociation. With this hypothesis and from Fig. 2, the Franck-Condon pattern of the dissociative state appears slighly shifted as compared to the predissociated one. This would emphasize a location of the dissociative potential surface almost parallel to that of the predissociated state, and slightly shifted toward high energy (as schematically drawn on Fig. 1).

The fact that no resonant TPI signal is detected in the 420-nm range on the Na_3 channel indicates that the predissociation lifetime is significantly less than 1 ns over the whole spectrum.

Let us now focus on the possible dissociation channels of Na_3. We observe in our experiment the predissociation $Na_3^* \rightarrow Na_2^* + Na$. The Na_2 ionization is performed with the same laser as the Na_3 excitation. The laser energy is $23\,200\ \mathrm{cm}^{-1} < h\nu_1 < 24\,100\ \mathrm{cm}^{-1}$, which excludes energetically all dissociation channels of the kind $Na^* + Na_2(X$ state) except for $Na^*(3p) + Na_2(X)$. The laser $h\nu_1$ has insufficient energy to ionize the Na in the $3p$ state and therefore the last channel cannot be observed in our experiment. It cannot be very dominant, however, because an intense signal is detected on Na_2^+. With Na_3 dissociation energy[17,18] taken into account (3000 cm^{-1}) and the Na_2 ionization potential (34480 cm^{-1}), a simple energy balance demonstrates that the Na_2 excited states resulting from the predissociation are located between 16200 and 20200 cm^{-1} above the Na_2 ground state. With use of the theoretical calculations of Jeung,[12] and recent spectroscopic results,[19–21] only four states can be candidates for this dissociation: the $a^3\Pi_u$, $A^1\Sigma_u^+$, $(1)^3\Sigma_g^+$, and $(2)^1\Sigma_g^+$ which are located at about 13600, 14700, 18400, and 19300 cm^{-1}, respectively, the $B^1\Pi_u$ state being slightly too high. In the case of the two first states (a and A states) ionization occurs only to fragments with a vibrational excitation exceeding 2600 and 1500 cm^{-1}, respectively. For this reason, the dissociation toward the two other states seems more probable. Let us notice, moreover, that the existence of an excited Na_3 state can be invoked to explain the recently observed very efficient relaxation process[22]

$$Na_2(B^1\Pi_u) + Na(3s) \rightarrow Na_2(2)^1\Sigma_g^+ + Na(3s).$$

If the assignment of the $(2)^1\Sigma_g^+$ state as the main dissociation channel could be confirmed, the presently observed predissociated Na_3 state would be the intermediate complex of the collision.

We have also recorded the Na_3 predissociation spectrum as a function of the cluster temperature by varying the carrier-gas pressure. The intensities of the small peaks observed between the intense bands of the main vibrational progression have the characteristic behavior of hot bands. The wave numbers of all the measured transitions are reported in Table I. The average distance between the main bands and the hot bands is 45 ± 3 cm^{-1}. This result is an indication for the Na_3 ground-state structure. It is in good agreement with hot bands which we observed in different Na_3 electronic states.[23]

In conclusion, we have shown that depletion spectroscopy combined with two-photon ionization techniques is a powerful tool to observe completely and

TABLE I. Wave numbers of all the measured transitions. E' is the energy difference between two consecutive cold bands and E'' the energy difference between hot and cold bands.

Running number	Cold bands $1/\lambda$ (cm^{-1})	E'	Hot bands $1/\lambda$ (cm^{-1})	E''
1	23 161.5	88	23 115.0	46.5
2	23 249.5	86.5	23 209.5	40
3	23 336.0	85	23 288.0	48
4	23 421.0	85.5	23 374.5	46.5
5	23 506.5	85	23 462.0	44.5
6	23 591.5	84	23 548.0	43.5
7	23 675.5	84.5	23 633.0	42.5
8	23 760.0	81.5	23 716.0	44
9	23 841.5	83	23 798.5	43
10	23 924.5		23 875.5	49

partially predissociated excited states of clusters. With inclusion of the present result, four spectroscopic systems are now known for Na_3. Three of them, ranging around 675, 625–550, and 475 nm, have been observed[5] by means of two-photon ionization spectroscopy. The corresponding excited states are not or only weakly dissociated with lifetimes larger than 1 ns. The fourth system is the presented 420-nm system which is completely predissociated. A systematic investigation of Na_3 by means of depletion spectroscopy, covering the whole spectral range to 330 nm, is in progress. In addition, in contrast to TPI spectroscopy of the trimer and smaller clusters which is limited by fragmentation, the present method may also be applied to larger clusters so long as the predissociative states are not overwhelmed by dissociative states.

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