Temperature Dependence of the Optical Response of Small, Open Shell Sodium Clusters

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The optical absorption of small, open sodium cluster ions (Na_n^+, $n = 4$, 7, and 11) exhibit an unexpectedly large temperature dependence. Clearly separated absorption lines observed for cold clusters ($T \sim 35$ K) are interpreted as transitions between electronic states of the Na_n^+ molecule. At the highest temperature ($T > 380$ K), however, the clusters are liquid, and broad absorption peaks are observed whose energy positions can be explained for $n > 7$ by the model of nearly free electrons oscillating in a spheroidal container.

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Alkali metal clusters offer a model system for studying the transition from atomic and molecular physics to the science of condensed matter [1–8]. Different concepts and methods have evolved in these traditionally well separated fields. Scientists with a solid state or nuclear physics background usually treat metal clusters as small spherical or spheroidal particles containing nearly free electrons [1–5]. The positions of the nuclei are either neglected or treated in some averaged way. The molecular or quantum-chemistry point of view is the complete opposite: The nuclei are assumed to have fixed positions, and their geometry strongly influences all physical properties [3,4,6,7]. This point of view is, in principle, more accurate but is limited to small cluster sizes, while the nearly free electron description can be extended to very large clusters [1,2]. An experiment is described in this Letter which shows that the nearly free electron or jellium model gives good agreement for hot, liquid clusters down to size $n = 7$, while very recent quantum-chemistry calculations give good agreement for cold Na_4^+ and partial agreement for cold Na_7^+ and Na_{11}^+. Thus not only the size but also the temperature is important in deciding which of the opposing theoretical approaches is more appropriate. This determination is deduced from these first temperature dependent measurements of optical spectra for open shell sodium cluster ions.

Two innovations have made this experiment possible: Firstly, a new variable temperature cluster ion source has been developed which can generate cluster ions with a canonical distribution of internal energies. Secondly, a new data acquisition method has been implemented, which is about a factor of 40 faster than earlier methods. This Letter is organized as follows: the cluster source is first described, then the way to change and measure the temperature is discussed, and finally the data are presented and interpreted.

The main idea of the variable temperature cluster ion source is to produce cluster ions and to cool them by immersion into a cold flow of helium gas. This concept has the advantages of (1) producing a cluster ensemble having a thermal distribution of internal energies and (2) avoiding the unknown change in internal energy upon ionization. No such cluster ion source has yet been described. As shown in Fig. 1, sodium is heated in an open container, producing a vapor pressure of about 10 Pa. The sodium container can be shifted horizontally in a liquid nitrogen cooled aggregation tube. Helium gas (about 4×10^{20} atoms/s) flows around the Na container, which also serves as a hollow cathode (HCD) of an electric discharge (~130 V, 1 mA). In this way neutral and charged clusters are formed by gas aggregation [4] and are cooled by collisions with the He gas. The distance between the sodium container and the exit hole is about 15 cm, long enough for efficient cooling. Estimates similar to those in Refs. [9–11] show that the cluster ions should be in thermal equilibrium with the helium gas implying a canonical distribution of internal energies. The gas velocity of about 1 m/s in the aggregation tube reaches near sound velocity in the exit hole, which has a diameter of about 6 mm. At a pressure of 100 Pa this produces a very mild supersonic expansion, so that only weak cooling effects are expected [4]. Once in

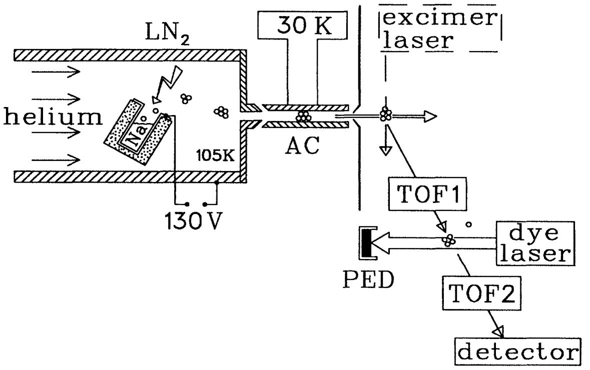

FIG. 1. Gas aggregation source to produce hot and cold sodium cluster ions and schematic of the experiment to measure their photoabsorption spectra. The aftercooler (AC) is removed for the 105 K operation. Photons from the excimer laser are used only if hot, liquid clusters are prepared. See text for details.

vacuum, the clusters retain their distribution of internal energies. They are cold enough that no atom can be evaporated. A thermocouple situated near the exit hole of the gas aggregation tube has been carefully calibrated [12] to correctly measure the gas temperature. Because of imperfect heat shielding, the gas temperature does not reach the expected temperature of the liquid nitrogen (77 K) but only 105 ± 7 K, in good agreement with the temperature obtained from the rovibrational spectrum of Na_2 [12]. Clusters prepared in this way were used for the intermediate temperature data shown in Fig. 2. A typical intensity is about 50 Na_{11}^+ clusters per pulse of our time-of-flight mass spectrometer.

In order to obtain a lower temperature, an "aftercooler" (AC) has been added, consisting of a 10 mm inner diameter, 10 cm long copper tube cooled by a closed cycle refrigerator. A similar setup was recently used by Martin *et al.* [10] for heating neutral clusters. With the aftercooler the ion intensity is reduced by a factor of about 5. A carbon resistor attached to the copper tube measures 30 ± 5 K, giving a lower bound to the cluster temperature. Judging from the result of Refs. [9–11], a cluster temperature 3 to 6 K higher than the copper tube is expected. A cluster temperature of 35 ± 5 K is therefore a reasonable estimate. At this temperature the atoms in the cluster can be expected to make only small amplitude oscillations, i.e., the cluster should be solid [13].

For the data recorded at the highest temperature, the electric discharge is switched off. Neutral clusters are ionized and further heated by photons from an excimer laser, which is indicated by the broken line in Fig. 1. An "evaporative ensemble" is thereby produced [14]. From the known dissociation energies $D(n)$ from Ref. [15] and by following the procedure described in Refs. [15,16], one can calculate the internal energy distribution, whose mean corresponds to a "temperature" of 700, 650, and 380 K for $n = 4$, 7, and 11, respectively. The absolute width is roughly equal to $D(n)$ giving ±600, ±450, and ±180 K for increasing n. As the melting point (371 K for bulk sodium [17]) decreases with cluster size [10], it is expected that most of the clusters produced by the evaporative ensemble technique will be liquid.

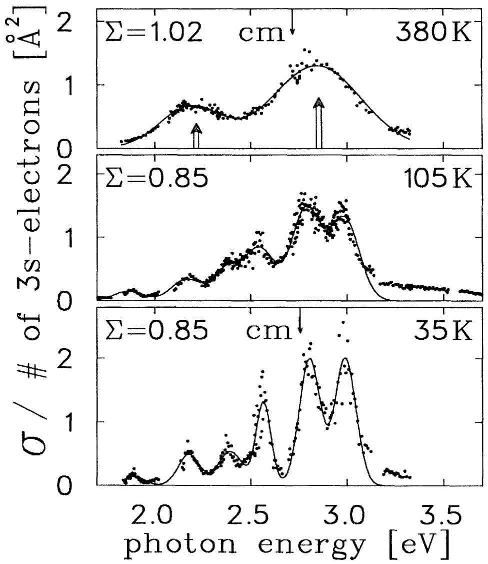

FIG. 2. Optical spectrum of Na_{11}^+ at three different temperatures. The six lines observed for cold clusters become broader with increasing temperature and merge into two broad peaks at the highest temperature. See also caption of Fig. 3.

The clusters and cluster ions traverse a skimmer, and a small packet of ions is ejected with a pulsed electric field into a reflectron time-of-flight mass spectrometer (TOF 1) having a resolution of $m/\Delta m \approx 2000$. The clusters are then irradiated by photons from an excimer pumped dye laser. The number of photons ϕ per area and pulse is measured absolutely using a calibrated pyroelectric detector (PED). The photon induced electronic transitions relax very quickly into nuclear motion, which leads to the ejection of an atom, as indicated schematically in Fig. 1. This so-called depletion spectroscopy [3,4,18] allows us to measure the absolute photoabsorption cross section σ by determining the laser fluence dependence of the ratio of the numbers of clusters with (N) and without (N_0) laser interaction: $N/N_0 = \exp(-\sigma\phi)$. The overlap b between cluster packet and laser pulse is reduced to about 90% to achieve a more stable and reproducible operation; beam instabilities and thermal drifts have a much smaller influence in this case. The absorption law then has to be modified:

$$N/N_0 = 1 - b + b\exp(-\sigma\phi). \qquad (1)$$

Two modes of data acquisition are used concurrently. In the first slow mode the ϕ dependence of N is measured accurately for one or two photon energies of each laser dye range. The value of N_0 is measured when the laser is off, using the measuring scheme described earlier [16]. From a fit by Eq. (1), the absolute cross section and the overlap b are obtained. It has been observed that b does not vary over the range of one laser dye, provided the laser beam profile in the interaction region is kept constant. This makes a second mode of data taking possible, which is faster by about a factor of 40. While scanning the wavelength, the laser intensity is automatically adjusted such that $N/N_0 \approx 0.5$–0.7. Taking the overlap b from the slow data taking procedure, the cross section can be obtained from Eq. (1). The pointing direction and the intensity of the laser have to be under computer control for this new, fast way of data acquisition; without it the lowest temperature experiment would not have been possible because of the heavy cluster ion loss in the aftercooler. The estimated error in the absolute value of the total cross section is less then 10%. The dominant contribution to this error stems from the uncertainty in calibrating the pyroelectric detector.

Optical spectra have been measured for several Na_n^+, $n \leq 15$, at three temperatures [$T \sim 35 \pm 5$, 105 ± 7 K, and T (evaporative ensemble)]. While the entire data set will be presented elsewhere [12], we focus here on the $n = 4$, 7 and 11 results (see Figs. 2 and 3), as they display the main observed features, which are as follows: (1) open shell clusters have a stronger temperature dependence of their optical spectrum than the closed shell clusters, for which a temperature dependence has been published earlier [19], (2) a small redshift of the mean absorption is seen with increasing temperature (4.4%, 5.7%, and 1.5% for $n = 4$, 7, 11, respectively), and (3) the sharp lines observed at low temperature broaden with increasing temperature by a factor of 4 or larger, and then merge into broad structures. The number of maxima stays the same for $n = 4$, while for the two heavier clusters only two maxima remain for high T. For Na_{11}^+ a spectrum at the intermediate temperature of 105 ± 7 K shows poorly resolved single lines, which become much sharper at a lower T. The peak positions of our high temperature Na_{11}^+ spectrum agree within 1% with those published earlier [18]. Fitting Gaussians by the high temperature data, one obtains for the ratios of the oscillator strengths [20] 1.6:1 for $n = 7$, and 1:2.8 for $n = 11$, in which the first number refers to the area under the lower energy peak.

As discussed in the introduction, there are two different methods used today for the calculation of optical spectra of small alkali clusters: quantum chemistry and methods based on the nearly free electron approximation. Very recently Bonačić-Koutecký *et al.* have calculated the spectra for Na_n^+, $2 \leq n \leq 21$, using the first method [21]. For Na_4^+ the calculated energies of the three dominant lines deviate 1% to 4% from the experimental result (see Fig. 3). The calculated peak heights are also in good agreement with experiment. Three absorption lines are calculated for $n = 7$ similar to those seen experimentally. For $n = 11$, the experimental and calculated spectra agree qualitatively, i.e., several resonances are present with increasing strength up to 3 eV with a small foot at higher energies. But a one-to-one correspondence of the peaks has not yet been achieved.

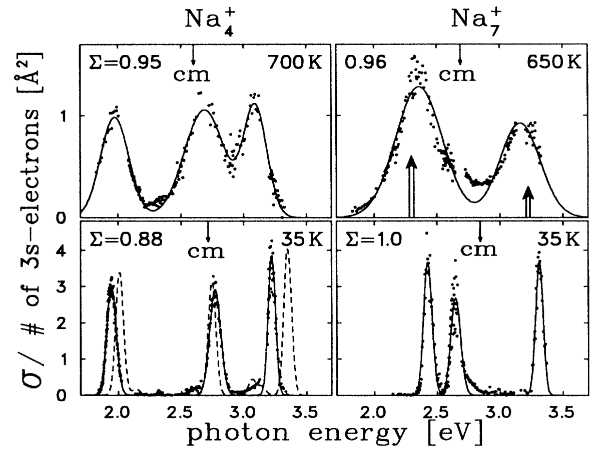

FIG. 3. Optical spectra of Na_4^+ and Na_7^+ at the lowest and highest temperatures. The solid line is a sum of Gaussians, fitted by the data. The dashed line for cold Na_4^+ gives the quantum-chemical results of Ref. [21], broadened by the experimental linewidth. The double arrows for hot $n = 7$ show the calculated energy and relative intensity of the modified jellium calculations of Ref. [25], while the arrows marked CM indicate the mean of the spectrum, which shifts slightly to the red with increasing temperature. Σ is the total oscillator strength per valence electron, obtained by fitting Gaussians by the data.

The decreasing agreement of calculated and measured spectra with increasing cluster size is to be expected in view of the complexity of these *ab initio* calculations. Nevertheless, one must conclude from the good agreement for cold Na_4^+ that its absorption spectrum arises from electronic transitions between the ground state and three electronically excited states of this molecule. It seems very likely that this interpretation can be extended to $n = 7$ and 11. Indeed, in a similar experiment with Li_7^+ we have recently resolved vibrational structure [12], which justifies this "molecular" interpretation. Also, as discussed below, the jellium type calculations are unable to reproduce the low temperature data.

Alternative approaches for the calculation of the optical spectra of sodium clusters neglect the ionic structure or treat it in some average way. The simplest approach is to assume the classical response of a spheroidal metal particle [3,18] allowing a calculation of the ratio of the spheroid's two axes from the experimental peak positions [22]. From the experiment with hot clusters, Na_7^+ is found to oblate, while Na_{11}^+ is prolate, with both results in good agreement with the Nilsson-Clemenger model [23]. The observed redshift of the mean of the optical spectrum is also compatible with the classical response of a spheroidal particle, if the bulk thermal expansion coefficient is used to calculate the temperature dependence of the density. The reduced electron density at higher temperature leads to a reduced mean absorption energy, which is 4%–5% for $n = 4$, 7 and 2.4% for $n = 11$, in qualitative agreement with experiment. The lower shift for $n = 11$ is due to the smaller temperature difference between hot and cold Na_{11}^+ compared to that for Na_4^+ and Na_7^+.

The more detailed local density calculations derive the confining potential for the electrons in the nearly free electron or jellium approximation, which has often been applied to alkali metals in bulk, surface, and cluster form [1–5]. A series of lines is obtained for the optical response of an open shell jellium cluster in the early calculation by Ekardt and Penzar [24] on Na_{10} and the more recent one by Reinhard [25] for Na_{11}^+. Both obtain five strong lines with positions and intensities in disagreement with the data at 35 or 105 K. This inability of the jellium model to explain the low temperature spectra is probably due to the basic assumption of the quasifree electron model: the neglect of ionic structure.

On the other hand, the global strength distribution of the unpublished calculations [25] based upon a smoothed edge jellium potential agrees within 2.5% with the experimental peak positions for hot $n = 7$ and 11 (thick arrows in Figs. 2 and 3). Thus this jellium model is able to explain the peak positions of the high temperature spectra. Apparently hot, liquid Na clusters are nature's best realization of the popular jellium model for clusters.

For a simple spheroidal deformation one expects a ratio of the dipole mode oscillator strength of 2:1 for oblate and 1:2 for prolate clusters [2,3]. But other than spheroidal deformations and the ionic structure mediate a redistribution of the oscillator strength up to 40% [25]. Thus the experimental ratios (1.6:1 for $n = 7$ and 1:2.8 for $n = 11$) appear to be compatible with the jellium model.

How can one understand that two theoretical approaches which are so different in concept give, nevertheless, good to satisfactory agreement with the data although at different ends of the temperature scale? A quantum-chemistry calculation is essentially performed at a temperature $T = 0$. An average over the thermally accessible cluster geometries is necessary for higher T. The jellium approach inverts the role of this sequence by first averaging over nuclear coordinates and then calculating the spectrum. As the averaging washes out any nuclear structure, it is not surprising that the jellium approach gives the spectrum of the liquid clusters, where the nuclei can move freely and are only confined by the electrons.

In summary, the range of validity of the two theoretical methods currently used for simple metal clusters (quantum chemistry versus jellium) has been experimentally tested. From a comparison of theoretical results with data on the temperature dependence of the optical spectra of Na_n^+, $n = 4$, 7, and 11, we deduce that small cold clusters are described best by *ab initio* quantum-chemical calculations, while the spectra of hot liquid clusters for $n \geq 7$ can be treated as oscillations of a nearly free electron gas in a spherical or spheroidal container. Two experimental innovations have been used: (1) a variable temperature source, which can generate cluster ions with a canonical distribution of internal energies and (2) an experimental procedure which speeds up the measurement of their optical spectrum.

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