Laser Spectroscopy of Alkali-Doped Helium Clusters

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A beam of He_N clusters ($10^3 \lesssim N \lesssim 10^4$) is seeded with one or more chromophores by sticky collisions with a low pressure gas and is probed, thereafter, by laser-induced fluorescence spectroscopy. Using sodium, we observe the spectra of atoms, dimers, and trimers and find that they are almost unshifted from their gas phase counterparts, but show cluster-induced broadenings in the range of tens of cm^{-1}. Upon formation on the cluster surface, a fraction of the dimers desorbs slowly and becomes part of the beam, allowing narrow, rotationally resolved, spectra to be obtained.

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Since the pioneering work of Becker, Klingelhöfer, and Lohse [1], large ($N \gtrsim 10^3$) helium clusters have been the object of several studies, which, using a variety of techniques [2–6], have aimed at detecting possible signatures of boson condensation in these, highly quantum, finite size, systems [7–9]. These clusters (which have a calculated temperature of 0.4 K [10] and are capable of capturing in flight foreign atoms or molecules [11]) have only recently been probed by spectroscopic means, both in our laboratory [12] and at the Max-Planck-Institut für Strömungsforschung in Göttingen [13,14]. These experiments, all of which have been carried out in the infrared, have been marred by resolution problems (due to the use of CO_2 lasers [12,13]) or by limited spectral coverage (due to the use of diode lasers [14]) and have stopped short of establishing the clusters' temperature or of demonstrating the physical effects of boson condensation.

In this Letter we would like to report on the use of high resolution laser-induced fluorescence, in the visible region of the spectrum, to probe large helium clusters doped with one or more alkali atoms. Alkalis have been chosen as probes because the spectroscopic and optical properties of their clusters are known [15–17], because a few spectroscopic studies also exist on alkali atoms and molecules dispersed in bulk helium [18], because the behavior of small metallic clusters is of substantial fundamental importance, and, finally, because the study of light metals dispersed in highly quantum matrices (He, H_2) is of considerable applied interest [19].

A schematic diagram of the experimental arrangement is displayed in Fig. 1. The apparatus, which has been used in previous experiments involving the infrared spectroscopy of SF_6 attached to helium clusters, has been described elsewhere [12,20,21]. Expanding He from a 10 μm nozzle, at temperatures down to 12 K and stagnation pressures up to 10^4 kPa, this apparatus can produce a beam of helium clusters ranging in average size up to 10^4 atoms/cluster. Doping the clusters with chromophores is achieved by placing a heated pickup cell directly behind the collimating skimmer. A heated tube connecting the pickup cell to an alkali reservoir establishes the necessary Na partial pressure of 10^{-3}–10^{-1} Pa inside the cell. The latter is normally kept at a temperature 100 K higher than the reservoir to avoid alkali atom distillation and to keep the alkali vapor free of dimers. According to the value of the alkali pressure in the cell, the larger clusters pick up one or more alkali atoms without being appreciably deflected from their path. For each alkali pickup, about 150 He atoms evaporate from the cluster [22]. A few centimeters downstream of the scattering cell, at the center of a two-mirror laser-induced fluorescence (LIF) detector of standard design [23], the clusters are crossed with the well baffled output beam of a tunable dye laser. The fraction of the photomultiplier signal which is phase related to the chopped cluster beam, is measured using a lock-in amplifier. A Langmuir-Taylor surface ionization detector, located beyond the LIF detector, is used to monitor the presence of the alkali atoms in the beam. It also aids in establishing the optimum cluster source and pickup cell conditions for maximum cluster flux and desired alkali dopant concentration in the clusters.

The excitation spectrum of the doublet transition ($3\,^2P_{1/2}, 3\,^2P_{3/2}$-$3\,^2S_{1/2}$) of sodium atoms attached to the helium clusters appears as fluorescence which is characterized by a very small shift and a 50 cm^{-1} wide blue tail (at a cluster source temperature of 14.5 K and a He stagnation pressure of 7×10^3 kPa). Following the scaling laws for cluster formation in supersonic jets [24–26], the cluster size distribution can be changed in the range from a few hundred to several thousand atoms by varying the He source conditions. Increasing the nozzle temperature

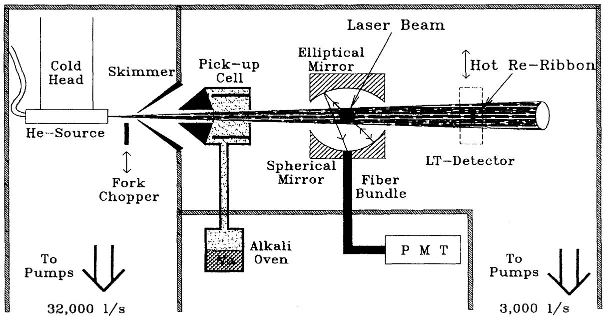

FIG. 1. Schematic diagram of the experimental setup.

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up to 27 K lowers the mean cluster size and decreases the linewidth to 15 cm^{-1}. The interpretation of these spectra requires the calculation of the elastic and inelastic interactions between the atoms and the superfluid helium cluster and will have to be postponed to a later time.

The more structured Na_2 spectra are more easily interpreted and, therefore, they form the core of the results reported and discussed here. What is already clear is that because of the almost total absence of spectral shifts, both atoms and molecules (see below) must reside on the cluster surface as suggested by the density functional calculations of Dalfovo [27], by the recent work of Cole and co-workers [28], by qualitative considerations based on the extreme weakness of the alkali helium interactions [29], and, last but not least, by the fact that the excitation spectra of alkali and other atoms immersed in liquid He *are* shifted to the blue by amounts variable from 700 cm^{-1} for the $B \leftarrow X$ transition of Na_2 [18] to 220 cm^{-1} for the D_1 line of Cs [18] to 270 cm^{-1} for the $6s6p\,{}^1P_1 \longleftarrow 6s^2\,{}^1S_0$ transition of Ba atoms [30].

Molecular sodium spectra have been obtained in the frequency range between 14 500 and 16 500 cm^{-1} by using initially a Spectra Physics 380 tunable ring dye laser at 5 GHz resolution. Figure 2 shows a spectrum at a cluster source temperature of 19 K and a He stagnation pressure of 7×10^3 kPa. The spectrum consists of three main groups of spectral features that will be discussed separately.

The first very strong group is detected between 15 800 and 16 500 cm^{-1} with a sharp intensity threshold near 15 800 cm^{-1}. This spectrum is about 100 times more intense than the bands observed at lower frequencies, which can be unambiguously identified as being produced by sodium dimers (see below). The intensity of this structure shows a higher order dependence on the Na partial pressure inside the pickup cell than the dimer bands. This suggests that the measured intensities may be due to a process involving three or more Na atoms. The *B*-*X* system of the trimer lies in this region, but has a completely different rovibrational structure [16,31]. Changes in the vibronic coupling in the trimer due to its interaction with the He_N cluster could alter the picture, in particular with respect to the pseudorotational behavior present in the free trimer. The sharp intensity threshold at 15 800 cm^{-1} is peculiar and may indicate a minimum energy requirement that will be the subject of further study in the near future.

The second group of features that follows the first moving toward the red can be identified as due to Na_2 $A\,{}^1\Sigma_u^+ - X\,{}^1\Sigma_g^+$ transitions. The threshold frequency of each subband and the spacings between these (center of Fig. 2) agree well with the corresponding quantities for gas phase Na_2. In contrast to the gas phase, where the width of a sub-Doppler line is limited only by its lifetime to 13 MHz [15], each of the bands measured here consists of a *relatively* sharp (≈ 1 cm^{-1}) line and an 80 cm^{-1} broad feature extending toward the blue. The spectrum is similar to the phonon wings of the vibrational bands of diatomics in solid rare gases as observed in matrix-isolation spectroscopy [32]. Decreasing the cluster size by raising the nozzle temperature to 22.5 K narrows the width to 25 cm^{-1}. The observation of these spectra is strictly correlated to the production of He clusters and the bands disappear for nozzle temperatures $T \gtrsim 25$ K. In spectroscopic experiments carried out by Takahashi *et al.* [18] of Na_2 in liquid helium, no absorption in this wavelength region has been reported, and the orange emission spectrum obtained could not unambiguously be assigned to either the $A\,{}^1\Sigma_u^+$ or $B\,{}^1\Pi_u$ state.

Since the low resolution scans indicated the presence of higher resolution structures, a Coherent 699-21 ring dye laser (~ 1 MHz bandwidth) was used to scan over a

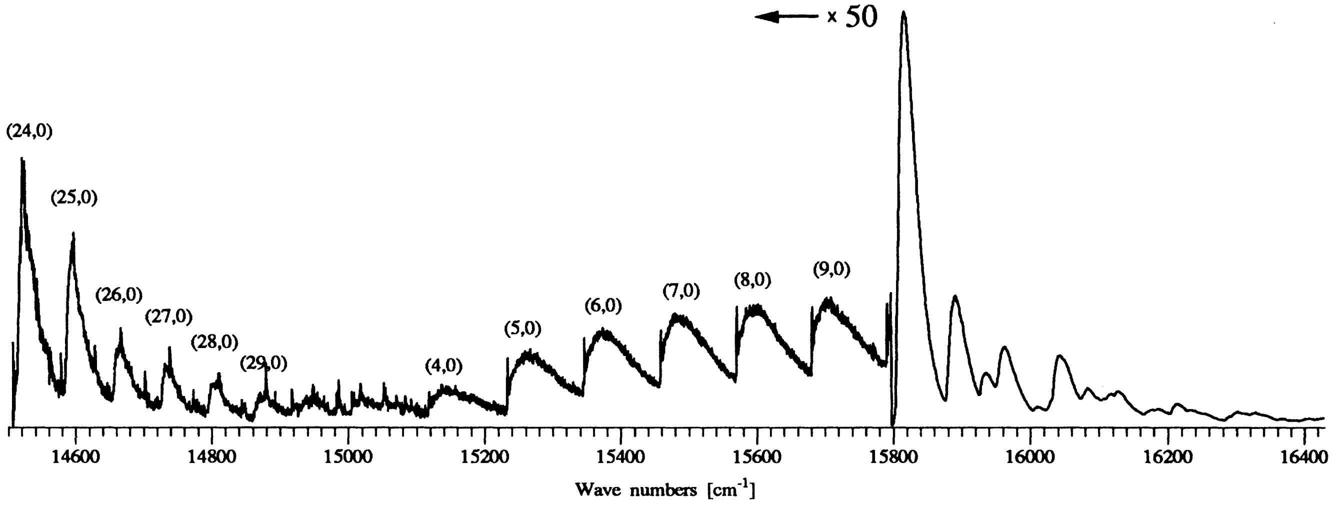

FIG. 2. Laser-induced fluorescence spectrum recorded at 5 GHz resolution showing the sodium dimer vibrational progression exciting the lowest triplet state (left) followed by the progression exciting the Na_2 singlet ground state (center) and a spectrum of the sodium trimer attached to a helium cluster.

6 cm^{-1} interval of the $A\,^1\Sigma_u^+ - X\,^1\Sigma_g^+$ (9, 0) vibrational band. The results are shown in Fig. 3. A very large fraction of the observed lines can be assigned as rotational lines of the (9, 0) band as indicated in the figure. The absolute line positions agree with those of the free sodium dimer [33] within the 0.01 cm^{-1} accuracy of the frequency measurement. The intensity of the narrow lines scales with the intensity of the broad band envelopes, and the lines disappear under the same conditions as the envelopes ruling out the pickup cell as a possible source of free dimers. The linewidth of the (Lorentian) rotational lines narrows with decreasing laser intensity to a value of 80 MHz obtained at 50 mW/cm^2 where some power broadening is likely to be present. A plot of the degeneracy corrected line intensities versus rotational quantum number revealed that a unique rotational temperature cannot be derived. The relative intensities of the four lowest states are consistent with a temperature of 3 K, but higher rotational states (up to $J = 12$) show intensities which are much greater than those expected for such a temperature.

Since the identified rotational lines exhibit no shift compared to the gas phase molecular line positions of Na_2 (and therefore the molecular constants have not changed) but the spectrum disappears in the absence of large He clusters, the Na atoms must first be picked up by the He clusters and must form sodium dimers on the cluster surface. The weak binding to the He cluster, the presence of large quantities of angular momentum from the pickup and the recombination process, together with the disposal of the recombination energy, cause the desorption of a fraction of the molecules from the cluster surface at a velocity which, due to the extreme softness of the helium surface and its low temperature, may be quite low. A fraction of these dimers then travels to the detector with the clusters and gives rise to features that reflect their gas phase nature. The small amount of kinetic energy associated with this evaporation process was detected as follows: the crossing point of the laser beam was shifted across the cluster beam profile and a larger divergency for the narrow lines compared to the broad features measurable even when the signal due to the broad features has become negligible, which shows that the presence of the free molecules is not due to a two photon process where the first photon would desorb the molecule and the second would detect it. Unfortunately the lack of equilibration of the molecular angular momentum does not allow the use of the intensity distribution of the rotationally resolved spectra for the determination of the clusters' temperature, but further analysis may provide very detailed dynamical information on the interaction of a diatomic molecule with a helium surface.

The broad line shown at the center of Fig. 3 corresponds to the "narrow" peaks located at the beginning of each vibrational band mentioned before. The redshift with respect to the gas phase band origin is constant for each vibrational band (2.4 cm^{-1} independently of cluster size). This indicates that the vibrational constants of the sodium dimer attached to the cluster are equal to those of the free molecule. If the line at the origin of each vibronic envelope is taken as a "zero phonon" line, then the 80 cm^{-1} band extending toward the blue can be attributed to a phonon sideband arising from an inelastic Stokes process involving the combined excitation of the Na_2 and the phonons of the helium cluster, which are coupled to the optical excitation of the Na_2 by the repulsive interaction between the valence electrons and the helium surface [34]. Naturally this sideband will be broadened and shaded toward the blue in a similar way as the atomic lines described above.

Finally, below 15 000 cm^{-1}, another vibrational progression is observed which is due to the presence on the clusters' surface of van der Waals bound triplet dimers which form with probability 3 times larger than the singlet molecules. The assignment of this progression to the $1\,^3\Sigma_g^+$-$1\,^3\Sigma_u^+$ transition of Na_2 and its interpretation is reported elsewhere [35]. The 30 cm^{-1} width of these bands indicates the smaller coupling of the triplet to the He cluster compared to the singlet molecule.

Beyond opening the door to the probing of properties of the host cluster, this work shows that liquid helium

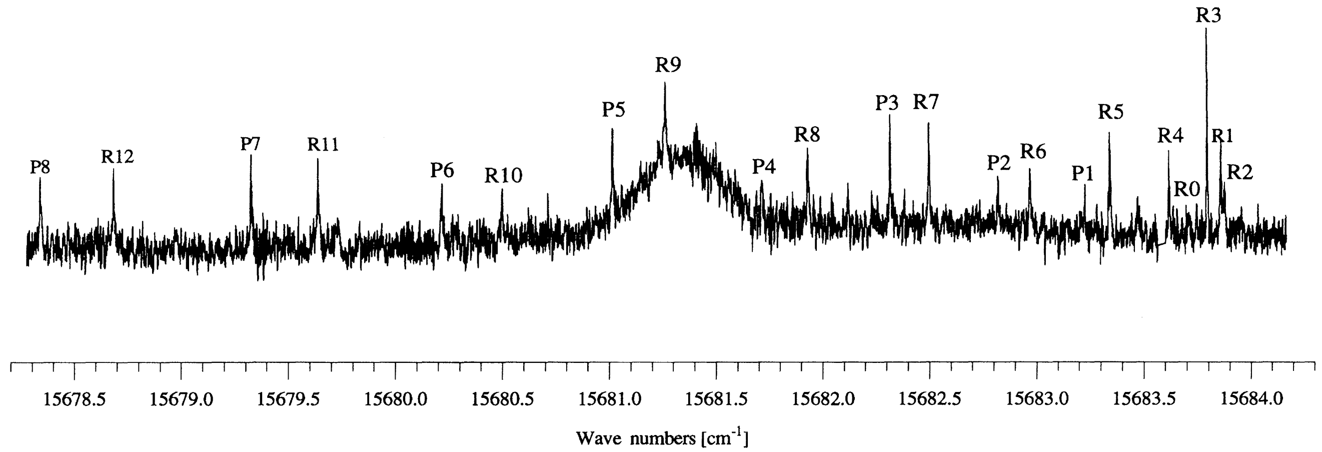

FIG. 3. Spectrum at the beginning of the (9, 0) band of the Na_2 singlet transition at 1 MHz spectral resolution.

weakly or strongly bound molecules can be formed and studied with both vibrational (on the cluster) and rotational (after evaporation) resolution.

The investigation of alkali trimers formed at the surface of a cold He cluster in their doublet state can reveal if the small interaction with the He neighbors affects the strong coupling of electronic and nuclear motion in these molecules. Furthermore, the study of the Na_3 quartet state may give us very detailed insight into the three-body component of the physical part of intermolecular forces. By using a second pickup cell, it will be possible to form mixed clusters of predetermined composition. For instance, mixed singlet and triplet dimers can be prepared, the latter being nearly impossible to form using the presently available methods. The new "matrix-isolation" technique described here has the advantage, over bulk-matrix methods, of providing to the spectroscopist all the flexibility of molecular beam based methods. Photoionization spectroscopy can be applied and large electric fields can be used without interference from electrical discharges and breakdown. Finally, we wish to note that access to the much desired cluster temperature measurement may be provided by experiments in which electronic spin transitions would be monitored. In summary, LIF spectroscopy of doped helium clusters appears to be a very promising technique for a large variety of experiments.

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