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Detachment of metastable helium molecules from helium nanodroplets

S. Yurgenson, C.-C. Hu, C. Kim[a], and J.A. Northby

Physics Department, University of Rhode Island, Kingston, RI 02881, USA

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Abstract. Metastable helium $a^3\Sigma_\mathrm{u}^+$ molecules are produced in helium nanodroplets by electron bombardment, and become attached to their surface. Photo induced electronic transitions release them, and they are subsequently detected when they eject secondary electrons upon reaching a nearby surface. We report here the first high resolution spectroscopic study of this system. It reveals a highly non-thermal rotational state distribution with $N = 1$ and $11 \leq N \leq 29$ populated but with the intermediate N states missing. Further studies of the bombarding electron energy appearance threshold for the high rotational states suggest that their precursor is the atomic 2^3P state.

PACS. 36.40.Vz Optical properties of clusters – 67.40.Yv Helium impurities and other defects

1 Introduction

The study of the interaction of superfluid helium with microscopic impurities has played a major role in developing our understanding of this most interesting liquid [1, 2]. With the introduction of cluster beam methods, it has become possible to study finite helium systems [3, 4], and it is natural also to want to understand the onset and nature of quantum liquid behavior in droplets which are too small for conventional operational definitions of superfluidity to apply. In this case, attached microscopic impurities provide almost the only method by which we can probe the system, since the bare clusters alone are highly inert. In the past decade considerable progress in this direction has been made by utilizing captured atoms and molecules [5–7], as well as charged states (ions) produced by electron bombardment [8–10]. Of particular interest are the experimental determination [11] of cluster temperature (~ 0.37 K) and the demonstration [12] that quantum liquid behavior is present in systems with as few as 100 atoms. In this paper we will describe our recent spectroscopic studies of metastably excited helium nanodroplets, whose characteristic size is $\sim 10^6$ atoms. In this case, while we have been motivated by a desire to learn about the nature of superfluidity in a surface dominated system, the more significant aspect of the experiments may be that we are able to study the interaction of a single excitation with the superfluid. As will be seen, cluster methods permit a range of experiments which are impossible in bulk helium because of interactions between excitations.

Previous studies [13, 14] have shown that in clusters, as in the bulk [15], triplet excitons produced by electron bombardment evolve into long lived metastable excitations attached to the clusters, which are believed to be $a^3\Sigma_\mathrm{u}^+$ helium dimer molecules. This assignment has been confirmed by our previous low resolution spectroscopic studies [16–18] which identified both the $b \leftarrow a$ and $c \leftarrow a$ electronic transitions of this molecule. These experiments also showed that the rotational distribution of these molecules was anomalous, with mostly only high rotational states populated. The mechanism which allows us to perform spectroscopic studies of this extremely dilute species has been elucidated in a recent paper [19]. We find that molecules in the lowest triplet electronic state reside on the surface of the droplets, and that the result of a photo induced electronic transition is to detach them. They then drift to metallic surfaces surrounding the beam where they decay by ejecting an electron. These secondary electrons are then counted. We measure the time of flight of the released molecules and find two velocity groups, one thermal and one much faster. We suggest that the slow group corresponds to molecules directly detached in the excited electronic state, and the fast group corresponds to those which are released in the subsequent decay process.

Here we will describe the first high resolution laser spectroscopic studies of this system. As will be seen, these provide a unique and detailed method of studying the interaction of this molecule with the surface of helium. We will concentrate here on some of the more qualitative aspects of

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[a] *Present address:* Physics Department, Brown University, Providence, RI 02886, USA

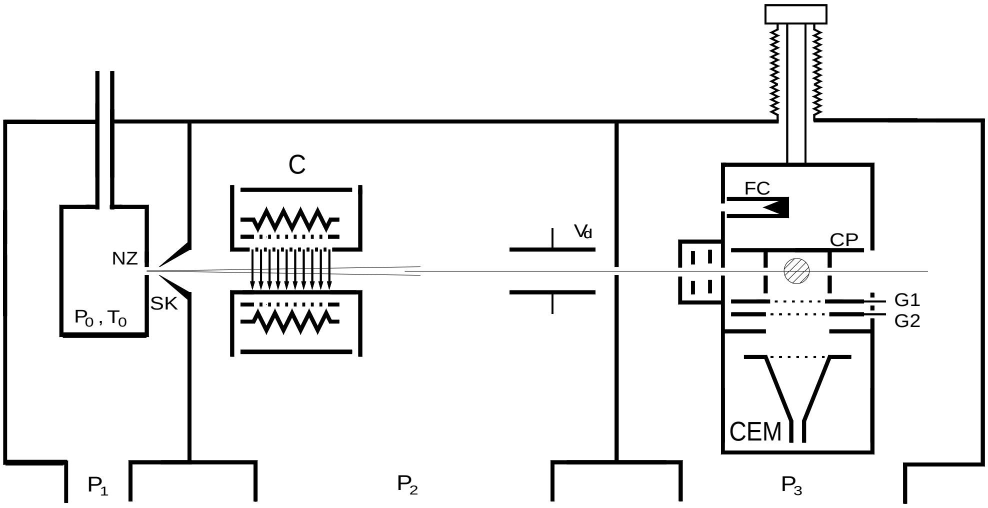

Fig. 1. Schematic of the apparatus. The laser beam (not shown) is normal to the page and intersects the cluster beam in the hatched region above the channel electron multiplier, CEM.

the initial data, with detailed quantitative discussion left for future communications.

2 Experiment

A schematic diagram of the apparatus is given in Fig. 1. Purified helium gas at $T_0 \sim 7.5\,\mathrm{K}$ and $P_0 \sim 20\,\mathrm{bar}$ expands through a $5\,\mu\mathrm{m}$ nozzle into a differentially pumped vacuum. Under these supercritical expansion conditions a broad droplet mass distribution is formed, with characteristic size $N \sim 10^6$ [20]. After skimming, the resulting beam passes through a radial electron impact excitation cell [17,18]. Its triode configuration allows us to vary the bombarding electron energy, E_e, and current independently, but the absolute energy and its distribution ($\Delta E_\mathrm{e} \sim 1\,\mathrm{eV}$) are only approximately known. A deflection field removes any charged products from the beam, and after a flight path of 76 cm and flight time of 4 ms, the neutral and metastably excited components enter the detection region. There they pass above a channel electron multiplier, CEM, which responds both to direct metastables and to secondary electrons emitted when metastable molecules strike surfaces surrounding the beam. Infrared light from a tunable external cavity diode laser [21] intersects the beam above the CEM in a multipass configuration. Its tuning range, 910 nm to 970 nm, coincides well with the $(0-0)$ rotational band of the $c^3\Sigma_\mathrm{g}^+ \leftarrow a^3\Sigma_\mathrm{u}^+$ electronic transition of the metastable $\mathrm{He}_2{}^*$ dimer. There is a background signal which results from spontaneously released molecules, but the signal increases sharply when the laser wavelength corresponds to several of the known electronic transitions of this molecule [22]. The light is mechanically chopped, and the light induced component of the signal as a function of wavelength is shown in Fig. 2. It is normalized to the laser power as measured by its internal monitor and also approximately normalized to the excited cluster current by dividing by the simultaneously measured background signal. The data are obtained point by point at fixed wavelengths, with an acquisition time of roughly 0.5 min per point. A low resolution scan (not shown) allowed us to identify the location of the peaks, but the density of points in the displayed figure is variable, and details of the curve are still being filled in. None the less, its main qualitative features are reproducible and ready for discussion.

Most of the peaks have been located to an accuracy of better than $0.1\,\mathrm{cm}^{-1}$ by simultaneous use of a temporarily borrowed wavemeter [23]. For the rest of the data we have used the laser's internal calibration which has a significantly lower accuracy ($\sim 1.0\,\mathrm{cm}^{-1}$). Whenever possible we have included a peak in our scan, and have shifted the data slightly until it coincides with its known location.

3 Results

The location of the known rotational transitions corresponding to the ground vibrational state of the molecule, measured in a room temperature discharge [22], are also indicated in Fig. 2. With two exceptions, all of our observed peaks are uniformly shifted to the blue by $2.7 \pm 0.1\,\mathrm{cm}^{-1}$ from one of these known peaks. The exceptions are the peak corresponding to the P(1) transition, which is blue shifted by about $2.4\,\mathrm{cm}^{-1}$, and the peak corresponding to R(1) which is also shifted by $\sim 2.4\,\mathrm{cm}^{-1}$ but split into three resolved components. The most notable qualitative feature of our data, however, is that numerous peaks visible in the gas are completely missing in the nanodroplet spectra. In particular, there is no evidence of peaks corresponding to the $N = 3, 5, 7$, and 9 transitions. The $N = 11$ transition is weakly visible at 939.2 nm in the P branch but we have not found the corresponding R branch peak at 912.8 nm where because of low laser power the noise is significantly greater. The other gas peak in our spectral range which we should see but do not is the R(31) peak. Finally, we note that there is no indication of any transitions in the first excited vibrational state$(1-1)$, whose rotational band head lies near 935 nm. Another qualitative feature of these data is that each peak has a very complex shape which is un-

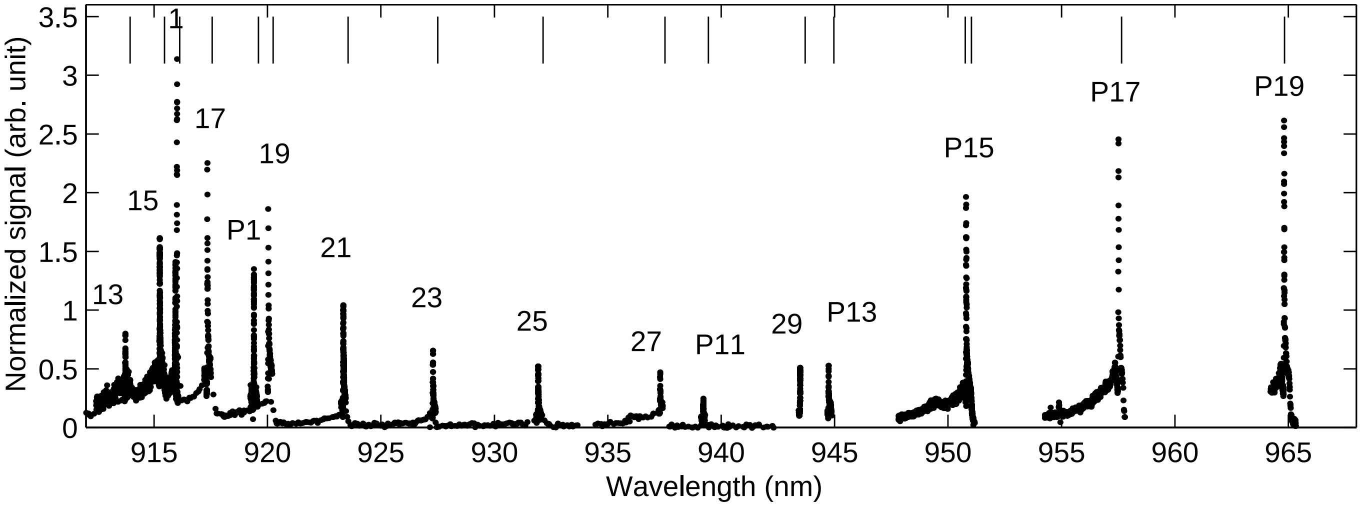

Fig. 2. Metastable detachment spectrum corresponding to the $c^3\Sigma_g^+ \leftarrow a^3\Sigma_u^+$ electronic transition of the He_2* molecule. Peaks are labeled with the N values of the corresponding free molecular rotational transitions in the $v = 0$ vibrational state. P branch peaks are indicated by a P; R branch peaks are unlabeled to save space.

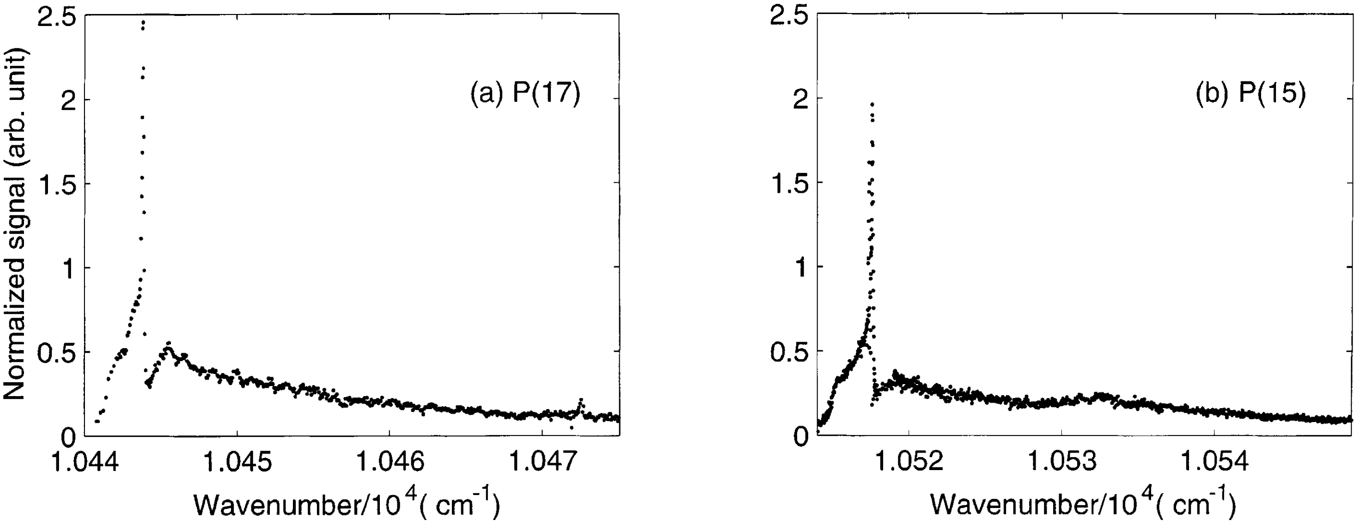

Fig. 3. Detailed spectra in the vicinity of (a) the P(17) peak and (b) the P(15) peak. The sharp peak feature in each case is shifted to higher energy by 2.7 cm^{-1} from the associated free molecular value.

doubtedly caused by the interaction of the molecule with the droplet. Examples of two of the P branch transitions, converted to an energy scale (cm^{-1}) are shown in Fig. 3. One can see that, because of the large rotational splitting in this molecule, the individual spectral lines *and their associated structure* are completely resolved. This should make them a uniquely valuable probe of the superfluid surface in the future.

4 Discussion

It is tempting to attribute the missing intermediate N spectral lines to some property of the underlying superfluid droplets, but in fact, similar highly anomalous rotational distributions also are found in studies of recombination in low temperature helium gas. Following the first reports by Callear and Hedges [24], other groups have studied this behavior as well [25]. They describe two groups of $v = 0$ molecules, those with $N < 11$ which appear to thermalize at a temperature comparable to the gas temperature and a group with $N \geq 11$, peaked around $N \sim 17 - 19$, which don't. In our case the molecules are very weakly attached to the clusters and it is likely that any molecule which undergoes a transition becomes detached. This in fact is probably the origin of our background signal. The models usually presented [25] to explain the origin of the highly rotationally excited states in the gas all involve ion-electron recombination, e.g., of He_3^+. This process is not sufficient to explain our results, however, as can be seen by the data in Fig. 4. There we examine the bombarding electron en-

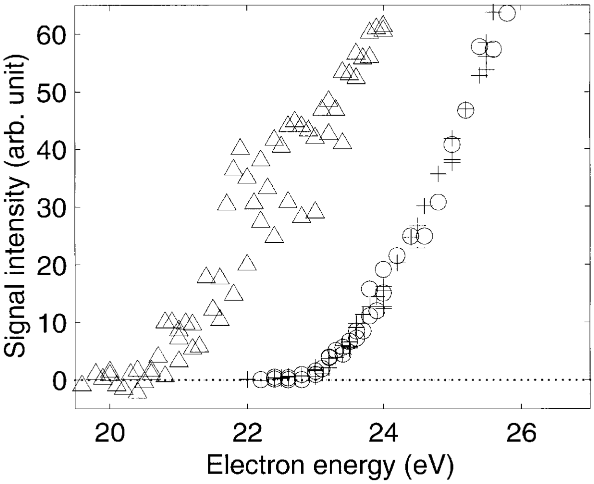

Fig. 4. Electron energy threshold for the appearance of the metastable detachment signal associated with the $N = 17$ transitions. +: at 917.3 nm. ○: at 957.3 nm. The triangles show the appearance of a metastable 2^3S_1 signal in helium gas with no clusters present, under the same electron beam conditions, which calibrates the energy scale.

ergy threshold for appearance of the P(17) and R(17) features [26] in our spectra compared with the threshold for producing atomic 2^3S_1 states in the room temperature gas measured under identical conditions. While such threshold comparisons are always somewhat ambiguous it apparently requires only about 2.2 ± 0.3 eV more energy to produce highly rotationally excited $v = 0$ molecules than to produce 2^3S_1 atoms in the gas. The least energetic process by which one can produce ions is by associative ionization [27] but this process requires excitation of the 3^3P state [28]. This state lies 3.2 eV above the 2^3S_1 state and thus ion recombination cannot play an essential role in forming the high rotational states found in our experiment. A possible explanation of the 2.2 eV shift can be had by assuming that the initial exciton is produced in the interior of the cluster. In order that the bombarding electron has enough energy to create the excitation and still escape the cluster it must retain enough energy to stay in the conduction band. Thus it must retain about 1.1 eV [14, 29] and we conclude that the excitation responsible lies 1.1 eV above the 2^3S_1 state. This coincides rather closely with the 2^3P state, and we suggest that eximer molecules derived from this state may be the relevant precursors.

The last free molecular peak which is not seen in our data is R(31). If shifted by the same amount as the others we would expect it to lie near 10 520 cm^{-1}, a region shown in Fig. 3b. In fact, there is a broad feature near 10 533 cm^{-1} for which we have no other explanation, and which might be an anomalously shifted and broadened R(31) peak. We note that the final state for this transition, $N = 32$, is probably the highest relatively long lived rotational state in the $c^3\Sigma_g^+$ state. A slight perturbation of the molecular potential induced by the surface might lead to enhanced predissociation, and possibly could explain such an increased shift and broadening.

In conclusion we note that these data contain a wealth of information about the formation of the helium "impurity" molecules and about their interaction with the nanodroplet surface. We have only discussed a very small part in this initial report. Hopefully it has been sufficient at least to demonstrate the power of this cluster based detachment spectroscopy. We would like to thank E. Chrissman for the loan of the wavemeter. This work was supported in part by the NSF (DMR9705242).

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