

Spontaneous and infrared induced electron detachment from negatively charged helium nanodroplets

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Received: 4 July 1996 / Final version: 15 September 1996

Abstract. A beam of helium nanodroplets, with sizes ranging up to $N = 10^7$ or more atoms, is produced by fragmentation of a low entropy supersonic expansion. It subsequently is excited by electron impact, producing various charged and metastable droplet states depending on the electron energy. We will describe experiments with negatively charged cluster ions, which are observed for low energy impacts when $N > 2 \times 10^5$. In these experiments, after a flight time in high vacuum of several milliseconds the droplets pass through a weak transverse field above an electron multiplier. A signal from spontaneously detached electrons is observed, which suggests that the ion, while long lived, is inherently metastable. Furthermore, when the beam is crossed with an infrared light beam above the detector, the detachment rate is significantly increased. The wavelength dependence of this light induced signal has a broad peak near $1.5 \mu\text{m}$. By deflection measurements it is found that the spontaneous detachment signal comes preferentially from smaller clusters, while the light induced signal comes predominantly from larger ones. By stopping potential measurements one can conclude that both kinds of detached electrons have energies below 1eV, with photo detached electrons the more energetic.

PACS: 67.40.Jg; 36.40.Wa

1 Introduction

When helium gas expands from a stagnation state with entropy less than the critical point entropy, its expansion isentropic enters the coexistence region from the liquid side and the material fragments into nanodroplets [1–5] with masses ranging up to 10^7 atoms or more. These will cool by evaporation, but because of the unique properties of helium they should remain in the liquid state. Much recent effort has been expended in developing methods to study these structures, such as by captured impurities [4, 6], synchrotron radiation [7, 8], and electronically excited metastable states of helium [9]. In the present paper we will describe our

recent experiments involving attachment of electrons to helium nanodroplets. Large, negatively charged helium clusters were first observed by Gspann [10]. Since the dominant short range part of the electron-helium interaction is strongly repulsive, understanding the mechanism of attachment is a challenge. Two possible delocalized states have been suggested for binding an electron to a droplet; an exterior electron state [11] similar to that known to exist on bulk helium surfaces [12], and an interior state [13, 14] in which the electron resides in a cavity, or bubble [15], inside of the droplet. The surface state is a weakly bound state, while the bubble state is inherently metastable. A third, stable structure, in which the electron is localized on a captured impurity also must be considered. Our previous studies of the negative ion mass distributions, and of the electron energy dependence of the capture process, have led us to argue that interior bubble state is the most likely structure [14]. We have also suggested that this state should be optically active in the infrared. In order to understand why this may be so, let us review briefly earlier spectroscopic studies of electron bubbles in the bulk liquid.

An excess electron in bulk liquid helium behaves as if it moved in a density dependent potential [15] which, for undisturbed helium, is about 1.1eV above the vacuum level [12]. The system energy is minimized by localizing the electron in a cavity of radius $\sim 17\text{\AA}$ [16]. Assuming a sharp cavity wall, the excited states are those of an electron in a 1.1eV deep spherical potential well. Photoexcitation into quasifree continuum states was first seen to be peaked near $1\mu\text{m}$ at vapor pressure [17]. Experiments at higher pressure [18] showed an enhanced effect which has been interpreted [19] to be a $1s \rightarrow 2p$ bound state transition. Most recently, Grimes and Adams [16] have studied the $1s \rightarrow 1p$ bound state transition.

It is reasonable to assume that if such a bubble structure also existed in a nanodroplet, excitation of a trapped electron to a quasifree continuum state could well detach the electron from the drop before it could rethermalize into another bubble. In fact, it seems probable that even a transition to an excited bound state could lead to an enhanced detachment probability, either via increased tunneling from the excited state, or via recoil associated with return to the

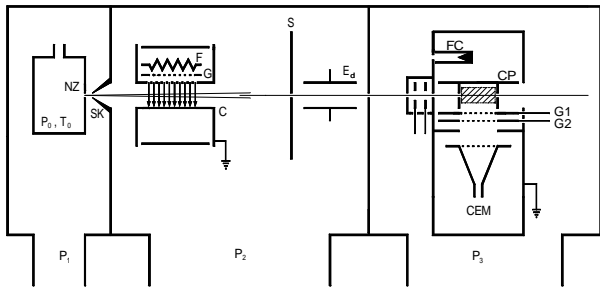


Fig. 1. Schematic of the apparatus.

ground state. Consequently we have undertaken a search for photodetachment of electrons from negatively charged helium nanodroplets induced by infrared light.

2 Apparatus

A schematic of our electron detachment apparatus is illustrated in Fig. 1. High purity (99.9999%) compressed helium gas at pressure P_0 is cooled to a low temperature T_0 by a commercial continuous flow helium cryostat in thermal contact with the stagnation chamber. The gas expands through a $5\mu\text{m}$ diameter supersonic nozzle, NZ, into a diffusion pumped expansion chamber ($P_1 \sim 6 \times 10^{-7}\text{bar}$), where it cools adiabatically and forms clusters. The nature of the cluster mass and velocity distributions is controlled by T_0 and P_0 . Under our typical source conditions, $T_0 = 7.5\text{K}$ and $P_0 = 20\text{bar}$, the expansion isentrope passes into the coexistence region from the liquid side and the clusters or nanodroplets which form by fragmentation can become large enough ($N > 2 \times 10^5$) to attach electrons. They all move with roughly the same velocity, and the resulting energy per atom is typically $\sim 1\text{meV}$. These nanodroplets should evaporate and cool to below 0.5K in less than a microsecond [20]. After about a centimeter the central beam is extracted through a 0.5mm diameter skimmer, SK, into a second differentially pumped chamber ($P_2 \sim 3 \times 10^{-9}\text{bar}$). The beam next passes through an electron impact ionizer located a few centimeters behind the skimmer. Electrons flow radially from filaments F through a control grid G and into a collector cage C at ground potential where they intersect the beam. Their kinetic energy in the nominally field free interaction region is determined by the filament voltage V_f , while the current is controlled by the grid potential. In the experiments described here, the electron energy is kept well below that required to electronically excite or positively ionize helium ($eV_f < 7\text{eV}$). Thus the only ions produced are nanodroplets negatively charged by electron capture. Since there is negligible momentum exchange associated with capture, these leave the interaction region with their velocity essentially unchanged. An aperture S further collimates the beam. It is also possible to deflect the low energy and hence low mass ions out of the beam by a transverse voltage E_d , before it enters the last differentially pumped chamber ($P_3 \sim 2 \times 10^{-10}\text{bar}$) which contains the detector assembly.

A perpendicular infrared light beam intersects the cluster beam in the hatched region above a channel electron multiplier, CEM. Electrons released in this region are directed

by a weak electric field through a series of grids and into the multiplier where they are counted. Some information about their energy can be obtained by using grid G2 as a stopping potential analyzer. Our light source is a 1000W quartz tungsten-halogen lamp. Broad band measurements were made by chopping the light and directing it through various infrared transmitting filters and a sapphire viewport to the interaction region. Narrow band measurements were made by placing a 0.25m Ebert grating monochromator in series with the filters. The power is measured with a thermocouple mounted in the chamber behind the interaction region. The entire detector assembly can be rotated about a vertical axis for alignment, and also moved vertically so that the total direct beam current, typically $\sim 1 \times 10^{-12}\text{A}$, can be measured by a Faraday collector, FC.

3 Experimental results

A Spontaneous detachment signal

Our first observation is that when there is a negatively charged direct beam, as measured by the Faraday cup, there is a significant (~ 200 counts/s) electron signal measured at the CEM detector - even with no light present. When we pulse the ionizer current, the corresponding CEM pulse, shown in the inset of Fig. 2, arrives delayed by the time of flight of the clusters. The width of the received pulse is accounted for by the finite ionizer and detector lengths, and by the ionizer pulse width. This indicates that the electrons arrive attached to the clusters and are released above the detector. The release mechanism is not related to the very weak field in the interaction region, since $\sim 15\%$ of the signal still remains even in its absence. It does not seem to be related to cluster collisions with collimating surfaces either. While such effects can be seen with poor alignment, careful adjustment apparently can eliminate them. Finally, we have tried to determine if background gas collisions could induce detachment, by deliberately increasing the background gas pressure. When the residual gas pressure is increased by lowering the liquid nitrogen level in various cold traps, however, the detachment signal decreases while the direct beam signal observed with the Faraday collector increases. We conclude that this release is truly spontaneous, indicating that the electrons are only metastably attached to pure clusters. Background gas impurity collisions actually appear to stabilize their attachment.

B Broad band light induced detachment signal

Our second observation is that when the infrared light is turned on, the counting rate from detached electrons increases. Since the total effect is small, we have made most of our measurements using filters to roughly determine the wavelength. The first filter, F1, is a heat transmitting glass which transmits between 0.8 and $2.6\mu\text{m}$. The second, F2, is a long pass interference filter which, together with the sapphire window, transmits between 2.5 and $6.0\mu\text{m}$. Figure 2 displays the electron detachment rate, normalized to its spontaneous background value, as a function of time. The light

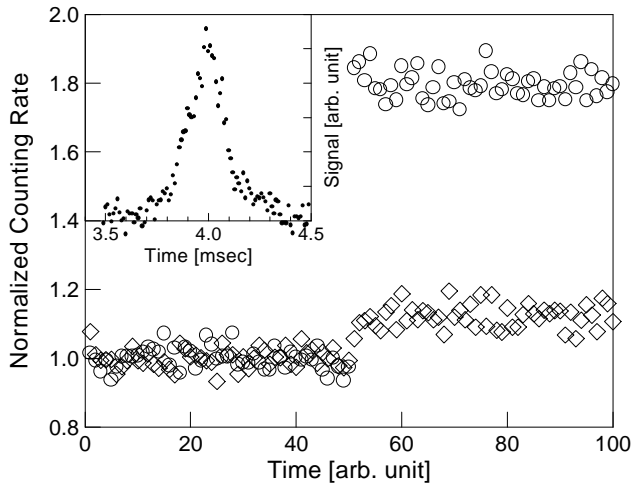


Fig. 2. Increase in electron detachment signal induced by infrared light: (\circ) with filter F1, (\diamond) with filter F2. Inset shows delayed response of spontaneous signal to ionizer pulse at $t = 0$

is turned on at 50 time units. With F1 in place the counting rate increases by 80%, and with F2 in place there is a 10% increase. We have not normalized these increases to the total power, which is considerably larger for F1 than F2. When the ionizing current is turned off, the signals disappear, which indicates that this is not surface photo effect induced by stray light. As the ionizing electron energy increases, all three signals (spontaneous and light induced with either filter) turn on simultaneously when the energy exceeds roughly 1eV. Also, impurities quench the light induced signal in the same way they do the spontaneous signal. These observations indicate that all signals derive from qualitatively similar ionic structures.

One way we can determine whether both spontaneous and light induced signals come from the same size clusters is to selectively remove the smaller clusters from the beam with the deflecting voltage E_d and see if both signals are attenuated equally. The applied deflection field removes all clusters whose size is less than $N_0 = aE_d$ where $a \sim 4 \times 10^5$ atoms/V. The results are shown in Fig. 3, with counting rates normalized at $E_d = 0V$. It is clear that the spontaneous signal is much more strongly attenuated when smaller clusters are removed than is the light induced signal obtained with F1. Thus it must come preferentially from the smaller clusters. The results for F2 are not as well defined and have been excluded from the figure. Qualitatively they lie in between the curves, but closer to the light induced signal.

We have tried to learn about the kinetic energy of the detached electrons by eliminating the field in the detachment region and utilizing grid G2 for a rough stopping potential energy measurement. It has not been possible to make accurate absolute measurements for such low energy randomly emitted electrons since we are sensitive only to one component of the motion. In addition, contact potentials and stray magnetic fields also distort the result. Nonetheless, the approximate magnitude and the differences between spontaneous and light induced signals should be significant. The results for the spontaneous and F1 light induced signals, normalized at $V_G = 0$, are shown in Fig. 4. Both have fairly sharp, low energy distributions, but the light induced elec-

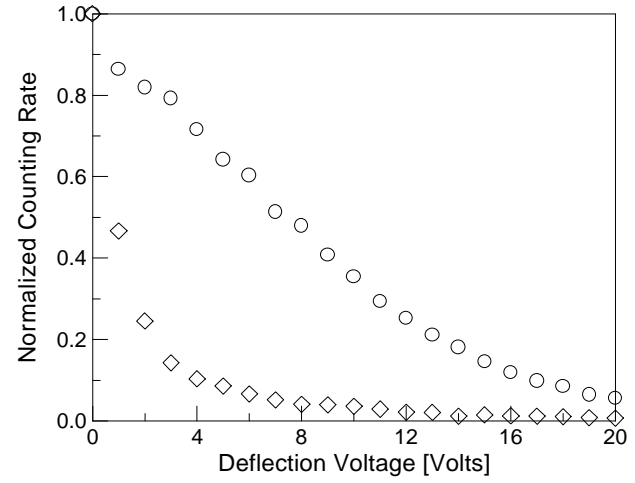


Fig. 3. Dependence of spontaneous signal(\circ) and infrared(F1) induced signal(\diamond) on deflection voltage E_d . $E_d = 2V$ removes clusters smaller than $\sim 8 \times 10^5$ atoms

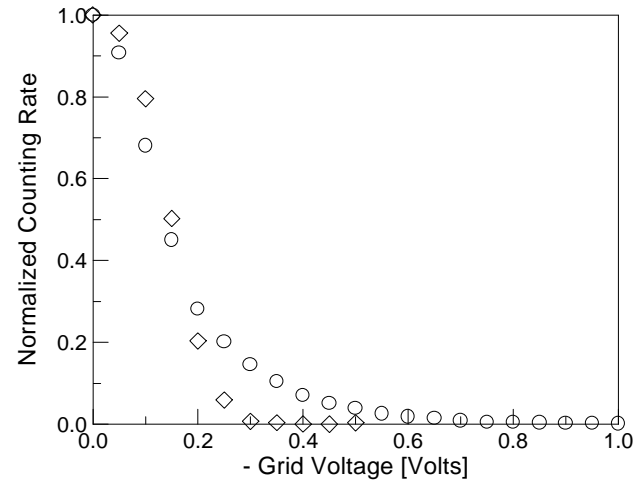


Fig. 4. Stopping potential energy measurement of the spontaneously detached electrons(\circ) and of the infrared(F1) light detached electrons (\diamond)

trons are significantly more energetic. Again, the signal taken with F2 is much weaker and is omitted from the figure for clarity. It appears to lie between the two curves, however, close to the spontaneous one.

C Narrow band light induced detachment signal

Finally, we have studied the wavelength dependence of the stronger of the two light induced signals by using the monochromator to narrow the bandwidth to a resolution of $0.1\mu m$. The result, normalized to the photon flux, is shown in Fig. 5. It shows only a single relatively broad peak centered at $1.5\mu m$. The peak power from our source is at $1.2\mu m$. In the region beyond $2.1\mu m$ the power is weaker and the S/N is not as good. We have searched for evidence of any narrow peaks out to $2.6\mu m$ but have found none. Similar efforts to determine the wavelength dependence of the F2 signal beyond $2.6\mu m$ were also unsuccessful.

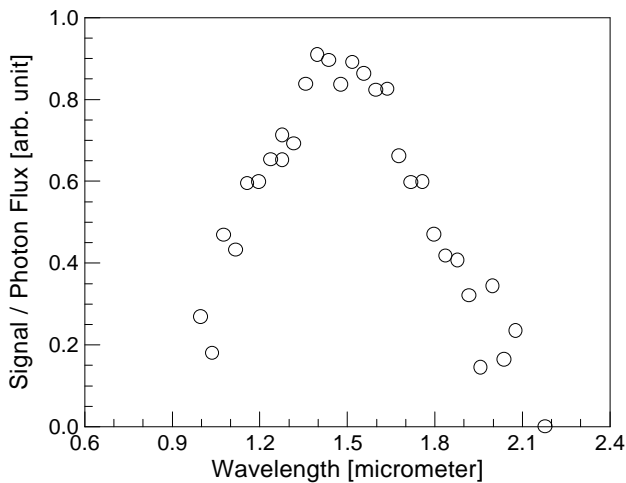


Fig. 5. Wavelength dependence of the infrared induced signal obtained with monochromator and filter F1

4 Discussion

We believe that the only one of the three suggested negative ion structures which is consistent with the experimental observations described above is the bubble electron model. Since the electronic ground state of the bubble electron lies roughly 0.1eV above the vacuum level it can tunnel through the barrier and become detached from the nanodroplet with a kinetic energy of 0.1eV. This interpretation is supported by the observed metastability of the negative ion and the fairly sharp low energy distribution of the spontaneously detached electrons. It is most reasonable to presume that the tunneling takes place when a thermal fluctuation brings the bubble close to the droplet surface. Since this situation occurs more frequently in small clusters we would expect spontaneous detachment to take place preferentially from the smallest clusters, in accord with our deflection field measurements. The observation that the spontaneous release rate decreases when the background gas pressure increases supports the idea that our observations concern pure clusters. Should an impurity atom be captured in flight by a negatively charged droplet the most likely effect will be to bind the electron more tightly to the complex. This is in accord with the observation that the direct beam current increases when the background pressure increases.

The qualitative existence of an infrared photodetachment process, as noted previously, is expected for the bubble structure. The quantitative details of the spectral response are more difficult to predict. There are mechanisms by which both (quasi)bound state and continuum conduction band transitions can lead to detachment, and it is not clear how to assign the single broad peak at $1.5\mu\text{m}$ (0.8eV) which we observe. If the droplet density is that of bulk helium we would expect that the conduction band lies above 1.1eV and the observed peak would seem to correspond to a

(quasi)bound state transition. However it has been suggested that the cluster density may be lower than for the bulk [5] and thus the possibility that it is a conduction band transition can not be ruled out. In fact, the location and shape of the peak corresponds rather closely to that calculated for a 18.7\AA bubble in a 0.7eV well [21]. The weak signal seen with filter F2 would indicate that other bound state transitions exist at longer wavelengths. Finally, we have seen that the kinetic energy of the photodetached electrons is greater than for spontaneously released electrons, but by an amount which is significantly less than the energy of the absorbed photon. This indicates that there is partial rethermalization of the excited electron before detachment.

It is important to note that model calculations of optical transitions of bubble electrons located in small clusters should be significantly influenced by the presence of the nearby vacuum interface. Understanding this effect will be necessary before structural information can be derived from measurements such as those presented above.

This work has been supported by NSF grants DMR9217525 and INT9311907.

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