Bubble Formation and Decay in ^{3}He and ^{4}He Clusters

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The energy transfer in ^{3}He and ^{4}He clusters electronically excited by monochromatic synchrotron radiation is investigated by luminescence spectroscopy. Depending on the cluster size and the isotopic constitution, either sharp, broadened, or shifted emission bands of single He molecules are observed. The spectral features show that He molecules emit light either within a bubble inside the cluster or in the vacuum after desorption from the cluster. From the luminescence intensity, the cluster diameter, and the radiative lifetime, an average velocity of ~ 7 m/s of bubbles in ^{4}He clusters could be deduced. In the nonsuperfluid ^{3}He clusters this velocity was observed to be significantly lower.

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Helium is known to possess various fascinating properties at low temperatures such as superfluidity, highly efficient heat transfer, and an extremely low density. Of special interest is the isotopic constitution. Although chemically identical, the two stable isotopes of He behave quite differently in many aspects. In particular, clusters of He atoms have recently been given much attention [1,2]. It turned out that some characteristics of liquid He were also observed in the He clusters. For instance, typical many-body properties such as superfluidity were identified in ^{4}He clusters of sizes larger than 60 atoms [3,4]. He clusters can also be used to pick up atoms and molecules and synthesize them to new, previously unknown complexes [5,6].

Another remarkable feature of bulk liquid He is the formation of bubbles around electrons, excited He atoms, and molecules [7,8]. Bubbles around He atoms and molecules have been identified spectroscopically after having excited liquid ^{4}He with high energetic electrons [9,10]. This formation of bubbles has been explained as follows: The excitation energy is transferred into localized atomic or molecular Rydberg states. The interaction between the Rydberg electron of the excited state and the surrounding ground state He atoms is repulsive at intermediate distances, because of the Pauli principle. Therefore the neighboring He atoms are pushed away and a bubble grows until equilibrium between the repulsive force and the surface tension of the bubble is established [2]. The enclosed excited He atoms and molecules interact with the ground state liquid helium so weakly that they remain rather long in their highly excited states. They finally decay to lower lying excited states leading to the emission in the visible and near infrared range (vis/ir). These emission lines are slightly shifted and broadened with respect to the gas phase due to the perturbation of the He atoms surrounding the bubble [11,12]. Further evidence for the existence of bubbles has been obtained by observing a dependence of the spectral line shifts on the pressure of the liquid He [13].

It is generally assumed that bubbles would also exist in He clusters, but no direct observations in *pure, neutral* ^{3}He or ^{4}He clusters were possible so far. Jiang *et al.* have shown that electrons of negatively charged He droplets are located in the interior of the cluster, probably surrounded by a bubble [14]. More recently, the detachment of negatively charged ^{3}He and ^{4}He droplets have been investigated by Fárník *et al.* [15]. Their explanation of the experimental results is based on oscillating motion of a bubble around the electron inside the droplets.

Here we report on spectroscopic investigations which prove the existence of bubbles in *pure* ^{3}He and ^{4}He drops for the first time. Our experiments revealed spectral lines either sharp, broadened, or shifted depending on both the cluster size and the isotopic constitution. From an analysis of the line intensities implications of the transport and motion of the bubbles could be made. As we show in this Letter, the energy transport of bubbles is different in ^{3}He and ^{4}He clusters, probably due to the superfluidity of ^{4}He clusters.

Our experimental setup allowed control over both initial and final states because the clusters were photoexcited with monochromatic synchrotron light and investigated using luminescence spectroscopy in the vis/ir spectral range. This simple and straightforward method explores the population of excited electronic levels at relatively high resolution. Recent luminescence studies of ^{4}He clusters electronically excited with monochromatic synchrotron radiation have revealed a discrete line vis/ir spectrum, similar to that of liquid He, however, sharp and unshifted from the free atom and molecule frequencies. This spectrum results from molecules and atoms formed after excitation, which subsequently desorb and emit in great distance from the cluster surface [16]. Emissions from atoms and molecules in bubbles similar to bulk liquid helium have not been observed in these first studies. However, at a specific cluster size there should no longer be any substantial difference to bulk liquid He and therefore one should generally also expect to find bubbles in He clusters.

The experimental apparatus described in earlier publications [16,17] has been modified in order to produce ^{3}He clusters and large droplets and to improve the efficiency of the vis/ir spectrometer. Briefly described, He gas, being continuously recycled, passes through a 5-μm-diameter cold nozzle at a pressure of 40 bars and temperatures from 7–32 K into a vacuum chamber. Under these conditions the He atoms form clusters in the size range from 10 to 10^7 atoms depending on the nozzle temperature and the isotope. The average cluster size $\overline{N}$ associated with a certain nozzle temperature has been derived from deflection scattering experiments carried out under similar expansion conditions [18]. 1 mm downstream from the nozzle the cluster beam is intersected by monochromatic synchrotron radiation. The photon energy is varied from 20–25 eV at a resolution of 0.5–2.5 Å (corresponding to 20–100 meV). The absorption of a photon is followed by luminescence in either the vacuum ultraviolet (vuv) or the vis/ir spectral range. For energy resolved luminescence spectroscopy the emitted vis/ir light is coupled out from the vacuum chamber by means of two achromatic LiF-Suprasil lenses and is analyzed with a $f = 275$-mm Czerny-Turner spectrometer. Using two different diffraction gratings, either overview spectra from 300–950 nm or high resolution spectra covering a range of 60 nm can be obtained. The spectral resolution at a slit width of 80 μm is $\sim$2 nm and $\sim$0.2 nm, respectively.

Spectra were taken at various excitation energies, cluster sizes, and isotopic constitutions. In the following discussion we concentrate on the aspects of the cluster size and isotopic constitution. In Fig. 1 highly resolved emission spectra of $\overline{N} = 10\,000$ large ^{3}He and ^{4}He clusters excited at a photon energy of 23.39 eV are presented. This excitation energy lies between the atomic $3p$ and $4p$ level. Free atoms or molecules do not absorb light at this energy. We have chosen this particular excitation energy, because the vis/ir yield is very high. The luminescence spectra of both isotopes show the unshifted $3d\,^1D \rightarrow 2p\,^1P$ atomic line and the rotational features of the molecular $D\,^1\Sigma_u^+ \rightarrow B\,^1\Pi_g$ transition indicating that the emitting atoms and molecules have been desorbed [16]. Although we were able to record the rotational line structure of many more molecular transitions, we show here the $D\,^1\Sigma_u^+ \rightarrow B\,^1\Pi_g$ transition representatively, because (i) it does not overlap significantly with other transitions, (ii) the rotational line structure is relatively simple, and (iii) it is discussed in the literature for electronically excited bulk liquid ^{4}He.

The spectrum of ^{3}He$_2$ does differ from that of ^{4}He$_2$, because of the different nuclear spins and moments of inertia. Lines with odd rotational quantum numbers of the P and R branch of ^{4}He$_2$ are absent, while for ^{3}He$_2$ all lines are to be seen. We have also run a simulation using the rotational and centrifugal stretching constants of the electronically excited states of the free He$_2$ molecule [19]. The line intensities were obtained through a Boltzmann distribution and line strength factors evaluated by Kovács for Hund's coupling case b [20]. It revealed that the ^{3}He and ^{4}He emission spectra matched best with the simulation at a rotational temperature of 350 K ($\pm$25 K). This temperature is 4 orders of magnitude larger than that of the He clusters (0.38 K and 0.15 K, respectively), indicating that the electronically excited molecule is not in thermal contact with the cluster. The fact that the spectral features reflect a Boltzmann distribution implicates the existence of a thermal equilibrium to a sort of heat sink at 350 K. It ought to be mentioned that the rotational temperature did not depend on the excitation energy.

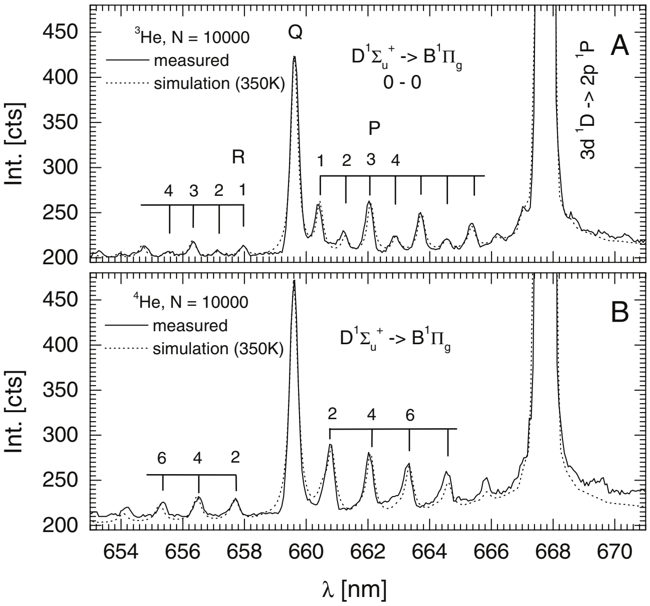

FIG. 1. Luminescence spectra of ^{3}He (A) and ^{4}He (B) droplets of the size $\overline{N} = 10\,000$ excited at 23.39 eV are shown. Simulated spectra are shown for the best fit using a rotational temperature $T_{\mathrm{rot}} = 350$ K. For a better fit of the ^{4}He$_2$ spectrum the (1-1) transition has also been simulated, using the same rotational temperature and an intensity of 10% of the (0-0) transition. Within the resolution of the spectrometer the line frequencies match the gas phase values indicating that the excited atoms and molecules do not emit inside or in the vicinity of the cluster.

In Fig. 2 luminescence spectra of large droplets are presented. All parameters, the excitation energy, spectral range, and resolution, are identical to Fig. 1, except the cluster size which is $\overline{N} = 10^7$ for ^{4}He droplets and $\overline{N} = 30\,000$ for ^{3}He droplets, respectively. Much the same as in Fig. 1 the luminescence spectrum of ^{4}He droplets exhibits the sharp, unshifted lines of the atomic $3d\,^1D \rightarrow 2p\,^1P$ line and the molecular $D\,^1\Sigma_u^+ \rightarrow B\,^1\Pi_g$ transition with the exception of a broad feature between the Q branch and the $R(2)$ line at a wavelength of 658.5 nm (see arrow). Compared with the vis/ir luminescence spectrum of bulk liquid He [9,10] it can be assigned to the $D\,^1\Sigma_u^+ \rightarrow B\,^1\Pi_g$ transition of He molecules enclosed in bubbles. However, the width is now only 1.5 nm (FWHM) as opposed to 2.5 nm observed for liquid He while the blueshift of 1 nm is almost identical in both cases.

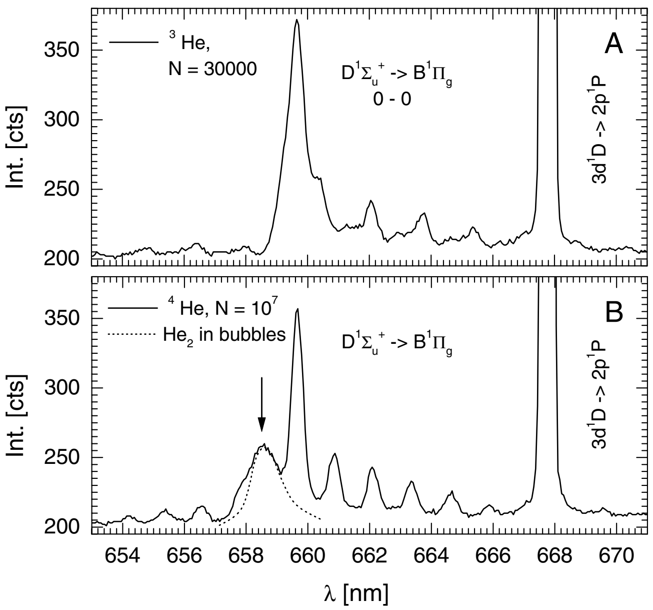

FIG. 2. Luminescence spectrum of ^{3}He (A) and ^{4}He (B) droplets of the size $\overline{N} = 30\,000$ and $\overline{N} = 10^7$, respectively, excited at 23.39 eV are shown. The ^{3}He molecular features (A) are clearly broadened with respect to Fig. 1. For ^{4}He (B) two components in the luminescence spectrum can be distinguished. The sharp lines resemble the features in Fig. 1. The broad feature (arrow) is very similar to the luminescence spectrum of bulk liquid helium. The dotted line is an arbitrary fit.

The luminescence spectrum of ^{3}He droplets containing 30 000 atoms shows the same sharp, unshifted atomic $3d^1D \rightarrow 2p^1P$ line, which is caused by the emission of desorbed excited He atoms. The molecular features, on the other hand, exhibit larger differences with respect to the smaller clusters of $\overline{N} = 10\,000$. The sharp lines of the $D^1\Sigma_u^+ \rightarrow B^1\Pi_g$ transition seem to be nearly completely overlapped by broadened structures. (This can be best seen when comparing the Q branch in Fig. 1A with that in Fig. 2A.) Although luminescence studies of liquid ^{3}He analogous to those performed by Dennis *et al.* [9,10] have not been performed yet, it is reasonable to assign the broadened feature to the $D^1\Sigma_u^+ \rightarrow B^1\Pi_g$ transition of ^{3}He$_2$ molecules enclosed in bubbles. The lines are only marginally blueshifted (~0.1–0.2 nm) and the envelope still reveals single resolved line patterns indicating that the excited molecular states are only very weakly perturbed, at least much less than for liquid ^{4}He. Hence, the bubble radius must be larger, which is expected at least from the lower surface tension $\gamma = 1.7 \times 10^{-8}$ J/cm^2 of liquid ^{3}He with respect to $\gamma = 3.6 \times 10^{-8}$ J/cm^2 for liquid ^{4}He [21]. The rotationally resolved line spectrum of the molecules enclosed in bubbles within ^{3}He droplets emission allows one to check their rotational temperature. We cannot as yet simulate the emission spectrum of ^{3}He$_2$ molecules in bubbles within ^{3}He droplets precisely. It is, however, possible to convolute the simulated spectrum of the free molecule with a Gaussian function to account roughly for the broadened features. The rotational temperature obtained in this manner is 350 K (±35 K) and similar to that of the desorbed molecules.

The observation of molecules emitting inside bubbles within He clusters and our findings of the size dependence of these processes give strong evidence that after electronic excitation the energy is first transferred into excited atomic and molecular states along with the formation of bubbles around them. If this occurs at or close to the surface, the bubbles would certainly not be formed completely or they would collapse immediately followed by subsequent desorption of the excited species. The spectra of the large droplets indicate that in their interior, in contrast, the bubbles remain stable, at least on a time scale similar to the radiative lifetime which is in the order of 10 ns [10]. A rough estimate of the time needed to create a bubble around an excited He atom or molecule may be derived by comparing it with the time calculated for the analogous case of an electron immersed into liquid helium which is 3.89 ps for liquid ^{4}He and 3.97 ps for liquid ^{3}He [21].

The $v = 0$ $D^1\Sigma_u^+$ state has an energy of 20.57 eV, which is 2.82 eV below the excitation energy (23.39 eV). This means that nonradiative decay must be responsible for the population of the emitting state releasing the excess energy of 2.82 eV into phonons, whereupon 5000 He atoms are evaporated. These decay processes must be very efficient, because the emission from higher lying states is only very weak. We conclude, therefore, that the formation of the bubble interrupts the nonradiative decay causing the relatively high quantum yield of the vis/ir emission. The total quantum yield of the vis/ir luminescence with respect to the vuv fluorescence has been determined at 10%–20% [22].

At present we cannot give a conclusive interpretation for the observed Boltzmann distribution of the rotational line intensities. The similarity between the rotational temperatures of the molecules inside and outside the clusters excludes that the molecules gain their internal energy from the energy which is stored inside the bubble and which becomes available when the bubble collapses. The energy of the bubble mainly stems from the surface tension and has been estimated for liquid ^{4}He to 30 meV corresponding to 350 K [12]. It is more likely that the formation process accounts for the temperature of 350 K. This means that in principle a He molecule could have any energy between 30 μV (0.4 K) and the excess energy of 2.79 eV. We ought to mention that other groups also observe unusual high rotational temperatures when exciting molecules at the surface of ^{4}He clusters [23,24].

In the case of ^{4}He droplets it is possible to obtain further information about the transport of the bubbles using the intensity ratio of the luminescence features, the radiative lifetime τ, and the droplet diameter. From the fact that excited metastable He atoms and molecules move ballistically through superfluid ^{4}He [8] we can assume that an excited molecule located in a bubble, which was created somewhere in a droplet, moves straight to the surface at a velocity v. On average this travel distance is almost equal to the cluster radius R. If we consider the intensity of the luminescence inside the droplet I_1 and outside I_2, respectively, the total luminescence I_0 is equal to $I_1 + I_2$ and the time dependence of the luminescence $I(t)$ is given by

$$I(t) = I_0 e^{-t/\tau}. \tag{1}$$

The luminescence intensity I_2 emitted by the molecule after desorption is obtained if the time t in Eq. (1) is expressed by the cluster radius R divided by the bubble velocity v. Hence v reads

$$v = \frac{R}{\ln(\frac{I_0}{I_2})\,\tau}. \tag{2}$$

If we take the radiative lifetime $\tau = 10$ ns [10], an intensity ratio $(I_1 + I_2)/I_2 = 2$, and the droplet radius $R = 480$ Å, a velocity of $7\,(^{-5}_{+1})$ m/s is obtained. This speed is close to that of Ba clusters which move at 10 m/s through liquid ^{4}He [25], and with Na_2 molecules which desorb from the ^{4}He cluster surface at a velocity less than 10 m/s [24]. It is interesting to note that the velocity is below Landau's critical velocity of 58 m/s. This is the maximum velocity at which particles can drag without friction through superfluid He. If the cluster, on the other hand, is treated as a classical liquid at 0.4 K the thermal velocity of the bubble (using an effective mass $m_{\mathrm{eff}} \sim 150$ m ^{4}He) would be 4.0 m/s. We assume that after their formation the bubbles inside the ^{4}He droplets are slowed down until their velocity is below 58 m/s. Then they move ballistically without friction towards the surface.

For the ^{3}He droplets of $N = 30\,000$ the intensity fraction of free molecules is probably less than 25%, and a much smaller velocity of 0.25 m/s is derived when the same procedure is applied. The thermal velocity, however, would be 2.1 m/s ($m_{\mathrm{eff}} \sim 270$ m ^{3}He). We believe, therefore, that in ^{3}He droplets the bubble does not move straight to the surface. Such a diffusive motion is presumably due to the nonsuperfluid phase of the ^{3}He droplets.

In conclusion, we observed the emission of excited He atoms and molecules either desorbed or inside bubbles after electronic excitation of ^{3}He and ^{4}He clusters by luminescence spectroscopy. The different transport properties of bubbles in ^{3}He and ^{4}He droplets are presumably controlled by the superfluidity of ^{4}He clusters. Our findings might suggest a new method for studying photochemical reactions between molecules at the center and on the surface of He clusters using bubbles as transport carriers [5]. After electronic excitation of the center molecule it will slowly move in a bubble to the cluster surface. Owing to the transport velocities elaborated by our experiments, it should be possible to have slow-motion control over the adjoining reactants involved by variation of the cluster size or the isotope.

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