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Line broadening of excimers bound to the surface of ^{4}He clusters investigated by comparison with corona discharge excitation spectra

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Abstract. A new method for assessing the site-specific emission from electronically excited helium droplets is presented. The fluorescence features of helium droplets show sharp rotationally resolved lines indicating desorption of excimers and emission far outside the droplets as well as blue-shifted and strongly broadened features due to emission of excimers confined in cavities within the droplets. A third feature is identified: slightly broadened rotational lines that we attribute to emission from excimers bound to the droplet surface. The line broadening arises from collisions with the helium gas within the surface layer of the helium droplets. These conditions are simulated using a high pressure gas cell in which helium gas is electronically excited using a corona discharge. Rotational line broadening of similar magnitude to that of large droplets (N $\sim 10^7$ atoms) is observed for gas pressures at about 8 bar and 80 K, corresponding to a number density of 7.24×10^{-4}Å^{-3}. We conclude that the excimers are located within a shell separated by 5 to 6 Å from the radius where the density has dropped to 50 % of its centre value. Helium droplets that are smaller (N $\sim 10^4$ atoms) exhibit rotational lines that are less broadened, which we attribute to the superposition of features originating from desorbed and from surface-bound excimers. A fit of the line widths reveals that between 20% and 50% excimers are bound to the surface of the smaller droplets.

1 Introduction

One of the many fascinating properties of liquid helium is the formation of cavities around helium atoms and excimers in Rydberg states. These highly excited species can radiate via transitions to the ground state or to low lying electronically excited states, giving rise to an emission spectrum in the vacuum ultra violet (VUV) [1] and in the visible and near infrared, respectively [2]. Visible emission caused by these transitions has been observed from superfluid helium that was excited with high energy electrons [3] as well as from liquid helium that was excited using corona discharges [4–6]. Visible emission originating from excimers in bubbles was also observed from large helium droplets that were photoexcited with monochromatised synchrotron radiation [7]. However, helium droplets also show spectral features that are not seen in fluorescence from the bulk phase. This droplet-specific luminescence originates from electronically excited atoms and excimers that are ejected after excitation of the clusters and that emit at great distance from the droplets, where their levels are essentially unperturbed. Their luminescence is characterised by sharp spectral lines, unshifted from the well known transitions of atoms and excimers in vacuum. Smaller droplets and helium clusters exclusively emit sharp lines [8]: no emission from bubbles is observed because the size of the droplets is too small to accommodate bubbles for a time long enough [9].

Careful examination of rotationally resolved fluorescence spectra of excimers ejected from electronically excited ^{4}He clusters shows that the "sharp" rotational lines are, in fact, slightly broadened [7]. The degree of broadening is on the one hand too small to be attributed to emission in bubbles, but on the other hand incommensurate with emission of unperturbed atomic and molecular species in vacuum. A plausible interpretation is that the features are sharp lines originating from ejected and unperturbed species superimposed with broadened features that originate from perturbations due to collisions. The only region where the density is sufficiently high to produce significant broadening is the surface of helium clusters and droplets. The existence of long lived excimers in the $a^3\Sigma_u^+$ state bound to the surface of helium droplets has already been proposed long ago [10] and we believe that the existence of bound states of excimers in higher excited states is similarly likely. The surface of helium droplets is very different from a sharp interface: the helium number density decreases smoothly from the bulk value to zero over a distance of about 6 to 7 Å [11].

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To asses the possibility of emission of excimers within the surface layer of helium clusters and droplets we have employed corona discharges to electronically excite helium in a high-pressure cell at hydrostatic pressures greater than 1 bar. A specific advantage of this technique is that the discharges run at high number densities: helium can be excited at pressures up to 100 bar both in the gas phase as well as in the liquid phase, where fluorescence from excited helium atoms and excimers can be observed. With this approach, rotationally resolved excimer spectra can be produced but, as opposed to helium droplets in supersonic beams, the sharp rotational lines can be assessed as a function of temperature, density and pressure. In this fashion, an excimer molecule within the outer surface region of a helium droplet as well as the perturbation of the hypothesised excimers within the surface layer can be simulated, the density at which the rotational line broadening is closest in each can be deduced and the radial position of the excimers bound to the surface of helium clusters can be determined.

2 Experiments

The data presented in this paper was obtained in two different experiments.

The first experiment was performed at the CLULU station at HASYLAB. The setup used in this experiment has been described earlier in the literature [7–9,12]; briefly, a continuous supersonic beam of He clusters was generated during the expansion of cold helium gas through a nozzle of 20 μm at a stagnation pressure of 12000 mbar. The beam was then irradiated with monochromatised and tunable synchrotron radiation in the energy range between 20 and 25 eV. Energy dispersed luminescence spectra were then recorded with a f=0.275 m spectrometer and subsequently analysed. The clusters generated with this setup ranged in size between 10^3 and 10^7 ^{4}He atoms [7]. The fluorescence recorded spans the UV region as well as the visible and near infrared.

The second experiment was performed in a high-pressure gas cell comprising a plane-tip electrode configuration embedded in a gaseous helium environment to establish a corona discharge (Fig. 1). The conception of the setup is similar to the experiments described in earlier reports [4,6,13]; deviations from the design reported in the literature included a smaller electrode distance of 5.4 mm and a sharper tip radius (as small as 200 nm). Fluorescence was emitted from a region close to the tip, collected by a lens assembly and focused onto an optical fibre mounted on a xyz manipulator to optimise collection efficiency. Spectra were recorded using a f=0.303 m Czerny-Turner spectrograph (L.O.T.) equipped with a Peltier-cooled CCD camera. A 1200 lines/mm grating was used in combination with a slit width of 20 μm, providing a spectral resolution of 0.1 nm.

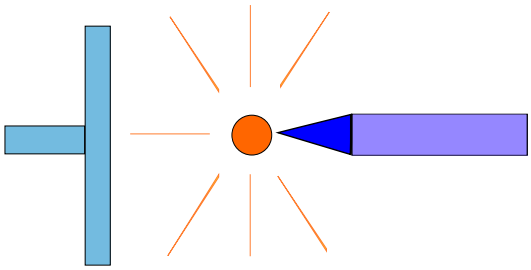

Fig. 1. (Color online) Schematic of corona discharge set-up in plane-tip electrode configuration. See text.

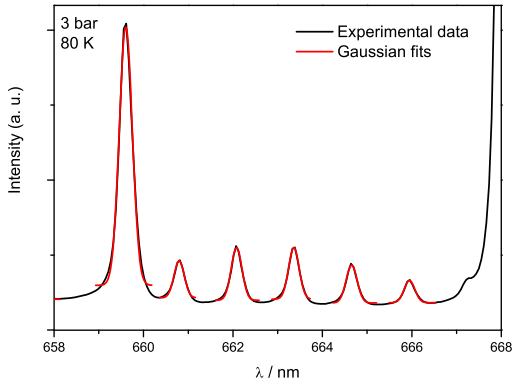

Fig. 2. (Color online) Example of the gaussian fits used in this paper.

3 Results

The rotational lines of the $D^1\Sigma_u^+ \rightarrow B^1\Pi_g$ transition were recorded for both corona discharge excitation spectra and photoexcited helium cluster spectra; gaussian lineshapes were fitted to each of the rotational lines to assess their broadening via the full width half maximum (FWHM). The precise form of the gaussian lineshape $y(x)$ fitted to our rotational transition is

$$y = y_0 + \frac{A}{w\sqrt{\pi/2}} e^{-\frac{2(x-x_c)^2}{w^2}}, \qquad (1)$$

In the equation y_0 is the background, A the amplitude, x_c the spectral position and w the linewidth. All the parameters in this formula were free, in particular, y_0, which amounted to a background subtraction for each of the rotational lines. While background substraction improved the quality of our fits the background level for the different P-lines under scrutiny did not differ too greatly (y_0 varies at most up to 11%). Similar results for the line width w would have been obtained by taking a fixed y_0. Summarising, the determination of the linewidth of the rotational lines depended only little on the way the lines were fitted. In Fig. 2 we give an example of one of the fits to give an idea of the accuracy of our fits.

Fig. 3 shows a comparison between three rotational spectra from a corona discharge obtained under similar

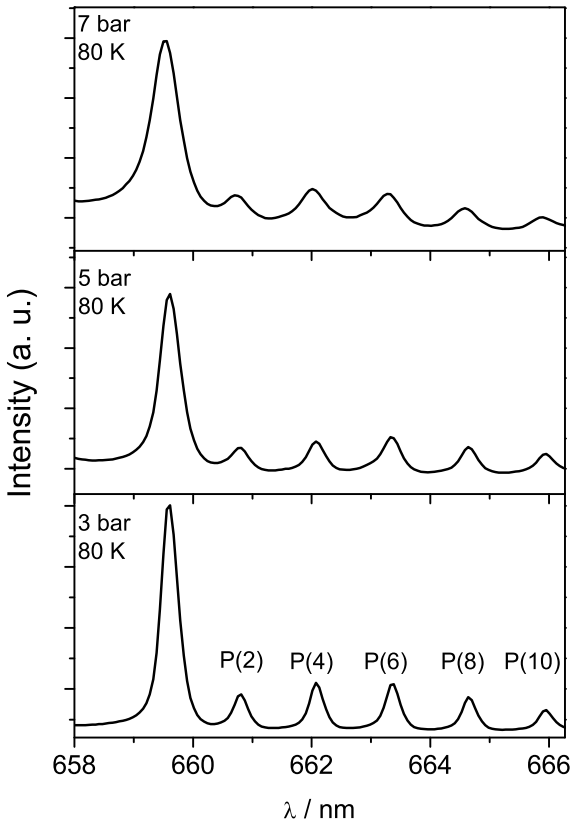

Fig. 3. Corona discharge spectra at several pressures. Pressure broadening is evident from this figure.

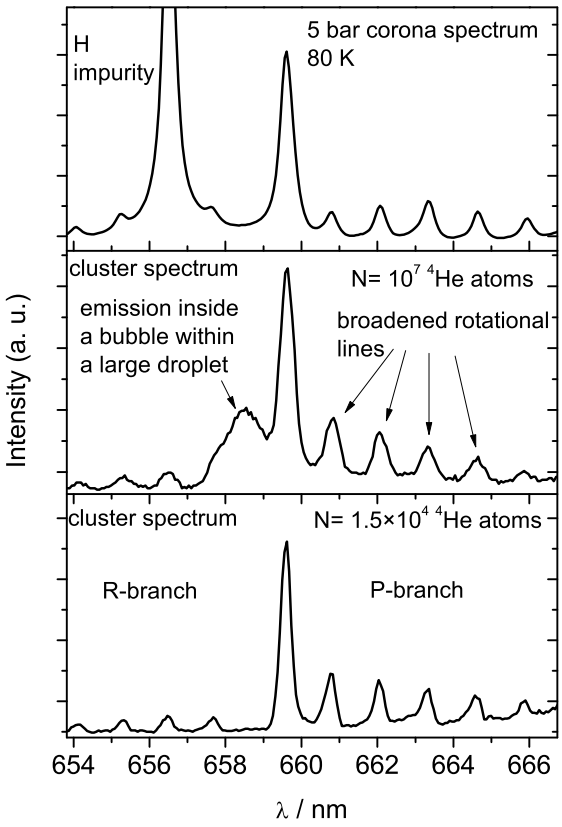

Fig. 4. Comparison of clusters' spectra and corona discharge excitation spectrum features. Some rotational lines within the R-branch in the corona spectrum are overshadowed by the H-α line from hydrogen impurities in the system.

conditions (80 K, a current of 550 μA, negative tip polarity) but for differing pressures.

Fig. 4 shows the same transition for small and large droplets as well as for the pressure at which the corona rotational spectrum shows a linewidth similar to that seen in the small cluster spectrum. The cluster spectra are identical to those published earlier [7]. However, following recent work [14] we correct the earlier size assignment for the smaller clusters to N = 1.5×10^4.

The rotational lines of the P-branch of the spectrum of the $N = 1.5 \times 10^4$ atom clusters are just resolvable by the spectrograph while the rotational lines of the larger droplets are distinctively broader. We interpret the broadening as due to lines that originate from excimers that are perturbed by collisions with a gas superimposed on the sharp lines that originate from excimers that emit away from the droplet surface. Although the shape of the rotational lines of the helium clusters is not exactly Gaussian, we apply Gaussian fits to assess the degree of homogeneous broadening; the lorenzian component should, in any case, be consistent from line to line under any given set of conditions. This procedure will account for the contribution of collisions to homogeneous line broadening. The average linewidth of the rotational P-lines of the corona discharge spectra that match the corresponding lines of the photoexcited helium spectra are 0.29 ± 0.04 nm and 0.44 ± 0.05 nm for the small and large droplet case, respectively; the error is determined as the standard deviation of the width of the aforementioned lines.

For the sake of the clarity of our reasoning, we show in Table 1 the results of the linewidth fits described above.

By studying the thermodynamic conditions at which the broadening seen in the corona spectra matches the rotational features of the large photoexcited helium droplets, we obtained an estimate of the density of the local environment surrounding the emitting excimer and – via the density profiles of droplets – a means to estimate the distance between the droplet and the excimer. From Table 1, the pressure at which there is a general match between the line broadening produced in the corona discharge experiment and that observed for large clusters is 8 bar, from an estimation of the linewidth between 7 and 9 bar. The number density corresponding to this situation is 7.24×10^{-4} Å^{-3}.

	small droplet	helium gas at 80 K				large droplet
	$N = 1.5 \times 10^4$	3 bar	5 bar	7 bar	9 bar	$N = 10^7$
P (2)	0.307	0.27	0.315	0.32885	1.767	0.387
P (4)	0.28	0.284	0.329	0.41608	0.59463	0.402
P (6)	0.335	0.278	0.334	0.37897	0.66267	0.45
P (8)	0.318	0.289	0.314	0.39603	0.6851	0.474
P (10)	0.227	0.282	0.312	0.38651	0.5211	0.496

Table 1. Result of the linewidth fits. The linewidths are given in nm.

4 Discussion

It has previously been reported that photoexcited helium droplet spectra exhibit sharp, unshifted lines. These lines can straightforwardly be explained as the emission of excited molecules and atoms far away from the cluster, indicating that they must have been ejected from the cluster. It can also be observed in the emission spectrum of very large droplets ($N > 10^6$) a blue-shifted feature very similar to the spectrum of bulk superfluid helium [3], which has been attributed to fluorescence of excimers in cavities. These features do not show rotational resolution but their envelope follows the well known P, Q, and R-branch pattern of the $D^1\Sigma_u^+ \rightarrow B^1\Pi_g$ transition. The band head is blue-shifted with respect to the free excimers transition but the blue shift is smaller for helium droplets than for bulk liquid helium.

The rotational lines of the small droplets are less broadened than the lines emitted by large droplets. The additional broadening of the large droplet lines cannot be explained as emission from cavities (since this particular emission is even broader and shifted) nor as emission from remotely ejected excimers. Bound excimer states have been suggested before and hence emission from these bound excimers will be considered in the following.

The binding energy and thus the location of an excimer on a helium cluster surface should be size-dependent. Qualitatively the situation is similar to the size-dependent binding energy of a single helium atom to a cluster [15]. This size dependence shows that clusters greater than 1000 atoms behave very much like the bulk. Therefore, the location of an excimer on the surface of a cluster of 10^4 atoms should be very similar to that of a much bigger droplet (10^7 atoms). For this reason, both the small and large droplets have the same ability to accommodate excimers on their surfaces.

The reason that clusters with 10^4 and 10^7 atoms exhibit different line broadenings can be understood as follows: the line features that we observe are a superposition of fluorescence from remote and surface-bound excimers and at the first sight it is not obvious how to disentangle the two contributions. We assume that the linewidth in the 10^7 droplet is dominated by the surface-bound excimers; this assumption can be substantiated by closer inspection of the lineshapes which show a more symmetric profile in the case of the big droplets and the more pronounced wing contribution for the smaller clusters. By means of the known density profile of the surface region of clusters and droplets we can deduce the distance of the excimers from the surface using the *linewidths measured for large droplets*.

Clearly the 10^4 cluster exhibits a much smaller contribution of surface-bound excimer emission; using the established linewidth of surface-bound excimer emission it is possible to disentangle the contributions from remote and surface-bound excimers for the 10^4 atom large clusters. In a very simple model we can represent the contributions from the remote and surface-bound excimers as gaussians, the former as sharp as the resolution of the instrument and the latter as broad as established above. Figure 5 shows a fit of the rotational lines of the N = 1.5 × 10^4 large cluster using two gaussian functions, one sharp and one broad, representing contributions from remote and surface-bound excimer emissions, respectively.

In concrete, and in analogy with the gaussian function used before, we fitted the function

$$y = y_0 + \frac{A}{w\sqrt{\pi/2}} e^{-\frac{2(x-x_c)^2}{w^2}} + \frac{A'}{w'\sqrt{\pi/2}} e^{-\frac{2(x-x_c)^2}{(w')^2}}, \quad (2)$$

where the first gaussian represents the remote contribution and the second one the surface-bound emission. The parameters A and A' give an estimation of the relative contributions of desorbed and surface-bound excimers, respectively. The analytical results can be found in Table 2. We can see that in general the remote contribution is always equal or greater than that from the surface-bound excimers except for the line P(8). The result on Table 2 yields the statement that the contributions between the remote and surface-bound excimers are in a ratio ranging from 1:1 to 4:1, approximately (the ratio in the case of P(6) is disregarded since the fitting of that line is not that good); the table also supports qualitatively that the emission from remote excimers is more important for the small droplets.

A possible mechanism for the noticeable larger broadening observed for the large droplets is the difference in the conditions of the release of the excimer: in the small droplet the size of the bubble is comparable to the size of the cluster so the bubble explodes very quickly after being formed ejecting violently the excimers [9,16]; on the other hand, within the large droplet the bubble travels at 7 m/s toward the surface [7] and thus the excimers are softly released, enabling a good amount of them to lie at the surface of the droplet; a low velocity makes soft-release of the excimers at the surface much more probable and hence

	A	A'
P (2)	3013.77423	2942.6733
P (4)	3552.76074	840.64669
P (6)	2719.00661	101.9927
P (8)	1485.62991	1758.54012
P (10)	1162.92453	701.47812

Table 2. Disentanglement of the contributions from remote and surface-bound excimers. The parameters A and A' designate the relative contributions of desorbed and surface-bound excimers, respectively. The linewidths are given in nm.

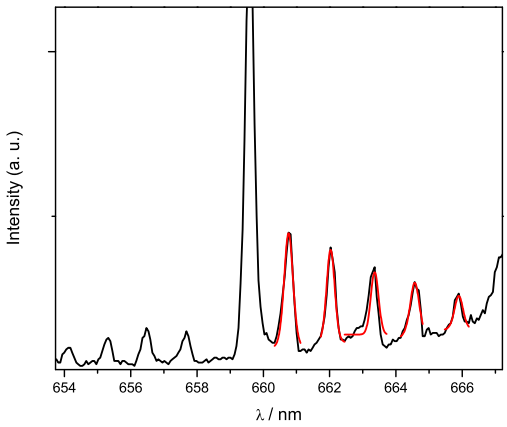

Fig. 5. (Color online) Result of the fitting procedure described in Eq. (2).

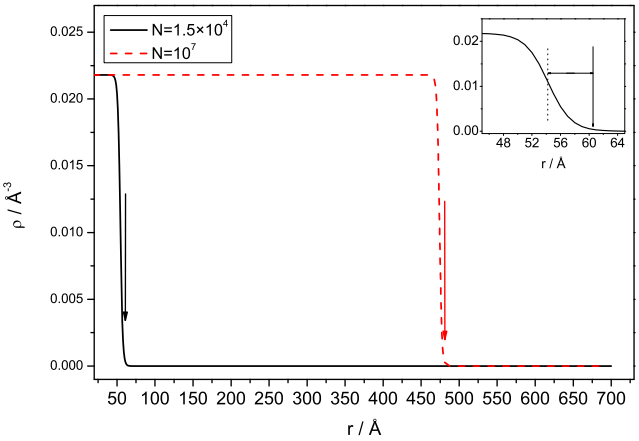

Fig. 6. (Color online) Arrows mark the hypothesised position of the emitting excimer at the surface of the cluster. The surface-bound excimers will produce some kind of dent in the droplet surface meaning that its distance to the droplet center will be slightly smaller than stated. The inset shows an expanded view of the density profile of the small cluster.

these excimers then have a chance to become attached in a bound state.

In Fig. 6 the location derived from comparing regions of similar density of the emitting excimer has been marked. The exercise was carried out for both small and large helium clusters; nevertheless, the estimated position obtained for the large droplet case is more representative because the droplets are more bulk-like.

5 Summary

Additional broadening observed in the spectra of photoexcited helium clusters is addressed. The location of an additional emission site for the emitting excimer is proposed by comparing the rotational linewidths of clusters' spectra with those of corona discharges. It is argued that emission can occur from isolated excimers bound to the outer surface of the clusters.

The corona discharge is used to simulate such surface interactions by changes in the pressure in such a way that the linewidths of the rotational features of both spectra match. For $N = 10^7$ the rotational linewidths match at 80 K and 8 bar. The corresponding density is 7.24×10^{-4} Å^{-3}. This density corresponds to a radial location of 5.39 ± 0.10 Å from the point at the droplet surface where the density drops to 50 % of the centre value.

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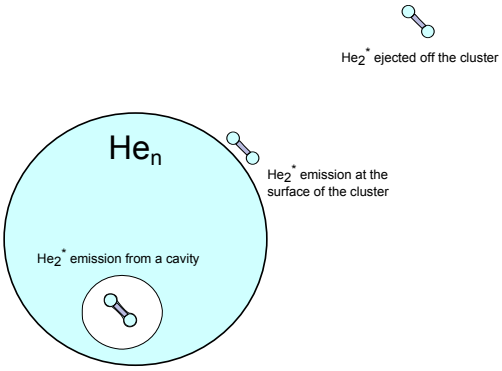

Fig. 7. (Color online) Qualitative model of the different locations of the emitting excimers with respect to the helium droplet.

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