Shape of atomic lines emitted by cryoplasma in Helium

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Abstract. Experimental data on spectral shape of the line 706nm emitted by corona discharge in liquid and gaseous cryogenic helium are presented. The data have their explanation in a framework of the bubble model. The long-range interaction between excited He* atoms and He atoms in the ground state was used for a description of the fluorescence measurements. The 'hump' like repulsive part of the inter-atomic potential at intermediate internuclear separations around 5 Å was calculated by using the full configuration interaction method as implemented in the MOLPRO code. The repulsion gives rise to the establishment of cavities around excited atoms in liquid helium and radius and profiles of the cavity boundaries were calculated for this potential and different pressures. The potential was used to simulate the atomic line fluorescence profile as a function of external pressure between 0.1 and 3.5 MPa. The fluorescence shows characteristic line shifts and widths as a function of pressure. By comparison with the theoretical predictions, we found evidence that for corona discharge-excited liquid helium the He* atoms reside in a cavity and hence emit from within the liquid phase. The measurements carried out at higher temperature 5.1K give spectra are characterised for the bubble states similar to the states were obtained in superfluid He II at 1.8 K.

1. Introduction
Emission spectroscopy is a powerful tool to obtain information about parameters that characterize non-equilibrium discharge plasma (corona) in high pressures. Spectroscopic observations of the light emitted by ionized gases can be used to determine conditions surrounding the emitted atoms or molecules. Spectroscopic studies of internal excitations in liquid helium have a long history [1–6]. Experimental techniques, such as α-particle bombardment [1, 7, 8], high energy electron bombardment [2–4], corona discharge [5, 6, 9–11], strong field ionization by femtosecond laser pulses [12, 13], and synchrotron radiation [14–16], have been employed. The latter technique has been applied to study intrinsic excitations in liquid helium droplets. Common to all these techniques is the first step, which involves direct ionization of helium atoms creating the corresponding positive ions and electrons in the liquid. This can directly lead to the formation of positive He⁺₂ and subsequently through electron-ion recombination He₂⁺*, or through electron impact ionization/excitation in the liquid electronically excited helium atoms He* may also form. These species are formed both in their singlet and triplet electronic manifolds and they relax towards lower energy states by emitting photons in the visible and infrared regions as well as in the VUV when the system returns back to its electronic ground state.
Such radiators undergo strong perturbation by surrounding atoms if they are placed in very dense medium as a liquid He. Though, atomic lines were observed in a lot of experiments and their width depends on external pressure applied to a liquid. This is possible because the excited species are established to reside inside voids ranging from (7 – 15) Å (“bubble states”), which are slightly smaller than for free electron in the liquid (18.5 Å) [17]. Such structures are the result of the repulsive Pauli exchange repulsion between the Rydberg electron and the surrounding closed shell helium atoms. These experiments have been carried out in a superfluid liquid He II at temperatures less than 2 K. It is well-known that electrons injected in dense helium remain localized in bubbles both in normal liquid He I at higher temperatures and in cryogenic gaseous He at temperatures less 20 K [18, 19]. In this work, we present results of spectroscopic experiments carried out in liquid and gaseous helium at low temperatures 4.2 – 5.2 K. The spectral line 706 nm of the transition $3^3S \rightarrow 2^3P$ is under the study. It will be shown that a shape (shift and width) of the line observed is strong different than in low density gas and it is related with bubble-like complex with excited atom in it.

2. Experimental facilities.

The experimental facilities used in our spectral investigations of corona discharges were described in details in [20]. The corona discharge (ionization of matter) occurs in vicinity of a tip cathode under action of high strength electric field. Tungsten needle electrode with point radii $r_p = 2.5\mu$m was used under dc high voltage. The point-plane inter-electrode distance was in the range of 0.65-0.8cm. The starting material was helium gas N60 (99.99990% pure, Air Liquide) which had an impurity concentration of about 0.1 ppm of oxygen. After the purification, the gas is liquefied in a cell housed in a cryostat. The temperature in the cell is measured by a germanium resistor and was fixed for each series of measurements. The measurements were carried out for different external pressures applied to the cell. The pressure increased until the spectral line was observed. Some measurements can be possible for the pressure 3.5 MPa. The voltage was supplied by a stabilized DC power supply (Spellman model RHSR/20PN60) giving either positive or negative tip polarity. The stabilized dc voltage (up to 20 kV) was connected to the tungsten point electrode. The Tektronix TDS540 oscilloscope or the Keithley 610C current meter was connected to the plane electrode.

An ionization zone near a tip electrode is a source of a light emitted by the corona. Gaseous and liquid Helium under pressures (0.1 -0.2) MPa at temperatures between of 4.2K and 5.2K was excited using the corona discharge both for negative and positive high voltages. The light emitted from the ionization zone of the discharge was analyzed. Both the helium cryostat and the copper beryllium cell were equipped with sapphire windows, which allowed the collection of light near the corona discharge zone by a short focal length lens. A second quartz lens was used to focus the light into a 300 mm focal length spectrograph (Acton Research Corporation; Spectra-Pro-300i with 150 gr/mm and 1200 gr/mm gratings). A liquid N$_2$ cooled charge coupled detector (CCD) was installed at the exit plane of the spectrograph (Princeton Instruments model 2D-CCDTKB-UV/AR). The spectral resolution with the 1200 gr/mm grating was 0.1 nm as determined from the spectral profiles of argon discharge lamp lines.

3. Results and discussion

The relevant atomic He* line observed in the experiments through fluorescence is the triplet Hel line 706 nm of the transition $3^3S \rightarrow 2^3P$. The line observed in liquid He is strongly different than the line observed in gaseous He, figure 1. Moreover, the shape of the line has strong pressure dependence in the LHe, figure 2. In figure 1 the experimental spectra obtained for 706 nm line in a negative corona under the same pressure and at different temperatures. Gas density at 570K is $4.4*10^{20}$ cm$^{-3}$. Liquid density at 4.2 K is $2*10^{22}$ cm$^{-3}$. The pressure dependence of the line width is a gas is a result of the linear relations between the gas density and the pressure. In the liquid variation of density with the pressure increasing is less than that in a gas. The pressure dependence of line width in a liquid has another reason.
Pressure broadening of spectral lines depends on the surrounding matter density. The “impact” interaction of radiator with surrounding atoms results in the Lorentzian symmetric profile of spectral lines emitted by a discharge in low pressure gases [21, 22]. In this case the width $\Delta \lambda$ (Full Width Half Maximum) of a line and its shift $S$ are proportional to gas density [23, 24]. The analysis of the line broadening and shift has been made in [25] for the Lennard-Jones potential of an interaction between excited atom and surrounded atoms in the ground state in the framework of the “impact” approximation. The shift sign (“red shift” for the shift toward longer wavelengths and “blue shift” for the shift toward shorter wavelengths) depends on character of radiator-perturbator interaction. The blue shift corresponds to significant repulsion. The “impact” interaction shifts the centre of line weaker than the broadening of the line. The ratio Shift/Width does not exceed 0.2 for “impact” distortion of the line shape. The low shift of line compare with its broadening is a feature of the “impact” broadening by pressure in a gas. Subsequent growth of the gas density is accompanied by distortion of the “impact” Lorentz profile of a line [26]. The asymmetry of a spectral line shape was described using “quasi-static” approach where perturbators are assumed immobile. The asymmetric shape of spectral lines has been observed in He gas under high pressures [27]. The lines had more intensive “blue wing” that was a result of repulsion between the excited atom and surrounding atoms. The number density of the liquid He is $2*10^{22}$ cm$^{-3}$, which is 45 times larger than gas density $4.4*10^{20}$ cm$^{-3}$ at temperature 570 K and pressure 3.2 MPa. So a linear extrapolation of the “gaseous” $\Delta \lambda = 2.6$ nm for the density $4.4*10^{20}$ cm$^{-3}$ up to the liquid density leads to non-real magnitude of the line width in the liquid and cannot explain the experimental data, figure 2.

![Figure 1](image1.png)  
**Figure 1.** Line 706nm observed in liquid He at 4.2K and in gaseous He at 570K under the same pressure 3.5 MPa.

![Figure 2](image2.png)  
**Figure 2.** Line 706nm observed in liquid He at 4.2K under different pressures. Shape of the lines is symmetric one.

![Figure 3](image3.png)  
**Figure 3.** Calculated [28, 29] He*-He potential as a function of a distance between atoms (lines with full symbols, left axis). Density profile of a cavity boundary (lines with empty symbols, right axis).

![Figure 4](image4.png)  
**Figure 4.** Blue shift of 706 nm line in liquid He at 4.2K. Points – experimental data [20]. Line – calculation according to bubble model [29].

The “blue” shift observed in our experiments with gaseous and liquid He is an indicator of inter-atomic repulsion. The interaction between excited He* and ground state helium atoms provides example where a long-range barrier in the intermediate distance regime occurs [28, 29]. Both He* and
He* species have been established to reside inside voids ranging from (7 – 15) Å (“bubble states”), which are slightly smaller than for free electron in the liquid (18.5 Å) [30-34]. Such structures are the result of the repulsive Pauli exchange interaction between the Rydberg electron and the surrounding closed shell helium atoms. Excited atom pushes away surrounding atoms. The bubble radius depends on external pressure the spectra are recorded systematically as a function of the pressure, figure 2. The long-range repulsion potential between 3s3S excited atom and 1s1S ground state atom calculated in [28, 29] is presented in figure 3 as a function of the distance between the atoms. The excited atom is located in the origin. Empty cavity surrounds the radiator. It is perturbed by weak part of a long-range tail of the potential, which occupies a non-zero density boundary of the cavity, figure 3. The boundary approaches to radiator with a pressure increasing and the perturbation leads to growth of shift and broadening of the emitted line. Such calculations give values of 706 nm line shift close to experimental, figure 4.

The phenomenon of localization of electron and excited atom in “bubble” was well known for liquid He at temperatures less then the temperature of the superfluid transition 2.17 K, i.e. in the superfluid Helium II. Our experiments at isotherm 4.2 K and high pressures showed that such phenomenon is possible in normal liquid Helium also. Localization of electrons injected in dense cryogenic He gas has been observed up to temperature 20 K [18, 19]. Our experiments have been made in the normal He I at 4.2 K showed that the localization of excited atoms is possible at that conditions.

It is natural that the localization of Rydberg-atoms should become weaker with growth of temperature and decreasing of gas density. The next step of our investigation is to discover the boundary of thermodynamic domain of the localization of excimers in cryogenic He gas. Moreover it is very interesting to study of atomic line shape in immediate vicinity of the critical point of Helium $T_{cr} \approx 5.2K$, $P_{cr} \approx 0.227$MPa. Figure 5 represents the density-pressure diagram with low temperature isotherms and circumscribes the domain of the observations. The isotherm 5.1 K shows that the boiling of He occurs at the pressure 0.21 MPa at this temperature. A liquid is realized under higher pressures but the liquid has properties similar to a supercritical fluid. As example, note a problem of the surface tension for such “liquid”. Figure 6 shows a shape of 706nm line emitted in liquid He at 5.1 K and different pressures. Shift of the lines increases with pressures and its magnitude is large enough to conclude that the radiator is in a cavity with rarefied gas inside. Such “pseudo-bubbles” were proposed to explain a nature of low mobility of electrons injected into dense cryogenic He gas [35].

![Figure 5](image5.png)  
**Figure 5.** Thermodynamic states of Helium in cryogenic conditions. $T_{cr} \approx 5.2K$, $P_{cr} \approx 0.227$MPa. Symbols show states where spectroscopic observations were made.

![Figure 6](image6.png)  
**Figure 6.** Line 706 nm observed in negative corona in liquid He at 5.1 K. Blue shift values are noted at intensity maxima. Isotherm 5.1 K is very close to the critical temperature 5.19 K.

4. Conclusions.
The experiments carried out in cryogenic Helium are described in the paper. The relevant $3s3S$ excimer which is an origin of 706 nm HeI line is presented in the liquid He as “impurity” created a cavity surround it. The corona micro-discharge in liquid and cryogenic gaseous helium is realized in our experiments and it was served as a source of emitted atoms. Shift and shape of an atomic line 706 nm
were measured for these conditions. The shape (broadening and shift) of the line emitted from the cryogenic He (liquid and dense gas) is different strongly of the line emitted from the gas at high temperature and pressure. The line has asymmetric shape with more intensive short-wavelength (blue) wing for a broadening characterized for high pressure gas. Blue shift (toward short-wavelengths) is small in a gas. Asymmetric shape of an atomic line 706 nm was recorded in our experiments in gaseous He at intermediate temperatures. Blue wing of the line recorded in negative corona was more intensive than its red wing. Spectral shift of the line was small for the range of applied pressure. The line shape observed in gaseous and liquid Helium for conditions closed to the boiling pressure at a fixed temperature was the same.

The spectra observed in cryogenic Helium have rather symmetric shape described by Gauss-function. Such spectra are characterized for light emitted by Rydberg-atoms localized inside of empty cavity (bubble). The bubble model has been developed for excimers in superfluid liquid He II at temperature 1.8 K. The model is modified for temperatures \( \approx 4 \) K and gives good agreement with measured width and shift of the 706 nm line. Such structure is the result of the Pauli repulsive exchange interaction between the Rydberg electron of excited atom and surrounding helium atoms. The excited atom and atoms from its environment are far enough each other in the “bubble state”. So, the long-length asymptotic of the repulsive potential is important in formation of this state. The He*-He pair interaction potential was calculated by using the full configuration interaction method as implemented in the MOLPRO code. The potential was used for calculation of the cavity shape and of perturbation of a radiator inside the cavity.

Thus, the spectra emitted corona discharge in liquid normal He I at 4.2 K are corresponded to bubble model which is developed for low temperature liquid He. Such limitation has physical basis because a temperature blurs of a static structure formed due to Pauli repulsion. In some respect the experimental evidence of the bubble-like spectra at 5.1 K is a significant step to develop of a theory of “pseudo-bubble” states of the Rydberg atoms in dense cryogenic supercritical fluid helium.

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References
[1] Surko C M and Reif F 1968 Phys. Rev. 175 229
[2] Dennis W S, Durbin J E, Fitzsimmons W A, Heybey O, and Walters G K 1969 Phys. Rev. Lett. 23 1083
[3] Soley F J and Fitzsimmons W A 1974 Phys. Rev. Lett. 32 988
[4] Keto J W, Soley F J, Stockton M, and Fitzsimmons W A 1974 Phys. Rev. A 10 872
[5] Zimmermann P H, Reichert J F, and Dahm A J 1977 Phys. Rev. B 15 2630
[6] Goncharov V A and Levitov V I 1975 Lvestiya Academii Nauk, Energetica i Transport 12 134
[7] Jortner J, Meyer L, Rice S A, and Wilson E G 1964 Phys. Rev. Lett. 12 415
[8] Moss F E and Hereford H L 1963 Phys. Rev. Lett. 11 63
[9] Kafanov S G, Parshin A Y, and Todoshenko I A 2000 JETP 91 991
[10] Parshin A Y, Todoshenko I A, and Kafanov S G 2000 Physica B 91 284
[11] Li Z-L, Bonifaci N, Aitken F, Denat A, von Haeften K, Atrashiev V M, and Shkhatov V A 2009 Eur. Phys. J. Appl. Phys. 47 2282
[12] Benderskii A V, Zadoyan R, Schwentner N, and Apkarian V A 1999 J. Chem. Phys. 110 1542
[13] Benderskii A V, Eloranta J, Zadoyan R, Schwentner N, and Apkarian V A 2002 J. Chem. Phys. 117 1201
[14] von Haeften K, de Castro A R B, Joppien M, Moussavizdeh L, von Pietrowski R, and Moller T 1997 Phys. Rev. Lett. 78 4371
[15] von Haeften K, Laarmann T, Wabnitz H, and Moller T 2002 Phys. Rev. Lett. 88 233401
[16] von Haeften K, Laarmann T, Wabnitz H, and Moller T 2005 J. Phys. B: At. Mol. Opt. Phys. 38
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[17] Eloranta J and Apkarian V A 2002 J. Chem. Phys. 117, 10139
[18] Levine J and Sanders T M 1967 Phys. Rev. 154, 138
[19] Harrison H R, Sander L M, and Springett B E 1973 J. Phys. B. 6, 908
[20] Li Z-L, Bonifaci N, Aitken F, Denat A, von Haeften K, Atrazhev V M and Shakhatov V A 2009 EEE Transactions on Dielectrics and Electrical Insulation 16, 742
[21] Traving G 1968 Interpretation of line broadening and line shift in Plasma Diagnostic (Chap. 2), edited by W. Lochte-Holtgreven, North-Holland Publishing Company, Amsterdam.
[22] Allard N and Kielkopf J 1982 Rev. Mod. Phys. 54, 1103
[23] Lindholm E 1945 Ark. Fys. A 32, 1
[24] Foley H M 1946 Phys. Rev. 69, 616
[25] Hindmarsh W R, Petford A D and Smith G 1967 Proc. of the Royal Soc. Series A 297
[26] Margenau H 1935 Phys. Rev. 48, 55
[27] Bonifaci N, Li Z-L, Denat A, von Haeften K, Atrazhev V M and Shakhatov V A 2011 Eur. Phys. J. Appl. Phys. 55, 13809
[28] Allard N F, Bonifaci N, and Denat A 2011 Eur. Phys. J. D 61, 365
[29] Bonifaci N, Aitken F, Atrazhev V M, S L, and Eloranta J 2012 Phys. Rev A 85, 042706
[30] Eloranta J and Apkarian V A 2002 J. Chem. Phys. 117, 10139
[31] Eloranta J, Schwentner N, and Apkarian V A 2002 J. Chem. Phys. 116, 4039
[32] Mateo D, Jin D, Barranco M, and Pi M 2011 J. Chem. Phys. 134, 044507
[33] Maris H J 2000 J. Low Temp. Phys. 120, 173
[34] Hickman A P, Steets W, and Lane N F 1975 Phys. Rev. B 12, 3705
[35] Khrapak A G and Iakubov I T 1979 Sov. Phys. – Usp. 22, 703