Spectroscopic studies of impurity-helium condensates containing stabilized N and O atoms

I.N. Krushinskaya, R.E. Boltnev, V.V. Khmelenko, and D.M. Lee

1Branch of Institute of Energy Problems of Chemical Physics, Chernogolovka, Moscow region, 142432, Russia
2Joint Institute for High Temperatures, Izhorskaya 13/19, 125412, Moscow, Russia
3Department of Physics and Astronomy, Texas A&M University, College Station, TX 77843, USA
E-mail: khmel@physics.tamu.edu

Abstract. We present optical spectra of impurity-helium condensates during the process of their formation by injection of gas mixtures N_2-Rg-He (Rg=Ne, Kr) into bulk superfluid helium after passing through a RF discharge. Atomic lines of He, Ne, Kr, N, O atoms as well as bands (1\( ^+ \) and 2\( ^+ \) systems of N\(_2\)) are present in the spectral range 320-1100 nm studied in these experiments. We also detected spectra emitted by the samples during their destruction, stimulated by warming through the temperature range 1.5 - 15 K. The luminescence spectra of the N-N\(_2\)-He and N-N\(_2\)-Ne-He samples contain only intense N(2D-4S) (\( \alpha \)-group) and O(1D-1S) (\( \beta \)-group) lines. For the N-N\(_2\)-Ne-He sample we observed the transformation of spectra of the \( \alpha \)-group. In thermo-stimulated luminescence spectra of the N-N\(_2\)-Kr–He samples, the intense \( \beta \)-group of O atoms and M-bands of NO molecules were found. Differences in the spectra obtained during destruction of N-N\(_2\)-Ne-He and N-N\(_2\)-Kr–He samples may be explained by a different shell structure of the nanoclusters formed during sample preparation.

1. Introduction
Impurity-helium condensates are quantum nanomaterials produced by injection of various atomic and molecular species (“the impurities”) into superfluid helium [1]. Structural and ultrasound studies revealed that the condensates are gel-like structures consisting of weakly interacting nanoclusters of impurities immersed into superfluid helium [2]. The Im-He condensates have attracted attention in various disciplines and practical applications for this material have been proposed. Very high concentrations of stabilized atoms can be achieved in Im-He condensates [1,3]. In the case of formation of condensates with stabilized N atoms the intense luminescence is observed during sample preparation and warming up of the samples. The detailed studies of the spectra of luminescence have been carried out earlier [4,5,6]. The luminescence of the samples during their destruction revealed interesting features. Upon destruction of N-N\(_2\)-Ar-He and N-N\(_2\)-Kr-He samples the M-bands of NO molecules were observed [7]. These studies were performed by recording spectra on Kodak film at the output of the spectrograph. This method does not allow studying changes of the spectra during the process of destruction and the registration of the each flash of the sample. In our work we obtained good quality optical spectra during Im-He sample destruction with repetition rate of 400 ms and proved that spectra during destruction of N-N\(_2\)-He and N-N\(_2\)-Ne-He samples differed substantially from that of N-N\(_2\)-Kr-He samples. The difference might be explained by the specific shell structure of nanoclusters that form Im-He solids.
2. Experimental Method
Impurity-helium condensates were formed by injection of gaseous mixtures (after passing through a discharge zone) into bulk superfluid helium. We used gas mixtures N2:He=1:100, N2:Ne:He=1:20:500 and N2:Kr:He=1:50:10000. The helium gas used in the experiments contained ~10 ppm of O2. The distance between the orifice for gas injection and the surface of the helium in the sample collection beaker was 2 cm. During 20 min sample preparation the superfluid helium in the beaker was replenished by using a fountain pump [1]. The temperature during sample preparation was about 1.6 K; the volume of the sample was a few cm³. After finishing sample preparation, we waited 15-20 minutes. During this waiting period, the sample afterglow disappeared. The warm-up process was initiated by decreasing of the pump rate of the cryostat and cutting-off the HeII supply to the beaker containing the sample. We observed thermoluminescence and spontaneous flashes from the samples upon warming from 1.5 to 15 K. The emission from the samples was collected by optical fiber connected to the entrance slit of a high resolution Ocean Spectra HR 2000+ ES spectrometer with enhanced sensitivity. The spectra were detected in the spectral range 200-1100 nm with resolution 1.3 nm. The exposure time for one spectrum was 400 ms. We were able to study the dynamics (with the temporal resolution 400 ms) of processes which initiate luminescence.

3. Results and Discussion
The luminescence spectrum obtained during N-N2-Ne–He sample preparation is shown in figure 1a. The most intense bands in this spectrum were assigned to the α-group, N(2D→4S) transitions, and β-group, O(1S→D) transitions. Also weak molecular nitrogen bands of the 1′ and 2′ systems (transitions B′Πg→A′Σu+ and C′Πg→B′Πg, respectively) and atomic He and Ne lines are displayed in this spectrum. Atomic lines of rare gas atoms correspond to Rg* emission from a gas jet. The luminescence spectrum during destruction of the N-N2-Ne–He sample is shown in figure 1b. The spectrum obtained during the destruction of the N-N2-He sample was very similar to that shown in figure 1b. Almost all luminescence during sample destruction was produced by oxygen atoms. Intense β-group as well as weak α′- and β″-groups of oxygen atoms are seen in the spectrum. The β′- and β″-groups correspond to electronic transitions O(1S→D) accompanied, respectively, by a simultaneous vibrational excitation (ν=0→ν=1) and de-excitation (ν=1→ν=0) in the neighbouring N2(X2Σg−) molecule [8]. A much less intense α-group and an even weaker α′-group were also present in the spectra. The α″-group is an electronic transition N(2D→4S) accompanied by a simultaneous vibrational excitation ν=0→ν=1 in the neighbouring N2(X2Σg−) molecule. The observation of β′ and β″ groups of oxygen atoms and the α′-group of nitrogen atoms is possible only if the emission of O and N atoms occur near a N2(X2Σg−) molecule. There was not any band of NO molecule in either spectrum.

The luminescence spectrum obtained during N-N2-Kr–He sample preparation is shown in figure 2a. The most intense lines in this spectrum belong to Kr atoms. Also atomic He, nitrogen α-group and oxygen β-group lines are presented in this spectrum. The luminescence spectrum during destruction of N-N2-Kr–He sample is shown in figure 1b. Again almost all luminescence during sample destruction was produced by oxygen atoms. The intense β-group is seen in the spectrum. The α-group is barely resolved in the spectra. But there are clearly seen the M-bands of NO molecules in this spectrum. The bands were reproduced in spectra of four different flashes observed during sample destruction.

The most surprising observation in these experiments was the substantial difference in the spectra during destruction of the samples studied. In the spectra of N-N2-He and N-N2-Ne-He samples, only the lines of single atoms O and N are present; however in the spectrum of N-N2-Kr-He sample in addition to the lines of O and N atoms, the bands of NO molecules are obtained. The thermoluminescence mechanism in the samples containing stabilized N and O atoms in an N2 matrix is well known. As temperature increases the thermal diffusion of N atom becomes possible and they recombine to create metastable N2(A′Σu+) molecules. The molecular excitation may be transferred through the N2 matrix to stabilized N and O atoms in their ground states. The emission from N2(D) and O(1S) so excited produce the α-group and the β-group, respectively. The intensity of β-group is larger.
than that of the \(\alpha\)-group because the probability of the transition \(O(1S \rightarrow 1D)\) is \(\sim 10^6\) times larger than that of \(N(2D \rightarrow 4S)\) transition, although the concentration of stabilized N atoms in the samples was from one to three orders of magnitude larger than that of stabilized O atoms. The absence of the NO bands in the N-N\(_2\)-He and N-N\(_2\)-Ne-He samples spectra means that N and O atoms in these samples are well separated. Let us analyse possible structures of the clusters formed by two impurities with different melting temperatures. In the case of N\(_2\) and Ne impurities, upon cooling down in the helium jet, first the nitrogen nanoclusters will be formed. The nitrogen atoms will be stabilized on the surfaces of N\(_2\) nanoclusters, and later the neon atoms will form the shell around nitrogen nanoclusters. The neon will influence only the spectral characteristics of the N atoms stabilized on the surfaces of N\(_2\) nanoclusters, and later the neon atoms will form the shell around nitrogen nanoclusters. The neon will influence only the spectral characteristics of the N atoms stabilized on the surfaces of N\(_2\) nanoclusters.

We observed the transformation of the shape of \(\alpha\)-group during destruction of N-N\(_2\)-Ne-He sample. At the beginning of the destruction the shape of \(\alpha\)-group was similar to that of N atoms stabilized in Ne matrix [6]. As time progressed, the shape of \(\alpha\)-group became similar to that of N atoms stabilized in N\(_2\) matrix [8].

In contrast for the case of N\(_2\) and Kr impurities cooling in the jet, first the Kr nanoclusters will be formed. The large surface of Kr nanoclusters will adsorb all N and O atoms and N\(_2\) molecules from the jet and significantly reduce the recombination of N atoms. The local concentration of N and O atoms on surface of Kr nanoclusters should be enhanced significantly. The N and O atoms stabilize close to each other. During warming up the N-N\(_2\)-Kr-He sample, the diffusion of N and O atoms leads to their recombination and creation of NO molecules. Further recombination of N atoms creates metastable \(N_2(A^3\Sigma_u^+)\) molecules, which transfer energy through the N\(_2\) matrix to excite \(O(1S)\) atoms and \(NO(a^3\Pi)\) molecules.

Figure 1. a) Luminescence spectra obtained during nitrogen-neon-helium sample preparation (gas mixture N\(_2\):Ne:He=1:20:500). b) Luminescence spectra during sample destruction.
Figure 2. a) Luminescence spectra obtained during nitrogen-krypton-helium sample preparation (gas mixture \( \text{N}_2: \text{Kr}: \text{He} = 1:50:10000 \)). b) Luminescence spectra during sample destruction. For sample destruction the spectra of four highest flashes are shown.

4. Conclusion

Optical spectra obtained for nitrogen–neon and nitrogen–krypton samples show evidence for different shell structure of nanoclusters in these samples and also the enhanced efficiency for stabilization atoms on the surfaces of Kr nanoclusters. Later effect was observed earlier for hydrogen atoms in hydrogen–krypton samples [3].

Acknowledgements The authors gratefully acknowledge the support by the Hackerman Foundation (Project # 010366-0137-2009) and the CRDF grant #16755.

[1] Khmelenko V V, Kunttu H, Lee D M 2007 J. Low Temp. Phys. 162 1
[2] Kiselev S I, Khmelenko V V, Lee D M, Kiryukhin V, Boltnev R E, Gordon E B, and Keimer B 2002 Phys. Rev. B 65 024517
[3] Boltnev R E, Bernard E P, Jarvinen J, Khmelenko V V and Lee D M 2009 Phys. Rev B 79 185506R
[4] Gordon E B, Pelmenev A A, Pugachev O F and Khmelenko V V 1981 Chem. Phys 61 35
[5] Boltnev R E, Gordon E B, Khmelenko V V, Krushinskaya I N, Martynenko M V, Pelmenev A A, Popov E A and Shestakov A F 1994 Chem. Phys. 189 367
[6] Boltnev R E, Gordon E B, Khmelenko V V, Martynenko M V, Pelmenev A A, Popov E A and Shestakov A F 1995 J. Chim. Phys. 92 362
[7] Boltnev R E, Krushinskaya I N, Pelmenev A A, Stolyarov D Yu and Khmelenko V V 1999 Chem. Phys. Lett. 305 217
[8] Oehler O, Smith D A and Dressler K 1977 J. Chem. Phys. 66 2097