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Luminescence of molecular nitrogen nanoclusters containing stabilized nitrogen, oxygen, hydrogen, and deuterium atoms.

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Abstract. We observed the appearance of a broad feature at 360 nm in spectra obtained during the destruction of ensembles of molecular nitrogen nanoclusters containing stabilized nitrogen, oxygen, hydrogen and deuterium atoms. We attribute this broad feature with a maximum at 360 nm to the N_4 polynitrogen molecules which are the product of the neutralization reaction of N_4^+ ions with electrons in solid N_2 .

1. Introduction

Relaxation processes in solid nitrogen containing stabilized atoms are of high interest in diverse fields of sciences. Nitrogen and nitrogen containing ices are present in large abundance in cosmic space [1], being exposed to solar wind and galactic cosmic rays. Another aspect of interest is related to polynitrogen compounds which are high-energy density materials (HEDM)[2,3]. HEDM materials with local concentrations of stabilized nitrogen atoms as high as 2×10^{21} cm⁻³ have been obtained in porous collections of nitrogen nanoclusters immersed in superfluid helium [4,5]. Most of the spectroscopic results obtained from studies of solid nitrogen containing stabilized atoms were explained by diffusion and chemical reactions of atoms and molecules in the process of annealing of solid matrices [6-9]. Only recently was the important role of radiation-induced charged particles (electrons and ions) suggested for these processes [10–15]. The explanation for some features in the observed luminescence spectra are still controversial. As an example, observed emission band at 360 nm had been assigned to the emission from the N_4^* polymer resulting from an N_4^+ neutralization process in solid N_2 irradiated by electrons [14]. However, earlier the band at 360 nm had been assigned to the $A^3\Pi, v' = 0 \rightarrow X^3\Sigma^-, v'' = 1$ transition of NH or ND radicals [16]. The NH radical has been observed by several methods. Also detected in the interstellar medium in 1991 [17], this radical has sparked the interest of astronomers and astrophysicists.

In this work we performed experimental studies of luminescence of nitrogen nanoclusters containing stablilized nitrogen atoms with small admixtures of hydrogen or deuterium atoms. The sample preparation method we used was the injection of the discharge products of nitrogen-

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helium or nitrogen-rare gas-helium mixtures into bulk superfluid (HeII) [18, 19]. This method creates nanoclusters of characteristic size ~ 5 nm with an overall density of impurity atoms and molecules in HeII of order 10^{20} cm⁻³ [20–22]. Nitrogen, oxygen, hydrogen, and deuterium atoms were formed in the discharge zone and were captured mostly on the surfaces of the molecular nitrogen nanoclusters [5, 23]. We found that a weak band at $\lambda = 360$ nm was present in the spectra observed during destruction of the nitrogen nanoclusters containing stabilized N and small admixtures of O atoms [9, 24]. This band is enhanced if hydrogen or deuterium atoms are present in the system. The addition of rare gases in the system did not significantly change the position of this band. On the basis of experimental observations described in this work, we conclude that the band at $\lambda = 360$ nm in the spectra obtained during the destruction of molecular nitrogen nanoclusters containing stabilized atoms, results from emission by N₄ polynitrogen.

2. Experimental Apparatus and Technique

The cryogenic part of the experimental setup consists of two silvered glass Dewars. Each Dewar has two slits for optical access. The inner Dewar is filled with liquid helium. By pumping on the helium bath with an Edwards E2M80 rotary vacuum pump, temperatures ~ 1.1 K are achievable.

The samples are created by injecting gas mixtures through a radio frequency (RF) discharge into a quartz beaker filled with HeII. The hydrogen-nitrogen-helium gas mixtures are prepared at room temperature in a gas handling system using Linde Electronics&Specialty research grade helium gas (99.9999% purity). We also used research purity nitrogen and hydrogen gases (99.9999%) from Matheson and deuterium gas $(99.6\% D_2 \text{ and } 0.4\% HD)$ from Cambridge Isotope Laboratory Inc. The oxygen content in the gas mixtures ~ 1 ppm results from contamination in this helium gas. A steady flux of 5×10^{19} atoms and molecules per second is maintained by a Brooks Instrument 5850E flow controller. The gas mixture enters the cryogenic system through a quartz capillary cooled by liquid nitrogen (LN₂). The RF discharge ($f \sim 50$ MHz, power ~ 75 W) is provided by a HP 8556B signal generator amplified by an E&I 3100L amplifier connected to electrodes surrounding the bottom of the quartz capillary. After passing through the discharge zone, the dissociated impurity atoms and excited molecules along with helium gas exit the quartz capillary through an orifice diameter ~ 0.75 mm and enter the helium Dewar. The pressure gradient ~ 2 Torr creates a well-formed jet which is injected into a beaker of superfluid HeII placed 2 cm below the orifice. The helium level in the beaker is maintained by a thermo-mechanical fountain pump which pumps HeII from the bottom of the main helium bath. During sample preparation a temperature of 1.5 K was maintained. The temperature inside the beaker was measured using a germanium thermometer.

After the sample is created, the fountain pump is turned off, ceasing the flow of HeII into the sample collection beaker. Over the course of ~ 15 - 20 minutes the liquid helium exits the beaker via film creep and evaporation, leaving a "dry" sample. At this moment, the pumping line to the Dewar is closed off, allowing the temperature of the sample to increase from 1.2 to ~ 15 K in ~ 50 s, and to initiate destruction of the sample, which is accompanied by thermoluminescence with a series of bright flashes.

The registration system for the luminescence spectra in the experimental setup consists of a bifurcated optical fiber which transfers the light emitted from the sample to the Andor Shamrock SR-500i and Ocean Optics HR2000+ spectrometers [24]. The Ocean Optics spectrometer can record spectra over a large wavelength range from 200 to 1100 nm, with spectral resolution 1.3 nm (generally used with a registration time from 100 to 300 ms). The Andor Shamrock SR-500i spectrometer with Newton EMCCD camera was used to obtain high resolution (0.53)nm, 1st grating) spectra. The higher sensitivity of the Andor spectrometer allows for a very short registration time (3 ms).

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Figure 1. Spectra observed by the Andor Spectrometer during destruction of the sample prepared from gas mixture $[H_2]:[N_2]:[He] = 1:330:33000$. a) Dynamics of luminescence spectra for the entire destruction process which were accumulated during period 1.5 s. b) Spectrum taken during destruction at t = 37.5 s. Temperature dependence on time during sample destruction is shown in the inset. c) Dynamics of emission taken during the final destruction of the sample with exposure time 3 ms. d) Spectrum taken at the end of sample destruction corresponds to t = 54.891 s with the most intense 360 nm band emission. Quantum efficiency of the Andor spectrometer is shown in the inset.

3. Experimental Results

First we studied the destruction process of the sample prepared from the gas mixture $H_2:N_2:He=1:330:33000$. Figure 1a shows the time dependence of the emission spectra of this sample in the spectral range from 240 to 580 nm. Spectra were obtained by the Andor spectrometer with exposure time 3 ms, but each spectrum shown in the Fig.1a is the sum of 500 spectra. Figure 1b shows the spectrum of sample luminescence corresponding to the 37th second after the beginning of destruction. The intense α -group of N atoms (transition ${}^{2}D \rightarrow {}^{4}S$), β -group of O atoms (transition ${}^{1}D \rightarrow {}^{1}S$) and Vegard-Kaplan (VK) bands of N₂ molecules (transitions $A^{3}\Sigma_{u} \rightarrow X^{1}\Sigma_{g}^{+}$) are present in the spectrum. Increasing the temperature of the sample initiates recombination of stabilized nitrogen atoms accompanied by luminescence. The warm-up thermogram during sample destruction is shown in the inset of Fig.1b. At the beginning of sample destruction, only the luminescence of the α -group of atomic nitrogen and VK

bands of N₂ can be seen in the spectra, and their intensities grow with increasing temperature. The intensity of the β -group emission of atomic oxygen is relatively small at the beginning of destruction but is increasing very strongly at the final stage of destruction. We also observed the appearance of the band with maximum at λ =360 nm at the end of destruction. All these features can be clearly seen in Figs. 1a and 1c. The spectrum taken at the end of destruction is shown in Fig. 1d. The main new effect observed in these experiments is the appearance of the strong band at $\lambda = 360$ nm.

As a next step we performed studies of the influence of the presence of molecular hydrogen in the initial gas mixtures on the appearance of the band at $\lambda = 360$ nm. We studied hydrogennitrogen-helium samples prepared from gas mixtures with different H₂/N₂ ratios: 1:200, 1:330, and 1:500. Figure 2 compares spectra of the largest flash observed during the destruction of samples prepared from different hydrogen-nitrogen-helium gas mixtures. All spectra were taken using the Ocean Optics spectrometer with the integration time 250 ms. In all samples the broad feature at ~ 360 nm, the α -group of N atoms, β -group of O atoms, and γ -line emission of N⁻ anions (transition ¹D \rightarrow ³P) [25] were observed. The largest intensity of the band at $\lambda = 360$ nm was observed for the sample prepared from gas mixture [H₂]:[N₂]:[He] = 1:330:33,000 (see Fig 2b), where it was found that reducing or increasing the hydrogen content present in this nitrogen-helium gas mixture decreased the intensity of all observed lines in the spectra of the largest flashes.



Figure 2. Comparison of spectra taken with the Ocean Optics spectrometer of the largest flash during the destruction of samples formed by different hydrogen-nitrogen-helium gas mixtures. a) $[H_2]:[N_2]:[He] = 1:200:20,000 \text{ b})$ $[H_2]:[N_2]:[He] = 1:330:33,000 \text{ c})$ $[H_2]:[N_2]:[He] = 1:500:50,000.$



Figure 3. Graph comparing spectra observed by the Andor Spectrometer with resolution 0.5 nm during the destruction of samples prepared from different gas mixtures: $[D_2]:[N_2]:[Ne]:[He] = 1:500:5000:100,000$ (blue), $[D_2]:[N_2]:[Ar]:[He] = 1:500:4500:225,000$ (red), and $[D_2]:[N_2]:[He] = 1:2,000:100,000$ (black).

We also studied the influence of addition of molecular deuterium to the nitrogen-helium make-up gas mixture on the luminescence spectra during sample destruction. It was found that the addition of D₂ molecules also leads to the appearance of the band at $\lambda = 360$ nm in the spectra. We studied spectra of thermoluminescence during destruction of samples prepared from deuterium-nitrogen-helium gas mixtures as well as mixtures also containing rare gases Ne and Ar. Figure 3 shows a comparison of spectra observed during the destruction of samples prepared from three different gas mixtures: deuterium-nitrogen-helium, deuterium-nitrogen-argon-helium, and deuterium-nitrogen-neon-helium. All spectra were taken using the Andor Spectrometer with

the integration time 300 ms. All spectra contain the 360 nm band, as well as the α , δ , and δ'' -groups of N atoms, the β -group of O atoms, the VK bands of N₂ molecules and the M bands of NO molecules.

4. Discussion

We have studied the optical luminescence spectra during the destruction of molecular nitrogen nanoclusters containing stabilized nitrogen, oxygen, hydrogen and deuterium atoms. As in earlier work [9, 24], the α -group of N atoms, β and β'' groups of O atoms and VK bands of N₂ molecules were present in the spectra of emitted light. The strong broad band with maximum at ~ 360 nm was observed in the spectra of samples which were prepared from gas mixtures containing hydrogen or deuterium. After analysis of our previous results we found that we observed only weak bands at 360 nm during the destruction of nitrogen nanoclusters containing only stabilized nitrogen atoms and small $(10^{-3} - 10^{-4})$ admixtures of oxygen atoms [9, 24]. The addition of H₂ or D₂ molecules in the gas mixture used during sample preparation resulted in enhancement of the intensity of the band appearing at $\lambda = 360$ nm in the luminescence spectra at the end of sample destruction (see Fig. 1c and Fig. 2). We found that the maximum intensity of the 360 nm band corresponds to some optimal quantity of H_2 or D_2 present in the make-up gas mixture. An important observation is that the addition of rare gases in the make-up gas mixture does NOT influence significantly the position of this band (see Fig. 3).

In the literature there are two explanations for the emission bands at $\lambda = 360$ nm. The first observation of this broad band was obtained when solid nitrogen was irradiated by 400 eV electrons, and the band was assigned to an unidentified impurity [26]. Later this luminescence band was studied during the excitation of solid nitrogen films by 500 eV electrons [14]. The band was assigned to the emission of polynitrogen N_4^* which was formed as a result of a neutralization reaction of N_4^+ with electrons. The scenario of "hole self-trapping" for N_2^+ ions with formation of N_4^+ in a nitrogen matrix was quite recently proposed [12, 13] because of the localized character of positive charge carriers in solid $N_2[27]$. This suggestion is in good accordance with both the study of gas-phase equilibria of solvation reactions of N_2^+ with N_2 molecules which revealed electrostatic bonding in the core clusters N_4^+ [28] and the laser-induced dissociation experiments showing N_4^+ as the ionic core for the even ion clusters $N_2^+ - (N_2)_n$ [29].

Another interpretation of the 360 nm band corresponding to the transition ND ($A^3\Pi v' = 0 \rightarrow$ $X^3\Sigma^- v'' = 1$) was suggested from the analysis of the luminescence spectra of the 0.1% N₂ doped solid deuterium irradiated by electrons [16]. Emission of NH (ND) radicals was also studied in different solid rare gases. It was found that the position of the (0-1) NH($A^3\Pi \rightarrow X^3\Sigma^-$) transition is shifted by tens of nanometers for different solid rare gases and that the band had a resolved structure [30].

In our experiments the spectra of the 360 band were not significantly influenced by the addition of rare gases or by the replacement of hydrogen isotopes in the nitrogen nanoclusters. This would give a preference for the interpretation of the observed band at 360 nm in our experiments as an emission of N_4 polynitrogen. However the question remains open as to why this emission was enhanced when the impurities of H_2 or D_2 were present in the molecular nitrogen nanoclusters. The exact identification of the transition of N_4 polynitrogen responsible for emission at $\lambda = 360$ nm requires additional experimental and theoretical work.

5. Conclusions

- (i) The process of stabilizing ground state atoms in molecular nitrogen nanoclusters provides a unique opportunity to study low temperature reactions and to produce a variety of unusual molecules in excited states.
- (ii) A weak broad band at 360 nm is observed during the destruction of ensembles of molecular nitrogen nanoclusters containing stabilized nitrogen and small admixtures of oxygen atoms.

This band was enhanced in the spectra of samples prepared from gas mixtures that contained hydrogen or deuterium.

(iii) Since this band is not changed significantly in rare gas matrices, we suggest that N_4^* polynitrogen molecule is responsible for the emission of the band at 360 nm. The exact shape and location of the 360 nm band is not altered by hydrogen isotope substitution These N_4 polynitrogen compounds are formed during the process of sample destruction accompanied by fast chemical reactions of nitrogen atoms and molecules.

6. Acknowledgments

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7. References

- Clark R N, Carlson R, Grundy W and Noll K 2013 Observed ices in the solar system The Science of Solar System Ices (Astrophysics and Space Science Library vol 356) ed Gudipati M S and Castillo-Rogez J (New York: Springer) pp 3–46 1st ed
- [2] Nguyen M T 2003 Coordination Chemistry Reviews 244 93 113
- [3] Zarko V E 2010 Combustion, Explosion, and Shock Waves 46 121–131
- [4] Boltnev R E, Krushinskaya I N, Pelmenev A A, Popov E A, Stolyarov D Y and Khmelenko V V 2005 Low Temp. Phys. 31 547–555
- [5] Mao S, Boltnev R E, Khmelenko V V and Lee D M 2012 Low Temp. Phys. 38 1313–1319
- [6] Bass A M and Broida H P 1956 Phys. Rev. **101**(6) 1740–1747
- [7] Oehler O, Smith D A and Dressler K 1977 J. Chem. Phys. 66 2097–2107
- [8] Khmelenko V V, Kunttu H and Lee D M 2007 J. Low Temp. Phys. 148 1–31
- [9] Khmelenko V V, Lee D M, Krushinskaya I N, Boltnev R E, Bykhalo I B and Pelmenev A A 2012 Low Temp. Phys. 38 688–699
- [10] Ponomaryov A N, Savchenko E V, Gumenchuk G B, Khizhniy I V, Frankowski M and Bondybey V E 2007 Low Temp. Phys. 33 532–537
- [11] Savchenko E, Khyzhniy I, Uyutnov S, Bludov M, Gumenchuk G and Bondybey V 2016 Radiation Measurements 90 1–5
- [12] Savchenko E V, Khyzhniy I V, Uyutnov S A, Barabashov A P, Gumenchuk G B, Ponomarov A N and Bondybey V E 2015 *Physica Status Solidi C* 12 49–54
- [13] Savchenko E V, Khyzhniy I V, Uyutnov S A, Barabashov A P, Gumenchuk G B, Beyer M K, Ponomaryov A N and Bondybey V E 2015 J. Phys. Chem. A 119 2475–2482
- [14] Savchenko E V, Khyzhniy I V, Uyutnov S A, Bludov M A, Barabashov A P, Gumenchuk G B and Bondybey V E 2017 J. Low Temp. Phys. 187 62–70
- [15] Pelmenev A A, Krushinskaya I N, Bykhalo I B and Boltnev R E 2016 Low Temperature Physics 42 224-229
- [16] Stenum B, Schou J, Sørensen H and Gürtler P 1993 J. Chem. Phys. 98 126-134
- [17] Meyer D M and Roth K C 1991 The Astrophysical Journal 376 L49
- [18] Gordon E B, Mezhov-Deglin L P and Pugachev O F 1974 JETP Lett. 19 63
- [19] Gordon E B, Mezhov-Deglin L P, Pugachev O F and Khmelenko V V 1976 Cryogenics 16(9) 555–557
- [20] Kiryukhin V, Keimer B, Boltnev R E, Khmelenko V V and Gordon E B 1997 Phys. Rev. Lett. 79 1774-1777
- [21] 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
- [22] Kiryukhin V, Bernard E B, Khmelenko V V, Boltnev R E, Krainyukova N V and Lee D M 2007 Phys. Rev. Lett. 98 195506–4
- [23] Bernard E P, Khmelenko V V and Lee D M 2008 J. Low Temp. Phys. 150 516-524
- [24] Meraki A, Mao S, McColgan P T, Boltnev R E, Lee D M and Khmelenko V V 2016 J. Low Temp. Phys. 185 269–286
- [25] Boltnev R E, Bykhalo I B, Krushinskaya I N, Pelmenev A A, Mao S, Meraki A, McColgan P T, Lee D M and Khmelenko V V 2016 Phys. Chem. Chem. Phys. 18 16013
- [26] Fugol I Y, Poltoratski Y B and Rybalko Y I 1978 Low Temp. Phys. 4 1048–1052
- [27] Loveland R J, Comber P G L and Spear W E 1972 Phys. Rev. B 6(8) 3121–3127
- [28] Hiraoka K and Nakajima G 1988 The Journal of Chemical Physics 88 7709–7714
- [29] David D E, Magnera T F, Tian R, Stulik D and Michl J 1986 Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 14 378 – 391
- [30] Bondybey V E and Brus L E 1975 The Journal of Chemical Physics 63 794-804