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Luminescence of ND radicals during the destruction of molecular nitrogen nanoclusters

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ABSTRACT

In this work we studied optical spectra of thermoluminescence accompanying the destruction of collections of molecular nitrogen nanoclusters containing stabilized nitrogen, oxygen, and deuterium atoms. These collections of nanoclusters were formed by the injection of products of a radio-frequency discharge in deuterium-nitrogen-helium gas mixtures into bulk superfluid ^{4}He. In the range from 200 to 1650 nm, the bands at 336 nm, 473 nm along with a new band at 1170 nm as well as the known bands of atomic nitrogen and oxygen, and bands of molecular nitrogen, oxygen, and NO were observed. These three bands were assigned to the emission of the ND radicals formed due to recombinations of nitrogen atoms in excited metastable states and deuterium atoms in the ground state during the destruction of ensembles of molecular nitrogen nanoclusters.

1. Introduction

The method of matrix isolation provides possibilities for studying exotic highly unstable species. In the past, considerable efforts were made to create systems with high concentrations of matrix-isolated free radicals [1]. Different practical applications were proposed for those systems such as clean energy storage and more efficient rocket fuel. The best results for obtaining high concentrations of stabilized atoms were achieved by condensing gas-phase products of a radio-frequency discharge into bulk superfluid helium [2,3]. This method allows the formation of a porous structure consisting of a collection of impurity nanoclusters inside superfluid helium (HeII). The characteristic size of the impurity nanoclusters is of order 5 nm and the overall density of impurity atoms and molecules inside HeII is of order 10^{20} cm^{-3} [4–6]. The pores in the structures formed by ensembles of nanoclusters which are also known as impurity-helium condensates, have a broad distribution of sizes ranging from 8 to 860 nm [7–9]. All of the pores are filled with liquid helium. Usually, most of the stabilized atoms reside on the surfaces of the nanoclusters [10,11]. The highest concentrations of stabilized atoms were achieved in nitrogen–helium condensates with relative concentration of stabilized nitrogen atoms ($N/N_2 \times 100$ %) in the range 10–30% [12]. High concentrations of nitrogen atoms stabilized in molecular nitrogen nanoclusters provide substantial chemical energy for promoting recombination reactions of stabilized atoms during warming of the samples [13–15]. The rapid release of stored chemical energy resulted in rapid heating and intense thermoluminescence of the samples. In the past, studies of thermoluminescence during the destruction of samples were performed for impurity-helium condensates containing N_2 molecules, N atoms, and rare gas atoms, as well as small amounts of oxygen atoms. Strong emissions from N atoms (α, α', δ, δ'-groups), O atoms (β, β', β'' groups), N_2 molecules (VK bands), NO molecules (M and β-bands), XeO molecules (green bands), O_2 molecules (second Herzberg bands), and N^- anions (γ-line) were observed in these experiments [16–22]. These studies provided examples of chemical reactions at low temperatures in collections of nanoclusters containing stabilized nitrogen and oxygen atoms.

In recent experiments small admixtures of hydrogen or deuterium were added into gas mixtures used for preparation of nitrogen-helium condensates in superfluid helium [23]. A new intense broad band at $\lambda\sim$ 360 nm was observed in these experiments. This band was assigned to the $2A_g \rightarrow 1A_g$ transition of $N_4(D_{2H})$ polymeric nitrogen. Additionally, in the experiments with the introduction of deuterium, the bands at λ = 336 and 473 nm were observed and were tentatively assigned to the ($A^3\Pi_i \rightarrow X^3\Sigma^-$) and ($b^1\Sigma^+ \rightarrow X^3\Sigma^-$) transitions of the ND radical [23]. The transition ($A^3\Pi_i \rightarrow X^3\Sigma^-$) at λ = 471 had previously been observed in the emission spectra of the NH(ND) radicals in noble-gas matrices

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[24–27]. However in the same experiment we observed the γ-line emission at 793 nm, which corresponds to the $^1D_2 \rightarrow {}^3P_2$ transition of N^- anions [22]. The presence of N^- anions during the destruction of the samples raised the possibility of observing other transitions of this species. Therefore the transition $^1S_0 \rightarrow {}^3P_{1,2}$ of N^- anions may be an alternative interpretation for the line at $\lambda = 473$ nm. If we assign the line at $\lambda = 473$ nm to the N^- ($^1S_0 \rightarrow {}^3P_{1,2}$) transition, and knowing the wavelengths of another transition N^- anion ($^1D_2 \rightarrow {}^3P_{1,2}$) [22], it is possible to calculate the wavelength of the transition $N^-(^1S_0 \rightarrow {}^1D_2)$. The calculated wavelength for $N^-(^1S_0 \rightarrow {}^1D_2)$ transition is equal to $\lambda = 1167$ nm. The position of this line is very close to the position of the band corresponding to the transition $b^1\Sigma^+ v' = 0 \rightarrow a^1\Delta^+, v'' = 0$ of the NH(ND) radical which was observed at $\lambda = 1170.47$ nm in an argon matrix [24].

To resolve the problem regarding the possibility of two alternative assignments of the emission at $\lambda = 473$ nm, we performed experiments with simultaneous registration of the spectra of emission in the ultraviolet (UV), visual and near infrared (NIR) regions during the destruction of pure nitrogen-helium samples and samples containing nitrogen and deuterium atoms. Analysis of these spectra provides convincing evidence for the assignment of the bands at $\lambda = 336$, 473, and 1170 nm to the ND radical.

2. Experimental setup

The experimental setup has been described in detail elsewhere [20]. Our experimental setup includes two concentric, silvered, glass Dewars. The inner Dewar is filled with liquid helium (LHe), and the outer Dewar with liquid nitrogen (LN_2). The helium Dewar is connected through a pumping line to an Edwards E2M80 mechanical pump. Using this pump, temperatures of 1.1 K are achievable inside the helium Dewar.

The gas mixtures that are used to create our samples are prepared at room temperature in a gas handling system. We increased the helium content of our gas mixtures to enhance the efficiency of dissociation of impurity molecules in the discharge. This system consists of a manifold connecting gas cylinders to gas mixing tanks, connection to an Edwards model 18 dual-stage rotary vane mechanical vacuum pump, and a Brooks 5850E mass flow controller. A stainless steel capillary connects the flow controller to the cryogenic portion of the setup. In our experiments we used Linde Electronics and Specialty Gases research-grade helium gas with 99.9999% purity. The oxygen present in our gas mixtures results from the ~1 ppm impurity in this gas.

Our samples are created by injecting a gas mixture into superfluid helium after passing through a 75 W radio-frequency (RF) ~50 MHz discharge zone. The RF discharge is provided by a HP 8656B signal generator supplemented with an Electronics & Innovations 3100L amplifier.

The discharge tube is made up of an outer quartz tube with an inner concentric quartz capillary. There are two discharge electrodes surrounding the capillary near the bottom of the quartz tube. The quartz tube is filled with LN_2 which simultaneously cools the discharge electrodes and the gas mixture passing through the capillary. The ~2 Torr pressure gradient between the discharge zone and the helium Dewar creates a well-formed jet as the excited atoms and molecules exit the orifice (ϕ~0.75 mm) of the discharge tube. Impurity atoms and molecules are rapidly cooled in the gas jet by the dense helium vapor and coalesce into nanoclusters. The beaker is placed ~2.5 cm below the orifice of the discharge tube. Inside the HeII, impurity nanoclusters aggregate into a porous structure. The level of HeII in the beaker is held constant by a thermo-mechanical fountain pump which supplies HeII from the bottom of the main bath. The temperature inside the sample beaker is maintained at 1.5 K by pumping on the main bath with the rotary pump, and is measured using a factory-calibrated Lake Shore Cryotronics GR-300-AA-0.3D germanium thermometer.

After the sample is created, the fountain pump is turned off, and the LHe is removed from the beaker by evaporation and the creeping film. When all of the LHe has left the beaker, the sample is said to be "dry". This process typically takes 15–20 min. With the dry sample, the valve to the pumping line is closed. Then the pressure and temperature increase inside the helium Dewar resulting in sample destruction, accompanied by luminescence of the sample, and concluding with bright flashes.

The emission of light in the UV and visible ranges is collected by a cryogenic fiber assembly [20] inside the Dewar which terminates at a vacuum feed-through. The opposite side of the vacuum feed-through is connected to a bifurcated fiber optical cable which simultaneously feeds an Ocean Optics HR2000 + spectrometer and an Andor SR500i spectrometer with a Newton EMCCD camera. The Ocean Optics spectrometer records spectra continuously in a wide spectral range (200–1100 nm) with a resolution of 1.3 nm. With this spectrometer the exposure time is generally between 250 and 500 ms. The Andor spectrometer can take high resolution spectra (0.53 nm, first grating) for a narrower spectral range ($\Delta\lambda = 340$ nm), but has a much higher sensitivity, allowing for an exposure time of 3 ms during registration. We have not presented spectra obtained by the Andor spectrometer in this paper.

The spectra of NIR emission is observed from the outside of the Pyrex Dewars through a strip window in the silvering. A collection lens focuses light emitted by the sample onto the entrance of a collimating lens where a fiber optic cable is attached. The fiber connects to an Avantes NIR 512-1.7 TEC spectrometer. This spectrometer can record spectra continuously in a spectral range from 900 to 1650 nm, with an exposure time of 250–500 ms, and a resolution of 5 nm.

3. Experimental results

We studied spectra during the destruction of two samples prepared from gas mixtures: $[N_2]$:[He] = 1:100 and $[D_2]$:$[N_2]$:[He] = 1:2000:100000. Usually the process of sample destruction lasted ~65–70 s. Fig. 1 shows integrated spectra obtained during the destruction in the UV and visual spectral ranges. Addition of deuterium in nitrogen-helium gas mixtures leads to a substantial reduction in the intensities of all bands previously observed from nitrogen–helium samples (see Fig. 1). In the integrated spectra of the nitrogen-helium sample the α, α'-groups of N atoms, β, β', and β''-groups of O atoms, γ-line of N^- anions, Vegard-Kaplan (V-K) bands of N_2 molecules, M-bands of NO molecules and the second Herzberg bands of O_2 molecules are present [20]. Only a few bands such as the α, α'-groups of N atoms and the β-group of O atoms, and γ-line of N^- anions [22] remain in the

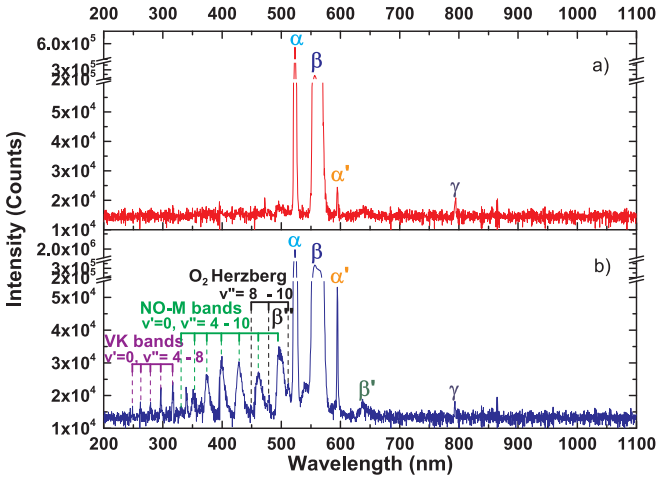

Fig. 1. Integrated spectra taken in the range 200–1100 nm by the Ocean Optics spectrometer during destruction of the samples prepared from different gas mixtures a) $[D_2]$:$[N_2]$:[He] 1:2000:100,000 (red), b) N_2:He 1:100 (blue). Each spectrum was accumulated during a period of 75 s.