

Formation of $(\text{Xe}_2\text{H})^*$ centers in solid Xe via recombination: nonstationary luminescence and «internal electron emission»

E.V. Savchenko¹, I.V. Khyzhniy¹, S.A. Uytunov¹, G.B. Gumenchuk², A.N. Ponomaryov², M.K. Beyer³, and V.E. Bondybey²

¹*Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine
47 Lenin Ave., 61103 Kharkov, Ukraine*

²*Lehrstuhl für Physikalische Chemie II TU München, Lichtenbergstraße 4, 85747 Garching, Germany*

³*Institut für Physikalische Chemie Christian-Albrechts-Universität Kiel, Olshausenstraße 40, 24098 Kiel, Germany*

E-mail: elena.savchenko.mytum@googlegmail.com

Received February 19, 2010

The formation of excimers $(\text{Xe}_2\text{H})^*$ in solid Xe doped with molecular hydrogen under electron beam is studied using the original two-stage technique of nonstationary (NS) cathodoluminescence (CL) in combination with the current activation spectroscopy method — thermally stimulated exoelectron emission (TSEE). Charged species were generated using a high-density electron beam. The species produced were then probed with a low-density beam on gradual sample heating. The near UV emission of the $(\text{Xe}_2\text{H})^*$ was used to monitor the neutralization process. It is found that the temperature behavior of the NS CL band of $(\text{Xe}_2\text{H})^*$ clearly correlates with the yield of TSEE measured after identical pre-irradiation of the sample. The fingerprints of the thermally stimulated detrapping of electrons — «internal electron emission» in the spectrum of NS CL point to the essential role of neutralization reaction in the stability of the proton solvated by rare-gas atoms.

PACS: 78.60.Hk Cathodoluminescence, ionoluminescence;

78.60.-b Radiative recombination;

79.75.+g Exoelectron emission.

Keywords: rare-gas hydride trimers, recombination, cathodoluminescence, thermally stimulated exoelectron emission.

1. Introduction

Ionic and neutral rare-gas hydride molecules, their formation and stability attract much interest in physical and chemical studies ([1–4] and references therein). Protonated and deuterated rare-gas species $(\text{Rg}_2\text{H})^+$ and $(\text{Rg}_2\text{D})^+$ have been prepared in cryogenic matrices using different techniques: ultraviolet (UV) excitation [5,6], deposition from discharge [7,8], electron bombardment [9]. For the most part the experiments were performed using the photolysis of molecular species containing an electronegative fragment (HF, HBr, etc.). In this case besides $(\text{Rg}_2\text{H})^+$ and their deuterated analogues $(\text{Y}_2\text{H})^-$ species were created in rare-gas matrices ($\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$). In a number of studies the production of protonated and deuterated rare-gas ionic species was detected by infrared (IR) spectroscopy. Several absorption lines were registered

and their possible ionic origin discussed [7,8]. Initially the authors were inclined to believe that the lines belong to neutral species. Their ionic nature was conclusively demonstrated in Refs. 10, 11 and became the subject of further studies, e.g., [12–14]. The observed lines in the infrared spectra shows an interesting behavior — they readily disappear on sample annealing, and «bleaching» of the lines, which belong to the protonated species, proceeds much faster than that for the deuterated species. This puzzling behavior has stimulated much interest to the question on stability of ionic species $(\text{Rg}_2\text{H})^+$ and $(\text{Rg}_2\text{D})^+$. Several mechanisms of their decay were proposed. It was suggested that the room-temperature black-body radiation induced diffusion of protons and deuterons [15]. The rate constants for an elementary step of the diffusion of H^+ and D^+ calculated with taking into account thermal activation and tunneling [16] supposed a dominant

contribution of tunneling into the diffusion. Another process, which is liable to be responsible for the decay of $(\text{Rg}_2\text{H})^+$ and $(\text{Rg}_2\text{D})^+$ ionic centers in the rare-gas matrices, is their neutralization by electrons. Such a possibility was considered in Ref. 17. It is suggested that the mechanism of neutralization involves tunneling of an electron from an electronegative fragment or another trap to the $(\text{Rg}_2\text{H})^+$ center.

The formation of protonated and deuterated rare-gas ionic dimers was also observed by IR absorption spectroscopy in rare-gas matrices doped only with H_2 and D_2 (without any admixture of electronegative species), e.g., [8]. Neutralization of protonated rare-gas dimers and their deuterated analogues results in an emergence of the excimers $(\text{Rg}_2\text{H})^*$, $(\text{Rg}_2\text{D})^*$. Their emission spectra, which fall in the vacuum ultraviolet (VUV) range, exhibit broad bands stemmed from the bound-free transition to a repulsive part of the ground state potential. Their kinetics and the excitation spectra were the subject of detailed studies [18–21] performed with synchrotron radiation. $(\text{Rg}_2\text{H})^*$ and $(\text{Rg}_2\text{D})^*$ were considered by Kraas and Gürtler as the ion-pair states $(\text{Rg}_2^+\text{H}^-)$ and $(\text{Rg}_2^+\text{D}^-)$. The most long-wave emissions at 4.92 and 4.9 eV were observed from the radiative decay of $(\text{Xe}_2\text{H})^*$ and $(\text{Xe}_2\text{D})^*$, correspondingly. The experiments mentioned above pointed to a quite efficient dissociation of H_2 and D_2 molecules in rare-gas matrices despite the «cage effect». The dissociation of D_2 molecule in solid Xe was observed in [22] by monitoring the emission of $(\text{Xe}_2\text{D})^*$ under irradiation of Xe– D_2 mixtures by an electron beam. The authors suggested an excitonic mechanism of D_2 dissociation which involves an intermediate complex $(\text{XeD}_2)^*$ formed due to localization of the Xe matrix exciton near the D_2 impurity center. Under nonselective excitation above the band gap energy E_g one could expect a contribution of the charge recombination (neutralization) reaction to the formation of excimers.

The present paper reports the results on nonstationary cathodoluminescence (NS CL) of solid Xe doped with molecular hydrogen H_2 without any admixture of electronegative species. The combination of nonstationary luminescence and the electric current method (thermally stimulated emission of electrons — TSEE) was used to monitor the neutralization process. It is based on some kind of «pump-probe» experiments with controlled *in situ* «injection» of electrons into the Xe matrix via their release from the traps stimulated by the sample heating.

2. Experimental details

Some details of the experimental technique were described recently [23]. High-purity gases: (99.999%) Xe and (99.999%) H_2 were used. The mixture of a desired concentration (usually 0.1% H_2) was prepared in a gas-handling system which was previously degassed by heating

under pumping. The base pressure in the sample chamber was $\sim 10^{-9}$ mbar. The samples of solid Xe doped with H_2 were grown from the gas phase by deposition on a MgF_2 thin layer coated metal substrate cooled by a closed-cycle 2-stage Leybold RGD 580 cryostat. The gas flow rate during deposition controlled by means of a Brokhorst Gas Flow Controller was 2 ml/min; the sample thickness, typically 50–100 μm , was independently determined by measuring the pressure decrease in a known volume of the container in the gas-handling system. The samples were of a high optical quality and looked transparent. To generate charge centers and dissociate H_2 molecules the samples were irradiated by a 1 keV electron beam at 6 K. The spectral measurements over the range from 200 to 1100 nm were performed using a CCD-based Ocean Optics S2000 spectrometer. The redistribution of intensity with the exposure time showed the formation of radiation-induced reactions products. The programmable temperature controller Leybold LTC 60 allowed us to maintain the desired temperature of deposition, irradiation and heating regimes. In the experiments, we used a constant heating rate of mostly 3.2 K/min. The temperature was measured with a calibrated silicon diode sensor, mounted on the substrate. Upon completion of irradiation we measured the yield of thermally stimulated exoelectron emission from the samples. The TSEE signal was detected by an Au-coated Faraday plate (kept at a small positive potential +9 V) and amplified by a FEMTO DLPCA 100 current amplifier.

3. Results and discussion

When the matrix is subjected to irradiation by a beam of electrons, some of them are inevitably stabilized in the traps of various depths, and remain there once irradiation is completed. Then these can be released either by gradual heating of the sample or by irradiating it by photons of an appropriate wavelength. These trapped electrons are indirectly detected via the appearance of thermally stimulated luminescence (TSL) and thermally stimulated exoelectron emission [24,25]. With this in mind, we have used a modified experimental approach [26] for probing the role of charge recombination reactions in the stability of positively charged ionic species including proton or deuteron solvated by rare-gas atoms.

The luminescence spectra of solid Xe doped with H_2 or D_2 were measured at 7 K. The spectra were successively detected with an exposure time (15 min). Figure 1 depicts the evolution of the emission band at 252 nm (with FWHM = 325 meV) which stems from the radiative transition of the $(\text{Xe}_2\text{H})^*$ to a repulsive part of the ground state. A pronounced increase of the band under irradiation by high-density electron beam was observed, demonstrating the efficient dissociation of the H_2 molecule and the formation of the rare-gas hydride molecule.

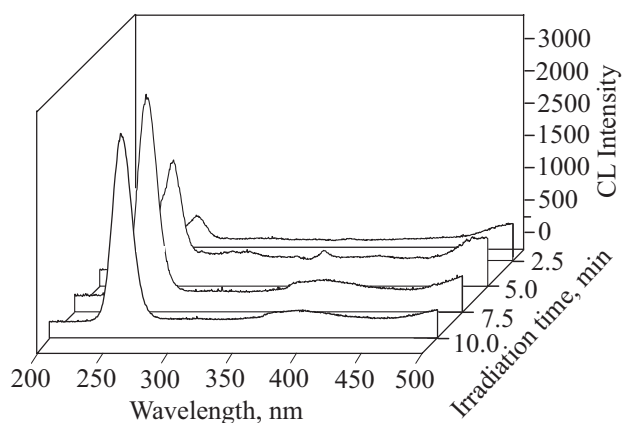
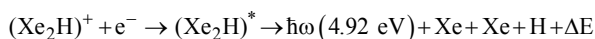


Fig. 1. Evolution of the $(\text{Xe}_2\text{H})^+$ emission band with exposure time.

In order to check a possible contribution from the neutralization reaction



special experiments were performed with «ejecting» electrons from shallow traps, i.e., defects in the rare-gas cryocrystals, by sample heating. In these kind of «pump-probe» experiments, the ionic species of interest were first generated with an intense electron beam of a high current density of 0.1 mA/cm^2 during 20 min. The time interval was large enough to create and to fill the shallow electron traps. The ionic species produced were then probed by the nonstationary luminescence (band at 252 nm) using a low-density electron beam (about $10 \mu\text{A/cm}^2$) to minimize the production of new ions. The «probing» was carried out on gradual linear heating of the sample in order to release electrons from progressively deeper traps and in doing so to enhance their recombination with positively charged centers $(\text{Xe}_2\text{H})^+$.

Figure 2 demonstrates changes of the $(\text{Xe}_2\text{H})^*$ emission band on such a heating which was performed at a rate of

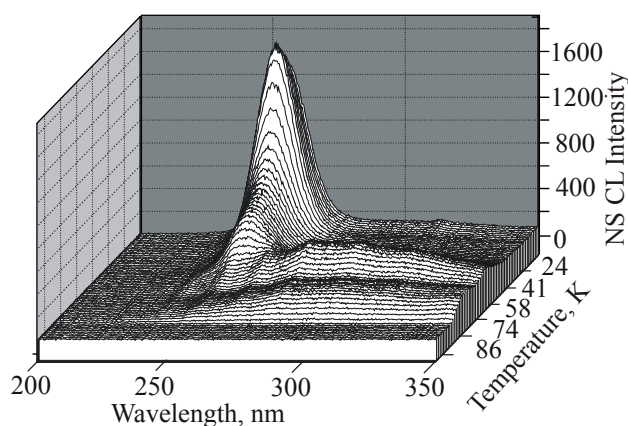


Fig. 2. Nonstationary luminescence (NS) in the range of $(\text{Xe}_2\text{H})^*$ emission measured under low-density electron beam at the sample heating with the rate of 3.2 K/min.

3.2 K/min. The spectra were recorded successively every 10 s. As seen in the figure, the intensity of the nonstationary luminescence band shows a nonmonotonic behavior — it first increases rapidly while heating and peaks at about 10 K. Further heating results in a decrease of the band intensity yielding however weak maxima at about 20 and 33 K. Upon reversing the temperature change to cooling, the intensity of nonstationary luminescence remains nearly constant.

One might expect the temperature dependence of the nonstationary luminescence intensity to «correlate» with peaks of thermally stimulated exoelectron emission due to the «internal electron emission». As an example, Fig. 3 illustrates the enhancement of the well-established $(\text{Xe}_2\text{H})^*$ emission band at 252 nm resulting from the recombination of $(\text{Xe}_2\text{H})^+$ species with detrapped electrons. The temperature behavior of the nonstationary luminescence band of $(\text{Xe}_2\text{H})^*$ measured under the low-density electron beam clearly correlates with the yield of TSEE measured after identical pre-irradiation of the sample. A rough estimation of the activation energy E_{act} associated with the low-temperature peak at about 10 K made by the half-width method [27] (using the ascending as well as the descending parts of the TSEE curve) resulted in $E_{\text{act}} \sim 10 \text{ meV}$. The distribution of electron traps depends on the matrix structure. The stability of ionic species with respect to neutralization is determined by the efficiency of detrapping and electron transport. The stabilization of positive charge centers in solid Xe in the presence of hydrogen atoms was discussed in Ref. 28. Note that the Xe matrices grown from discharge contain a high concentration of ionic centers and electrons in traps, which manifest themselves in strong thermoluminescence and photon-induced bleaching of ionic centers [29].

The results presented demonstrate the essential role of electron traps in the stability of the proton solvated by rare-gas atoms. A similar behavior is observed for the deuterated species $(\text{Xe}_2\text{D})^*$. An important process res-

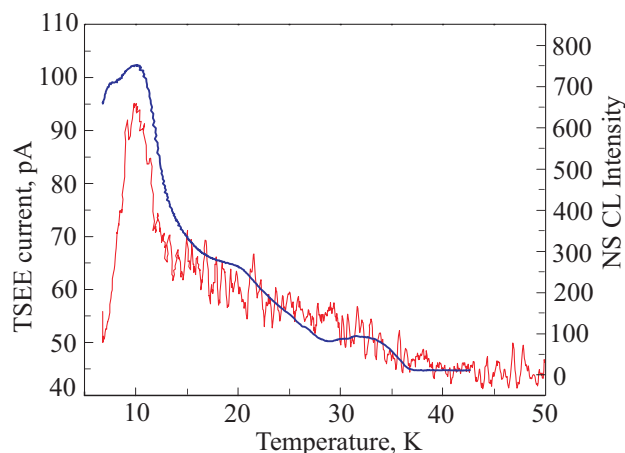


Fig. 3. Comparison of the $(\text{Xe}_2\text{H})^*$ emission band temperature behavior with the TSEE yield from the pre-irradiated sample.

possible for the proton and deuteron thermal stability is shown to be the thermally stimulated release of electrons from the traps followed by the charge recombination reactions.

The authors thank Markku Räsänen and Leonid Khriachtchev for valuable comments. E.V.S., I.V.Kh. and S.A.U. would like to acknowledge DFG for travel grant.

1. V.A. Apkarian and N. Schwentner, *Chem. Rev.* **99**, 1481 (1999).
2. V.E. Bondybey, M. Räsänen, and A. Lammers, *Ann. Rep. Progr. Chem.* **C95**, 331 (1999).
3. L. Khriachtchev, M. Pettersson, N. Runeberg, J. Lundell, and M. Räsänen, *Nature (London)* **406**, 874 (2000).
4. B. Gerber, *Ann. Rev. Phys. Chem.* **55**, 55 (2004).
5. D.E. Milligan and M.E. Jacox, *J. Chem. Phys.* **53**, 2034 (1970).
6. D.E. Milligan and M.E. Jacox, *J. Chem. Phys.* **55**, 2550 (1971).
7. V.E. Bondybey, G.C. Pimentel, and P.N. Noble, *J. Chem. Phys.* **55**, 540 (1971).
8. V.E. Bondybey and G.C. Pimentel, *J. Chem. Phys.* **56**, 3832 (1972).
9. T.D. Fridgen and J.M. Parnis, *J. Chem. Phys.* **109**, 2155 (1998).
10. D.E. Milligan and M.E. Jacox, *J. Mol. Spectrosc.* **46**, (1973).
11. C.A. Wight, B.S. Ault, and L. Andrews, *J. Chem. Phys.* **65**, 1244 (1976).
12. H. Kunttu, J. Seetula, M. Räsänen, and A. Apkarian, *J. Chem. Phys.* **96**, 5630 (1992).
13. M. Räsänen, J. Seetula, and H. Kunttu, *J. Chem. Phys.* **98**, 3914 (1993).
14. Henrik M. Kunttu and Jorma Seetula, *Chem. Phys.* **189**, 273 (1994).
15. M.K. Beyer, E.V. Savchenko, G. Niedner-Schatteburg, and V. Bondybey, *Fiz. Nizk. Temp.* **25**, 1087 (1999) [*Low Temp. Phys.* **25**, 814 (1999)].
16. M.K. Beyer, V.E. Bondybey, and E.V. Savchenko, *Fiz. Nizk. Temp.* **29**, 1045 (2003) [*Low Temp. Phys.* **29**, 792 (2003)].
17. Leonid Khriachtchev, Antti Lignell, and Markku Räsänen, *J. Chem. Phys.* **123**, 064507 (2005).
18. M. Kraas and P. Gurtler, *Chem. Phys. Lett.* **174**, 396 (1990).
19. M. Kraas and P. Gurtler, *Chem. Phys. Lett.* **183**, 264 (1991).
20. M. Kraas and P. Gurtler, *Chem. Phys. Lett.* **187**, 527 (1991).
21. Mathias Kraas, Dissertation, Hamburg, DESY (1992).
22. A.G. Belov, M.A. Bludov, and E.I. Tarasova, *Fiz. Nizk. Temp.* **35**, 1230 (2009) [*Low Temp. Phys.* **35**, 957 (2009)].
23. A. Ponomaryov, G. Gumenchuk, E. Savchenko, and V.E. Bondybey, *Phys. Chem. Chem. Phys.* **9**, 1329 (2007).
24. I.V. Khyzhniy, O.N. Grigorashchenko, A.N. Ponomaryov, E.V. Savchenko, and V.E. Bondybey, *Fiz. Nizk. Temp.* **33**, 701 (2007) [*Low Temp. Phys.* **33**, 529 (2007)].
25. I.V. Khyzhniy, S.A. Uytunov, E.V. Savchenko, G.B. Gumenchuk, A.N. Ponomaryov, and V.E. Bondybey, *Fiz. Nizk. Temp.* **35**, 433 (2009) [*Low Temp. Phys.* **35**, 335 (2009)].
26. O.N. Grigorashchenko, S.A. Gubin, A.N. Ogurtsov, and E.V. Savchenko, *J. Electron Spectrosc. Related Phenom.* **79**, 107 (1996).
27. D.R. Vij, in: *Luminescence of Solids: Thermoluminescence*, D.R. Vij (ed.), Plenum Press, New York (1998).
28. M. Beyer, A. Lammers, E. Savchenko, G. Niedner-Schatteburg, and V. Bondybey, *Phys. Chem. Chem. Phys.* **1**, 2213 (1999).
29. E.V. Savchenko, N. Caspary, A. Lammers, and V.E. Bondybey, *J. Low Temp. Phys.* **111**, 693 (1998).