Observation of Fluorescence from Heavy Rare-Gas Hydrides and Deuterides in Electron-Irradiated Matrices of Solid Hydrogen and Deuterium

J. Schou, B. Stenum, and H. Sørensen
Physics Department, EURATOM-Risø National Laboratory, DK-4000 Roskilde, Denmark

P. Gürtler
Hamburger Synchrotronstrahlungslabor (HASYLAB), Deutsches Electronen Synchrotron (DESY),
D-2000 Hamburg 52, Federal Republic of Germany

(Received 30 May 1989)

The first detection of neutral heavy rare-gas hydrides and deuterides produced in a solid is reported. XeD, XeH, and KrD were generated in Xe- and Kr-doped matrices of the solid hydrogens irradiated by 2-keV electrons. The fluorescence bands peak close to the wavelength value of the bound-free hydride $B\,^2\Pi \rightarrow X\,^2\Sigma^+$ transition in the gas phase.

PACS numbers: 33.20.Lg, 34.50.Gb, 78.60.Fi

The production of neutral rare-gas hydrides and deuterides[1-10] is a relatively new feature. Only ArH and ArD have been known for more than a decade.[9] These simple molecules are characterized as Rydberg molecules because of the hydrogenlike structure of the excited states.[2] A feature common to all the molecules is the strongly repulsive ground state which has made the observations of the unstable molecules difficult. Usually, the hydrides and deuterides have been produced by electronic excitations in gaseous mixtures[1-5,9] or by neutralization of charged beams.[6-8] The only existing observation of a rare-gas hydride and deuteride produced in a gas-solid environment was made by Brooks and coworkers.[10,11] They reported discrete spectra from HeH and HeD formed at the interface of the solid hydrogens and dense He gas, or in macroscopic large bubbles in the solids. The authors demonstrated that the vapor pressure of hydrogen or deuterium is of importance, and that a ratio 10^8:1 for He to H or D pressure leads to a maximum in spectral intensity.

Here we present the first spectra of the heavy rare-gas hydrides and deuterides produced in the bulk of samples of the solid hydrogens doped with a small amount of rare gases. XeD and probably XeH are produced by a mechanism entirely different from the formation of helium hydrides and deuterides observed by Brooks and coworkers.[10,11]

Our measurements represent to our knowledge the first example of an identified uv fluorescence from doped samples of the solid hydrogens. We have previously reported a broad feature in purified deuterium around 275 nm (Ref. 12) which we have tentatively assigned to a bound-free transition in D_3. Brooks[13] observed transitions in the visible region from nitrogen and oxygen impurities in solid deuterium and hydrogen. Since the intrinsic luminescence from these two materials is extremely weak,[12] solid hydrogen and deuterium are ideal hosts for studies of impurities. The disadvantage of using these materials as host is their high volatility even at liquid-helium temperature.

The experimental setup is similar to that previously utilized by us for studies of sputtering of solidified gases by keV electron bombardment.[14] A modification allows us to observe light emission from samples of the hydrogens with high sensitivity at the expense of high resolution. The luminescence in the region 200–600 nm is recorded with a cooled Valvo XP2020Q photomultipler coupled to a $f/3.5$ Jobin Yvon monochromator. Thick films ($\approx 1\ \mu$m) of the appropriate gas mixtures are produced by letting a jet of gas hit a gold substrate or a quartz-crystal microbalance suspended below a pumped liquid-helium cryostat. The films may be irradiated by a continuously rastered electron beam of energy 1–3 keV and current typically 50–300 nA, so that beam-induced evaporation of the volatile solid is largely reduced. During irradiation, the temperature of the solid was 3–4 K depending on the beam current.

The concentration of the rare gas was determined from the gas mixture at room temperature. However, since the gases were purified by a cryotrap in the gas inlet system, the concentration of the rare gas in the frozen sample might have been reduced relative to the gas mixture.

Figure 1 shows the spectrum for Xe-doped solid deuterium. The most pronounced peak has a maximum at 269 nm which is close to the gas-phase value of about 271 nm of the bound-free $B\,^2\Pi \rightarrow X\,^2\Sigma^+$ transition of XeH reported by Möller, Beland, and Zimmerer.[1] The broad peak at 420–450 nm is a structureless oxygen-impurity feature.[12] Brooks[13] observed the molecular transition $A'\,^3\Delta_u \rightarrow X\,^3\Sigma_g^-$ of O_2 in solid H_2 and D_2 in the same wavelength region, but the peak seen by us has no discrete emission band. The clear concentration dependence of the peak at 269 nm demonstrates that the peak is a XeD transition. No other gases, e.g., the stated impurities in our research-purity Xe gas, show a similar peak in solid deuterium or hydrogen. At our best resolution of 4 nm we have been unable to resolve any fine

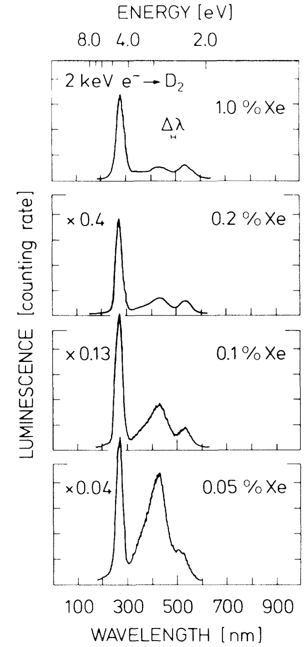

FIG. 1. Fluorescence of XeD for several Xe concentrations in solid D_2. (The peak at 540 nm is second order of XeD.)

structure of the two peaks.

The spectra from Kr-doped solid deuterium show the same characteristic dependence on the Kr concentration, but the KrD emission is weaker than that from the broad oxygen-induced impurity peak except for the highest Kr concentration (2%), and substantially weaker than the XeD emission in Xe-doped deuterium (Fig. 2). The energy position of the maximum at 260 ± 2 nm is close to that of the $B\,^2\Pi \rightarrow X\,^2\Sigma^+$ transition of KrH in the gas phase. A similar peak for Ar-doped deuterium was observed at 285 nm for only a high concentration (2%). For concentrations smaller than that the peak is not clearly identifiable, and for large Ar concentrations the N_2 impurity content of the Ar leads to a strong superposition of the molecular N_2 transitions $A\,^3\Sigma_u \rightarrow X\,^1\Sigma_g^+$ (Ref. 15) on the possible ArD peak. Although this wavelength is not far from the gas-phase value of about 276 nm, we have no argument for assigning the peak to an ArD transition other than that the appearance is similar to the heavy rare-gas hydrides.

The precise emission wavelengths of the bound-free transition for the rare-gas hydrides and deuterides in a matrix are not known. However, the atomic and molecular lines observed by Brooks[13] in the solid hydrogens were shifted very little, and the molecular transitions of the N_2 impurity observed by us lay within 1 nm of the known values in solid N_2. This means that the gas-solid shifts are small in solid H_2 and D_2, supporting our assignments, since our observed transition lies close to the reported gas values of $B\,^2\Pi \rightarrow X\,^2\Sigma^+$ from Möller, Beland, and Zimmerer[1] (Table I).

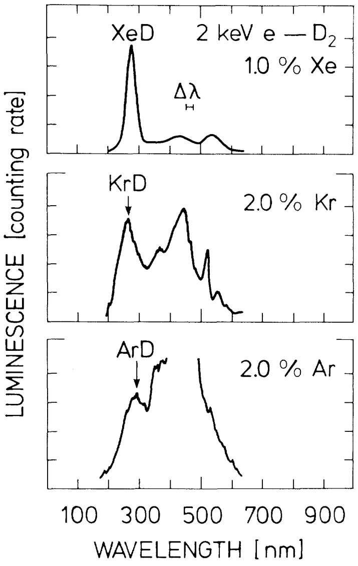

FIG. 2. Fluorescence of XeD, KrD, and possibly ArD in solid D_2. The vertical scale is different for the three molecules.

The intensity of the XeH emission was about a factor of 4 lower than that for XeD (Table I). This is in agreement with the expectation that predissociation is much more probable for H than for D atoms. We did not succeed in producing XeH peaks for high concentrations, whereas XeD peaks with a superimposed N_2-impurity structure were produced up to concentrations of about 15%. The intensities normalized to beam current and concentration are listed in Table I.

A striking fact is the weak intensity of the KrD peak and the possible ArD peak. The intensity is about 2 orders of magnitude less than the corresponding one for Xe at the same concentration. The reason for the difference is that for Xe a variety of excited states ($5d,6p,6s$) are well below the Lyman-α level for single D atoms as well as the lowest excited, nonrepulsive state $B\,^1\Sigma_u^+$ of D_2.

TABLE I. Normalized intensities for different concentrations c of the rare-gas hydrides and deuterides. The intensities were derived by dividing the measured value by the beam current and the concentration.

c (%)	XeD	XeH	KrD	ArD
0.05	0.5	0.15	0.007	⋯
0.1	0.85	⋯	⋯	⋯
0.2	1	⋯	0.005	⋯
0.75	⋯	0.25	⋯	⋯
1.0	0.45	⋯	0.007	⋯
2.0	⋯	⋯	0.025	0.004
λ (nm)	269		260	285
λ (Ref. 1)	271			276

For Kr, only the lowest excited states ($5s\ ^3P_1, ^3P_2$) are below the B state of D_2, and for Ar, all excited states are above the lowest excited states of D and D_2.[16] After excitation, the system will relax down to the lowest excited states, which are the $6s\ ^3P_1, ^3P_2$ of the Xe. Then XeD may be produced by the following reaction:

$$\mathrm{Xe}^* + \mathrm{D} + \mathrm{D}_2 \rightarrow \mathrm{XeD}^* + \mathrm{D}_2 . \qquad (1)$$

The generation of hydride and deuteride ions from $H_3{}^+$ ions and $D_3{}^+$ ions may be possible as well. The neutralization of RH^+ and RD^+ has been utilized in the neutral-beam experiments, and such a process may work for all rare gases and not only for Xe. The process (1) requires deuterons in the solid matrix. These atoms are liberated as a result of $D_3{}^+$ generation from molecular ions that were produced by the primary electrons,

$$\mathrm{D}_2{}^+ + \mathrm{D}_2 \rightarrow \mathrm{D}_3{}^+ + \mathrm{D} , \qquad (2)$$

or from dissociative excitation or ionization of D_2.

Our measurements have shown that the intensity increased by a factor of 2 during the first period, of the order of 10 min, of irradiation. This time development agrees well with that observed by Brooks *et al.*[17] for the formation of $D_3{}^+$ alone or embedded in small clusters. This is the expected time behavior for the concentration of single D atoms as well, if the majority of the D atoms originate from the formation of $D_3{}^+$ clusters.

In contrast to the measurements of Brooks and coworkers[10,11] on helium hydrides and deuterides, the generation of XeD molecules in not dependent on the existence of a surface. We did not observe any significant change in the intensity when our Xe-doped sample was covered with a D_2 film. However, we may not exclude the possibility that the XeD molecules are generated close to or in microscopic cavities that always are present in samples produced in this way.

A surprising feature is the small full width at half maximum (≈ 20 nm) of the fluorescence band of XeD produced in the solid compared with that in the gas phase (≈ 100 nm). However, the spectra from Möller, Beland, and Zimmerer[1] have been obtained with a low counting rate and probably contain contributions from more than one vibrational level of the $B\ ^2\Pi$ state. The present observations originate from a solid in which fast relaxation to the lowest level is expected. This could explain the difference between the solid and the gas phases.

In summary, we have presented the first measurements on the neutral heavy rare-gas deuterides and hydrides produced in a solid. The high intensity of the XeD peak compared with other deuterides indicates that the rare-gas deuteride is primarily formed from excited Xe atoms in the D_2 matrix, and not from the neutralization of rare-gas deuteride ions known from neutral-beam experiments.

---

[1] T. Möller, M. Beland, and G. Zimmerer, Phys. Rev. Lett. **55**, 2145 (1985); Chem. Phys. Lett. **136**, 551 (1987).

[2] G. Herzberg, Annu. Rev. Phys. Chem. **38**, 27 (1987).

[3] R. H. Lipson, Chem. Phys. Lett. **129**, 82 (1986); I. Dabrowski, G. Herzberg, and R. H. Lipson, Mol. Phys. **63**, 289 (1988).

[4] M. Douay, S. A. Rogers, and P. F. Bernath, Mol. Phys. **64**, 425 (1988).

[5] I. Dabrowski, G. Herzberg, B. P. Hurley, R. H. Lipson, M. Vervloet, and D. C. Wang, Mol. Phys. **63**, 269 (1988).

[6] W. Ketterle, H. Figger, and H. Walther, Phys. Rev. Lett. **55**, 2941 (1985); W. Ketterle, Phys. Rev. Lett. **62**, 1480 (1989).

[7] W. J. van der Zande, W. Koot, D. P. de Bruijn, and C. Kubach, Phys. Rev. Lett. **57**, 1219 (1986).

[8] S. F. Selgren, D. E. Hipp, and G. I. Gellene, J. Chem. Phys. **88**, 3116 (1988).

[9] J. W. C. Johns, J. Mol. Spectrosc. **36**, 488 (1970); C. R. Lishawa, J. W. Feldstein, T. N. Stewart, and E. E. Muschlitz, Jr., J. Chem. Phys. **83**, 133 (1985).

[10] R. L. Brooks, J. L. Hunt, and J. J. Miller, Phys. Rev. Lett. **58**, 199 (1987).

[11] R. L. Brooks and J. L. Hunt, J. Chem. Phys. **88**, 7267 (1988); **89**, 7077 (1988).

[12] B. Stenum, J. Schou, H. Sørensen, and P. Gürtler, Radiat. Eff. Def. Solids (to be published).

[13] R. L. Brooks, J. Chem. Phys. **85**, 1247 (1986).

[14] J. Schou, H. Sørensen, and P. Børgesen, Nucl. Instrum. Methods Phys. Res., Sect. B **5**, 44 (1984); J. Schou, P. Børgesen, O. Ellegaard, H. Sørensen, and C. Claussen, Phys. Rev. B **34**, 93 (1986).

[15] Yu. B. Poltoratskii and I. Ya. Fugol', Fiz. Nizk. Temp. **5**, 925 (1979) [Sov. J. Low Temp. Phys. **5**, 439 (1979)]; F. Coletti and A. M. Bonnot, Chem. Phys. Lett. **45**, 580 (1977); H. Kühle, J. Bahrdt, R. Fröhling, N. Schwentner, and H. Wilche, Phys. Rev. B **31**, 4858 (1985).

[16] N. Schwentner, E.-E. Koch, and J. Jortner, *Electronic Excitations in Condensed Rare Gases* (Springer-Verlag, Berlin, 1985), pp. 125–127; C. E. Moore, in *Atomic Energy Levels,* edited by C. C. Keiths, NBS Circular No. 467 (U.S. GPO, Washington, DC, 1949, 1952, 1958).

[17] R. L. Brooks, S. K. Bose, J. L. Hunt, J. R. MacDonald, J. D. Poll, and J. C. Waddington, Phys. Rev. B **32**, 2478 (1985).