

Diffusion of hydrogen in rare gas solids: neutral H atoms and H⁺ protons

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In this letter we review and compare the available information about the stability and spectroscopy of the hydrogen atoms and protons in rare-gas solids. Mechanism of the H⁺ diffusion involving protonated rare-gas dimer Rg₂H⁺ formation in the lattice is discussed. We suggest that the puzzling differences in their behavior and the stability are due to the fact that diffusion of hydrogen atoms is thermally activated, while that of the protons is activated by vibrational excitation of the Rg₂H⁺ under ambient temperature black body radiation.

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Diffusion in solids is of fundamental interest from the purely academic point of view and it is also important in nature and in numerous industrial situations and processes. While molecular species in solid matrices at low temperatures are usually stable, and can be maintained isolated for indefinite periods, some atoms exhibit even below 10 K a considerable degree of mobility [1,2]. Rare-gas solids, with their well-known potentials [3] and well-defined structures thus represent a very suitable model system for studying diffusion. Particularly interesting is the mobility of the lightest and most abundant atom of them all — the hydrogen atom. Atomic hydrogen can, in fact, exist in the matrix at least in two varieties — as neutral atoms [4–12] and as charged protons [13–18], and both of them have been studied in-depth spectroscopically.

Neutral hydrogen atoms are easily detected either by their ESR spectra [4], or by optical UV spectroscopy [5,6,9,11,12], and can occur in matrices in several distinct sites [4,19]. Protons in rare gases are tightly solvated by two rare gas atoms that form well-defined Rg₂H⁺ cations [20]. Both states, neutral and charged, have been investigated by many researchers, and it is well known that under suit-

able conditions both forms can be mobilized, and their depletion due to diffusion can be followed spectroscopically [8,9,11,12,16,17]. Somewhat surprisingly, not only the weakly interacting neutral atoms, but also the strongly bound protons can be quite easily destroyed by diffusion [16,17]. Examination of the available data reveals, however, that the diffusion of the two species exhibits some very surprising differences. The purpose of the present paper is to compile and review some of the available evidence, and propose an explanation for the observed differences and unexpected trends in the behavior of neutral atoms and protons.

In an early study of matrices produced by discharging or photolysing deuterium halides infrared absorptions appearing at 645 and 607 cm⁻¹ were observed in solid argon and krypton, respectively [13]. The carrier clearly involved a single deuterium atom, and the lines shifted to 907 and 851 cm⁻¹ when normal hydrogen halides were substituted for the deuterides. At first, an assignment to a neutral H atom trapped in an interstitial site in the rare-gas solid was preferred, since it was not understood how ions could be produced under the conditions of some of the experiments. Later stud-

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ies, however, have shown rather conclusively that the absorptions are, in fact, due to the positively charged protons [14,15], which form strongly bound, linear centrosymmetric RgH^+Rg cations in the matrix. These are characterized by a very intense asymmetric stretching infrared absorption ν_3 , accompanied by a progression of $\nu_3 + n\nu_1$ combination bands [16,21].

Neutral hydrogen atoms in rare gases were extensively studied by means of ESR spectroscopy [4] since the early days of matrix spectroscopy. These studies suggested that while in neon a single matrix site is observed, in the heavier rare gases, Ar, Kr, and Xe the H atoms can be trapped in at least two different trapping sites, presumably substitutional and octahedral interstitial [4,19]. Atoms produced by dissociation with excess kinetic energy [22,23] can apparently propagate through the matrix for distances of the order of 100 Å [10]. Atoms in thermal equilibrium with the lattice, on the other hand, appear to be at the lowest temperatures indefinitely stable [8]. They can in fact be stabilized at sufficiently high concentrations for the detection of H...H spin-pair diradicals, with a distribution of internuclear distances of $r > 7$ Å [24]. Besides ESR, it was recently shown that H atoms can also be detected by optical absorption and emission spectroscopy. While in the gas phase the lowest resonant transition of hydrogen atoms requires 10.2 eV (α -Lyman), in rare-gas solids the transition is shifted to much lower energies, with onsets of strong structured absorptions near 9.7, 8.0, and 6.2 eV in solid argon, krypton and xenon, respectively. Excitation of these bands by tunable synchrotron radiation results in broad and intense, strongly red-shifted emission bands [7].

The ability to monitor spectroscopically hydrogen atoms and bare protons allows us to study their stability and diffusion as a function of temperature, and indeed numerous such studies have been reported. Both the neutral H atoms and H^+ cations can be destroyed due to diffusion, but comparison of the two processes indicates some surprising trends and differences. Careful studies of the mobilities of hydrogen atoms produced in solid krypton and xenon by x-ray irradiation were carried out by Creuzburg and coworkers [9,11]. They found that annealing of the matrix leads to disappearance of the H atoms at a rate which is in solid xenon below 32 K unobservably slow, but changes by six orders of magnitude between 32 and 45 K, with a similar rapid rate change occurring in solid Kr between 22 and 27.5 K. The disappearance of the atoms is presumably due to radical-radical recombi-

nation, with formation of the HXeH hydride being an alternative channel in xenon [11,25–27]. From an Arrhenius plot of the data, the authors were able to deduce activation energies of 66 and 123 meV (Ref. 11) (6.4 and 11.9 kJ/mol) for the bleaching process in Kr and Xe, respectively, which they explain in terms of thermally activated diffusion. Most interestingly, they find no observable difference between the bleaching of hydrogen and deuterium atoms, a result which was recently confirmed by Vaskonen et al. [12].

While no experimental values for the H^+ diffusion activation barriers are available, one might expect them to be considerably higher than those of the neutral atom. This was indeed confirmed by recent theoretical calculations, predicting a barrier of about 10 kJ/mol in solid neon, and about 30–35 kJ/mol in the heavier rare-gas solids [20]. As noted above, the asymmetric stretching absorption of the Rg_2H^+ cations allows easy monitoring of the «matrix isolated» protons. Rather surprisingly, despite the relatively high barriers, a rather efficient bleaching of the absorption is observed; it exhibits, however, quite different properties than the neutral hydrogen depletion [16,17]. In the first place, the Rg_2H^+ destruction does not exhibit a pronounced temperature dependence, and persists down to the lowest matrix temperatures. Furthermore, unlike the neutral hydrogens, whose diffusion shows no isotopic dependence, the charged protons decay up to an order of magnitude faster than the corresponding deuterons.

The fast disappearance at low temperatures could possibly be explained if one argued that not the proton diffusion but some alternative process is responsible. Since the positively charged cations are present, negatively charged centers must also be present, and these centers are usually unidentified. One might understand the bleaching if it was due to diffusion of electrons located in shallow traps. While such a process could have a very low activation energy, it cannot explain the strong hydrogen isotopic effect [16].

We propose as one possible explanation that while the matrix may be at a low temperature of only a few K, it is still invariably in the room-temperature-range (about 300 K) radiative field of the apparatus walls. This radiation might be efficiently absorbed by the very intense infrared transition and lead to the observed diffusion. The computed lowest energy path shown in Fig. 1 involves essentially a ligand-switching reaction, where the Rg_2H^+ solvated proton exchanges one of its rare-gas ligands. Stretching modes of triatomic molecules almost in-

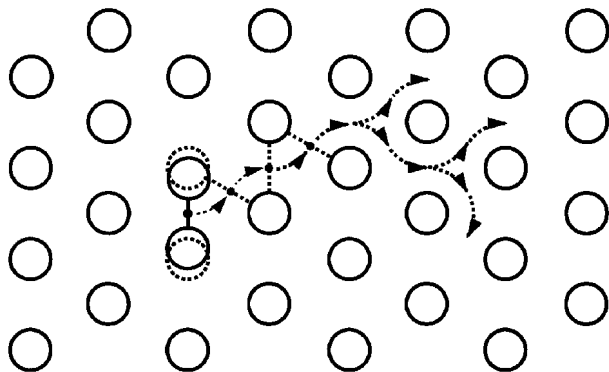


Fig. 1. Schematic diagram of proton diffusion in the host, for simplicity constrained to two dimensions. Only three rare-gas atoms are involved in each diffusion step, in which only one H^+ -Rg bond needs to be rearranged. Barriers calculated in the gas phase for an Rg_3H^+ complex are given in Ref. 20 and Table 1. While the proton has moved considerably in the rare-gas environment, the displacement of the rare-gas atoms involved is minor.

variably relax via the lower frequency bending modes, and the excitation step can be followed by tunneling of the vibrating proton in the excited molecule from one Rg-Rg bond to an adjacent one. The infrared absorption thus provides the energy needed to lower the activation barrier. This interpretation also helps to rationalize the strong isotopic dependence by combination of several effects: factor of 2 change in the reduced mass, with the corresponding $\sqrt{2}$ change in the vibrational frequency, the change in the overlap with the 300-K Planck curve, as shown in Fig. 2, and change of the oscillator strength due to the mass effects. Equally important may be the zero-point effects and, in

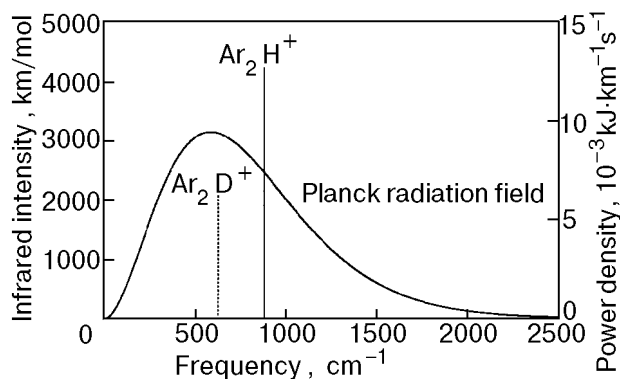


Fig. 2. Overlap of the vibrational modes of Ar_2H^+ and Ar_2D^+ with the Planck blackbody radiation field. The lower infrared intensity of the deuterated species is partly compensated by the better overlap with the radiation field.

particular, the effect of mass upon the tunneling process.

This observation of a process activated by blackbody radiation would not be without precedence. Like in the matrix, where the «collision energies» are too low to activate chemical reactions, in the high vacuum of an FT-ICR mass spectrometer collisions are too infrequent for the classical Lindeman-Hinshelwood mechanism of chemical activation to be operative. We have recently shown that in such an ultrahigh environment, where at pressures of $\approx 10^{-10}$ mbar collisions are reduced to about 1 per 100 s, the absorbed blackbody radiation becomes the dominant source of activation energy [28]. Thus, for example, fragmentation of ionic water clusters, as well as a variety of chemical reactions within the clusters, like hydrogen formation [29–32] or aldol condensation [33], are activated by blackbody radiation. In addition, a whole range of other processes in low-temperature rare-gas solids, where collisional activation is in view of the low temperatures of 5–20 K, inefficient processes, such as isomerization and structural rearrangements, are known to be efficiently activated by infrared absorption.

To estimate the amount of energy absorbed by the ions, we have used the infrared frequencies ν and line intensities $I(\nu)$ of Rg_2H^+ species from our previous paper [20], and for the purpose of this work we have calculated the values for deuterated Rg_2D^+ species on the same level of theory (B3LYP in Gaussian-94 [34]). For the calculation of the power absorbed from blackbody radiation, the frequencies are multiplied with a scaling factor of 0.8 to account for the strong matrix shift [20].

The power absorbed by these modes from 298-K blackbody radiation can be calculated from the Planck distribution, taking into account that half of the 4π steric angle around the molecule is occupied by the low-temperature mirror on which the host is deposited, reducing the steric angle of radiation to 2π . With ν in cm^{-1} , this amounts to:

$$P(\nu, I, T) = \frac{4\pi h c^2 \nu^3 I \cdot 10^6}{\exp(100ch\nu/kT) - 1}$$

The vibrational frequencies, infrared intensities, the photon energy and the power absorbed by the vibrational modes are listed in Table, together with the activation barrier for proton diffusion. Examination of the data for Ne_2H^+ reveals that absorption of a single ν_3 photon is sufficient to overcome the diffusion barrier, and that about 0.4 of these photons are absorbed by each Ne_2H^+ site per second, which might account for the fact that the H^+ protons were

Vibrational frequencies ν (cm^{-1}), infrared intensities $I(\nu)$ (km/mol), the photon energy $E(\nu)$ (kJ/mol), the absorbed power $P(\nu)$ ($\text{kJ}/\text{mol}\cdot\text{s}$), and the barrier for proton diffusion $E(TS)$ (kJ/mol)

Ion	$0.8\nu_3^a$	$I(\nu_3)^a$	$E(\nu_3)$	$P(\nu_3)$	$0.8\nu_2^a$	$I(\nu_2)^a$	$E(\nu_2)$	$P(\nu_2)$	$P(\nu_2) + P(\nu_3)$	$E(TS)^a$
Ne_2H^+	1329	2319	15.9	6.7	620	248	7.4	2.33	9.0	11.5
Ne_2D^+	950	1153	11.4	7.6	444	115	5.3	1.00	8.6	13.8
Ar_2H^+	878	4227	10.5	31.3	549	42	6.6	0.40	31.7	29.7
Ar_2D^+	625	2117	7.5	19.9	390	19	4.7	0.15	20.0	29.9
SECP ^b										
Ar_2H^+	950	4385	11.4	28.9	518	47	6.2	0.44	29.4	30.7
Ar_2D^+	678	2196	8.1	20.2	369	21	4.4	0.16	20.3	31.6
Kr_2H^+	857	5094	10.3	38.9	486	17	5.8	0.15	39.1	32.3
Kr_2D^+	606	2551	7.3	24.1	345	8	4.1	0.06	24.1	32.8
Xe_2H^+	758	5873	9.1	50.6	444	3	5.3	0.03	50.6	35.5
Xe_2D^+	537	2941	6.4	27.6	314	1	3.8	0.01	27.6	35.9

^a The values for protonated species were taken from Ref. [20]; for deuterated species from this work.

^b The values above the horizontal line were computed considering all electrons explicitly. The computation below the divider were carried out using for the heavier rare-gas atoms the quasi-relativistic effective core potentials of the Stuttgart/Dresden group [35].

thus far not observed in solid neon. The proton activated by the absorption of room-temperature blackbody radiation may acquire in solid neon a considerable mobility, and find an electron or an anion for recombination or a neutral molecule for reactions within a few seconds. Among possible «sinks» for H^+ could be the formation of H_2^+ or H_3^+ molecular ions [36].

The situation is a little more complicated in solid Ar, Kr, and Xe, where the ν_3 photon energy is considerably lower than the computed H^+ activation energy, and where the H^+ ions have been studied experimentally. Even though in the heavier hosts the absorbed power is higher, amounting to about 3–5 photons/(ion·s) due to higher oscillator strength, multiphoton processes are quite unlikely to be important in overcoming the barrier. Here, however, the absorptions due to the $\nu_3 + n\nu_1$ combination bands might be a contributing factor. It is also possible that the actual barrier in the bulk may be lower than that computed for Rg_nH^+ clusters with $n = 3$, and, as suggested by the strong isotopic dependence, tunneling through the barrier may very well be involved.

The proposed infrared activation would thus be essentially consistent with the observations: bulk matrix temperature independence, and a strong isotopic effect of the proton absorption bleaching. A similar mechanism would not work for neutral hydrogen atoms, whose vibrational modes lie at considerably lower frequencies, and whose infrared

absorptions are surely many orders of magnitude weaker than those of H^+ in the complex Rg_2H^+ .

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1. W. C. Easley and W. Weltner, Jr., *J. Chem. Phys.* **52**, 197 (1970).
2. E. T. Ryan and E. Weitz, *J. Chem. Phys.* **99**, 1004 (1993).
3. H. H. von Grünberg and H. Gabriel, *Chem. Phys. Lett.* **192**, 503 (1992).
4. S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, *J. Chem. Phys.* **32**, 963 (1960).
5. M. Creuzburg, F. Koch, and F. Wittl, *Chem. Phys. Lett.* **156**, 387 (1989).
6. M. Creuzburg and F. Wittl, *J. Mol. Struct.* **222**, 127 (1990).
7. M. Kraas and P. Gürtler, *Chem. Phys. Lett.* **174**, 396 (1990).
8. D. LaBrake and E. Weitz, *Chem. Phys. Lett.* **211**, 430 (1993).
9. F. Wittl, J. Eberlein, T. Eppe, M. Dechant, and M. Creuzburg, *J. Chem. Phys.* **98**, 9554 (1993).
10. D. LaBrake, E. T. Ryan, and E. Weitz, *J. Chem. Phys.* **102**, 4112 (1995).
11. J. Eberlein and M. Creuzburg, *J. Chem. Phys.* **106**, 2188 (1997).
12. K. Vaskonen, J. Eloranta, T. Kiljunen, and H. Kunttu, *J. Chem. Phys.* **110**, 2122 (1999).

13. V. E. Bondybey and G. C. Pimentel, *J. Chem. Phys.* **56**, 3832 (1972).
14. D. E. Milligan and M. E. Jacox, *J. Mol. Spectrosc.* **46**, 460 (1973).
15. C. A. Wight, B. S. Ault, and L. Andrews, *J. Chem. Phys.* **65**, 1244 (1976).
16. H. Kunttu, J. Seetula, M. Räsänen, and V. A. Apkarian, *J. Chem. Phys.* **96**, 5630 (1992).
17. H. M. Kunttu and J. A. Seetula, *Chem. Phys.* **189**, 273 (1994).
18. T. D. Fridgen and J. M. Parnis, *J. Chem. Phys.* **109**, 2155 (1998).
19. F. J. Adrian, *J. Chem. Phys.* **32**, 972 (1960).
20. M. Beyer, A. Lammers, E. V. Savchenko, G. Niedner-Schatteburg, and V. E. Bondybey, *Phys. Chem. Chem. Phys.* **1**, 2213 (1999).
21. J. Nieminen, E. Kauppi, J. Lundell, and H. Kunttu, *J. Chem. Phys.* **98**, 8698 (1993).
22. F. Magnotta, D. J. Nesbitt, and S. R. Leone, *Chem. Phys. Lett.* **83**, 21 (1981).
23. G. W. Flynn and R. E. Weston, Jr., *Ann. Rev. Phys. Chem.* **37**, 551 (1986).
24. L. B. Knight, Jr., W. E. Rice, L. Moore, E. R. Davidson, and R. S. Dailey, *J. Chem. Phys.* **109**, 1409 (1998).
25. M. Pettersson, J. Lundell, and M. Räsänen, *J. Chem. Phys.* **103**, 205 (1995).
26. V. I. Feldman, F. F. Sukhov, and A. Y. Orlov, *Chem. Phys. Lett.* **280**, 507 (1997).
27. M. Pettersson, J. Lundell, and M. Räsänen, *Eur. J. Inorg. Chem.* (in print).
28. T. Schindler, C. Berg, G. Niedner-Schatteburg, and V. E. Bondybey, *Chem. Phys. Lett.* **250**, 301 (1996).
29. M. Beyer, C. Berg, H. W. Görlitzer, T. Schindler, U. Achatz, G. Albert, G. Niedner-Schatteburg, and V. E. Bondybey, *J. Am. Chem. Soc.* **118**, 7386 (1996).
30. C. Berg, U. Achatz, M. Beyer, S. Joos, G. Albert, T. Schindler, G. Niedner-Schatteburg, and V. E. Bondybey, *Int. J. Mass Spectrom Ion Process.* **167/168**, 723 (1997).
31. C. Berg, M. Beyer, U. Achatz, S. Joos, G. Niedner-Schatteburg, and V. E. Bondybey, *Chem. Phys.* **239**, 379 (1998).
32. M. Beyer, U. Achatz, C. Berg, S. Joos, G. Niedner-Schatteburg, and V. E. Bondybey, *J. Phys. Chem.* **A103**, 617 (1999).
33. U. Achatz, S. Joos, C. Berg, T. Schindler, M. Beyer, G. Albert, G. Niedner-Schatteburg, and V. E. Bondybey, *J. Am. Chem. Soc.* **120**, 1876 (1998).
34. *Gaussian 94, Revision D.4*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA (1995).
35. A. Nicklass, M. Dolg, H. Stoll, and H. Preuss, *J. Chem. Phys.* **102**, 8942 (1995).
36. M. Beyer, E. V. Savchenko, G. Niedner-Schatteburg, and V. E. Bondybey, *J. Chem. Phys.* **110**, 11950 (1999).