

The contribution of tunnelling to the diffusion of protons and deuterons in rare gas solids

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The stability and diffusion of protons and deuterons in rare gas matrices are reexamined. These are known to be stabilized in rare gas matrices in the form of linear, centrosymmetric Rg_2H^+ cations. The elementary step in their diffusion, displacement from one Rg–Rg bond to a neighboring one, can be modelled as an isomerization of the triangular Rg_3H^+ cation. Using an analytic approximation for thermally averaged transmission coefficients for tunnelling through and reflection by a truncated parabolic potential barrier (R.T. Skodje and D.G. Truhlar, *J. Phys. Chem.* **85**, 624 (1981)) we calculate the rate constants for this elementary diffusion step. The calculated rate constants are consistent with all experimental observations, and confirm that tunnelling makes the dominant contribution to the diffusion of protons and deuterons in rare gas solids. Deuteration reduces the tunnelling rates by 5 to 8 orders of magnitude, which agrees with the observation that D^+ in rare gas solids is significantly more stable than H^+ .

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Introduction

Infrared absorptions associated with deuterons and protons in solid rare gases have been known for more than thirty years, and in fact some of the puzzling aspects of their earliest observations were linked with their diffusion behavior. Initially, a strong infrared absorption near 644 cm^{-1} was detected, whenever argon with a small amount of deuterium was discharged and deposited on a cold substrate held at 14 K. However, no comparable absorption appeared when normal hydrogen was used instead [1,2]. This problem turned out to lie in the fact that grating infrared spectrometers used at the time required typically some 60 minutes to scan the usual IR-range from $4000\text{--}400\text{ cm}^{-1}$. When, on the other hand, the spectral scan was started directly in the expected region, the corresponding absorption due to normal hydrogen was detected near 905 cm^{-1} , shifted almost exactly by the appropriate $\sqrt{2}$ ratio. While the hydrogen absorption decreases in intensity with a half-life of a few minutes, the deuteron band is much more stable, with its rate of decrease being slower by several orders of magnitude.

Initially there also was some doubt as to the charge state of the carrier of the absorption bands, but subsequent evidence pointed increasingly towards positively charged protons [3–7]. Similar absorptions were also found in solid krypton [2], and more recently in xenon [5], and it is now well established that the transitions are due to the ν_3 asymmetric stretch and $\nu_3 + n\nu_1$ combination bands with the low frequency symmetric stretching mode of the linear, centrosymmetric Rg_2H^+ cations. Already the first investigation of these absorptions pointed out the iso-electronic nature of Rg_2H^+ species with the well-known HX_2^- dihalide anions. From the chemical point of view, protons — or deuterons — are essentially dimensionless charges, and show therefore a clear preference for a coordination number of two, that is they are strongly solvated by two and only two strongly bound rare gas ligands [8].

As noted above, both H^+ and D^+ are observable in solid argon, krypton and xenon. H^+ is quite short-lived in argon, and disappears on a much slower, 10^3 s time-scale in solid Kr and Xe, whereas D^+ is much more long-lived in argon, and essentially stable in the

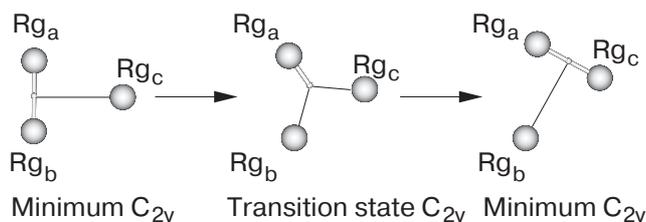


Fig. 1. Cluster model for proton diffusion in rare gas matrices. The proton changes its connectivity when it goes through the transition state of the Rg_3H^+ ion. A large number of these elementary steps lead to a random motion of the proton through the matrix. Reproduced from ref. [8] by permission of the PCCP owner societies.

heavier rare gases, with the orders of magnitude difference in the stability between protons and deuterons being suggestive of a tunnelling process. Interestingly, neither protons, nor deuterons have thus far been observed in solid neon. We have recently discussed these phenomena in this journal [9], and suggested that diffusion might be activated by room temperature black-body radiation, which exhibits a strong overlap with the ν_3 band of Rg_2H^+ . At that time, we did not quantify the effect of tunnelling, but suggested that it might contribute to the observed differences.

A proton or a deuteron in a rare gas solid is inserted between two neighboring atoms to form the linear, centrosymmetric Rg_2H^+ entity. Interestingly, the distance between the two atoms with the proton inserted is in fact considerably shorter than the distance between two nearest neighbour atoms in an unperturbed rare gas lattice. An elementary step of diffusion through the solid then requires displacement of the proton from one Rg–Rg bond to a neighboring one, and can be modelled as an isomerization of a triangular Rg_3H^+ cation, as shown schematically in Fig. 1. In the T -shaped, C_{2v} cation, the proton is displaced stretching the $\text{Rg}_b\text{–H}^+$ and shortening the $\text{Rg}_c\text{–H}^+$ distance to reach the equally C_{2v} transition state. We have computed the barrier heights and frequencies of this transition state in our recent investigation [8,9]. In the present work, we use these results to estimate the transmission rate constants for H^+ and D^+ in solid neon, argon, krypton and xenon through the diffusion barrier, accounting for thermal activation and tunnelling.

Computational details

Thermally averaged transmission coefficients for truncated parabolic potential barriers are calculated with the analytic approximation by Skodje and Truhlar [10], which resolves some problems associated

with the earlier approaches by Wigner [11] and Bell [12]. As an input into this formalism, the barrier height and the imaginary frequency of the transition state are needed. The transition states of Rg_3H^+ have been calculated in our previous work [8,9] with the B3LYP functional and the 6-311++G(3df, 3pd) basis set on hydrogen, neon and argon, and the Stuttgart/Dresden relativistic effective core potential basic set [13] on argon, krypton, and xenon, employing the Gaussian94 [14] program suite. In all cases, frequencies are scaled by a factor of 0.8 to account for the influence of the rare gas solid [9].

Results and discussion

As argued previously [8,9], the reaction sequence depicted in Fig. 1 for Rg_3H^+ represents one step in the diffusion of protons or deuterons in rare gas solids. Zero-point corrected barrier heights V_0 and imaginary frequencies ν are given in the Table. The key parameter to describe tunneling is the transmission coefficient $\kappa(T)$ at temperature T [10], which is more instructively called the enhancement of the transfer rate due to tunneling by Lill and Helms [15]. With

$$\alpha = -2\pi/h\nu \quad (1)$$

and

$$\beta = 1/kT \quad (2)$$

it is easily shown that the conditions $\alpha < \beta$ and $\beta V_0 > 1$ are fulfilled for the species discussed in this work. According to Skodje and Truhlar [10], $\kappa(T)$ is then approximated by the equation:

$$\kappa(T) = [\beta/(\beta - \alpha)] \exp [(\beta - \alpha)V_0]. \quad (3)$$

At $T = 10$ K this yields the exceedingly large numbers which are listed in the Table. They indicate that at these low temperatures, tunnelling is the only contribution to the diffusion of protons as well as deuterons.

In order to get a quantitative estimate of the rate constants involved in the diffusion process, classical Arrhenius rate constants are calculated. Since the bending mode ν_2 of the protonated rare gas dimer corresponds to the imaginary mode in the transition state, its frequency is chosen as the Arrhenius A -factor, i.e. the frequency with which the barrier is probed. The Arrhenius rate constant k_A then amounts to:

$$k_A(T) = c\nu_2 \exp(-\beta V_0). \quad (4)$$

Calculated values for k_A are listed in the Table. They illustrate that thermal activation is in no case sufficient to overcome the diffusion barrier, and significant energy input e.g. from room temperature

Table

Matrix, dopant H^+ or D^+ , barrier height V_0 in $\text{kJ}\cdot\text{mol}^{-1}$, scaled imaginary frequency ν in cm^{-1} , scaled bending frequency ν_2 in cm^{-1} (scaling factor 0.8 in both cases), enhancement of the transfer rate due to tunnelling $\kappa(10\text{ K})$, classical Arrhenius rate constant $k_A(10\text{ K})$ in s^{-1} , semiclassical rate constant which accounts for thermal activation and tunnelling $k_{SC}(10\text{ K})$ in s^{-1} .

Matrix	Dopant	$V_0 / \text{kJ}\cdot\text{mol}^{-1}$	$-\nu/\text{cm}^{-1}$	ν_2/cm^{-1}	$\kappa(10\text{ K})$	$k_A(10\text{ K})/\text{s}^{-1}$	$k_{SC}(10\text{ K})/\text{s}^{-1}$
Ne	H^+	11.5 ^a	609	620 ^a	$6.25\cdot 10^{55}$	$1.98\cdot 10^{-47}$	$1.24\cdot 10^9$
Ne	D^+	13.8 ^b	441	444 ^b	$9.66\cdot 10^{64}$	$1.37\cdot 10^{-59}$	$1.33\cdot 10^6$
Ar	H^+	29.7 ^a	506	549 ^a	$6.03\cdot 10^{141}$	$1.50\cdot 10^{-142}$	$9.06\cdot 10^{-1}$
Ar	D^+	29.9 ^b	366	390 ^b	$3.97\cdot 10^{137}$	$9.64\cdot 10^{-144}$	$3.83\cdot 10^{-6}$
SECP ^c							
Ar	H^+	30.7 ^a	506	518 ^a	$3.59\cdot 10^{146}$	$8.48\cdot 10^{-148}$	$3.05\cdot 10^{-1}$
Ar	D^+	31.6 ^b	364	369 ^b	$1.97\cdot 10^{145}$	$1.20\cdot 10^{-152}$	$2.37\cdot 10^{-7}$
Kr	H^+	32.3 ^a	471	486 ^a	$1.32\cdot 10^{153}$	$3.49\cdot 10^{-156}$	$4.60\cdot 10^{-3}$
Kr	D^+	32.8 ^b	335	345 ^b	$1.10\cdot 10^{149}$	$6.06\cdot 10^{-159}$	$6.63\cdot 10^{-10}$
Xe	H^+	35.5 ^a	441	444 ^a	$1.36\cdot 10^{167}$	$6.15\cdot 10^{-173}$	$8.35\cdot 10^{-6}$
Xe	D^+	35.9 ^b	313	314 ^b	$2.70\cdot 10^{161}$	$3.54\cdot 10^{-175}$	$9.57\cdot 10^{-14}$

Comment: ^a From Ref. [8]; ^b From Ref. [9]; ^c The values above the horizontal line were computed considering all electrons explicitly. The computations below the divider were carried out using the quasi-relativistic effective core potential basis sets of the Stuttgart/Dresden group [13].

black-body radiation [9] would be required to explain the diffusion. However, the enhancement of transfer rate due to tunnelling described by $\kappa(T)$ is sufficiently large to balance these low Arrhenius rate constants. With the assumption that the quantum mechanical barrier is probed at the same rate as the classical barrier, the semi-classical thermally averaged rate constant k_{SC} which accounts for thermal activation and tunnelling amounts to:

$$k_{SC} = \kappa(T) k_A(T) = c\nu_2[\beta/(\beta - \alpha)] \exp(-\alpha V_0). \quad (5)$$

These values are again given in the Table, and are shown in Fig. 2. Since most parameters, like V_0 and ν , are in the argument of the exponential function, the accuracy of these results cannot be better than a few orders of magnitude. Nevertheless, the numbers clearly reflect the experimental observations: In solid neon, the deuteron changes place on a timescale of μs , and the proton on a timescale of ns , both consistent with the fact that neither H^+ nor D^+ have been observed in solid neon. In either case, the charged particle is rapidly diffusing through the matrix and may find species like electrons, X^- impurities, neutral hydrogen atoms, H_2O or H_2 [16] to recombine.

The barrier V_0 is much higher for argon, krypton and xenon than for neon. Consequently, diffusion rate constants are reduced by 10 orders of magnitude or more. Within this group of heavier, more polarizable

rare gases, there is still a significant increase in the lifetime of the charge carrier for argon via krypton to xenon, since the barriers slightly increase, and more importantly, the frequencies in the transition state considerably decrease. This is consistent with the experimental observation that H^+ is relatively short-lived in argon, and much easier to observe in krypton and xenon. In the simultaneous presence of hydrogen

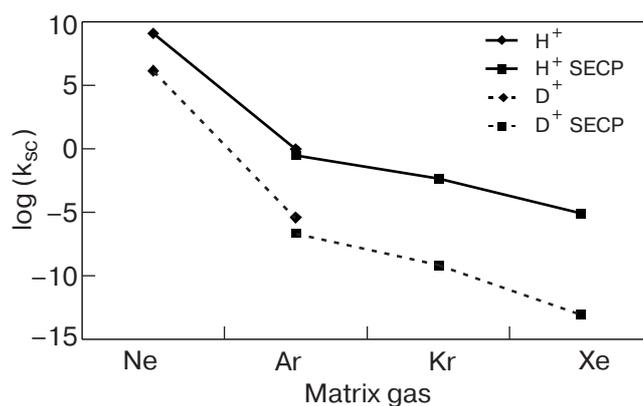


Fig. 2. Semi-classical rate constant of the elementary diffusion step for Ne, Ar, Kr, and Xe. While both H^+ and D^+ have a high mobility in a neon matrix, diffusion is considerably slowed down in argon, krypton, and xenon. Deuteration reduces the rate constants by 5 to 8 orders of magnitude, which stabilizes D^+ relative to H^+ in matrices of heavier rare gases.

and deuterium, also the rate of deuteron disappearance is increased, suggesting that also the neutral sinks for the charge carrier are diffusing in part by tunnelling.

As expected, however, deuteration reduces the diffusion rate constants k_{SC} by 5 to 8 orders of magnitude, which means that in cases where H^+ is short-lived, D^+ becomes long-lived. If H^+ is long-lived, D^+ becomes essentially stable, as observed experimentally for xenon by Räsänen and coworkers [5].

In the presence of two different rare gases, that is in terms of Fig. 1, if Rg_b is different from Rg_c , then the two minima on the right and left hand sides will no longer be equivalent, but will have substantially different energies. Under these circumstances the diffusion should stop, and the positive charge would remain localized near the heavier, more polarizable rare gas atom. Species like XeH^+ and Xe_2H^+ should therefore be observable in solid neon.

Conclusions

The calculations of rate constants which account for thermal activation as well as for tunnelling show that the latter process, tunnelling, dominates the diffusion of protons and deuterons in rare gas solids. At a temperature of 10 K, tunnelling is faster than thermal activation by 55 orders of magnitude for H^+ in neon, up to 167 orders of magnitude for H^+ in xenon. The values are consistent with all experimental observations. Deuteration reduces the tunnelling rates by 5 to 8 orders of magnitude, which is consistent with the observed, significantly higher stability of D^+ in comparison with H^+ in rare gas solids. The results also indicate that the transition states proposed earlier are indeed relevant for the diffusion of protons and deuterons in rare gas solids.

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1. V.E. Bondybey, G.C. Pimentel, and P.N. Noble, *J. Chem. Phys.* **55**, 540 (1971).
2. V.E. Bondybey and G.C. Pimentel, *J. Chem. Phys.* **56**, 3832 (1972).
3. D.E. Milligan and M.E. Jacox, *J. Mol. Spectrosc.* **46**, 460 (1973).
4. C.A. Wight, B.S. Ault, and L.E. Andrews, *J. Chem. Phys.* **65**, 1244 (1976).
5. H. Kunttu, J. Seetula, M. Räsänen, and V.A. Apkarian, *J. Chem. Phys.* **96**, 5630 (1992).
6. H.M. Kunttu and J.A. Seetula, *Chem. Phys.* **189**, 273 (1994).
7. T.D. Fridgen and J.M. Parnis, *J. Chem. Phys.* **109**, 2155 (1998).
8. M. Beyer, A. Lammers, E.V. Savchenko, G. Niedner-Schatteburg, and V.E. Bondybey, *Phys. Chem. Chem. Phys.* **1**, 2213 (1999).
9. M. Beyer, E.V. Savchenko, G. Niedner-Schatteburg, and V.E. Bondybey, *Fiz. Nizk. Temp.* **25**, 1087 (1999) [*Low Temp. Phys.* **25**, 814 (1999)].
10. R.T. Skodja and D.G. Truhlar, *J. Phys. Chem.* **85**, 624 (1981).
11. E. Wigner, *Z. Phys. Chem.* **B19**, 203 (1932).
12. R.P. Bell, *Trans. Faraday Soc.* **55**, 1 (1959).
13. A. Nicklass, M. Dolg, H. Stoll, and H. Preuss, *J. Chem. Phys.* **102**, 8942 (1995).
14. *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).
15. M.A. Lill and V. Helms, *J. Chem. Phys.* **115**, 7985 (2001).
16. M. Beyer, E.V. Savchenko, G. Niedner-Schatteburg, and V.E. Bondybey, *J. Chem. Phys.* **110**, 11950 (1999).