Supporting Information

Fast Proton Hopping Detection in Ice I_h by Quasi-Elastic Neutron Scattering

Itay Presiado,[†] Jyotsana Lal,[§] Eugene Mamontov,[‡] Alexander I. Kolesnikov,[‡] and Dan Huppert[†]*

†*Raymond and Beverly Sackler Faculty of Exact Sciences, School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel*

§*Materials Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA*

‡*Neutron Scattering Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN* 37831*, USA*

*Corresponding author: Dan Huppert

e-mail: huppert@tulip.tau.ac.il

phone: 972-3-6407012

fax: 972-3-6407491

Supporting Information Available

1. The Smoluchowski model
2. Figure and table 1 of proton hopping times versus the temperature in HCl-doped ice.

We derived the proton diffusion coefficient in ice, $D_{H^+}^{ice}$, from the photochemical reaction of an excess proton with a large organic compound, flavin mononucleotide (FMN). The molecular structure of FMN is shown in scheme 1. It consists of a heterocyclic chromophore connected to a sugar with a phosphate substituent. In a previous study,[1] we found that the intensity of the green-yellow emission of FMN depends on the pH of the sample at pH levels below 4. The fluorescence lifetime decreases in the presence of a strong mineral acid in both liquid H_2O and in the ice phase. We found that the average decay time decreases linearly with the acid concentration.

We analyzed the time-resolved emission signal of FMN in H_2O ice using the simple chemical equation:

$$\mathrm{FMN}^* \xrightarrow{k} \mathrm{FMNH}^+(g)$$

where FMN* denotes an electronically excited FMN molecule. The reaction with the proton leads to the protonated ground-state molecule, $FMNH^+$. The overall observation is an increase in the emission decay rate when acid is added to the ice. The reaction rate constant, k, is time-dependent. At short times, it is larger than at long times, $k_{t=0} > k_{\infty}$. The model explaining this behavior was introduced many years ago by von Smoluchowski.

The Smoluchowski Model

The Smoluchowski model is used to describe the diffusion-assisted irreversible reaction $A + B \rightarrow AB$, where the concentration of B is in a great excess over A. In this study it is used to qualitatively explain the time-resolved emission decay of the FMN*, form in the presence of an excess proton in water and ice samples.

We assumed that the excess proton transport toward the FMN* is the rate limiting step. The mathematical and computational details of the Smoluchowski model are given elsewhere.[2] According to the Smoluchowski model, the survival probability of a single (static) donor, an excited FMN* molecule (the A particle), due to its irreversible reaction with a $c = [H^+]$ concentration of protons (B is the excess proton in liquid and ice) is given by[3,4,5]

$$S(t) = \exp\left(-c\int_0^t k(t')dt'\right) \tag{1}$$

where $k(t)$ is the time-dependent rate coefficient for the donor-acceptor pair

$$k(t) = k_a\, p(a,t) \tag{2}$$

whose intrinsic proton-recombination rate constant is k_a. The pair (RO^-/H^+) density distribution, $p(r, t)$, is governed by a three-dimensional Smoluchowski equation (diffusion in a potential $U(r)$).[6]

When $U(r) = 0$, the above equations are analytically solvable for $k(t)$.[4] Szabo[5] found an approximate expression for the time-dependent rate constant for the instances when $U(r) \neq 0$.

When a potential is introduced, it behaves correctly at both $t = 0$ and $t = \infty$, i.e.,

$$k(0) = k_a e^{-\beta U(a)}, \quad k(\infty) = [k(0)^{-1} + k_D^{-1}]^{-1} \tag{3}$$

where $k_D = 4\pi\, D a_e$ (4)

is the diffusion-controlled rate constant, and a_e is an effective radius that depends on the Coulomb pair attraction potential. $U(a)$ and a_e depend on the dielectric constant[7] with

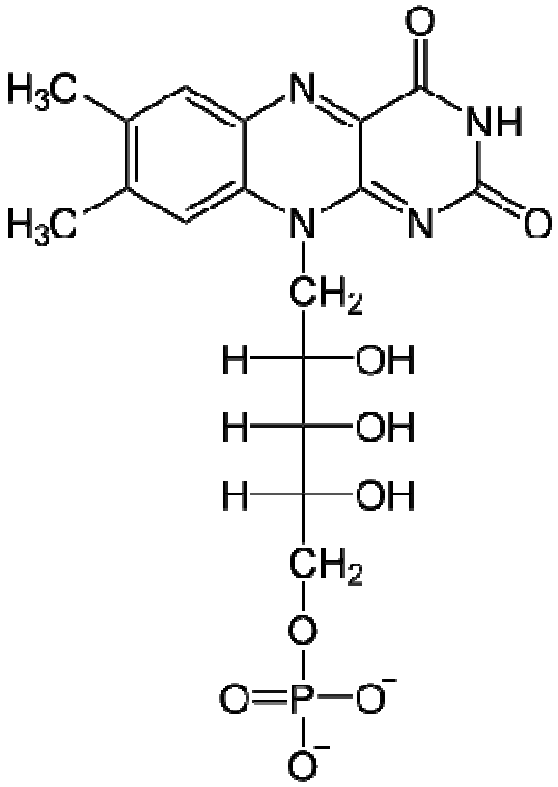
$$a_e = R_D / \left(1 - \exp\left(-R_D / a\right)\right) \tag{5}$$

and $$R_D = \frac{ze^2}{\varepsilon_s k_B T} \tag{6}$$

where a is the actual encounter radius of the specific reaction. $a = 6\,\mathring{A}$ is a commonly used value for a proton reaction in aqueous solutions.[8] R_D is the Debye radius, z is the charge of the molecule in electronic units and e is the charge of the electron.

The analysis of the time-resolved FMN emission provided the $D_{H^+}^{ice}$ at different temperatures. We used equation 2 in the main text to calculate the average hopping time, τ_{hop}, of the proton from $D_{H^+}^{ice}$. The values of these hopping times at low and high temperatures are given in table 1. At T ≥ 240 K the hopping times are on the order of 200 fs and amost temperature independent. At lower temperatures, we found that values of the hopping times increase as the temperature decreases. A plot of hopping time values versus 1/T is given in figure 1.

The average activation energy of a hopping step at T < 235 K is ~22 kJ/mol. We were unable to measure the hopping times at temperatures below 175 K, since the time-window of the fluorescence measurements is limited by the excited-state lifetime. We also found that in acidic ice a slight temperature-independent shortening of the lifetime occurs. It could be explained by the reaction of FMN* with a proton to form the $FMNH^+$ form. The reacting proton is not homogenously distributed in the ice bulk, but rather a proton that is trapped next to the FMN molecule. The phosphate group has a pK_a value of ~3 in liquid H_2O. Possibly, a proton trapped by the phosphate group, reacts with the alloxazine upon its slow release from the phosphate. It is important to note that we previously measured many photoacids that undergo the following reaction: $RO^{-}* + H^+ \rightarrow ROH*$ in liquid and in ice. This reaction is diffusion-controlled, and that is why $D_{H^+}^{ice}$ is measurable. The experiments on photoacids at T ≥ 220 K thus far provided similar $D_{H^+}^{ice}$ values independent of the proton reactive molecule within a reasonable experimental error. We used FMN to evaluate the value of $D_{H^+}^{ice}$ at T < 240 K, since photoacids recombine with a proton only after they first transfer a proton to the ice. Only after this transfer can they recombine with an excess proton in liquid or ice. The ESPT rate strongly depends on the temperature. Therefore, photoacids cannot be used to measure $D_{H^+}^{ice}$ at low temperature. FMN is not a photoacid, but it does react a proton in its excited-state, so it can be used for the purpose of measuring $D_{H^+}^{ice}$ at low and high temperatures. The $D_{H^+}^{ice}$ values obtained from the FMN experiment are compared in the article with the results from the neutron scattering experiment.



Scheme 1

FMN

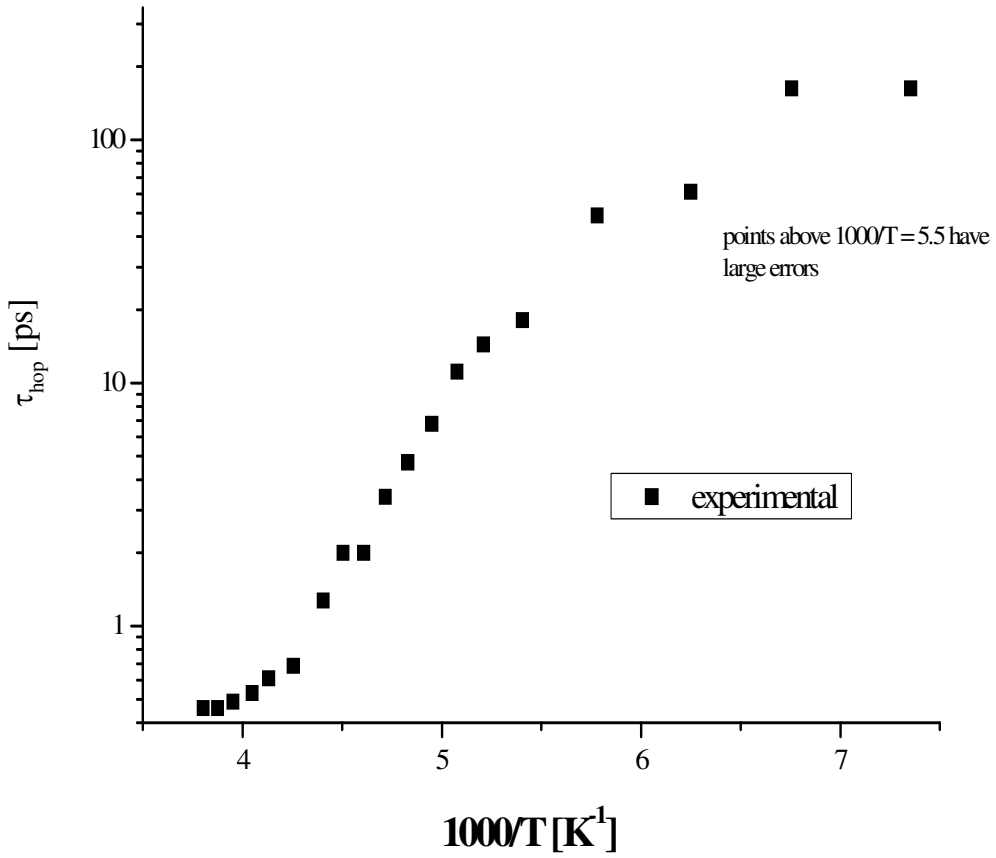


Figure 1. The proton hopping time in ice versus 1000/T.

T [K]	1000/T [K^{-1}]	Hopping time [ps]
263	3.80	0.24
258	3.88	0.24
253	3.95	0.25
247	4.05	0.28
242	4.13	0.32
235	4.26	0.36
227	4.41	0.66
222	4.51	1.1
217	4.61	1.1
212	4.72	1.9
207	4.83	2.7
202	4.95	4.0
197	5.08	6.7
192	5.21	10
185	5.41	13
173	5.78	47
160	6.25	75

Table 1. Proton hopping times in ice doped with 1 mM HCl measured by photochemical methods.[1]

1 . Uritski, A.; Presiado, I; Erez, Y.; Gepshtein, R.; Huppert, D. *J. Phys. Chem. C* **2009**, *113*, 10285.

2. Cohen, B.; Huppert, D.; Agmon, N. *J. Phys. Chem. A* **2001**, *105*, 7165.

3. Von Smoluchowski, M. *Z. Phys. Chem.* **1917**, *92*, 129.

4. Tachiya, M. *Radiat. Phys. Chem.* **1983**, *21*, 167.

5. Szabo, A. *J. Phys. Chem.* **1989**, *93*, 6929.

6. Agmon, N.; Szabo, A. *J. Chem. Phys.* **1990**, *92*, 5270.

7. Agmon, N. *J. Phys. Chem. A,* **2005**, *109*, 13.

8. Weller, A. *Prog. React. Kinet.*, **1961**, *1*, 189.