Proton Conductivity in Phosphoric Acid: The Role of Quantum Effects

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Phosphoric acid has one of the highest intrinsic proton conductivities of any known liquids, and the mechanism of this exceptional conductivity remains a puzzle. Our detailed experimental studies discovered a strong isotope effect in the conductivity of phosphoric acids caused by (i) a strong isotope shift of the glass transition temperature and (ii) a significant reduction of the energy barrier by zero-point quantum fluctuations. These results suggest that the high conductivity in phosphoric acids is caused by a very efficient proton transfer mechanism, which is strongly assisted by quantum effects.

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Understanding the proton transport mechanisms in liquids and biological systems is important for many technological applications, including energy and biotechnology [1–8]. Proton transport differs qualitatively from the transport of other ions because it requires the existence and rearrangements of hydrogen bonds in the system [1,2]. Two types of proton transport mechanisms have been recognized [1,2]: (i) the vehicular mechanism where an excess proton is transported by a molecule (vehicle); and (ii) the proton transfer mechanism which involves a shuttling of a proton between different molecular units through a transient hydrogen bond network. The proton transfer mechanism can also be collective, involving several chain-like proton transfer events, in which case it is called Grotthuss-like. In addition, there are extensive discussions in literature about the importance of quantum effects in proton transport [3,9–18]. Quantum tunneling depends exponentially on the mass of the moving particle; therefore, a proton is expected to have a rather high probability for tunneling between different sites [1,17]. These quantum effects should give rise to strong isotope effects, and, accordingly, the conductivity of protic materials should be systematically higher than that of their deuterated analogs. This issue, however, remains controversial [3,19,20].

Phosphoric acid (PA), H_3PO_4, and its aqueous solutions have one of the highest intrinsic proton conductivities among known materials, and the mechanism of this unique conductivity remains a puzzle [1,8,21]. NMR studies of PA found that the average proton mobility is more than 4 times higher than phosphorus mobility, clearly indicating a proton transfer mechanism of conductivity [22]. Recent detailed analysis based on *ab initio* molecular dynamics studies [21] suggested that, indeed, proton transport in PA involves the intermolecular Grotthuss-like proton transfer mechanism. Therefore, substitution of a hydrogen atom by deuterium in PA should lead to a measurable change in conductivity. In the case of the vehicular mechanism, however, this isotope substitution should have a negligible effect on conductivity, because of the very small change in the total mass of the molecule (vehicle).

This Letter presents a detailed study of the isotope effect on the conductivity σ of PA with varying water contents. Our studies discovered an enormous (more than 100 times) effect of D/H substitution on the conductivity of PA at low temperatures that decreases to the level expected for the classical proton transfer mechanism ($\sigma_H/\sigma_D \sim 1.4$) at high temperatures. The presented analysis shows that the observed strong change in conductivity at lower temperatures is caused by two effects: (i) an unusually large isotope-induced change in viscosity $\eta(T)$ and in the glass transition temperature T_g; and (ii) the so-called "trivial quantum effect"—a decrease in the activation energy barrier due to zero-point quantum fluctuations [1]. Thus, the presented results explicitly demonstrate that the intermolecular proton transfer process is the major mechanism of charge transport in phosphoric acids, while quantum effects also play a significant role in enhancing proton mobility.

The 85 wt% H_3PO_4 in H_2O and 85 wt % D_3PO_4 in D_2O systems were purchased from Sigma-Aldrich (99% purity). The protonated sample was used as received, and we added $\sim$1.2 wt % of D_2O to the deuterated sample to bring it to the same molar ratio of water to phosphorus pentoxide $R \approx 5$ ($R =$ Molar ratio of water to P_2O_5). Other acid concentrations were achieved by hydration of phosphorus pentoxide (98.0% purity, Sigma-Aldrich) with deionized H_2O (Fischer Scientific) and D_2O (99.9 atom% D, Sigma-Aldrich). P_2O_5 was weighed under argon atmosphere. Hydrated or deuterated water was added by vapor absorption in a closed chamber for 96 h. The remaining amounts of water were added via micropipette and the samples were stirred for 45 min at 180 °C to ensure uniform mixing.

Differential scanning calorimetry (DSC) measurements were performed using the TA-Instruments Q1000 calorimeter with a temperature cycle rate of 5 °C/ min. The calorimetric T_g was determined as the midpoint of the step in specific heat associated with the glass transition on heating. Broadband dielectric spectroscopy (BDS) measurements in the frequency range of 10^{-2} to 10^{7} Hz were performed using a Novocontrol Alpha analyzer. The samples were placed in a parallel-plate dielectric cell, and temperature was controlled using a Quatro Cryosystem from Novocontrol. The same temperature protocol was used for all samples: First they were equilibrated in the cell in the molten state at $T = 80\,°\mathrm{C}$ for 10 min and then quenched to ~30 K below T_g to avoid crystallization. The samples were equilibrated for 20 min at each T before measurement of each dielectric spectrum. Linear shear viscosity measurements for $R = 5$ protonated and deuterated systems were carried out via a stress-controlled AR2000ex rheometer from TA Instruments in a frequency range 10^{-1}–10^{2} Hz using a parallel-plate geometry with a disk diameter of 4 mm and a gap of 1 mm. During rheological measurements the temperature was stabilized within ±0.2 K. A much stronger crystallization tendency of pure deuterated PA ($R = 3$) prevented us from acquiring accurate results for its viscosity.

The dielectric spectra of both protonated (H-PA) and deuterated (D-PA) PA ($R = 3$) at select temperatures are presented in Fig. 1. The real part of the dielectric permittivity $\varepsilon'(\nu)$ shows an electrode polarization effect at lower frequencies and a conductivity relaxation process at higher frequencies [Fig. 1(a)]. The latter appears as a peak in the imaginary part of the complex electric modulus, $M''(\nu)$ [Fig. 1(c)] with a characteristic time constant $\tau_\sigma = 1/(2\pi\nu_{\max})$, while dc conductivity manifests as a frequency independent plateau $\sigma(T)$ in the real part of the complex conductivity, $\sigma'(\nu)$ [Fig. 1(b)]. The raw data (Fig. 1) reveal a significant isotope effect with D/H substitution in PA.

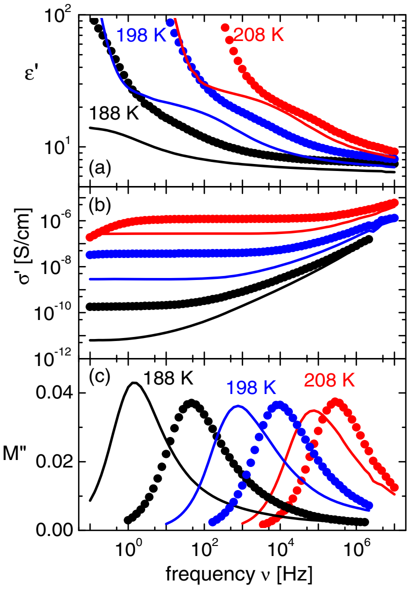

FIG. 1. Dielectric spectra of $R = 3$ H-PA (solid symbols) and D-PA (lines) at select temperatures. (a) Real part of the dielectric permittivity $\varepsilon'(\nu)$; (b) real part of the conductivity $\sigma'(\nu)$; and (c) imaginary part of the electric modulus $M''(\nu)$.

The conductivity $\sigma(T)$ at high temperatures displays a Vogel-Fulcher-Tammann (VFT)-like behavior, $\sigma(T) = \sigma_0 \exp[-B/(T - T_0)]$ that crosses over to an Arrhenius-like temperature dependence at lower T, $\sigma(T) = \sigma_0 \exp(-E_a/kT)$ [Fig. 2(a)]. The same behavior is observed for $\tau_\sigma(T)$ [Fig. 2(b)] that is directly related to inverse conductivity, $\tau_\sigma \approx \varepsilon'\varepsilon_0/\sigma$. This type of temperature dependence is typical for ionic conductivity upon crossing the glass transition

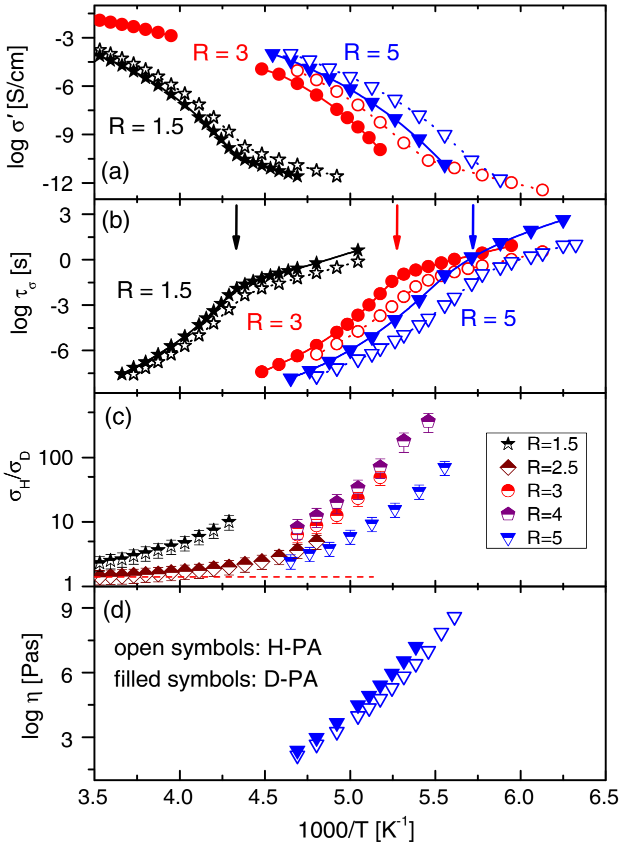

FIG. 2. Temperature dependence of (a) conductivity and (b) of the conductivity relaxation time in H-PAs (open symbols) and in D-PAs (closed symbols) for several selected water content R values. Arrows in (b) indicate T_g values for H-PAs from DSC measurements. (c) The ratio of conductivities in protonated σ_{H} and deuterated σ_{D} samples with different R. The horizontal dashed line in (c) presents the value 1.4 expected for classical proton transfer mechanism. (d) Temperature dependence of viscosity in H-PA (open triangles) and D-PA (closed triangles) with $R = 5$.

temperature [23,24]. Indeed, analysis of the DSC data indicates that the calorimetric T_g lies in the vicinity of this crossover temperature [Fig. 2(b)]. Thus this crossover in the temperature dependence of conductivity and τ_σ provides another way to estimate T_g of our materials.

Comparison of conductivities in deuterated and hydrogenated PAs [Fig. 2(c)] reveals a strong isotope effect at all studied temperatures and compositions R. This result agrees with earlier studies [22], where a decrease of conductivity was reported in partially deuterated PAs, although these measurements were limited to high temperatures only. The observed strong isotope effect [Fig. 2(c)] contradicts the vehicular mechanism for proton conductivity, for which no measurable isotope effect is expected due to very small changes of the mass of molecular units (vehicle) upon D/H substitution. It should be noted that the observed VFT behavior is characteristic of the temperature dependence of structural relaxation time τ_α and viscosity [Fig. 2(d)] in liquids. Similar temperature behavior in conductivity [Fig. 2(a)] suggests that a similar friction mechanism also controls motion of charges in these PAs. This VFT behavior, however, does not imply a vehicular mechanism of conductivity but rather suggests that the dominating proton transport mechanism at $T > T_g$ requires some local rearrangements of the molecules and is strongly affected by the liquid's viscosity.

The unexpectedly strong isotope effect in conductivity of PA and its aqueous solutions is intriguing. The ratio of conductivities reaches the expected value $\sigma_H/\sigma_D \sim (M_D/M_H)^{1/2} \sim 1.4$ for the proton transfer mechanism only at high temperatures [Fig. 2(c)] (here M_D and M_H are the masses of deuterium and proton). However, the isotope effect increases sharply upon cooling, with the ratio σ_H/σ_D reaching several hundred times. Such a strong effect is not expected in the classical picture of proton conductivity. To unravel the mechanism of such a strong change in conductivity, we note that the isotope substitution can also affect structural relaxation time τ_α and viscosity η of a liquid. Thus, we need to compare σ_H and σ_D not at a constant temperature, but at the same η or structural relaxation time τ_α.

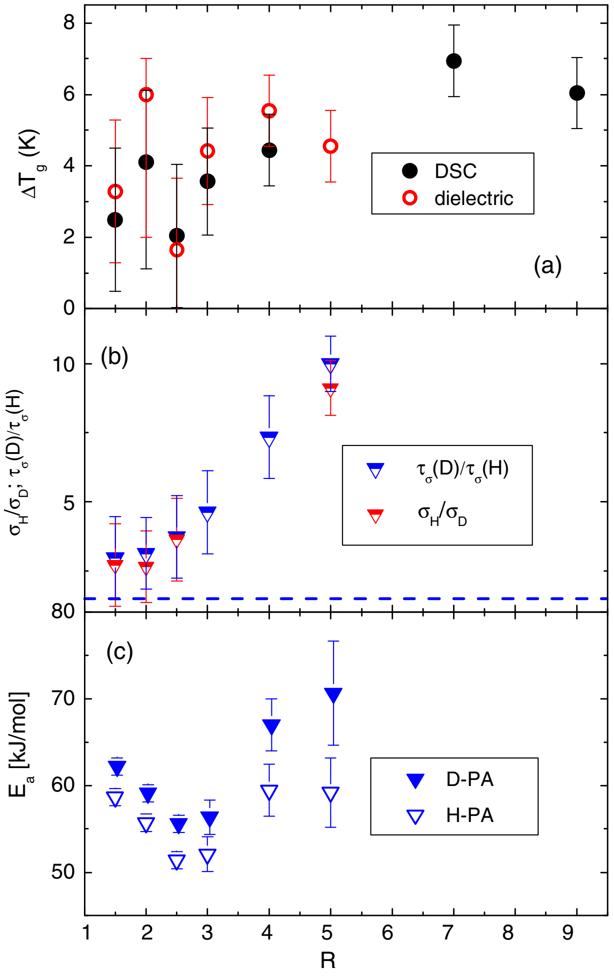

FIG. 3. Dependence of the isotope effect on molar content of water R: (a) Isotope shift of the glass transition temperature $\Delta T_g = T_g(D) - T_g(H)$ measured by DSC (closed symbols) and BDS (open symbols). The error bars for the shift in T_g are larger for samples with low R due to significantly higher sensitivity of T_g in theses samples to the water content. (b) The ratio of the conductivities and conductivity relaxation times at T_g. The dashed line shows the ratio $\sigma_H/\sigma_D \sim 1.4$. (c) The activation energy for the conductivity relaxation time in the Arrhenius regime $T < T_g$ for D-PAs (closed symbols) and H-PAs (open symbols). Accuracy of estimated E_a for $R = 4$ and 5 is low due to more limited temperature range investigated below T_g.

The viscosity data exhibit a strong isotope effect [Fig. 2(d)], which is further substantiated by the significant increase in calorimetric T_g upon D/H substitution. The shift in T_g, $\Delta T_g = T_g(D) - T_g(H)$, increases from ~2 K at $R = 1.5$ to ~6–7 K at $R \geq 7$ [Fig. 3(a)]; i.e., it increases with the increase in water content. We note large data scattering and large error bars in ΔT_g for samples with $R < 3$ [Fig. 3(a)]. This is caused by very strong sensitivity of T_g to water content at $R < 2$, which decreases by more than 3 times for $R > 4$. In any case, our results reveal an unusually large isotope effect in T_g for a hydrogen bonding liquid. For example, the isotope shift of T_g with D/H substitution in the hydrogen bonding liquids ethanol, glycerol, and propylene glycol is less than 1 K [25–28]. However, the observed strong isotope shift of T_g in PAs [Fig. 3(a)] agrees well with the recent studies [25] that revealed an anomalously large isotope effect in the glass transition of water, $\Delta T_g \sim 10$ K. This was explained by a possible quantum mechanical tunneling effect in structural relaxation of water at low temperatures [25,29]. The observed strong isotope shift of T_g in PAs indicates significant slowing down of their structural dynamics upon D/H substitution that can be caused by a decrease in quantum effects [25,29] or by changes in the hydrogen bonding network. However, a detailed discussion of the mechanism of the isotope shift in T_g of PAs is out of the scope of this Letter.

To disentangle the isotope effects on proton conductivity from those on structural relaxation, we can compare the values of conductivity at the same viscosity. Analysis of our data clearly demonstrates that σ_{D} is significantly lower than σ_{H} even when compared at the same η (Fig. 4). The difference increases from ∼2 times at higher temperature $T \sim 210$ K (lower viscosity), to ∼5 times at $T \sim 190$ K (higher viscosity), and reaches ∼10 times at T_g [$\eta(T_g) \sim 10^{12}$ Pa s] for sample with $R = 5$ (inset of Fig. 4). These results clearly exclude the vehicular mechanism of conductivity in PAs. The same conclusion can be achieved from comparison of conductivities at T_g of each sample. In this case we compare conductivities at similar structural relaxation time of the systems [$\tau_\alpha(T_g) \sim 100$ s]. The ratio of conductivities at T_g increases from $\sigma_{\mathrm{H}}(T_g)/\sigma_{\mathrm{D}}(T_g) \sim 2.5$ times in samples with $R \sim 1.5$–2 up to ∼10 times for samples with $R \sim 5$ [Fig. 3(b)]. Accurate measurements of conductivity at T_g is strongly limited by the lower frequency measurements [Fig. 1(b)], while much more accurate data can be obtained for the conductivity relaxation time [Fig. 2(b)] that provides similar information. It essentially reflects the rate of ion motions. As expected, our analysis shows that the isotope effect on conductivity relaxation time at T_g agrees well with the data on conductivity at T_g [Fig. 3(b)]: $\tau_{\sigma\mathrm{D}}(T_g)/\tau_{\sigma\mathrm{H}}(T_g)$ increases from ∼3 for $R = 1.5$ to ∼10 for $R = 5$.

Such a strong isotope effect in conductivity at the same viscosity and at T_g clearly suggests that the proton transfer mechanism dominates the conductivity mechanism in PAs. The most surprising result is that the isotope effect at low temperatures far exceeds the expected classical value of $\sigma_{\mathrm{H}}/\sigma_{\mathrm{D}} \sim 1.4$, even after corrections for viscosity and T_g (Figs. 3, 4). Is it possible that quantum effects are the reason for the observed strong isotope effect at lower T? To answer this question we analyze the temperature dependence of the conductivity relaxation time [Fig. 2(b)]. First of all, the super-Arrhenius (VFT) behavior at $T > T_g$ and Arrhenius behavior $\tau(T) = \tau_{\sigma 0}\exp(E_a/kT)$ at $T < T_g$ can be well described by the usual over-barrier relaxation and have reasonable $\tau_{\sigma 0} \sim 10^{-13}$–$10^{-16}$ s. A sub-Arrhenius temperature dependence and $\tau_{\sigma 0}$ significantly longer than the usual microscopic τ_0 are expected in the case of tunneling (for details see, e.g., Refs. [3,29] and references therein). We note also that tunneling at low temperatures can be directly observed in neutron scattering spectroscopy (see, e.g., Refs. [30,31]), but only when it is in the ps-ns time range. We don't expect such fast proton motion in the PAs studied here at low temperatures. Thus, despite the strong isotope effect, we do not find any signs of tunneling in our data (Fig. 2). Recent *ab initio* molecular dynamics simulations revealed strong dependence of quantum effects in water on electric field and presence of ions [32,33]. Strong ionization of phosphoric acids can create significant electric fields which might affect the probability of proton tunneling in PAs.

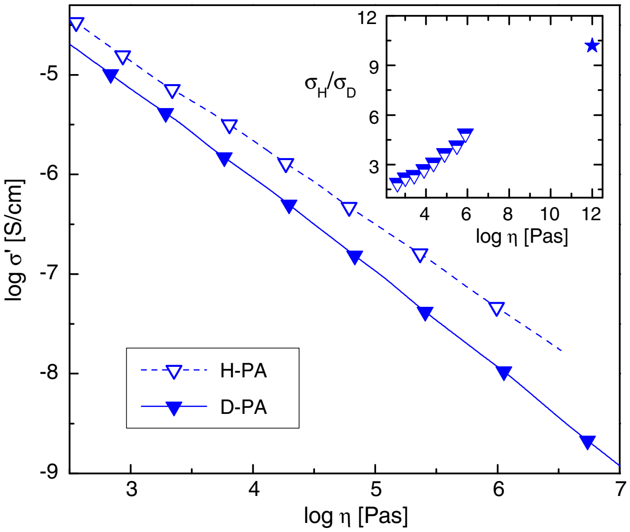

FIG. 4. Conductivity vs viscosity in protonated (open symbols) and deuterated (closed symbols) PA with $R = 5$. Inset shows the ratio of conductivities at the same viscosity that increases with decrease in temperature (increase in viscosity), and the star shows the ratio of conductivities at T_g that should correspond to $\eta \sim 10^{12}$ Pa s.

It appears that the activation energy E_a in the Arrhenius regime of τ_σ at $T < T_g$ [Fig. 2(c)] in deuterated PAs is always higher than in protonated PAs by ∼5–10 kJ/mol [Fig. 3(c)]. This difference in activation energy provides a hint for understanding the mechanism of this strong isotope effect on the conductivity of PAs. From a quantum mechanical perspective of activated hopping, a particle jumps over energy barriers not from the bottom of the potential well, but from the energy level of zero-point quantum fluctuations $E_0 = h\nu_0/2$. This effective decrease in the activation energy is usually referred to as the trivial quantum effect [1,3]. The zero-point energy for O-H vibrations is $E_0 \sim 21$ kJ/mol, and is $\sim(M_{\mathrm{D}}/M_{\mathrm{H}})^{1/2} \sim 1.4$ times lower for O-D vibrations [1,34]. Thus, substitution of hydrogen by deuterium leads to a decrease of the zero-point energy and an "effective" increase of the activation energy by ∼6 kJ/mol. Similar decrease of activation energy by ∼3–5 kJ/mol have been reported for hydrogen and deuterium diffusion and conductivity in various materials [1,3,34]. The observed difference in E_a between deuterated and hydrogenated PAs [Fig. 3(c)] agrees with the value expected for the isotope effect on the zero-point energy. In that case, the importance of this change in activation energy barrier upon isotopic substitution increases with decreasing temperature. This explains the increase of the isotope effect with temperature decrease even when compared at the same viscosity (inset Fig. 4). It also explains the observed increase of the isotope effect at T_g with increasing water content [Fig. 3(b)] by a simple decrease in T_g of the samples.

The presented study revealed an unexpectedly strong isotope effect on proton conductivity of phosphoric acids over broad temperature and composition ranges. The ratio σ_H/σ_D starts from the value $\sim$1.4 at high temperatures and reaches several hundred at lower temperatures (Fig. 2). These results clearly demonstrate that the intermolecular proton transfer is the dominating mechanism of proton conductivity in PA and its aqueous solutions. The value 1.4 is expected in the classical picture of an intermolecular proton transfer mechanism. We demonstrate that the observed strong isotope effect in conductivity at low temperatures is primarily caused by an increase in viscosity and T_g upon D/H substitution. However, the isotope effect on conductivity of PAs at low T remains unexpectedly high even after accounting for the change in viscosity and T_g, and reaches the value $\sigma_H(T_g)/\sigma_D(T_g) \sim 10$ for the sample with $R = 5$, far exceeding the classical value. We emphasize that our results revealed no signs of proton or deuterium tunneling, and the observed large isotope effect can be well explained by the trivial quantum effect—the decrease of the quantum zero-point energy with D/H substitution that leads to an effective increase of the energy barrier. This result clearly emphasizes the important role that quantum effects play in proton conductivity of phosphoric acids by reducing the energy barrier for proton transport by $\sim$20 kJ/mol. Classical MD simulations usually neglect quantum effects and adapt the model parameters to compensate for zero-point energy. The presented results demonstrate that contribution of zero-point vibrations are not negligible and should be explicitly accounted for in any model that aims to describe the proton transport in PAs.

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