

SUPPORTING INFORMATION

Can a Secondary Isotope Effect Be Larger than a Primary?

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Equations. Bigeleisen and Mayer derived the relationship between EIEs and partition functions Q of reactant and product, as expressed in eq S1,² where the asterisk signifies isotopic label. Because the EIE is defined as $K_{\text{light}}/K_{\text{heavy}}$, the ratio of partition functions must be Q/Q^* , but eq S1 can be converted to eq S2, with the more familiar ratio Q^*/Q . The ratio of partition functions of an N -atomic species can be expressed as a product over all the vibrations, as in eq S3, where $u_i = h\nu_i/kT$.

$$\text{EIE} = \left(\frac{Q}{Q^*}\right)_{\text{product}} / \left(\frac{Q}{Q^*}\right)_{\text{reactant}} \quad (\text{S1})$$

$$\text{EIE} = \left(\frac{Q^*}{Q}\right)_{\text{reactant}} / \left(\frac{Q^*}{Q}\right)_{\text{product}} \quad (\text{S2})$$

$$\frac{Q^*}{Q} = \prod^{3N-6} \frac{u_i^*}{u_i} \left(\frac{1 - e^{-u_i}}{1 - e^{-u_i^*}}\right) e^{(u_i - u_i^*)/2} = \text{MMI} \cdot \text{EXC} \cdot \text{ZPE} \quad (\text{S3})$$

The three factors in eq S3—the mass and moment of inertia factor (MMI), the excitation factor (EXC), and the zero-point-energy factor (ZPE)—can all be determined from the vibrational frequencies. The second factor, EXC, represents the contribution from excited vibrational states. These are occupied only for low frequencies or at high temperatures, so that EXC can be ignored, leading to eq S4. The MMI factor of eq S5 is also often ignored, leading to eq S6, in terms of only the ZPE factor. Substituting eq S6 into eq S2 then gives eq S7, expressing the EIE in terms of only ZPEs.

$$\frac{Q^*}{Q} = \prod^{3N-6} \frac{u_i^*}{u_i} e^{(u_i - u_i^*)/2} \quad (\text{S4})$$

$$\text{MMI} = \prod^{3N-6} \frac{u_i^*}{u_i} \quad (\text{S5})$$

$$\frac{Q^*}{Q} \sim \prod^{3N-6} e^{(u_i - u_i^*)/2} \quad (\text{S6})$$

$$\text{EIE} \sim \text{ZPE} \sim \frac{\prod^{3N-6} e^{(u_i - u_i^*)/2}_{\text{reactant}}}{\prod^{3N-6} e^{(u_i - u_i^*)/2}_{\text{product}}} \quad (\text{S7})$$

The MMI factor accounts for the rotational and translational partition functions. The form in eq S5, involving only vibrational frequencies, is convenient for computation. It results from applying the Redlich-Teller product rule to the alternative form in eq S8, where m is the mass of an atom, M is the total mass of the species, and I_x , I_y , and I_z are its moments of inertia along the three principal axes.³ The contribution of the last two factors of eq S8 to the EIE in eq S2 is the mass factor M of eq S9. Because the atoms are identical on both sides of a reaction, the ratio of the masses m must equal 1. Moreover, the factor including the ratio of the total masses, M , on the two sides of the equation is usually negligibly different from unity. For example, for the EIE on the acidity of formic acid-¹⁸O the M factor contributes 1.0014 to both the 1° and 2° EIEs. Therefore the mass factor M can be ignored, and the major contributor to MMI is the first factor in eq S8. Its contribution to the EIE of eq S2 is then the MI factor of eq S10. Finally, restoring this MI factor, in the form of eq S5, to the overall EIE leads to eq 4.

$$\text{MMI} = \left(\frac{I_x^* I_y^* I_z^*}{I_x I_y I_z} \right)^{1/2} \left(\frac{M^*}{M} \right)^{3/2} \prod^{3N} \left(\frac{m}{m^*} \right)^{1/2} \quad (\text{S8})$$

$$M = \frac{\left(\frac{M^*}{M} \right)^{3/2} \prod^{3N} \left(\frac{m}{m^*} \right)^{1/2}_{\text{reactant}}}{\left(\frac{M^*}{M} \right)^{3/2} \prod^{3N} \left(\frac{m}{m^*} \right)^{1/2}_{\text{product}}} \sim 1 \quad (\text{S9})$$

$$\text{MI} = \frac{\left(\frac{I_x^* I_y^* I_z^*}{I_x I_y I_z} \right)^{1/2}_{\text{reactant}}}{\left(\frac{I_x^* I_y^* I_z^*}{I_x I_y I_z} \right)^{1/2}_{\text{product}}} \quad (\text{S10})$$

$$\text{EIE} = \frac{\prod^{3N-6} \left(\frac{u_i^*}{u_i} \right)_{\text{reactant}} e^{(u_i - u_i^*)/2}_{\text{reactant}}}{\prod^{3N-6} \left(\frac{u_i^*}{u_i} \right)_{\text{product}} e^{(u_i - u_i^*)/2}_{\text{product}}} \quad (4)$$

Details of Computation. Calculations were performed on species both with and without constraint to the expected point-group symmetry.⁴ If the difference between the unconstrained and constrained energies was ≤ 10 cal/mol, the symmetrized structure was used. No scaling factor was applied to vibrational frequencies,⁵ because the correction is small and does not affect the comparison here between 1° and 2° EIEs.

The acid/base reactions of formic, nitrous and nitric acids were also calculated using the B3LYP/aug-cc-pVTZ basis set, and the polarized continuum model (PCM) of both chloroform and water, to assess the effect of solvation on the vibrational frequencies and the EIEs. This was repeated for two Lewis acids by calculating the vibrational frequencies of water, nitrosonium ion, carbon dioxide, nitrous acid, and bicarbonate. Each EIE on acidity was calculated using eq 4, excluding the contribution from excitation that is in the central parentheses of eq S3, but including the MMI factor.

Species with a three-fold or higher axis of symmetry, including CO_3^{2-} , NO_3^- , BH_3 , HB(OH)_3^- , B(OH)_3 , H_3PO_4 , PO_3^- , CO_2 , B(OH)_4^- and PO_4^{3-} , have degenerate frequencies. In some cases, errors in the calculations result in vibrational frequencies that differ slightly. However, these errors are too small to be significant for the calculations herein.

Deprotonation of some acids—borinic (hydroxyborane, H_2BOH), boronic (dihydroxyborane, HB(OH)_2), boric (B(OH)_3), and phosphenic (O_2POH)—is only hypothetical, since the acid preferentially reacts as a Lewis acid. The calculated energy differences between the Lewis adduct and the Brønsted products (water + Brønsted conjugate base) are listed in Table S1. The strong preference for Lewis acidity is confirmed by the calculations, although it should be mentioned that diarylborinic acids can be deprotonated by butyllithium to Ar_2BO^- .⁶

Table S1. B3LYP/aug-cc-pVTZ energy preference (kcal/mol) for select acids to react as Lewis acids over Brønsted acids.

Acid HA	$E(\text{A}^- + \text{H}_2\text{O}) - E(\text{HAOH}^-)$
H_2BOH	25.4
HB(OH)_2	17.2
B(OH)_3	15.8
O_2POH	24.8

Treatment of Isotopomers and Isomers. The number of inequivalent oxygen atoms in an acid or conjugate base represents the number of mono- ^{18}O isotopomers for that species. For example, formic acid, HCOOH , has two inequivalent oxygen atoms, C=O and C-OH , which result in two mono- ^{18}O isotopomers depending on which oxygen is labeled. Those have identical electronic energy but different ZPEs. In contrast, some acids or conjugate bases have isotopomers that differ only by single-bond rotation. These are conformational isomers if the structures differ in their electronic energy, or conformational isotopomers if the structures differ only in their ZPEs.

An example of conformational isomers arises in the (hypothetical) deprotonation of boronic acid, which can result in *cis* and *trans* boronate anions, shown in Figure S1. The designations *cis* and *trans* identify the relationship between the hydroxyl proton and the hydrogen on the boron. (Alternatively, these can be designated as *E* and *Z*, respectively, if double-bond

character is associated with the B–OH bond.). These are conformational isomers, which differ in their absolute energies, analogous to the *cis* and *trans* isomers of an amide RCONHR'. The *trans* boronate HB(OH)O[−] is calculated to be more stable than the *cis* by nearly 3 kcal/mol. This difference is inherent in the structures, without any consideration of vibrational ZPE or isotopic substitution. The energy difference corresponds to a strong preference for removal of the *cis* (*E*) proton in boronic acid over the *trans* (*Z*), by a factor of 156 at room temperature. Therefore the *cis* boronate anion can be ignored.

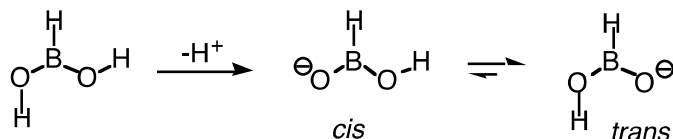


Figure S1. Deprotonation of boronic acid to two conformational isomers of boronate anion.

Conformational isotopomers have the same electronic energy, but because of the isotopic labeling, they differ in ZPE. However, this difference is found to be very small, so that there is a negligible preference for one isotopomer over another, and all are populated nearly equally at room temperature. An example of conformational isotopomers arises with bicarbonate anion. It has three mono-¹⁸O-labeled isotopomers; two with the ¹⁸O in anionic carbonyls and one with ¹⁸O in the hydroxyl. The hydroxyl oxygen is not equivalent to the carbonyl oxygens, and the isotopomer with ¹⁸O-labeled hydroxyl has a substantially different ZPE, so it is an isotopomer, not a conformational isotopomer, of the other two. In contrast, the two isotopomers with an ¹⁸O-labeled carbonyl have identical electronic energies and differ only by the *trans* or *cis* orientation of ¹⁸O relative to the hydroxyl proton, as shown in Figure S2. These are conformational isotopomers that differ only in their ZPEs. The overall EIE must be an average of the EIEs of these two isotopomers, weighted in principle by their populations. How large is the energetic preference for ¹⁸O in one position over the other? The answer depends on the ZPEs. The *trans* isotopomer is more stable than the *cis*, but by < 3 cal/mol. At room temperature this corresponds to a *trans*:*cis* ratio of 1.004:1. Such a ratio is general for conformational isotopomers, which can be accurately modeled as an equimolar mixture, and their EIEs can be evaluated as simple averages over all the conformational isotopomers.

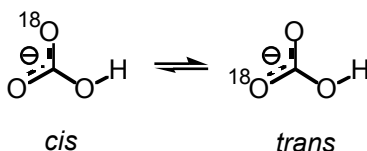


Figure S2. Two conformational isotopomers of bicarbonate anion with ¹⁸O in carbonyl.

Brønsted Acids Centered on Carbon. Formic acid in Figure S3 and acetic acid in Figure S4 are straightforward. Formic acid, acetic acid, and acetate were constrained to the C_s point group, and formate anion was constrained to the C_{2v} point group. The deprotonation step for either the 1° or 2° EIE results in the same anion, with equivalent oxygens and the same vibrational frequencies and ZPEs regardless of which oxygen is ¹⁸O-labeled.

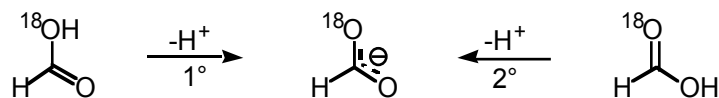


Figure S3. Reactions associated with the primary and secondary EIEs on the acidity of formic acid.

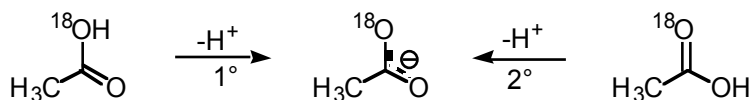


Figure S4. Reactions associated with the primary and secondary EIEs on the acidity of acetic acid.

In highly acidic solutions carboxylic acids can be protonated on the carbonyl oxygen.⁷ This was modeled using protonated formic acid, in Figure S5, undergoing deprotonation to formic acid. The lowest-energy form of protonated formic acid has one OH proton *cis* to the C-H and the other OH *trans*. The two formic acid structures formed after deprotonation of one OH or the other are conformational isomers related by single-bond rotation, and they differ considerably in energy. Only the more acidic *cis* proton of protonated formic acid is removed, leading to the formation of the more stable *trans* (*Z*) conformation of formic acid.

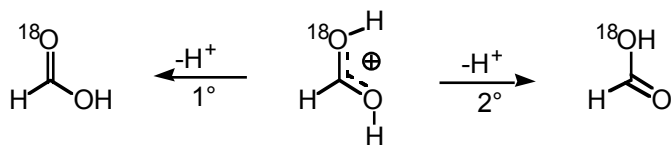


Figure S5. Reactions associated with the primary and secondary EIEs on the acidity of protonated formic acid.

Figure S6 shows the deprotonation of carbonic acid to bicarbonate anion, which can undergo further deprotonation to form carbonate dianion. Carbonic acid has C_{2v} symmetry, with both protons syn to the C=O.⁸ Then identical vibrational frequencies are obtained regardless of which OH is labeled. Bicarbonate has C_s symmetry, with anionic oxygens that are inequivalent because one oxygen is *cis* to the hydrogen and the other is *trans*. Labeling one or the other of those oxygens then produces two conformational isotopomers, as in Figure S2. Because the total ZPEs of the two conformational isotopomers are calculated to differ by <3 cal/mol, both contribute equally, and both the 1° EIE and the 2° C=O EIE of carbonic acid are averages of EIEs for deprotonation to the *cis* and *trans* ^{18}O -labeled products.

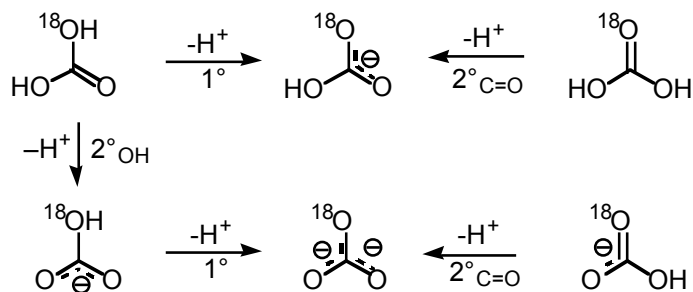


Figure S6. Reactions associated with the one primary and two secondary EIEs on carbonic acid acidity and the primary and secondary EIEs on bicarbonate acidity.

Because carbonate dianion has D_{3h} symmetry, the vibrational frequencies and ZPEs are the same regardless of the placement of a single ^{18}O label. The 1° EIE for the deprotonation of bicarbonate anion has only one possible reactant and product, so no averaging is required. The 2° EIE requires averaging over the two possible conformational isotopomers that differ in whether the ^{18}O is *cis* or *trans* to the OH hydrogen.

Brønsted Acids Centered on Nitrogen. Deprotonation of nitrous acid, of C_s symmetry, to form the nitrite anion, as in Figure S7, is very similar to that of formic acid in Figure S3. There are two mono- ^{18}O isotopomers of nitrous acid, one leading to the 1° EIE and the other leading to the 2° EIE. No averaging is required for either EIE. The nitrite anion has C_{2v} symmetry, so the vibrational frequencies and ZPEs of the product are identical regardless of the mono-labeled precursor.

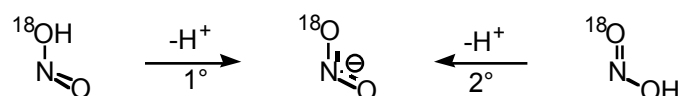


Figure S7. Reactions associated with the primary and secondary EIEs on the acidity of nitrous acid.

The primary and secondary EIEs for deprotonation of nitric acid, of C_s symmetry, to nitrate anion, as in Figure S8, closely parallel those of bicarbonate in Figure S6. There are three isotopomers of mono- ^{18}O labeled nitric acid, but each one results in the same mono-labeled nitrate anion. The 1° EIE is the result of the unique isotopomer with the ^{18}O label at the OH position. The 2° EIE requires averaging over two conformational isotopomers, with the ^{18}O in a nitryl oxygen either *trans* or *cis* to the OH hydrogen.

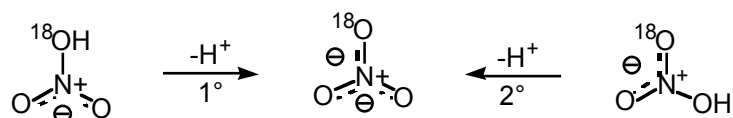


Figure S8. Reactions associated with the primary and secondary EIEs on the acidity of nitric acid.

Brønsted Acids Centered on Boron. The next three boron cases are hypothetical and of only comparative and theoretical value. For all of them, as documented in Table S1, deprotonation is less favorable than water addition combined with H^+ loss, as in eq 3, which is considered later. Deprotonation of borinic acid in Figure S9 has only a 1° EIE. There is only one isotopomer for either the mono- ^{18}O substituted reactant or product.

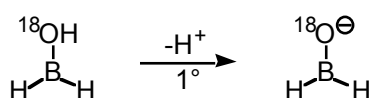


Figure S9. Reaction associated with the primary EIE for deprotonation of borinic acid.

Deprotonation of boronic acid in Figure S10 has some unique features. The lowest-energy conformation of boronic acid has one OH proton *cis* to the BH and one OH proton *trans*, with the *cis,cis* calculated to be 1.8 kcal/mol higher in energy. The two possible deprotonated products are conformational isomers that differ substantially in energy. If the *trans* proton were removed, a less stable anion would result. Therefore, the *cis* OH proton is more acidic than the *trans* and is the only proton removed. This results in a 1° ¹⁸O EIE that comes from deprotonation of the *cis* OH in the conformational isotopomer labeled at the *cis* OH, while the 2° EIE comes from deprotonation of the *cis* OH in the conformational isotopomer labeled at the *trans* OH. Each reaction leads to a different isotopomer of the anion, and all species have C_s symmetry.

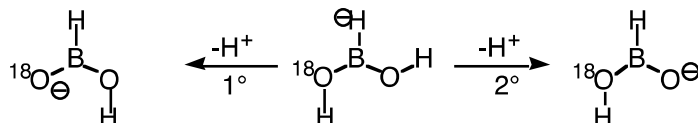


Figure S10. Reactions associated with the primary and secondary EIEs on the acidity of boronic acid.

Deprotonation of boric acid, of C_{3h} symmetry, in Figure S11, is straightforward, except that a bond rotation must occur after deprotonation to obtain the lowest-energy anion, *cis,cis* B(OH)₂O[−], of C_{2v}, symmetry, with both OH protons *cis* to the O[−]. Both the 1° and the 2° ¹⁸O EIE are calculated from the vibrational frequencies of the mono-labeled boric acid and of the species with ¹⁸O in either the anionic oxygen (1°) or in one of the two hydroxylic oxygens, which are equivalent. No averaging is required.

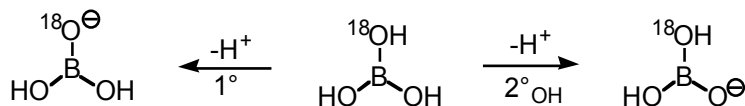


Figure S11. Reactions associated with the primary and secondary EIEs for deprotonation of boric acid.

Brønsted Acids Centered on Phosphorus. The deprotonation of phosphinic acid, in Figure S12, to phosphinate is straightforward. Phosphinic acid is not symmetric (C₁ symmetry). The C_s symmetric structure, with the hydrogen in the OPO plane, can be rejected because it is over 90 cal/mol higher in energy. However, phosphinate anion has C_{2v} symmetry, so the anionic phosphoryl oxygen atoms in phosphinate are equivalent, and no averaging is required to obtain either the 1° or 2° ¹⁸O EIE.

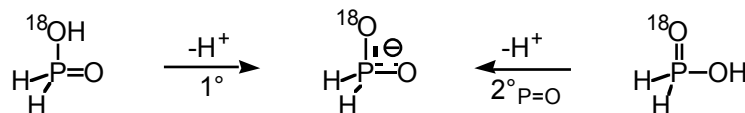


Figure S12. Reactions associated with the primary and secondary EIEs on the acidity of phosphinic acid.

Deprotonation of phosphonic acid, in Figure S13, shows a 1° and two 2° ¹⁸O EIEs. The

C_1 -symmetric structure is more stable than the C_s -symmetric structure, albeit by only 25 cal/mol. The lack of symmetry means that the two mono- ^{18}OH isotopomers of the acid are conformational isotopomers, which differ in ZPE by < 3 cal/mol and so are of comparable acidity. Therefore it is necessary to average over these two conformational isotopomers to calculate the EIEs. Also, because hydrogen phosphonate anion is of C_1 symmetry, there are two conformational isotopomers with ^{18}O at one or the other phosphoryl oxygen. These differ by whether the ^{18}O is synperiplanar or anticlinal to the hydroxyl H. Then it is necessary to average over these two conformational isotopomers to calculate the 1° and 2° P=O EIEs. Combining all possibilities from the acid and anion thus requires averaging over four reactions for the 1° EIE, and two reactions for either of the 2° EIEs.

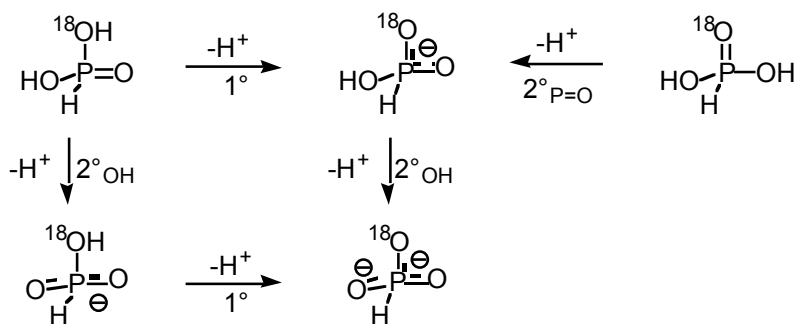


Figure S13. Reactions associated with the primary and secondary EIEs on the acidities of phosphonic acid and hydrogen phosphonate anion.

Phosphoric acid in Figure S14 has C_3 symmetry, so the hydroxyl groups are equivalent. Dihydrogen phosphate anion has C_2 symmetry, with both of the phosphoryl groups and both of the hydroxyl groups equivalent. Therefore no averaging is required for any of the three EIEs.

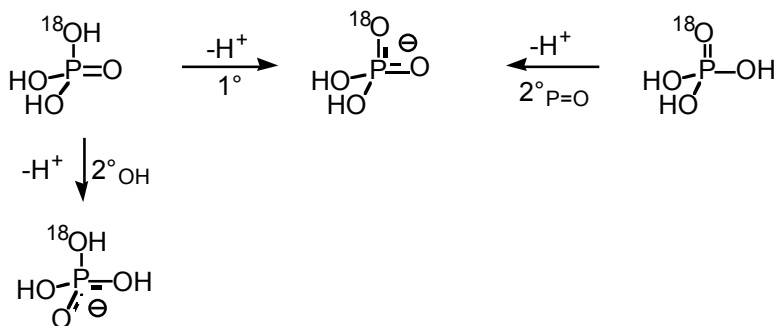


Figure S14. Reactions associated with the primary and secondary EIEs on the acidity of phosphoric acid.

Further deprotonation of dihydrogen phosphate anion of C_2 symmetry, in Figure S15, to hydrogen phosphate dianion, like the first deprotonation of phosphoric acid, has three different EIEs, a 1° and two 2° . Two phosphoryl oxygens in the dianion, of C_s symmetry, are equivalent and the third is inequivalent because of proximity to the OH hydrogen. Therefore an average must be taken over all three conformational isotopomers, two of which are identical. The 1° and the 2° P=O EIEs both require averaging over the three possible structures. The 2° P-OH EIE does

not require averaging.

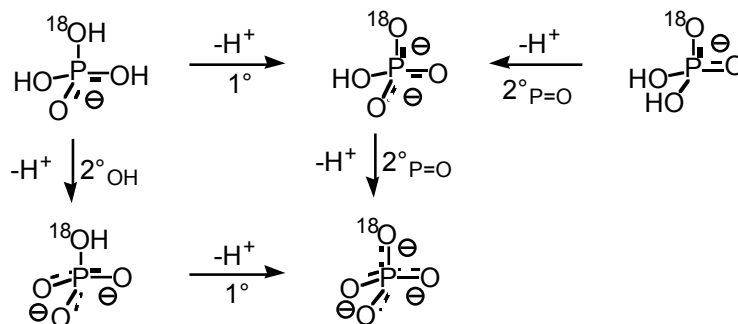


Figure S15. Reactions associated with the primary and secondary EIEs on the acidities of dihydrogen phosphate anion and hydrogen phosphate dianion.

Hydrogen phosphate dianion in Figure S15 can be further deprotonated to phosphate trianion. Because the dianion has C_s symmetry, it is necessary to average over three conformational isotopomers, two of which are identical. Because the four oxygens in the T_d -symmetric phosphate trianion are equivalent, no averaging is necessary for the 1° EIE, but there are three 2° EIEs to average.

Deprotonation, of phosphenic acid, in Figure S16, is only hypothetical because this is a Lewis acid. Like bicarbonate anion in Figure S6, phosphenic acid has C_s symmetry, with phosphoryl oxygens that are inequivalent because of their different relations to the H. Labeling either the *cis* or the *trans* oxygen then produces two conformational isotopomers. The deprotonation product, phosphenate, has D_{3h} symmetry, so the 1° EIE has only one possible product, and no averaging is required. The 2° EIE requires averaging over the two conformational isotopomers.

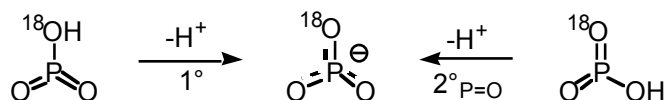


Figure S16. Reactions associated with the primary and secondary EIEs on the acidity of phosphenic acid.

Lewis Acids Centered on Carbon. The addition of water to carbon dioxide to form the C_s bicarbonate anion + H^+ , in Figure S17, has only one 1° EIE, from addition of $^{18}OH_2$ to unlabeled CO_2 . The 2° EIE must be averaged over the two conformational isotopomers of bicarbonate anion. In these figures, as in subsequent ones, only the net reaction of adding OH^- to the Lewis acid is shown, although the overall reaction, as in eq 3, is the combination of H_2O addition and H^+ loss.



Figure S17. Reactions associated with the primary and secondary EIEs on the Lewis acidity of

carbon dioxide.

Lewis Acids Centered on Nitrogen. Nitrosonium (NO^+) and nitronium (NO_2^+) ions can add water, resulting in nitrous and nitric acids, respectively, + H^+ . The 1° EIEs arise from reaction of unlabeled cation, in Figure S18 or S19, with $^{18}\text{OH}_2$, to produce nitrous acid or nitric acid with ^{18}O in the N–OH. The 2° EIE for NO^+ arises from reaction of ^{18}O -labeled nitrosonium ion with unlabeled OH_2 , to produce nitrous acid with ^{18}O in the nitryl oxygen. No averaging is necessary. Mono- ^{18}O -labeled nitronium is also a single isotopomer, so no averaging is necessary for its 1° EIE. However, its 2° EIE involves the two conformational isotopomers of nitric acid, in Figure S8, with very similar energies, so that averaging over both is required.



Figure S18. Reactions associated with the primary and secondary EIEs on the Lewis acidity of the nitrosonium cation.



Figure S19. Reactions associated with the primary and secondary EIEs on the Lewis acidity of the nitronium cation.

Lewis Acids Centered on Boron. Addition of water to borane, as in Figure S20, shows only a 1° EIE, and no averaging is required.

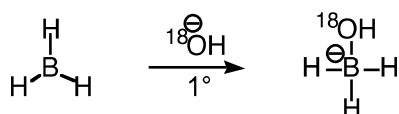


Figure S20. Reaction associated with the primary EIE for borane.

Water addition to borinic acid, as in Figure S21, produces an anion with C_2 symmetry, and calculation of its EIEs requires no averaging.

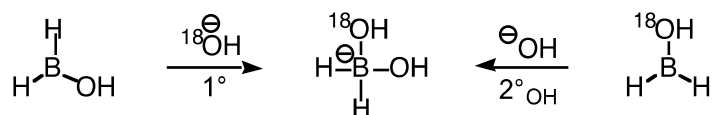


Figure S21. Reactions associated with the primary and secondary EIEs on the Lewis acidity of borinic acid.

Water addition to boronic acid, as in Figure S22, lacks the complexity in Figure S10 of its deprotonation. The two mono- ^{18}O labeled isotopomers of boronic acid are conformational isotopomers, with a ZPE difference of < 3 cal/mol), so they can be averaged. The 1° EIE arises

from addition of $^{18}\text{OH}_2$ to the unlabeled acid, to form the anion of C_3 symmetry, and no averaging is necessary. The 2° EIE is an average over the two conformational isotopomers of the acid.

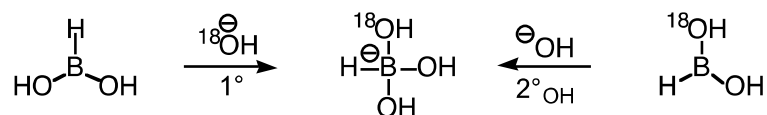


Figure S22. Reactions associated with the primary and secondary EIEs on the Lewis acidity of boronic acid.

For boric acid, in Figure S23, of C_{3h} symmetry, the 1° EIE arises from addition of $^{18}\text{OH}_2$, and the 2° EIE arises from OH_2 addition to mono- ^{18}O -labeled boric acid. Both reactions lead to the same mono- ^{18}O labeled adduct, of S_4 symmetry, and no averaging is required.

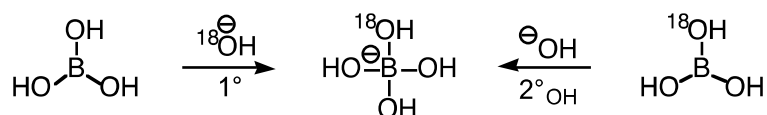


Figure S23. Reactions associated with the primary and secondary EIEs on the Lewis acidity of boric acid.

Lewis Acids Centered on Phosphorus. The addition of water to phosphenic acid, in Figure S24, to produce dihydrogen phosphate anion + H^+ , requires averaging the 2° $\text{P}=\text{O}$ EIE over two conformational isotopomers of the acid. Mono- ^{18}O phosphenic acid has three possible isotopomers, one with $\text{P}-^{18}\text{OH}$ and two conformational isotopomers where $\text{P}=\text{O}$ resides either *cis* or *trans* to the OH hydrogen. Mono- ^{18}O dihydrogen phosphate anion has C_2 symmetry, so no averaging is required. The EIEs for the 1° and 2° $\text{P}-\text{OH}$ do not require any averaging, but the 2° $\text{P}=\text{O}$ EIE is the average over the two conformational isotopomers of the acid.

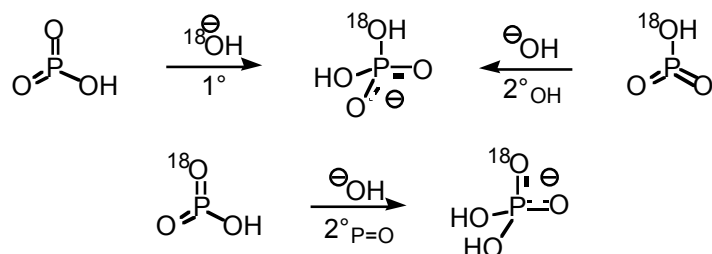


Figure S24. Reactions associated with the primary and secondary EIEs on the Lewis acidity of phosphenic acid.

Results

Energy, optimized geometry (Cartesian coordinates), and vibrational frequencies obtained for each of the various acids and their conjugate bases are listed below. Although neither the

energy nor the optimized geometry changes with isotopic substitution, vibrational frequencies differ for each mono- ^{18}O isotopologue. Although each of the vibrational frequencies was calculated with four digits after the decimal point, which were retained in all calculations, all tables round to the nearest cm^{-1} .

Water. Water reacts with each Lewis acid, with loss of H^+ . It was calculated both in vacuum (Tables S2 and S3) and with solvation (Tables S4-7), using the polarized continuum model (PCM) for solvation by chloroform (CHCl_3) or by water.

Table S2. Energy and optimized coordinates (\AA) for H_2O .

$E = -76.4661983477 \text{ A.U.}$			
Atom	x	y	z
O	0.000000	0.000000	0.116992
H	0.000000	0.763520	-0.467967
H	0.000000	-0.763520	-0.467967

Table S3. Vibrational frequencies (cm^{-1}) for unlabeled and ^{18}O -labeled water.

H_2^{16}O	H_2^{18}O
1627	1621
3797	3789
3899	3883

Table S4. Energy and optimized coordinates (\AA) for H_2O , using the PCM for solvation by chloroform.

$E = -76.4746962429 \text{ A.U.}$			
Atom	x	y	z
O	0.000000	0.000000	0.118382
	0.000000	0.766331	-0.473530

H	0.000000	-0.766331	-0.473530
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Table S5. Vibrational frequencies (cm^{-1}) for unlabeled and ^{18}O -labeled H_2O using the PCM for solvation by chloroform.

H_2^{16}O	H_2^{18}O
1585	1578
3667	3659
3747	3731

Table S6. Energy and optimized coordinates (\AA) for H_2O using the PCM for solvation by water.

$E = -76.4784287664 \text{ A.U.}$			
Atom	x	y	z
O	0.000000	0.000000	0.119142
H	0.000000	0.767649	-0.476570
H	0.000000	-0.767649	-0.476570

Table S7. Vibrational frequencies (cm^{-1}) for unlabeled and ^{18}O -labeled H_2O using the PCM for solvation by water.

H_2^{16}O	H_2^{18}O
1563	1557
3597	3590
3663	3648

Formic Acid, Protonated Formic Acid, and Formate. Formic acid was calculated under a variety of isotopic substitutions, including deuterium and tritium at both CH and OH. Each of these isotopologues has the same energy and optimized geometry, listed in Table S8, except for those modeled with solvation, in Tables S16 and S18. The vibrational frequencies for the O isotopologues of each acid are in Tables S9, S11-15, S17, and S19. Table S10 presents the

decrease in vibrational frequencies upon mono- ^{18}O labeling. Table S20 presents $\text{HCOO}^{1/2}\text{H}$ as a hypothetical case in which $^{1/2}\text{H}$ is a fictitious atom with half the mass of a proton. It models an acid whose OH hydrogen bonds to solvent.

The energy and optimized geometry for protonated formic acid, $\text{HC}(\text{OH})_2^+$, and the vibrational frequencies for its mono- ^{18}O isotopologues are included in Tables S21 and S22.

Formate anion was calculated as various CH and ^{18}O isotopologues, which have identical energy and optimized geometry but different vibrational frequencies, both with and without PCM solvation (Tables S23-S29). Vibrational frequencies for di- ^{18}O labeled formic acid and formate anion are included, but only mono- ^{18}O isotopologues were calculated for all other species.

Table S8. Energy and optimized coordinates (Å) for formic acid and its H-isotopologues, HCOOH , HCOOD , HCOOT , DCOOH , DCOOD , DCOOT , and $\text{HCOO}^{1/2}\text{H}$.

$E = -189.845117682 \text{ A.U.}$			
Atom	x	y	z
C	0.000000	0.421051	0.000000
O	-1.028178	-0.446130	0.000000
O	1.158545	0.117328	0.000000
H	-0.383223	1.447894	0.000000
H	-0.659714	-1.343779	0.000000

Table S9. Vibrational frequencies (cm^{-1}) for all O isotopologues of formic acid, HCOOH .

$^{16}\text{O}_2$	$\text{C}-^{18}\text{OH}$	$\text{X}=^{18}\text{O}$	$^{18}\text{O}_2$
629	620	616	607
675	670	674	669
1052	1051	1050	1049
1121	1091	1117	1088
1298	1292	1296	1290
1402	1400	1395	1393

1811	1810	1775	1774
3048	3048	3048	3048
3716	3704	3716	3704

Table S10. Decrease in calculated vibrational frequencies (cm^{-1}) of formic acid upon mono- ^{18}O labeling.

ν	Mode	$\Delta\nu_{^{18}\text{OH}}$	$\Delta\nu_{\text{C}=\text{O}}$
3716	ν_{OH}	11.6	0.0
3048	ν_{CH}	0.0	0.0
1811	$\nu_{\text{C}=\text{O}}$	0.6	36.2
1402	δ_{CH}	2.2	6.8
1298	δ_{OH}	6.0	1.9
1121	$\nu_{\text{C}-\text{O}}$	30.1	3.8
1052	γ_{CH}	0.8	1.9
675	π_{OH}	4.3	1.0
629	δ_{OCO}	8.3	12.6
Sum		63.9	64.1

Table S11. Vibrational frequencies (cm^{-1}) for O isotopologues of formic acid-OD, HCOOD.

$^{16}\text{O}_2$	$\text{C}-^{18}\text{OH}$	$\text{C}=\text{O}$
531	525	529
561	558	551
999	973	992
1050	1049	1048

1186	1169	1184
1392	1392	1387
1805	1805	1768
2702	2685	2702
3049	3049	3049

Table S12. Vibrational frequencies (cm⁻¹) for O78, HCOOT.

¹⁶ O ₂	C- ¹⁸ OH	C= ¹⁸ O
473	467	471
506	505	497
931	906	923
1049	1048	1047
1171	1153	1170
1391	1391	1385
1804	1803	1766
2269	2248	2269
3049	3049	3048

Table S13. Vibrational frequencies (cm⁻¹) for O isotopologues of formic-*d* acid, DCOOH.

¹⁶ O ₂	C- ¹⁸ OH	C= ¹⁸ O
623	615	610
664	660	663
886	884	883
985	972	983

1157	1137	1149
1294	1287	1292
1779	1778	1742
2267	2267	2265
3716	3704	3716

Table S14. Vibrational frequencies (cm^{-1}) for O isotopologues of formic-*d* acid-OD, DCOOD.

$^{16}\text{O}_2$	C- ^{18}OH	C= ^{18}O
513	508	512
557	554	547
886	884	883
960	939	957
1049	1040	1043
1179	1164	1175
1775	1774	1738
2266	2266	2264
2702	2686	2702

Table S15. Vibrational frequencies (cm^{-1}) for O isotopologues of formic-*d* acid-OT, DCOOT.

$^{16}\text{O}_2$	C- ^{18}OH	C= ^{18}O
451	446	451
503	502	495
886	884	883
918	894	912

1012	1006	1008
1173	1157	1168
1774	1773	1737
2260	2246	2259
2274	2268	2273

Table S16. Energy and optimized coordinates (Å) of formic acid, HCOOH, using the PCM for solvation by chloroform.

$E = -189.856535535$ A.U.			
Atom	x	y	z
C	0.000000	0.419408	0.000000
O	-1.030693	-0.428245	0.000000
O	1.162168	0.100745	0.000000
H	-0.360210	1.457017	0.000000
H	-0.691591	-1.353462	0.000000

Table S17. Vibrational frequencies (cm^{-1}) for O isotopologues of formic acid, HCOOH, using the PCM for solvation by chloroform.

$^{16}\text{O}_2$	C- ^{18}OH	C= ^{18}O
635	627	622
657	653	656
1061	1060	1059
1128	1098	1124
1293	1286	1291
1400	1398	1393

1760	1759	1726
3009	3009	3009
3399	3388	3399

Table S18. Energy and optimized coordinates (Å) of formic acid, HCOOH, using the PCM for solvation by water.

$E = -189.861654500$ A.U.			
Atom	x	y	z
C	0.000000	0.418245	0.000000
O	-1.032194	-0.419706	0.000000
O	1.163938	0.093270	0.000000
H	-0.350009	1.460884	0.000000
H	-0.703939	-1.358867	0.000000

Table S19. Vibrational frequencies (cm^{-1}) for O isotopologues of formic acid, HCOOH, using the PCM for solvation by water.

$^{16}\text{O}_2$	C- ^{18}OH	C= ^{18}O
638	630	625
644	640	643
1065	1064	1063
1130	1099	1126
1285	1277	1284
1399	1397	1392
1736	1736	1703
2984	2983	2983

3192	3182	3192
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Table S20. Vibrational frequencies (cm^{-1}) for O isotopologues of formic acid- $\text{O}^{1/2}\text{H}$, $\text{HCOO}^{1/2}\text{H}$.

$^{16}\text{O}_2$	$\text{C}-^{18}\text{OH}$	$\text{C}=\text{}^{18}\text{O}$
663	651	649
890	887	889
1063	1063	1062
1149	1120	1146
1385	1385	1380
1665	1661	1646
1862	1860	1841
3048	3048	3048
5201	5193	5201

Table S21. Energy and optimized coordinates (\AA) of protonated formic acid, $\text{HC}(\text{OH})_2^+$.

$E = -190.139682836 \text{ A.U.}$			
Atom	x	y	z
C	0.000000	0.425878	0.000000
O	-1.145431	-0.105207	0.000000
O	1.049173	-0.292999	0.000000
H	0.028761	1.514045	0.000000
H	-1.148805	-1.086026	0.000000
H	1.890103	0.202362	0.000000

Table S22. Vibrational frequencies (cm^{-1}) for O isotopologues of protonated formic acid, $\text{HC}(\text{OH})_2^+$, where *cis* and *trans* represent the relationship between the CH and OH protons.

$^{16}\text{O}_2$	C^{18}OH (<i>cis</i>)	C^{18}OH (<i>trans</i>)
608	598	600
658	655	658
774	774	768
1090	1088	1089
1169	1165	1160
1187	1177	1172
1363	1347	1362
1463	1454	1452
1691	1685	1679
3166	3166	3166
3593	3592	3581
3659	3647	3659

Table S23. Energy and optimized coordinates (\AA) for formate, HCO_2^- , and formate-*d*, DCO_2^- , anions.

$E = -189.288234807 \text{ A.U.}$			
Atom	x	y	z
C	0.000000	0.000000	0.315782
O	0.000000	1.135734	-0.209106
O	0.000000	-1.135734	-0.209106
H	0.000000	0.000000	1.451001

Table S24. Vibrational frequencies (cm^{-1}) for O isotopologues of formate anion, HCO_2^- .

$^{16}\text{O}_2$	C^{18}O	$^{18}\text{O}_2$
744	729	714
1042	1040	1038
1338	1315	1295
1371	1368	1364
1649	1637	1624
2573	2573	2573

Table S25. Vibrational frequencies (cm^{-1}) for O isotopologues of formate-*d* anion, DCO_2^- .

$^{16}\text{O}_2$	C^{18}O
737	722
902	899
1005	1001
1325	1302
1646	1634
1877	1877

Table S26. Energy and optimized coordinates (\AA) of formate anion, HCO_2^- , using the PCM for solvation by chloroform.

$E = -189.375445734 \text{ A.U.}$			
Atom	x	y	z
C	0.000000	0.000000	0.329956
O	0.000000	1.129703	-0.214365
O	0.000000	-1.129703	-0.214365
H	0.000000	0.000000	1.450108

Table S27. Vibrational frequencies (cm^{-1}) for O isotopologues of formate anion, HCO_2^- , using the PCM for solvation by chloroform.

$^{16}\text{O}_2$	C^{18}O
739	724
1059	1057
1350	1325
1385	1382
1605	1594
2733	2733

Table S28. Energy and optimized coordinates (\AA) for formate anion, HCO_2^- , using the PCM for solvation by water.

$E = -189.398019909 \text{ A.U.}$			
Atom	x	y	z
C	0.000000	0.000000	0.336238
O	0.000000	1.127147	-0.216869
O	0.000000	-1.127147	-0.216869
H	0.000000	0.000000	1.452472

Table S29. Vibrational frequencies (cm^{-1}) for O isotopologues of formate anion, HCO_2^- , using the PCM for solvation by water.

$^{16}\text{O}_2$	C^{18}O
735	720
1064	1062
1351	1326

1384 1382

1581 1571

2774 2774

Acetic Acid and Acetate. The energy and optimized geometry for acetic acid and acetate anion and the vibrational frequencies for their mono- ^{18}O isotopologues are included in Tables S30-S33.

Table S30. Energy and optimized coordinates (Å) for acetic acid, CH_3COOH .

<u>$E = -229.185826803 \text{ A.U.}$</u>			
<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
O	-0.177979	1.345665	0.000000
O	1.241742	-0.392899	0.000000
C	0.000000	0.155272	0.000000
C	-1.069439	-0.899095	0.000000
H	1.874810	0.340146	0.000000
H	-2.046447	-0.427450	0.000000
H	-0.960916	-1.535944	0.877880
H	-0.960916	-1.535944	-0.877880

Table S31. Vibrational frequencies (cm^{-1}) for O isotopologues of acetic acid, CH_3COOH

<u>$^{16}\text{O}_2$</u>	<u>$\text{C}-^{18}\text{OH}$</u>	<u>$\text{C}=^{18}\text{O}$</u>
70	70	70
424	417	420
546	546	545
584	578	572

663	659	661
858	845	849
999	991	998
1070	1070	1069
1201	1188	1196
1335	1330	1332
1408	1408	1408
1472	1472	1471
1478	1478	1478
1812	1811	1780
3052	3052	3052
3109	3109	3109
3159	3159	3159
3738	3726	3738

Table S32. Energy and optimized coordinates (Å) for acetate anion, CH_3CO_2^- .

$E = -228.621929709 \text{ A.U.}$			
Atom	x	y	z
C	0.010174	0.209370	0.000000
O	0.000616	0.751942	1.131436
O	0.000616	0.751942	-1.131436
C	0.000616	-1.350532	0.000000
H	0.482359	-1.746039	0.896053
H	-1.039308	-1.692021	0.000000
H	0.482359	-1.746039	-0.896053

Table S33. Vibrational frequencies (cm^{-1}) for O isotopologues of acetate anion, CH_3CO_2^- .

$^{16}\text{O}_2$	C^{18}O
17	17
436	430
599	594
630	624
863	851
998	995
1033	1032
1321	1316
1347	1333
1462	1462
1474	1473
1638	1627
2998	2998
3054	3054
3075	3075

Carbonic Acid, Bicarbonate, Carbonate, and Carbon Dioxide. The energies and optimized geometries for carbonic acid, bicarbonate anion, carbonate dianion, and carbon dioxide and the vibrational frequencies for their mono- ^{18}O isotopologues are included in Tables S34-S49.

Table S34. Energy and optimized coordinates (\AA) for carbonic acid, H_2CO_3 .

$E = -265.121949794 \text{ A.U.}$			
Atom	x	y	z

C	0.000000	0.000000	0.101961
O	0.000000	0.000000	1.305151
O	0.000000	1.088369	-0.679396
O	0.000000	-1.088369	-0.679396
H	0.000000	1.854613	-0.091320
H	0.000000	-1.854613	-0.091320

Table S35. Vibrational frequencies (cm^{-1}) for O isotopologues of carbonic acid, H_2CO_3 .

$^{16}\text{O}_2$	C- ^{18}OH	C= ^{18}O
526	524	526
547	538	542
596	594	587
601	596	596
800	797	795
975	956	965
1150	1139	1150
1289	1284	1280
1453	1449	1452
1818	1817	1789
3787	3776	3787
3790	3788	3790

Table S36. Energy and optimized coordinates (\AA) for bicarbonate anion, HCO_3^- .

$$E = -264.573364416 \text{ A.U.}$$

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	0.000000	0.172464	0.000000
O	-1.001262	0.893888	0.000000
O	1.223692	0.427397	0.000000
O	-0.295390	-1.245700	0.000000
H	0.583674	-1.639471	0.000000

Table S37. Vibrational frequencies (cm^{-1}) for O isotopologues of bicarbonate anion, HCO_3^- , where *cis* and *trans* indicate the relationship between the C^{18}O oxygen and the OH proton, as in Figure S2.

$^{16}\text{O}_2$	$\text{C}-^{18}\text{OH}$	C^{18}O (<i>cis</i>)	C^{18}O (<i>trans</i>)
536	535	536	536
546	537	537	538
620	601	613	612
820	818	816	816
841	834	832	831
1194	1185	1187	1191
1290	1290	1268	1269
1750	1749	1742	1736
3794	3782	3794	3794

Table S38. Energy and optimized coordinates (\AA) for the bicarbonate anion, HCO_3^- , using the polarized continuum solvation method of chloroform.

$E = -264.661682633 \text{ A.U.}$			
Atom	<i>x</i>	<i>y</i>	<i>z</i>
C	0.000000	0.149537	0.000000

O	-1.012810	0.869647	0.000000
O	1.212064	0.462383	0.000000
O	-0.273199	-1.234305	0.000000
H	0.591557	-1.679023	0.000000

Table S39. Vibrational frequencies (cm^{-1}) for O isotopologues of the bicarbonate anion, HCO_3^- , using the PCM for solvation by chloroform, where *cis* and *trans* indicate the relationship between the C^{18}O oxygen and the OH proton, as in Figure S2.

$^{16}\text{O}_2$	$\text{C}-^{18}\text{OH}$	C^{18}O (<i>cis</i>)	C^{18}O (<i>trans</i>)
509	506	509	508
568	559	559	560
648	632	638	637
823	821	819	819
896	881	887	887
1206	1198	1204	1200
1302	1302	1278	1284
1679	1678	1670	1666
3595	3584	3595	3595

Table S40. Energy and optimized coordinates (\AA) for the bicarbonate anion, HCO_3^- , using the PCM for solvation by water.

$E = -264.686036386 \text{ A.U.}$			
Atom	x	y	z
C	0.000000	0.139373	0.000000
O	-1.021682	0.855853	0.000000
O	1.204595	0.483241	0.000000

O	-0.258619	-1.231964	0.000000
H	0.605651	-1.693280	0.000000

Table S41. Vibrational frequencies (cm^{-1}) for O isotopologues of the bicarbonate anion, HCO_3^- , using the PCM for solvation by water, where *cis* and *trans* indicate the relationship between the C^{18}O oxygen and the OH proton.

$^{16}\text{O}_2$	C- ^{18}OH	C^{18}O (<i>cis</i>)	C^{18}O (<i>trans</i>)
496	494	496	495
575	566	565	568
654	640	645	643
823	821	819	819
922	904	913	913
1200	1192	1198	1192
1306	1306	1283	1291
1639	1638	1630	1627
3435	3424	3435	3435

Table S42. Energy and optimized coordinates (\AA) for the carbonate dianion, CO_3^{2-} .

$E = -263.792764512 \text{ A.U.}$			
Atom	x	y	z
C	0.000000	0.000000	0.000000
O	0.000000	1.306138	0.000000
O	1.131149	-0.653069	0.000000
O	-1.131149	-0.653069	0.000000

Table S43. Vibrational frequencies (cm^{-1}) for O isotopologues of the carbonate dianion, CO_3^{2-} .

$^{16}\text{O}_3$	C^{18}O
638	624
638	630
858	855
1011	991
1296	1284
1296	1295

Table S44. Energy and optimized coordinates (\AA) for carbon dioxide, CO_2 .

$E = -188.663386958 \text{ A.U.}$			
Atom	x	y	z
C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.160469
O	0.000000	0.000000	-1.160469

Table S45. Vibrational frequencies (cm^{-1}) for O isotopologues of carbon dioxide, CO_2 .

$^{16}\text{O}_2$	C^{18}O
674	669
674	669
1369	1330
2400	2383

Table S46. Energy and optimized coordinates (\AA) for carbon dioxide, CO_2 , with the PCM for solvation by chloroform.

$$E = -188.666091910 \text{ A.U.}$$

Atom	x	y	z
C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.160233
O	0.000000	0.000000	-1.160233

Table S47. Vibrational frequencies (cm^{-1}) for O isotopologues of carbon dioxide, CO_2 , with the PCM for solvation by chloroform.

$^{16}\text{O}_2$	C= ^{18}O
667	662
667	662
1370	1331
2364	2347

Table S48. Energy and optimized coordinates (\AA) for carbon dioxide, CO_2 , with the PCM for solvation by water.

$$E = -188.667189144 \text{ A.U.}$$

Atom	x	y	z
C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.160146
O	0.000000	0.000000	-1.160146

Table S49. Vibrational frequencies (cm^{-1}) for O isotopologues of carbon dioxide, CO_2 , with the PCM for solvation by water.

$^{16}\text{O}_2$	C= ^{18}O
665	660

665	660
1371	1331
2349	2332

Nitrogen-Centered Acids and their Conjugate Bases. The energies and optimized geometries for nitrous acid, the nitrosonium cation, nitrite anion, nitric acid, the nitronium cation, and nitrate anion and the vibrational frequencies for their mono- ^{18}O isotopologues are included in Tables S50-S71.

Table S50. Energy and optimized coordinates (Å) for nitrous acid, HONO.

$E = -205.790627265 \text{ A.U.}$			
Atom	x	y	z
N	0.000000	0.546973	0.000000
O	1.084475	0.090252	0.000000
O	-1.013492	-0.408799	0.000000
H	-0.567872	-1.280438	0.000000

Table S51. Vibrational frequencies (cm^{-1}) for O isotopologues of nitrous acid, HONO.

$^{16}\text{O}_2$	N- ^{18}OH	N= ^{18}O
623	606	613
683	679	682
864	854	859
1330	1320	1320
1708	1707	1669
3578	3567	3578

Table S52. Energy and optimized coordinates (Å) for nitrous acid, HONO, using the PCM for

solvation by chloroform.

$$E = -205.798586215 \text{ A.U.}$$

Atom	<i>x</i>	<i>y</i>	<i>z</i>
N	0.000000	0.540345	0.000000
O	1.087553	0.078907	0.000000
O	-1.012968	-0.389973	0.000000
H	-0.596676	-1.293891	0.000000

Table S53. Vibrational frequencies (cm^{-1}) for O isotopologues of nitrous acid, HONO, using the PCM for solvation by chloroform.

$^{16}\text{O}_2$	N- ^{18}OH	N= ^{18}O
648	631	637
668	664	667
868	857	863
1334	1324	1325
1673	1672	1635
3254	3244	3254

Table S54. Energy and optimized coordinates (\AA) for the nitrosonium cation, NO^+

$$E = -129.587323609 \text{ A.U.}$$

Atom	<i>x</i>	<i>y</i>	<i>z</i>
N	0.000000	0.000000	-0.563691
O	0.000000	0.000000	0.493230

Table S55. Vibrational frequencies (cm^{-1}) for O isotopologues of the nitrosonium cation, NO^+ .

^{16}O	N^{18}O
2477	2412

Table S56. Energy and optimized coordinates (Å) for the nitrosonium cation, NO^+ , using the PCM for solvation by chloroform.

$E = -129.693786365 \text{ A.U.}$			
Atom	x	y	z
N	0.000000	0.000000	-0.562637
O	0.000000	0.000000	0.492307

Table S57. Vibrational frequencies (cm^{-1}) for O isotopologues of the nitrosonium cation, NO^+ , using the PCM for solvation by chloroform.

^{16}O	N^{18}O
2484	2418

Table S58. Energy and optimized coordinates (Å) for the nitrite anion, NO_2^- .

$E = -205.242086246 \text{ A.U.}$			
Atom	x	y	z
N	0.000000	0.000000	0.457240
O	0.000000	1.069661	-0.200043
O	0.000000	-1.069661	-0.200043

Table S59. Vibrational frequencies (cm^{-1}) for O isotopologues of nitrite anion, NO_2^- .

$^{16}\text{O}_2$	N^{18}O
796	778

1283 1264

1325 1312

Table S60. . Energy and optimized coordinates (Å) for the nitrite anion, NO_2^- , using the PCM for solvation by chloroform.

$E = -205.328271379 \text{ A.U.}$			
Atom	x	y	z
N	0.000000	0.000000	0.459542
O	0.000000	1.066314	-0.201050
O	0.000000	-1.066314	-0.201050

Table S61. Vibrational frequencies (cm^{-1}) for O isotopologues of nitrite anion, NO_2^- , using the PCM for solvation by chloroform.

$^{16}\text{O}_2$	N^{18}O
802	784
1252	1236
1341	1325

Table S62. Energy and optimized coordinates (Å) for nitric acid, HNO_3 .

$E = -281.007114831 \text{ A.U.}$			
Atom	x	y	z
N	0.000000	0.155887	0.000000
O	1.167566	0.464330	0.000000
O	-0.979722	0.835576	0.000000
O	-0.265660	-1.232965	0.000000

H	0.622530	-1.626743	0.000000
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Table S63. Vibrational frequencies (cm^{-1}) for O isotopologues of nitric acid, HNO_3 , where *cis* and *trans* represent the relationship between N^{18}O and the OH proton

$^{16}\text{O}_3$	$\text{N}-^{18}\text{OH}$	$\text{N}^{18}\text{O} (cis)$	$\text{N}^{18}\text{O} (trans)$
485	483	485	485
585	576	575	578
647	625	641	639
783	781	779	779
896	890	884	884
1316	1311	1291	1312
1342	1340	1337	1320
1744	1743	1736	1730
3711	3699	3711	3711

Table S64. Energy and optimized coordinates (\AA) for nitric acid, HNO_3 , using the PCM for solvation by chloroform.

$E = -281.017685088 \text{ A.U.}$			
Atom	x	y	z
N	0.000000	0.142125	0.000000
O	1.158279	0.488884	0.000000
O	-0.991522	0.817676	0.000000
O	-0.247535	-1.224820	0.000000
H	0.646225	-1.648793	0.000000

Table S65. Vibrational frequencies (cm^{-1}) for O isotopologues of nitric acid, HNO_3 , using the PCM for solvation by chloroform, where *cis* and *trans* represent the relationship between N^{18}O and the OH proton.

$^{16}\text{O}_3$	$\text{N}-^{18}\text{OH}$	N^{18}O (<i>cis</i>)	N^{18}O (<i>trans</i>)
454	452	454	453
604	594	593	596
670	649	663	660
788	786	784	783
905	896	894	894
1318	1316	1294	1291
1334	1328	1328	1334
1680	1679	1673	1668
3349	3338	3349	3349

Table S66. Energy and optimized coordinates (\AA) for the nitronium cation, NO_2^+ .

$E = -129.587323609 \text{ A.U.}$			
Atom	x	y	z
N	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.115776
O	0.000000	0.000000	-1.115776

Table S67. Vibrational frequencies (cm^{-1}) for O isotopologues of the nitronium cation, NO_2^+ .

$^{16}\text{O}_2$	$\text{N}=^{18}\text{O}$
653	648
653	648
1447	1405

2438 2418

Table S68. Energy and optimized coordinates (Å) for the nitrate anion, NO_3^- .

<u>$E = -280.481786765 \text{ A.U.}$</u>			
<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
N	0.000000	0.000000	0.000000
O	0.000000	1.258044	0.000000
O	1.089498	-0.629022	0.000000
O	-1.089498	-0.629022	0.000000

Table S69. Vibrational frequencies (cm^{-1}) for O isotopologues of nitrate anion, NO_3^- .

<u>$^{16}\text{O}_3$</u>	<u>N^{18}O</u>
707	691
707	697
843	840
1062	1041
1364	1352
1364	1364

Table S70. Energy and optimized coordinates (Å) for the nitrate anion, NO_3^- , using the PCM for solvation by chloroform.

<u>$E = -280.563583342 \text{ A.U.}$</u>			
<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
N	0.000000	0.000000	0.000000
O	0.000000	1.237600	0.000000

O	1.071793	-0.618800	0.000000
O	-1.071793	-0.618800	0.000000

Table S71. Vibrational frequencies (cm^{-1}) for O isotopologues of nitrate anion, NO_3^- , using the PCM for solvation by chloroform.

$^{16}\text{O}_3$	N^{18}O
712	696
712	702
841	838
1073	1052
1341	1328
1341	1341

Boron-centered Acids and their Conjugate Bases. The energies and optimized geometries for the various boron species— BH_3 , BH_3OH^- , H_2BOH , H_2BO^- , $\text{H}_2\text{B}(\text{OH})_2^-$, $\text{HB}(\text{OH})_2$, $\text{HB}(\text{OH})\text{O}^-$, $\text{HB}(\text{OH})_3^-$, $\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_2\text{O}^-$, and $\text{B}(\text{OH})_4^-$ —and the vibrational frequencies for their mono- ^{18}O isotopologues, along with select moments of inertia, are included in Tables S72-S96.

Table S72. Energy and optimized coordinates (\AA) for borane, BH_3 .

$E = -26.6243786243 \text{ A.U.}$			
Atom	x	y	z
B	0.000000	0.000000	0.000000
H	0.000000	1.188050	0.000000
H	1.028881	-0.594025	0.000000
H	-1.028881	-0.594025	0.000000

Table S73. Vibrational frequencies (cm⁻¹) for borane, BH₃.

1161
1204
1204
2565
2692
<u>2692</u>

Table S74. Energy and optimized coordinates (Å) for hydroxytrihydroborate anion, H₃BOH⁻, the hydroxide adduct of borane.

<u>$E = -102.572342758$ A.U.</u>			
<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
B	-0.052466	0.741654	0.000000
O	-0.052466	-0.772228	0.000000
H	0.523532	1.204725	1.007431
H	0.523532	1.204725	-1.007431
H	-1.224393	1.127401	0.000000
H	0.859387	-1.067294	0.000000

Table S75. Vibrational frequencies (cm⁻¹) for O isotopologues of hydroxytrihydroborate anion, H₃BOH⁻, the the hydroxide adduct of borane.

<u>¹⁶O</u>	<u>B-¹⁸OH</u>
222	221
829	812
842	837
944	941

1119	1113
1155	1155
1171	1171
1196	1195
2104	2104
2162	2162
2264	2264
3842	3830

Table S76. Energy and optimized coordinates (Å) for borinic acid, H₂BOH.

$E = -101.958955219$ A.U.			
Atom	x	y	z
B	0.052746	0.714038	0.000000
O	0.052746	-0.638879	0.000000
H	-0.976288	1.322753	0.000000
H	1.115450	1.250539	0.000000
H	-0.824856	-1.032451	0.000000

Table S77. Vibrational frequencies (cm⁻¹) for O isotopologues of borinic acid, H₂BOH.

¹⁶ O	B- ¹⁸ OH
777	774
888	887
1058	1058
1174	1160

1183	1170
1367	1354
2560	2560
2657	2657
3826	3813

Table S78. Energy and optimized coordinates (Å) for the borinate anion, H_2BO^- , the product of deprotonation of borinic acid.

$E = -101.376865776 \text{ A.U.}$			
Atom	x	y	z
B	0.000000	0.000000	-0.591894
O	0.000000	0.000000	0.694457
H	0.000000	1.041479	-1.298094
H	0.000000	-1.041479	-1.298094

Table S79. Vibrational frequencies (cm^{-1}) for O isotopologues of borinate anion, H_2BO^- , the product of deprotonation of borinic acid.

^{16}O	B- ^{18}O
960	956
992	991
1196	1190
1522	1492
2019	2019
2152	2152

Table S80. Energy and optimized coordinates (Å) for dihydroxydihydroborate anion, $\text{H}_2\text{B}(\text{OH})_2^-$, the hydroxide adduct of borinic acid.

$E = -177.883582970 \text{ A.U.}$			
Atom	x	y	z
B	0.000000	0.000000	0.596826
O	0.000000	-1.240096	-0.251895
O	0.000000	1.240096	-0.251895
H	-1.021172	-0.074639	1.301110
H	1.021172	0.074639	1.301110
H	0.803824	-1.225341	-0.778014
H	-0.803824	1.225341	-0.778014

Table S81. Vibrational frequencies (cm^{-1}) for O isotopologues of dihydroxydihydroborate anion, $\text{H}_2\text{B}(\text{OH})_2^-$, the hydroxide adduct of borinic acid.

$^{16}\text{O}_2$	B- ^{18}OH
281	280
292	291
479	470
794	793
836	819
847	844
942	941
1097	1094
1136	1133
1180	1179
1205	1205

2170	2170
2211	2211
3812	3800
3812	3812

Table S82. Energy and optimized coordinates (Å) for boronic acid, HB(OH)₂.

$E = -177.288987050$ A.U.			
Atom	x	y	z
B	0.000000	0.484651	0.000000
O	-1.223983	-0.104059	0.000000
O	1.121480	-0.299412	0.000000
H	0.056951	1.674926	0.000000
H	-1.179995	-1.066998	0.000000
H	1.943067	0.196576	0.000000

Table S83. Vibrational frequencies (cm⁻¹) for O isotopologues of boronic acid, HB(OH)₂, where *cis* and *trans* represent the relationship between the OH and BH protons.

¹⁶ O ₂	B- ¹⁸ OH (<i>cis</i>)	B- ¹⁸ OH (<i>trans</i>)
475	466	468
531	529	531
629	629	624
927	925	926
966	964	963
1005	997	988
1113	1103	1109

1232	1220	1226
1430	1425	1420
2631	2631	2631
3804	3804	3792
3866	3853	3866

Table S84. Moments of inertia (atomic units) of boronic acid isotopomers.

Acid	I_x	I_y	I_z	$I_x I_y I_z$
Boronic	29.080	176.190	205.270	1051729
Boronic- <i>cis</i> - ^{18}OH	29.479	185.279	214.758	1172981
Boronic- <i>trans</i> - ^{18}OH	29.213	186.103	215.316	1170597

Table S85. Energy and optimized coordinates (Å) for boronate, $\text{HB}(\text{OH})\text{O}^-$, the product of deprotonation of boronic acid.

$E = -176.707148460 \text{ A.U.}$				
Atom	x	y	z	
B	0.000000	0.470565	0.000000	
O	1.246422	0.136294	0.000000	
O	-1.104569	-0.466168	0.000000	
H	-0.453396	1.620020	0.000000	
H	-0.681430	-1.333852	0.000000	

Table S86. Vibrational frequencies (cm^{-1}) for O isotopologues of boronate, $\text{HB}(\text{OH})\text{O}^-$, the product of deprotonation of boronic acid.

$^{16}\text{O}_2$	B- ^{18}OH	B- ^{18}O
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484	478	474
595	591	594
880	879	878
909	885	906
1059	1057	1057
1109	1105	1103
1518	1517	1489
2278	2278	2278
3758	3747	3758

Table S87. Moments of inertia (atomic units) of boronate anion isotopomers.

Acid	I_x	I_y	I_z	$I_x I_y I_z$
Boronate	26.288	172.475	198.763	901185
Boronate- $^{18}\text{O}^-$	26.597	182.508	209.105	1015016
Boronate- <i>trans</i> - ^{18}OH	26.398	182.625	209.022	1007671

Table S88. Energy and optimized coordinates (Å) for trihydroxyhydroborate anion, $\text{HB}(\text{OH})_3^-$, the hydroxide adduct of boronic acid.

$E = -253.200687350 \text{ A.U.}$			
Atom	x	y	z
B	0.000000	0.000000	0.432348
O	0.000000	1.406696	-0.076747
O	1.218234	-0.703348	-0.076747
O	-1.218234	-0.703348	-0.076747
H	-1.646370	-0.075139	-0.663753

H	0.000000	0.000000	1.671445
H	0.888258	-1.388229	-0.663753
H	0.758112	1.463368	-0.663753

Table S89. Vibrational frequencies (cm^{-1}) for O isotopologues of trihydroxyhydroborate anion, $\text{HB}(\text{OH})_3^-$, the hydroxide adduct of boronic acid.

$^{16}\text{O}_3$	B- ^{18}OH
127	127
127	127
386	384
391	386
391	387
538	532
814	801
832	826
832	831
1009	1007
1009	1008
1086	1085
1166	1163
1166	1165
2227	2227
3830	3820
3835	3832
3835	3835

Table S90. Energy and optimized coordinates (Å) for boric acid, B(OH)₃.

$E = -252.611166552$ A.U.			
Atom	x	y	z
B	0.000000	0.000000	0.000000
O	0.000000	1.370689	0.000000
O	-1.187052	-0.685345	0.000000
O	1.187052	-0.685345	0.000000
H	-0.884567	1.745916	0.000000
H	-1.069724	-1.639015	0.000000
H	1.954291	-0.106900	0.000000

Table S91. Vibrational frequencies (cm⁻¹) for O isotopologues of boric acid, B(OH)₃.

¹⁶ O ₃	B- ¹⁸ OH
428	420
428	423
447	447
533	531
533	533
670	668
876	860
1015	1005
1015	1012
1019	1018
1442	1432

1442	1441
3852	3840
3852	3852
3853	3853

Table S92. Energy and optimized coordinates (Å) for the lowest-energy conformer of dihydrogen borate, *cis,cis* B(OH)₂O⁻ (where *cis* represents the relationship between the OH and the O⁻), from deprotonation of boric acid.

$E = -252.027069013$ A.U.			
Atom	<i>x</i>	<i>y</i>	<i>z</i>
B	0.000000	0.000000	0.108766
O	0.000000	1.172804	-0.725424
O	0.000000	-1.172804	-0.725424
O	0.000000	0.000000	1.408180
H	0.000000	-1.902430	-0.101239
H	0.000000	1.902430	-0.101239

Table S93. Vibrational frequencies (cm⁻¹) for O isotopologues of the lowest-energy conformer of dihydrogen borate, *cis,cis* B(OH)₂O⁻, from deprotonation of boric acid.

¹⁶ O ₃	B- ¹⁸ OH	B- ¹⁸ O
418	411	414
459	455	449
496	494	496
520	520	520
704	701	700
794	778	786

960	951	960
1072	1068	1064
1200	1198	1199
1523	1522	1500
3847	3835	3847
3849	3848	3849

Table S94. Energy and optimized coordinates (Å) of *cis/trans*-dihydrogen borate, $\text{B}(\text{OH})_2\text{O}^-$, where *cis* and *trans* represent the relationships between the OH and the O^- .

$E = -252.024134192 \text{ A.U.}$			
Atom	x	y	z
B	0.000000	0.173458	0.000000
O	1.344696	-0.340299	0.000000
O	-0.931108	-0.952165	0.000000
O	-0.351102	1.414294	0.000000
H	1.299703	-1.299669	0.000000
H	-1.799582	-0.542260	0.000000

Table S95. Energy and optimized coordinates (Å) for borate, $\text{B}(\text{OH})_4^-$, the hydroxide adduct of boric acid.

$E = -328.518395869 \text{ A.U.}$			
Atom	x	y	z
B	0.000000	0.000000	0.000000
O	0.000000	1.252369	0.801039
O	1.252369	0.000000	-0.801039

O	0.000000	-1.252369	0.801039
O	-1.252369	0.000000	-0.801039
H	-0.912912	-1.436339	1.031131
H	0.912912	1.436339	1.031131
H	1.436339	-0.912912	-1.031131
H	-1.436339	0.912912	-1.031131

Table S96. Vibrational frequencies (cm^{-1}) for O isotopologues of borate, $\text{B}(\text{OH})_4^-$, the hydroxide adduct of boric acid.

$^{16}\text{O}_4$	$\text{B}-^{18}\text{OH}$
171	171
221	220
289	288
289	289
350	345
404	401
474	468
474	471
507	500
726	716
844	837
844	844
962	959
1002	1000
1047	1045

1187	1184
1187	1186
3850	3840
3853	3851
3853	3853
3856	3855

Phosphorus-centered Acids and their Conjugate Bases. The energies and optimized geometries for phosphinic acid, phosphinate anion, phosphonic acid, hydrogen phosphonate anion, phosphonate dianion, phosphoric acid, dihydrogen phosphate anion, hydrogen phosphate dianion, phosphate trianion, phosphenic acid, and phosphenate anion, and the vibrational frequencies for their mono- ^{18}O isotopologues are included in Tables S97-116.

Table S97. Energy and optimized coordinates (Å) for phosphinic acid, H_2POOH .

$E = -493.743114960 \text{ A.U.}$			
Atom	x	y	z
P	-0.122760	0.369069	0.016441
O	-1.282687	-0.548872	-0.029767
O	1.347558	-0.303584	-0.061600
H	-0.063736	1.170312	1.178028
H	0.011205	1.291324	-1.039621
H	1.374959	-1.178029	0.345918

Table S98. Vibrational frequencies (cm^{-1}) for O isotopologues of phosphinic acid, H_2POOH .

$^{16}\text{O}_2$	P- ^{18}OH	P= ^{18}O
177	176	176
395	388	387

780	779	777
856	824	854
885	884	884
996	993	995
1090	1087	1086
1163	1163	1155
1272	1272	1239
2413	2413	2413
2445	2445	2445
3802	3790	3802

Table S99. Energy and optimized coordinates (Å) for phosphinate anion, H_2POO^- .

$E = -493.203535644 \text{ A.U.}$			
Atom	x	y	z
P	0.000000	0.000000	0.292156
O	0.000000	1.329482	-0.427315
O	0.000000	-1.329482	-0.427315
H	1.098528	0.000000	1.227349
H	-1.098528	0.000000	1.227349

Table S100. Vibrational frequencies (cm^{-1}) for O isotopologues of phosphinate anion, H_2POO^- .

$^{16}\text{O}_2$	P^{18}O
442	433
783	779

905	903
1039	1013
1068	1066
1158	1158
1224	1208
2137	2137
2206	2206

Table S101. Energy and optimized coordinates (Å) for phosphonic acid, HP(OH)₂O.

$E = -569.047095052$ A.U.			
Atom	x	y	z
P	0.007661	0.105718	0.275654
O	0.295864	1.459540	-0.236302
O	1.091262	-1.007676	-0.156915
O	-1.406016	-0.537137	-0.129458
H	-0.067247	-0.065247	1.660815
H	1.832321	-0.607995	-0.628368
H	-1.728868	-0.230345	-0.985849

Table S102. Vibrational frequencies (cm⁻¹) for O isotopologues of phosphonic acid, HP(OH)₂O, where the designations (1) and (2) represent similar groups that have slightly different ZPEs.

¹⁶ O ₃	P- ¹⁸ OH (1)	P- ¹⁸ OH (2)	P= ¹⁸ O
111	110	111	111
248	247	247	248
364	359	360	361

400	398	395	392
467	463	463	462
847	824	825	843
895	885	884	895
939	939	939	938
987	986	985	986
1044	1041	1043	1042
1076	1075	1073	1071
1289	1289	1289	1252
2517	2517	2517	2517
3801	3794	3789	3801
3806	3801	3806	3806

Table S103. Energy and optimized coordinates (\AA) for the hydrogen phosphonate anion, HP(OH)O_2^- .

$E = -568.511481548 \text{ A.U.}$			
Atom	x	y	z
P	-0.131100	0.091032	0.218148
O	0.491971	1.397384	-0.207447
O	1.010281	-1.097083	-0.107043
O	-1.467031	-0.397307	-0.253387
H	-0.117515	0.028370	1.642655
H	1.802242	-0.617802	-0.371854

Table S104. Vibrational frequencies (cm^{-1}) for O isotopologues of the hydrogen phosphonate

anion, $\text{HP}(\text{OH})\text{O}_2^-$, where the designations (1) and (2) represent similar groups that have slightly different ZPEs.

$^{16}\text{O}_3$	P- ^{18}OH	P ^{18}O (1)	P ^{18}O (2)
284	281	283	282
372	367	367	369
411	407	405	403
522	519	516	515
736	712	735	735
955	954	954	955
1000	998	997	997
1047	1045	1025	1044
1075	1074	1069	1054
1267	1267	1256	1250
2286	2285	2285	2285
3818	3806	3818	3818

Table S105. Energy and optimized coordinates (Å) for the phosphonate dianion, HPO_3^{2-} .

$E = -567.768301111 \text{ A.U.}$			
Atom	x	y	z
P	0.000000	0.000000	0.175865
O	0.000000	1.505051	-0.178873
O	1.303412	-0.752525	-0.178873
O	-1.303412	-0.752525	-0.178873
H	0.000000	0.000000	1.654984

Table S106. Vibrational frequencies (cm^{-1}) for O isotopologues of the phosphonate dianion, $\text{HPO}_3^{=}$.

$^{16}\text{O}_3$	P^{18}O
428	417
428	425
540	535
906	887
955	953
955	955
1057	1038
1057	1056
1895	1895

Table S107. Energy and optimized coordinates (\AA) for phosphoric acid, H_3PO_4 .

$E = -644.344009049 \text{ A.U.}$			
Atom	x	y	z
P	0.000000	0.000000	0.115540
O	0.000000	0.000000	1.588956
O	0.000000	1.435598	-0.591970
O	1.243264	-0.717799	-0.591970
O	-1.243264	-0.717799	-0.591970
H	-0.485878	2.091731	-0.079151
H	2.054431	-0.625082	-0.079151
H	-1.568553	-1.466648	-0.079151

Table S108. Vibrational frequencies (cm^{-1}) for O isotopologues of phosphoric acid, H_3PO_4 .

$^{16}\text{O}_4$	P- ^{18}OH	P= ^{18}O
159	158	158
159	159	158
296	295	296
368	363	364
368	364	364
444	440	441
451	446	445
451	448	445
826	811	820
912	895	912
912	912	912
1043	1040	1039
1047	1045	1047
1047	1047	1047
1302	1301	1264
3817	3805	3817
3817	3817	3817
3819	3819	3819

Table S109. Energy and optimized coordinates (\AA) for dihydrogen phosphate anion, H_2PO_4^- .

$E = -643.811123850 \text{ A.U.}$			
Atom	x	y	z
P	0.000000	0.000000	0.167658

O	0.000000	1.332462	0.854473
O	-1.287657	-0.014787	-0.892110
O	1.287657	0.014787	-0.892110
O	0.000000	-1.332462	0.854473
H	1.561876	0.934626	-0.956342
H	-1.561876	-0.934626	-0.956342

Table S110. Vibrational frequencies (cm^{-1}) for O isotopologues of the dihydrogen phosphate anion, H_2PO_4^- .

$^{16}\text{O}_4$	P- ^{18}OH	P ^{18}O
197	196	197
312	306	309
314	314	314
378	375	373
422	418	417
485	479	478
490	485	484
745	728	742
771	765	771
1039	1035	1033
1056	1053	1046
1076	1076	1063
1296	1296	1282
3830	3818	3830
3831	3830	3831

Table S111. Energy and optimized coordinates (Å) for hydrogen phosphate dianion, HPO_4^{2-} .

$E = -643.072524090 \text{ A.U.}$				
Atom	x	y	z	
P	0.023455	0.164723	0.000000	
O	-0.545220	0.762864	1.295012	
O	1.553629	-0.084458	0.000000	
O	-0.545220	-1.505583	0.000000	
O	-0.545220	0.762864	-1.295012	
H	0.304412	-1.956335	0.000000	

Table S112. Vibrational frequencies (cm^{-1}) for O isotopologues of the hydrogen phosphate dianion, HPO_4^{2-} , where the designations (1), (2), and (3) represent similar groups that have slightly different ZPEs.

$^{16}\text{O}_4$	P- ^{18}OH	P ^{18}O (1)	P ^{18}O (2)	P ^{18}O (3)
208	207	208	208	208
326	321	321	321	323
330	324	328	328	324
475	462	466	466	471
479	474	475	475	475
493	490	487	487	484
600	593	598	598	598
912	912	898	898	887
988	984	981	981	983
1089	1089	1073	1073	1089
1109	1107	1107	1107	1102

3817 3805 3817 3817 3817

Table S113. Energy and optimized coordinates (Å) for the phosphate trianion, PO_4^{3-} .

$E = -642.144630480 \text{ A.U.}$			
Atom	x	Y	z
P	0.000000	0.000000	0.000000
O	0.920623	0.920623	0.920623
O	-0.920623	-0.920623	0.920623
O	-0.920623	0.920623	-0.920623
O	0.920623	-0.920623	-0.920623

Table S114. Vibrational frequencies (cm^{-1}) for O isotopologues of the phosphate trianion, PO_4^{3-} .

$^{16}\text{O}_4$	P^{18}O
338	333
338	333
479	473
479	473
479	474
805	787
837	825
837	837
837	837

Table S115. Energy and optimized coordinates (Å) for phosphenic acid, O_2POH .

$$E = -567.811846750 \text{ A.U.}$$

Atom	x	y	z
P	0.000000	0.139260	0.000000
O	-0.228044	-1.435678	0.000000
O	1.412258	0.536600	0.000000
O	-1.260547	0.877839	0.000000
H	0.610667	-1.918994	0.000000

Table S116. Vibrational frequencies (cm^{-1}) for O isotopologues of phosphenic acid, O_2POH , where *cis* and *trans* represent the relationship between the proton and the $\text{P}=\text{}^{18}\text{O}$ oxygen.

$^{16}\text{O}_2$	$\text{C}-^{18}\text{OH}$	$\text{C}=\text{}^{18}\text{O}$ (<i>cis</i>)	$\text{C}=\text{}^{18}\text{O}$ (<i>trans</i>)
394	387	389	390
422	420	418	418
436	433	428	427
511	508	510	511
887	856	881	881
1043	1037	1043	1040
1174	1171	1147	1154
1444	1444	1428	1423
3765	3753	3765	3765

Table S117. Energy and optimized coordinates (\AA) for phosphenate anion, PO_3^- , the product of deprotonation of phosphenic acid.

$$E = -567.305477200 \text{ A.U.}$$

Atom	x	y	z
P	0.000000	0.000000	0.000000

O	0.000000	1.498337	0.000000
O	1.297597	-0.749168	0.000000
O	-1.297597	-0.749168	0.000000

Table S118. Vibrational frequencies (cm^{-1}) for O isotopologues of the phosphenate anion, PO_3^- , the product of deprotonation of phosphenic acid.

$^{16}\text{O}_3$	P^{18}O
469	457
469	466
469	466
989	968
1254	1230
1254	1254

Reliability of Calculations. Before drawing any conclusions, the reliability of the calculated EIEs must be examined. This can be done by comparing the EIEs calculated here with the EIEs determined experimentally for some fully ^{18}O -labeled acids. The comparisons are presented in Table S119. Because the calculated EIEs in Table 5 are for mono- ^{18}O -labeled acids, it is necessary to compare the product of all those EIEs with the experimental EIEs of fully ^{18}O -labeled acids. For formic, formic-*d*, and acetic acids this EIE is the product of the 1° and $2^\circ\text{C}=\text{O}$ EIEs. Calculating the EIE for fully ^{18}O -labeled dihydrogen phosphate anion, with its four ^{18}O labels, requires taking the product of 1° , one 2°OH , and two $2^\circ\text{P}=\text{O}$ EIEs. Similarly, calculating the EIE for the fully ^{18}O -labeled hydrogen phosphate dianion requires taking the product of one 1° and three $2^\circ\text{P}=\text{O}$ EIEs.

Table S119. Experimentally measured EIEs on acidities of various fully ^{18}O -labeled acids compared to the product of the calculated primary and secondary EIEs.

^{18}O Acid	K_a^{16}/K_a^{18}	$1^\circ \prod 2^\circ$
$\text{HC}^{18}\text{O}_2\text{H}$	1.0222 ± 0.0002^a	1.0294
$\text{HC}^{18}\text{O}_2\text{D}$	1.0291 ± 0.0001^a	1.0363

CH ₃ C ¹⁸ O ₂ H	1.0172 ± 0.0004 ^b	1.0257
H ₂ P ¹⁸ O ₄ ⁻	1.019 ± 0.001 ^c	1.0489
HP ¹⁸ O ₄ ²⁻	1.019 ± 0.001 ^c	1.0556

^aRef. ⁹ ^bRef. ¹⁰ ^cRef. ¹¹.

The calculated EIEs with only two ¹⁸O labels—formic, formic-*d*, and acetic acid—are similar to the experimental values, but overshoot the actual value. For the acids with four ¹⁸O labels—dihydrogen phosphate anion and hydrogen phosphate dianion—the calculated EIEs are much larger than their experimental counterparts. This may be due to solvation playing a larger role in the di- and tri-anions. Despite this discrepancy, the computational values are good representatives of the experimental EIEs.

Another way to assess the reliability of these calculations is to verify that they reproduce values of Q^{18}/Q^{16} calculated previously on the basis of experimental vibrational frequencies using eq S3, including the EXC factor. Table S120 compares our values with those obtained by Urey at 273K.¹² The agreement is quite close, and the difference for CO₃²⁻ can be attributed to the difficulty in estimating frequencies for an ion.

Table S120. Q^{18}/Q^{16} for select species.

Species	this work	Ref. 12
H ₂ O	1.0658	1.0667
CO ₂	1.1201	1.1172
CO ₃ ²⁻	1.0805	1.0945

Errors can also arise from incomplete convergence in the calculations, despite the imposition of a very tight optimized geometry and an ultrafine optimization grid. Errors can be manifested as small differences in degenerate vibrational frequencies that ought to be identical. Species exhibiting degenerate frequencies include CO₃²⁻, NO₃⁻, BH₃, HB(OH)₃⁻, B(OH)₃, H₃PO₄, PO₃⁻, CO₂, B(OH)₄⁻, and PO₄³⁻, each of which has a three-fold or higher axis of symmetry. The species with a four-fold axis of symmetry or higher, CO₂, B(OH)₄⁻, and PO₄³⁻, have degenerate frequencies that are calculated to be identical within 0.0001 cm⁻¹. The species with the largest error is CO₃²⁻, which shows a 0.08-cm⁻¹ variation in its 1296 cm⁻¹ mode. This is too small to appear in the rounded off values in Table S43. It translates to a possible error of ±1.0002 in the EIE, large enough to affect the values in Tables 5 and 6, but still too small to have any impact on the comparison of 1° with 2° EIEs. These results indicate that the convergence errors obtained in these calculations do not substantially affect the EIEs obtained.

Other errors in the calculations can arise from inadequacy of the basis set, but the

agreement in Table S119 between experimental and calculated EIEs suggests that the basis set is adequate, as had been found.¹³

Inclusion of the EXC Factor. Tables S121 and S122 present the EIEs calculated with the full eq S3.

Table S121. Calculated ^{18}O EIEs on deprotonation of various mono- ^{18}O -substituted carbon-, nitrogen-, boron-, and phosphorus-containing acids using eq S3 at 298.15 K.

Name	Acid	Base	1°	2° $\text{X}=\text{O}$	2° $\text{X}-\text{OH}$
Formic	HCOOH	HCO_2^-	1.0135	1.0181	—
Formic ^a	HCOOH	HCO_2^-	1.0137	1.0159	—
Formic ^b	HCOOH	HCO_2^-	1.0132	1.0152	—
Formic·H ⁺	$\text{HC}(\text{OH})_2^+$	HCOOH	1.0183	—	1.0256
Acetic	CH_3COOH	CH_3CO_2^-	1.0100	1.0170	—
Carbonic	H_2CO_3	HCO_3^-	1.0111	1.0130	1.0264
Bicarbonate	HCO_3^-	CO_3^{2-}	1.0052	1.0204	—
Nitrous	HONO	NO_2^-	1.0016	1.0288	—
Nitrous ^a	HONO	NO_2^-	1.0017	1.0262	—
Nitric	HNO_3	NO_3^-	0.9982	1.0184	—
Nitric ^a	HNO_3	NO_3^-	0.9991	1.0159	—
Borinic	H_2BOH	H_2BO^-	1.0235	—	—
Boronic	$\text{HB}(\text{OH})_2$	$\text{HB}(\text{OH})\text{O}^-$	1.0183	—	1.0199
Boric	$\text{B}(\text{OH})_3$	$\text{B}(\text{OH})_2\text{O}^-$	1.0194	—	1.0140
Phosphinic	H_2POOH	H_2PO_2^-	1.0062	1.0090	—
Phosphonic	$\text{HP}(\text{OH})_2\text{O}$	$\text{HP}(\text{OH})\text{O}_2^-$	1.0044	1.0079	1.0118
Hydrogen phosphonate	$\text{HP}(\text{OH})\text{O}_2^-$	HPO_3^{2-}	1.0054	1.0128	—
Phosphoric	H_3PO_4	H_2PO_4^-	1.0063	1.0064	1.0129
Dihydrogen Phosphate	H_2PO_4^-	HPO_4^{2-}	1.0060	1.0126	1.0166
Hydrogen phosphate	HPO_4^{2-}	PO_4^{3-}	1.0063	1.0169	—
Phosphenic	O_2POH	PO_3^-	1.0091	1.0093	—

^awith PCM for solvation by CHCl_3 . ^bwith PCM for solvation by H_2O .

Table S122. Calculated ^{18}O EIEs at 298.15 K for H_2O addition to various carbon, nitrogen, boron, and phosphorus-containing Lewis acids using eq S3 at 298.15 K.

Name	Acid	Base	1°	2° $\text{X}=\text{O}$	2° $\text{X}-\text{OH}$
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Carbon Dioxide	CO ₂	HCO ₃ ⁻	0.9813	1.0159	—
Carbon Dioxide ^a	CO ₂	HCO ₃ ⁻	0.9727	1.0166	—
Carbon Dioxide ^b	CO ₂	HCO ₃ ⁻	0.9695	1.0172	—
Nitrosonium	NO ⁺	HONO	0.9862	1.0267	—
Nitrosonium ^a	NO ⁺	HONO	0.9839	1.0296	—
Nitronium	NO ₂ ⁺	HNO ₃	0.9778	1.0183	—
Borane	BH ₃	H ₃ BOH ⁻	0.9940	—	—
Borinic	H ₂ BOH	H ₂ B(OH) ₂ ⁻	0.9901	—	1.0218
Boronic	HB(OH) ₂	HB(OH) ₃ ⁻	0.9876	—	1.0207
Boric	B(OH) ₃	B(OH) ₄ ⁻	0.9811	—	1.0166
Phosphenic	O ₂ POH	H ₂ PO ₄ ⁻	1.0206	1.0509	1.0523

^awith PCM for solvation by CHCl₃. ^bwith PCM for solvation by H₂O.

Effect of Solvation. The effect of solvent was assessed using the PCM for solvation by chloroform and water. According to the results in Table 5, the 1° EIEs are nearly the same with the PCM as in the gas phase. The 2° X=O EIEs experience a decrease with solvation, resulting in values that are closer to unity, although still greater than the 1° EIEs. The solvation effect on the individual vibrational frequencies can be measured by $\Delta\Delta\nu$, as defined in eq S9, where ν_{16} represents a vibrational frequency of the unlabeled species, ν_{18} represents a vibrational frequency of the 1° or 2° mono-¹⁸O labeled species for either the gas phase or in solvent. Table S123 lists $\Delta\Delta\nu$ values for nitrous acid, expressing the change of the isotope effect on vibrational frequencies on going from gas phase (Table S51) to chloroform (Table S53).

$$\Delta\Delta\nu = (\nu_{16} - \nu_{18})_{\text{gas}} - (\nu_{16} - \nu_{18})_{\text{PCM}} \quad (11)$$

Table S123. Changes in vibrational frequencies, $\Delta\Delta\nu$, for 1° and 2° EIEs of nitrous acid between gas phase and chloroform

Mode	$\Delta\Delta\nu_{1^\circ}$	$\Delta\Delta\nu_{2^\circ}$
Bend	-0.2	-1.0
Bend	-0.3	0.0
N-O	-0.9	0.5
Bend	0.1	0.3
N=O	-0.2	1.2

O–H	0.9	0.0
Sum	–0.6	1.0

According to the results in Table 6, the effect of solvation is that the 1° EIE for Lewis acids deviates even more from unity (becomes more inverse), while the 2° EIE remains largely unchanged. As without solvation, the magnitudes of the 1° EIEs are greater than the magnitudes of the 2° EIEs.

The calculated EIEs in Table S119 overestimate the experimental values. This is a common phenomenon because these calculations are gas-phase and ignore solvation, but solvation can be modeled with the polarized continuum model (PCM). The product of the computed 1° and 2° EIEs for solvated formic acid in Table 5 can be compared with the experimental EIE. This results in overall EIEs of 1.0275 for chloroform and 1.0263 for water, which are closer to the experimental EIE (1.0222) than are the gas phase calculations (1.0294). However, the PCM values are still quite different from the experimental value. Likewise, the solvation effects on the calculated EIEs on the Brønsted acidity of nitrous acid in Table 5 or on the Lewis acidity of nitrosonium cation in Table 6 are small. Even though vibrational frequencies do change with solvation, as seen by comparing Tables S51 and S53, $\Delta\Delta\nu$, the isotope effect on the changes of vibrational frequency in Table 6, is quite small and is associated with bending modes. Consequently it is impossible to attribute the solvent effect to specific vibrations.

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