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Improved Methods for Feynman Path Integral Calculations of Vibrational−Rotational Free Energies and Application to Isotopic Fractionation of Hydrated Chloride Ions†

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We present two enhancements to our methods for calculating vibrational−rotational free energies by Feynman path integrals, namely, a sequential sectioning scheme for efficiently generating random free-particle paths and a stratified sampling scheme that uses the energy of the path centroids. These improved methods are used with three interaction potentials to calculate equilibrium constants for the fractionation behavior of Cl^- hydration in the presence of a gas-phase mixture of H_2O, D_2O, and HDO. Ion cyclotron resonance experiments indicate that the equilibrium constant, K_{eq}, for the reaction $Cl(H_2O)^- + D_2O \rightleftharpoons Cl(D_2O)^- + H_2O$ is 0.76, whereas the three theoretical predictions are 0.946, 0.979, and 1.20. Similarly, the experimental K_{eq} for the $Cl(H_2O)^- + HDO \rightleftharpoons Cl(HDO)^- + H_2O$ reaction is 0.64 as compared to theoretical values of 0.972, 0.998, and 1.10. Although $Cl(H_2O)^-$ has a large degree of anharmonicity, K_{eq} values calculated with the harmonic oscillator rigid rotator (HORR) approximation agree with the accurate treatment to within better than 2% in all cases. Results of a variety of electronic structure calculations, including coupled cluster and multireference configuration interaction calculations, with either the HORR approximation or with anharmonicity estimated via second-order vibrational perturbation theory, all agree well with the equilibrium constants obtained from the analytical surfaces.

1. Introduction

Although great progress has been made in developing systematic, accurate methods for quantum mechanical electronic structure calculations, less attention has been paid to quantum mechanical treatments of vibrational motion and vibrational−rotational coupling. The Feynman path integral (PI) method[1−4] is especially well suited for the computational thermochemistry of vibrations,[5−17] and in the present article we present further improvements of the methods[13,18−24] we have developed for such calculations and we apply them to isotopic fractionation of monohydrated chloride ions.

The strong hydrogen bonds between anions and water play an important role in solvation,[25,26] and clustering has interesting effects on chemical reactivity;[27] one simple system that has been studied extensively, both experimentally[26,28−30] and theoretically,[31−41] to learn about clustered anions is monohydrated chloride ion. For this system, a significant theoretical−experimental discrepancy remains between the equilibrium constants, K_{eq}, for isotopic fractionation measured by ion cyclotron resonance (ICR) spectroscopy[28] and those calculated with electronic structure calculations and employing the harmonic oscillator rigid rotator (HORR) approximation.[31] Zhao et al.[31] suggested that the effects of anharmonicity and vibrational−rotational coupling, which can be large in noncovalently bound systems, might be one source of this discrepancy. This explanation is not qualitatively inconsistent with the complex anharmonic effects observed later[30] in the experimental vibrational spectra of microhydrated anions, although the five observed fundamentals[30] have frequencies that differ on average by only 4% from the earlier[31] calculated harmonic vibrational frequencies. In the present work we calculate anharmonic and vibrational−rotational coupling effects by employing PI methods to calculate accurate vibrational−rotational partition functions for three analytical potential energy surfaces. By combining vibrational−rotational partition functions with translational partition functions, one can calculate absolute free energies and equilibrium constants. Specifically, we considers the equilibrium constants for the following three reactions:

$$Cl(H_2O)^- + D_2O \rightleftharpoons Cl(D_2O)^- + H_2O \qquad (R1)$$

$$Cl(H_2O)^- + HDO \rightleftharpoons Cl(HDO)^- + H_2O \qquad (R2)$$

and

$$Cl(D_2O)^- + HDO \rightleftharpoons Cl(HDO)^- + D_2O \qquad (R3)$$

There are only two independent equilibrium constants, but for comparison with experiment we will tabulate results for all three reactions.

In order to obtain further understanding of the accuracy of the employed potential surfaces and the vibrational anharmonicity, we also calculated the partition functions by harmonic and approximate anharmonic methods with force constants and geometries obtained both from potential energy surfaces and from a number of new electronic structure calculations that address the sensitivity of the vibrational−rotational partition functions for this system to the level of the treatment of electron correlation and to the basis set.

2. Theoretical Methods

We briefly review our previously published PI methodology for calculating partition functions, and we discuss two enhance-

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ments to our methods, namely a sequential sectioning scheme for efficiently generating random free-particle paths and a stratification scheme using the energies of the path centroids.

2.1. Review of PI Calculations. Feynman path integral calculations were performed to obtain the vibrational–rotational partition function, Q, which may be calculated as

$$Q = \frac{1}{\sigma_{\mathrm{sym}}} \int_{-\infty}^{\infty} \mathrm{d}\mathbf{x}\, \rho(\mathbf{x}, T) \tag{1}$$

where T is the temperature, $\mathbf{x}$ is an N-dimensional configuration space point (with the center-of-mass motion removed so that N is $3N^{\mathrm{A}} - 3$ with N^{A} equal to the number of atoms), σ_{sym} is an identical-atom permutational symmetry number (2 for H_2O, D_2O, $Cl(H_2O)^-$, and $Cl(D_2O)^-$, and 1 for HDO and $Cl(HDO)^-$), and $\rho(\mathbf{x},T)$ is the quantum mechanical coordinate-space density at temperature T. We use rectilinear coordinates scaled to a reduced mass μ so that the kinetic energy is

$$K = \frac{\mu}{2} \sum_{m=1}^{N} \left(\frac{\mathrm{d}x_i}{\mathrm{d}t}\right)^2 \tag{2}$$

The quantum mechanical density may be calculated as[2]

$$\rho = \oint D[\mathbf{x}(s)] \exp\left\{-\frac{1}{\hbar} \int_0^{\beta\hbar} \mathrm{d}s \left(\frac{\mu}{2}\left(\frac{\mathrm{d}\mathbf{x}}{\mathrm{d}s}\right)^2 + V[\mathbf{x}(s)]\right)\right\} \tag{3}$$

where $\beta = 1/k_{\mathrm{B}}T$, k_{B} is Boltzmann's constant, V is the potential energy, $\hbar$ is Planck's constant divided by 2π, and $\oint D[\mathbf{x}(s)]$... denotes a path integral, that is, the summation over all closed paths beginning and ending at $\mathbf{x}$ and parametrized by imaginary time s.

The partition function may then be re-expressed as[2]

$$Q = \frac{1}{\sigma_{\mathrm{sym}}} \int_{-\infty}^{\infty} \mathrm{d}\mathbf{x} \oint D[\mathbf{x}(s)] \Phi^{\mathrm{fp}}[\mathbf{x}(s)] \exp\left\{-\frac{1}{\hbar} \int_0^{\hbar\beta} \mathrm{d}s V[\mathbf{x}(s)]\right\} \tag{4}$$

where $\Phi^{\mathrm{fp}}[\mathbf{x}(s)]$ denotes the contribution of a particular path to the density ρ^{fp} of a free particle, i.e.,

$$\rho^{\mathrm{fp}} = \oint D[\mathbf{x}(s)] \Phi^{\mathrm{fp}}[\mathbf{x}(s)] = \oint D[\mathbf{x}(s)] \exp\left[-\frac{1}{\hbar} \int_0^{\hbar\beta} \mathrm{d}s\, \frac{\mu}{2}\left(\frac{\mathrm{d}\mathbf{x}}{\mathrm{d}s}\right)^2\right] \tag{5}$$

It is convenient for Monte Carlo sampling to multiply and divide the right-hand side of eq 4 by the partition function of a free particle and to restrict the configuration space to a finite domain Γ. This yields

$$Q = \frac{Q_{\mathrm{fp}}(T)}{\sigma_{\mathrm{sym}}} \frac{\int_{\Gamma} \mathrm{d}\mathbf{x} \oint D[\mathbf{x}(s)] \Phi^{\mathrm{fp}}[\mathbf{x}(s)] \exp\left\{-\frac{1}{\hbar} \int_0^{\hbar\beta} \mathrm{d}s V[\mathbf{x}(s)]\right\}}{\int_{\Gamma} \mathrm{d}\mathbf{x} \oint D[\mathbf{x}(s)] \Phi^{\mathrm{fp}}[\mathbf{x}(s)]} \tag{6}$$

where Q_{fp} is the contribution to a free-particle partition function that comes from paths that begin and end at a point within Γ; this quantity may be calculated as

$$Q_{\mathrm{fp}} = V_{\Gamma} \left(\frac{\mu}{2\pi\beta\hbar^2}\right)^{N/2} \tag{7}$$

where V_{Γ} is the volume of the restricted domain.

If the integration over the paths is done by trapezoidal-rule quadrature (with $\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_{P+1}$ denoting the points on the path, and with $\mathbf{x}_{P+1} \equiv \mathbf{x}_1$), then eq 6 becomes

$$Q^{[P]} = \frac{Q_{\mathrm{fp}}(T)}{V_{\Gamma}\sigma_{\mathrm{sym}}} \frac{\int_{\Gamma} \mathrm{d}\mathbf{x}_1 \oint D[\mathbf{x}(s)] \Phi^{\mathrm{fp}}[\mathbf{x}(s)] \exp\left\{-\frac{\beta}{P} \sum_{i=1}^{P} V(\mathbf{x}_i)\right\}}{\oint D[\mathbf{x}(s)] \Phi^{\mathrm{fp}}[\mathbf{x}(s)]} \tag{8}$$

The approximate partition function $Q^{[P]}$ is frequently derived[3,4,20] by recourse to a symmetric[42] Trotter approximation[43] and a subsequent trapezoidal rule integration, and we refer to $Q^{[P]}$ as the Trapezoidal Trotter (TT) partition function. Partition functions calculated in the TT approximation converge as $O(1/P^2)$.[42] Note that the $P = 1$ approximation is equivalent to symmetry-corrected classical mechanics.

The outer quadrature in eq 8 involves the initial path position, but—when developing importance sampling schemes—the paths are more effectively characterized by their centroid position $\mathbf{x}_{\mathrm{C}}$;[1] the specific value of the centroid position for the path $\mathbf{x}_1', \mathbf{x}_2', ..., \mathbf{x}_P'$ is given by

$$\mathbf{x}_{\mathrm{C}}' = \frac{1}{P} \sum_{i=1}^{P} \mathbf{x}_i' \tag{9}$$

Thus, we recast eq 8 as

$$Q^{[P]} = \frac{Q_{\mathrm{fp}}(T)}{V_{\Gamma}\sigma_{\mathrm{sym}}} \left[\int_{\Gamma} \mathrm{d}\mathbf{x}_{\mathrm{C}} \oint D[\mathbf{x}(s)] \Phi^{\mathrm{fp}}[\mathbf{x}(s)] \exp\left\{-\frac{\beta}{P} \sum_{i=1}^{P} V(\mathbf{x}_i)\right\} \delta\left\{\mathbf{x}_{\mathrm{C}} - \frac{1}{P} \sum_{i=1}^{P} \mathbf{x}_i\right\}\right] \Big/ \left(\oint D[\mathbf{x}(s)] \Phi^{\mathrm{fp}}[\mathbf{x}(s)]\right) \tag{10}$$

2.2. Monte Carlo Sampling. Our Monte Carlo sampling scheme employs a combination of correlated and uncorrelated importance sampling. Uncorrelated sampling (unlike the popular Metropolis algorithm[44]) allows straightforward uncertainty estimates, and the small amount of correlation we introduce in our procedure is done in a controlled fashion that still allows uncertainty estimates as will be discussed below. We employ two types of importance sampling to improve efficiency, one for sampling configuration space and one for sampling the paths relative to their centroids in configuration space. The inner integral in eq 10 involves the sampling of the relative paths, and the Monte Carlo integration of this integral is carried out by sampling according to a free-particle distribution. When this is done, the entire Monte Carlo integration of eq 10 with uniform sampling of $\mathbf{x}_{\mathrm{C}}$ may conveniently be expressed as

$$Q^{[P]} = \frac{Q_{\mathrm{fp}}(T)}{\sigma_{\mathrm{sym}}}\left\langle \exp\left\{-\frac{\beta}{P}\sum_{i=1}^{P} V(\mathbf{x}_i)\right\}\right\rangle_{\mathrm{fp},\mathbf{x}_C} \qquad (11)$$

where $\langle ... \rangle_{\mathrm{fp},\mathbf{x}_C}$ indicates an average of the bracketed quantity with relative paths sampled according to a free-particle distribution (as discussed in section 2.3) and with centroid positions chosen uniformly from within Γ.

However, in the present work, the outer integral in eq 10, was importance sampled using an importance function denoted f. Thus, eq 10 becomes

$$Q^{[P]} = \frac{Q_{\mathrm{fp}}(T)\langle f\rangle}{\sigma_{\mathrm{sym}}}\left\langle \frac{1}{f(\mathbf{x}_C)}\exp\left\{-\frac{\beta}{P}\sum_{i=1}^{P} V(\mathbf{x}_i)\right\}\right\rangle_{\mathrm{fp},f(\mathbf{x}_C)} \qquad (12)$$

where $\langle f\rangle$ denotes the average value of f over the integration domain, i.e.,

$$\langle f\rangle = \frac{1}{V_\Gamma}\int_\Gamma \mathrm{d}\mathbf{x}_C\, f(\mathbf{x}_C) \qquad (13)$$

For the calculations presented here, we employ mass-scaled Jacobi coordinates

$$\mathbf{x}_C = \sqrt{\frac{\mu_1\mu_2\mu_3}{\mu^3}}\mathbf{y}_1 \otimes \mathbf{y}_2 \otimes \mathbf{y}_3 \qquad (14)$$

where $\mathbf{y}_1$ is a (unscaled) 3-vector pointing from H_1 to H_2, $\mathbf{y}_2$ is a 3-vector pointing from the O atom to the center of mass of the two hydrogen atoms, $\mathbf{y}_3$ is a 3-vector pointing from the Cl atom to the center of mass of water, μ is a scaling mass explained in conjunction with eq 2, and the μ_i are reduced masses given by $m_i\tilde{m}_i/(m_i + \tilde{m}_i)$, where m_i and $\tilde{m}_i$ are the masses of the fragments connected by $\mathbf{y}_i$.

We elected to use an importance function that is a product of Gaussians involving the magnitudes $y_i^{\mathrm{M}} = |\mathbf{y}_i|$ of the unscaled 3-vectors and the angle, θ, between $\mathbf{y}_1$ and $\mathbf{y}_2$, i.e.,

$$f(\mathbf{x}) = \exp\left[-\frac{(\theta-\theta_0)^2}{2\Delta_\theta^2}\right]\prod_{i=1}^{3}\exp\left[-\frac{(y_i^{\mathrm{M}} - y_{i,0}^{\mathrm{M}})^2}{2\Delta_i^2}\right] \qquad (15)$$

This importance sampling is implemented using a ziggurat[45] sampling method discussed in detail previously[23] that allows samples to be drawn, with nearly negligible rejection, from distributions that are a product of a Gaussian and the Jacobian for the sampled coordinate (for the choices here, either the square of the magnitude of the sampled Jacobi vector or the sine of the sampled angle).[23] Note that the importance function is broad enough to cover both $[\mathrm{Cl}\cdots\mathrm{H_aOH_b}]^-$ geometries and $[\mathrm{Cl}\cdots\mathrm{H_bOH_a}]^-$ geometries because it does not include dependence on angles involving the Cl atom. Reasonably efficient center parameters (θ_0 and $y_{i,0}^{\mathrm{M}}$) of the Gaussian importance function are estimated from the values in equilibrium structures, and the width (Δ) parameters are optimized based on results obtained with a small number of samples. Our sampling domain, Γ, is chosen as a direct product of three-dimensional annuli in each of the Jacobi magnitudes.[23] In practice, the upper and lower bounds on these annuli need not be carefully optimized because the importance sampling function confines most samples to lie within reasonable portions of configuration space.

During sampling we simultaneously collected data for several P, in particular, $P = 32$, 48, 64, 96, and 192. Using the enhanced same path (ESP) scheme,[22] the data for the lowest four values of P are obtained for virtually no additional expense as a byproduct of the $P = 192$ calculation. A small extrapolation correction[19,20,22] was applied to obtain the converged quantum mechanical (QM) partition function using the result of a fit of the three largest values of P to

$$Q^{[P]} = Q^{[p=\infty]}(T) + \frac{A(T)}{P^2} + \frac{B(T)}{P^3} \qquad (16)$$

If P' is a divisor of P, the ESP scheme permits lower-order partition function estimates, $Q^{[P',P]} \approx Q^{[P']}$, to be obtained as an average of the P/P' possible trapezoidal quadrature estimates attainable using the already available potential evaluations, and these estimates converge monotonically on a path-by-path basis,[22] which facilitates highly accurate extrapolation. In the limit that the weighting factor for the configuration space importance sampling at the centroid of each subset of P' points agrees with the weighting factor at the centroid of all P points, we have $Q^{[P',P]} = Q^{[P']}$ and the results for P' are the usual trapezoidal Trotter values. Outside this limit the lower-order results are valid quadrature estimates of the partition function, but extrapolation according to eq 16 may be less accurate.

For low temperatures, low P', and sharply varying importance functions, the ESP partition functions for $P' < P$ can manifest a non-negligible dependence on P and the importance function; in particular, calculations for $P' = 1$ in the ESP scheme are not accurate estimates of the classical limit (however, a valid estimate of the classical limit may be readily obtained simultaneously with other calculations at the cost of a single extra potential evaluation at the centroid position). For many applications even $P' = 2$ in the ESP scheme yields values indistinguishable from TT partition functions. In the present study ESP data for all values of P' are indistinguishable from TT values, so hereafter they are simply labeled $Q^{[P']}$.

2.3. Free-Particle Path Sampling via Sequential Sectioning.

In past work[20] we have generated random free-particle paths using an isomorphism of Coalson[20,46] that permits evenly spaced points on free-particle paths to be obtained by finite Fourier expansions calculated with $O(P \log P)$ operations via fast Fourier sine transforms. This scheme allows formation of sequences of paths that vary in the number of path expansion parameters, P, such that extrapolations to infinite P are well behaved and accurate.[20] One merit of this extrapolation approach is that it has no restrictions on the P values that may be used. However, provided that we only use $Q^{[P]}$ for P values that are divisors of some specific $P^{\max}$, we can employ the ESP scheme for extrapolation. The ESP scheme employs subsets of points from a single path of $P^{\max}$ points to generate correlated estimates of $Q^{[P]}$ in such a way that we do not require the Fourier expansion properties of our earlier approach. Thus, we are interested in finding the least expensive path generation scheme for a given single value of P.

For the special case where P is a power of 2, free-particle paths may be generated in $O(P)$ operations via the bisection algorithm,[47−49] but this restriction can occasionally be inconvenient; fortunately, as we will now show, even greater efficiency is possible with no restrictions on P. Sampling points $\mathbf{x}(s)$ on a free particle path at arbitrary imaginary time slices s_i may be accomplished via[50]

$$\mathbf{x}(s_i) = \frac{(s_k - s_i)}{(s_k - s_j)}\mathbf{x}(s_j) + \frac{(s_i - s_j)}{(s_k - s_j)}\mathbf{x}(s_k) + \sqrt{\frac{(s_k - s_i)(s_i - s_j)\hbar}{(s_k - s_j)\mu}}\mathbf{g} \quad (17)$$

for $s_j < s_i < s_k$ where **g** denotes a vector whose components are Gaussian random numbers with a mean of zero and a variance of 1 and μ is the reduced mass introduced in eq 2. For each path we have $s_1 = 0$, $s_{P+1} = \hbar\beta$, and $\mathbf{x}(s_1) = \mathbf{x}(s_{P+1}) = 0$. Equation 17 allows one to generate a point $\mathbf{x}(s_i)$ on the path using two previously generated ones, $\mathbf{x}(s_j)$ and $\mathbf{x}(s_k)$, subject to the constraint that s_j and s_k are the closest times before and after s_i, respectively, for which points have previously been generated; the order in which we generate the points is at our discretion. The bisection algorithm generates points in the order $i = P/2$, $P/4$, $3P/4$, etc., with the goal of detecting unimportant paths with as few evaluations as possible to facilitate efficient rejection. In our algorithm we wish to initially importance sample based on the centroid position of the path, so we calculate all of the points of a random free-particle path, calculate the centroid of this random path, and then shift the path to the desired centroid position, after which we make further decisions about the ultimate suitability of this path. In cases such as this where the entire path must be formed, it is more efficient to sample the points sequentially from 1 to P than to use the bisection algorithm because then the middle term on the right-hand side of eq 17 is always zero. In particular, for the case of P evenly distributed points $\mathbf{x}_i$, sampling sequentially via eq 17 gives

$$\mathbf{x}_i = \left(\frac{P + 1 - i}{P + 2 - i}\right)\mathbf{x}_{i-1} + \sqrt{\left(\frac{P + 1 - i}{P + 2 - i}\right)\left(\frac{\hbar^2\beta}{\mu P}\right)}\mathbf{g} \quad (18)$$

Paths obtained via bisection require about 5 NP floating-point operations whereas calculations using eq 18 require about 3 NP floating-point operations and benefit from a simpler loop structure than that for bisection. Energies may then be evaluated according to a different ordering such that the initial evaluations are widely distributed along the path in order to avoid unnecessary computation for paths that have negligible contributions to the partition function.[18]

2.4. Centroid Energy Stratification.

Stratified sampling is a standard technique for improving the performance of Monte Carlo integration of multidimensional integrals.[51] To employ it here, we first partition Γ into several disjoint strata k of volume V_k and generalize eq 12 to

$$Q^{[P]} = \frac{1}{\sigma_{\text{sym}}}\sum_{k=1}^{N^{\text{strata}}} Q_k^{\text{fp}}(T)\langle f\rangle_k \left\langle \frac{1}{f(\mathbf{x}_\text{C})}\exp\left\{-\frac{\beta}{P}\sum_{i=1}^{P} V(\mathbf{x}_i)\right\}\right\rangle_{\text{fp},f(\mathbf{x}_\text{C});k} \quad (19)$$

where the final average is over all $\mathbf{x}_\text{C}$ values within a particular stratum, k, Q_k^{fp} denotes the contribution of stratum k to the free-particle partition function, and

$$\langle f\rangle_k = \frac{1}{V_k}\int_{\Gamma_k} \mathrm{d}\mathbf{x}_\text{C} f(\mathbf{x}_\text{C}) \quad (20)$$

In past work[7,13,18−23,52] we have employed stratification in a single coordinate and, in favorable circumstances, this resulted in modest improvements in efficiency of approximately a factor of 2. If f is a function of the magnitudes of the 3-vectors that constitute the Jacobi coordinates or angles between these vectors, and stratification is also in one of these coordinates, the $\langle f\rangle_k$ can be determined either analytically or with an inexpensive set of one-dimensional quadratures.

Stratification based on the centroid energy rather than a particular coordinate can offer substantial improvements in efficiency, but it suffers from a number of complicating factors. We define strata based on evenly spaced intervals of the centroid energy, except for the final stratum, which also includes all samples with a centroid energy higher than the upper bound of other strata. One complication is that the volumes of the individual strata, V_k, which are needed to calculate the Q_k^{fp} as well as the $\langle f\rangle_k$, are not readily available; indeed, the boundaries of the individual strata are complicated functions of the PES, and a given stratum may consist of multiple noncontiguous domains. To mitigate these difficulties, we recast eq 19 as

$$Q^{[P]} = \frac{Q^{\text{fp}}(T)\langle f\rangle}{\sigma_{\text{sym}}}\sum_{k=1}^{N^{\text{strata}}} \alpha_k\left\langle \frac{1}{f(\mathbf{x}_\text{C})}\exp\left\{-\frac{\beta}{P}\sum_{i=1}^{P} V(\mathbf{x}_i)\right\}\right\rangle_{\text{fp},f(\mathbf{x}_\text{C});k} \quad (21)$$

where

$$\alpha_k = \frac{\langle f\rangle_k V_k}{\langle f\rangle V} \quad (22)$$

The α_k are calculated by Monte Carlo integration as the fraction of candidate centroid samples obtained with importance function f that fall within stratum k; in particular, these quantities are estimated on the fly (and updated as the calculation progresses) and typically converge much more rapidly than the partition function does. Thus, the uncertainties in the α_k values are negligible compared to the uncertainties in the rest of the calculation.

Another complication with stratification in the centroid energy is that locating a sample that lies within a desired stratum is nontrivial; we employ rejection for this sampling, and at low temperatures this can involve the calculation of a large number of energies ($>10^3$) at candidate configurations before a suitable sample is obtained. One way to ameliorate the costs associated with this is to evaluate multiple paths for each accepted centroid. The contributions of all paths at a given centroid are correlated and are immediately averaged. The averaged contributions from different centroid positions are uncorrelated, so we gather statistics on these averaged quantities for which error estimates may be obtained using the standard formulas for uncorrelated sampling. The calculation of the statistical uncertainties is reviewed in the Supporting Information. Generally, the variance reduction with increasing numbers of samples is greatest for completely uncorrelated sampling and degrades as the number of paths per centroid increases, so a tradeoff is involved between the cost of obtaining valid samples and the number of samples that will be required to achieve a given accuracy. In the high T limit or for $P = 1$, there is no benefit from knowing the results of multiple paths at each centroid. However, in the low temperature limit, where locating important centroid configurations is the most difficult, the degradation in the variance reduction from sampling many paths per centroid is quite modest

TABLE 1: Parameters Used in the PI Calculations

	note	$Cl(H_2O)^-$	$Cl(D_2O)^-$	$Cl(HDO)^-$	H_2O	D_2O	HDO
$N^{centroids}$	*a*	1×10^7	5×10^6	1×10^7	1×10^8	1×10^7	1×10^7
$N^{centroids}_{passive}$	*b*	1×10^6	1×10^6	1×10^6	1×10^7	1×10^6	1×10^6
N^{paths}	*c*	20	20	20	10	10	10
y_1^M domain (a_0)	*d*	1−5	1−5	1−5	1−5	1−5	1−5
y_2^M domain (a_0)	*d*	0−4	0−4	0−4	0−4	0−4	0−4
y_3^M domain (a_0)	*d*	4−8	4−8	4−8	n/a	n/a	n/a
$y_{1,0}^M$ (a_0)	*e*	2.798	2.798	2.798	2.798	2.798	2.798
$y_{2,0}^M$ (a_0)	*e*	1.187	1.187	1.260	1.107	1.107	1.260
$y_{3,0}^M$ (a_0)	*e*	5.8098	5.7284	5.8164	n/a	n/a	n/a
θ_0	*e*	90	90	64.22	90	90	64.22
Δ_1 (a_0)	*f*	0.3	0.3	0.3	0.3	0.3	0.3
Δ_2 (a_0)	*f*	0.2	0.2	0.2	0.2	0.2	0.2
Δ_3 (a_0)	*f*	0.6	0.6	0.6	n/a	n/a	n/a
Δ_θ	*f*	5	5	5	5	5	5
N^{strata}	*g*	20	20	20	30	30	30
strata size (kcal/mol)		1	1	1	0.5	0.5	0.5
$E^{screen}_{centroid}$ (kcal/mol)	*h*	20	20	20	12	12	12

[a] The total number of accepted centroid samples. [b] The number of accepted centroid samples prior to using adaptively optimized stratified sampling. [c] The number of paths that are sampled at each accepted centroid position. [d] The domain range of the magnitude of a particular $\mathbf{y}_i$ vector for the three annuli that determine the sampling domain. [e] Center parameters for the importance function of eq 15. [f] Width parameters for the importance function of eq 15. [g] The number of strata used in the centroid energy stratification scheme. [h] An energy cutoff; if the energy of a centroid is higher than this value, contributions to the partition function for all paths at this point are neglected.

(a few percent) when we used 20 paths per centroid and allows the centroid sampling costs to be reduced by an order of magnitude.

We employ a centroid-energy cutoff above which the contributions of all paths at that centroid are neglected. In all other respects our stratification approach is the same as the adaptively optimized stratified sampling scheme discussed previously.[18] In particular, we calculate a small portion of samples in an initial exploratory phase using only passive stratification and then use these results to estimate an optimal distribution of the remaining samples among the various strata. These samples are calculated in batches during which candidates are only accepted if they fall within a stratum that is estimated to be undersampled, and after each batch is finished a new estimate is made for the best distribution of the remaining samples. For some of the calculations presented below, the improvements in efficiency resulting from energy stratification are about a factor of 100.

3. Interaction Potentials and Electronic Structure

In this section we detail the potentials to be used in the PI calculations and then we discuss the various types of electronic structure calculations that are considered.

3.1. Potential Energy Surfaces. We consider three analytical potential energy surfaces (PESs) for the $Cl(H_2O)^-$ system. The first is the Dorsett−Watts−Xantheas (DWX) PES,[33] the functional form for which is presented clearly in the Appendix of the work of Schenter et al.[35] The DWX PES is the only one of the three potentials that is capable of treating hydration by more than one water molecule, but it yields the least accurate agreement with experimental fundamental frequencies for the single-water complex. The second PES we consider is the morphed DWX (MDWX) surface of Bowman and Xantheas,[38] which is a modification of the DWX PES that was fit so that anharmonic frequency calculations better match the expt3;erimental[29,30] $Cl(H_2O)^-$ fundamental frequencies. Both the DWX and MDWX surfaces yield the Reimers−Watts−Klein (RRK2) water potential[53] upon dissociation of the chloride. The third PES that we consider is that of Rheinecker and Bowman (RB).[40,41] The RB surface was fit to 50270 energies calculated at the CCSD(T)/aug-cc-pVTZ level of electronic structure theory; in contrast to the other two PESs, the RB surface is not a global fit and does not dissociate to a reasonable water potential.

We calculate partition functions for the isotopomers of water using the spectroscopically accurate PES of Partridge and Schwenke (PS).[54] It would be more consistent (although probably less accurate) to use the RRK2 PES for calculations obtained with the DWX and MDWX PESs; however, as we will show in the following, the calculated equilibrium constants vary by only a few percent depending on the choice of the water potential used.

3.2. Electronic Structure Calculations. In addition to the PI calculations we also performed a number of electronic structure calculations to assess the sensitivity of the potential energy surface to treatment at various levels of theory or with various basis sets. We employed correlation consistent basis sets;[55−57] we began with the aug-cc-pVTZ set because it was used to calculate the data upon which the RB surface fit is based, and we also used the aug-cc-pV(T+d)Z, aug-cc-pV(Q+d)Z, and aug-cc-pV(5+d)Z sets. Results for some systems that contain second-row atoms have been observed[58,59] to display significant sensitivity to the inclusion of tight d functions; the cc-pV(*n*+d)Z and aug-cc-pV(*n*+d)Z families of basis sets, which include such tight d functions, were introduced by Dunning et al.[57] to correct for this deficiency in the earlier correlation consistent basis sets. Møller−Plesset second-order electronic perturbation theory[60] (MP2) and density functional theory (DFT) calculations with the mPW1PW functional[61] were performed in conjunction with second-order vibrational perturbation theory (PT2)[62,63] estimates of anharmonicity. The PT2 calculations are carried out using the implementation of Barone[63] in the Gaussian 03 program suite.[64] The anharmonic calculations are especially sensitive to the accuracy of the density functional integration grid, and we chose to use a grid with 199 radial and 974 angular points.

Additional calculations of harmonic frequencies, using the MOLPRO suite of programs,[65] were performed for MP2, coupled cluster theory with single and double excitations plus a quasi-perturbative treatment of connected triple excitations [CCSD(T)],[66] and internally contracted[67,68] multireference configuration interaction with single and double excitations (icM-

TABLE 2: Vibrational−Rotational Partition Functions, $Q^{[P]}$ at 298 K, Extrapolated Values, and 2σ Uncertainties for Isotopomers of Water Obtained with the PS PES

P	H_2O	D_2O	HDO
32	$(1.095 \pm 0.002) \times 10^{-8}$	$(1.005 \pm 0.001) \times 10^{-5}$	$(6.4925 \pm 0.0051) \times 10^{-7}$
48	$(9.454 \pm 0.015) \times 10^{-9}$	$(9.482 \pm 0.012) \times 10^{-6}$	$(5.8602 \pm 0.0047) \times 10^{-7}$
64	$(8.965 \pm 0.014) \times 10^{-9}$	$(9.289 \pm 0.012) \times 10^{-6}$	$(5.6478 \pm 0.0046) \times 10^{-7}$
96	$(8.624 \pm 0.014) \times 10^{-9}$	$(9.150 \pm 0.012) \times 10^{-6}$	$(5.4986 \pm 0.0045) \times 10^{-7}$
192	$(8.425 \pm 0.013) \times 10^{-9}$	$(9.068 \pm 0.012) \times 10^{-6}$	$(5.4102 \pm 0.0045) \times 10^{-7}$
extrapolated	$(8.358 \pm 0.013) \times 10^{-9}$	$(9.042 \pm 0.012) \times 10^{-6}$	$(5.3811 \pm 0.0045) \times 10^{-7}$

TABLE 3: Vibrational−Rotational Partition Functions, $Q^{[P]}$ at 298 K, Extrapolated Values, and 2σ Uncertainties for Isotopomers of Water Obtained with the RRK2 PES

P	H_2O	D_2O	HDO
32	$(1.154 \pm 0.002) \times 10^{-8}$	$(1.035 \pm 0.001) \times 10^{-5}$	$(6.7754 \pm 0.0054) \times 10^{-7}$
48	$(9.990 \pm 0.016) \times 10^{-9}$	$(9.774 \pm 0.013) \times 10^{-6}$	$(6.1261 \pm 0.0050) \times 10^{-7}$
64	$(9.480 \pm 0.015) \times 10^{-9}$	$(9.576 \pm 0.013) \times 10^{-6}$	$(5.9081 \pm 0.0048) \times 10^{-7}$
96	$(9.129 \pm 0.015) \times 10^{-9}$	$(9.437 \pm 0.013) \times 10^{-6}$	$(5.7549 \pm 0.0047) \times 10^{-7}$
192	$(8.922 \pm 0.014) \times 10^{-9}$	$(9.353 \pm 0.013) \times 10^{-6}$	$(5.6643 \pm 0.0047) \times 10^{-7}$
extrapolated	$(8.854 \pm 0.014) \times 10^{-9}$	$(9.326 \pm 0.013) \times 10^{-6}$	$(5.6345 \pm 0.0047) \times 10^{-7}$

TABLE 4: Vibrational−Rotational Partition Functions, $Q^{[P]}$ at 298 K, Extrapolated Values, and 2σ Uncertainties for Isotopomers of $Cl(H_2O)^-$ Obtained with the DWX PES

P	$Cl(H_2O)^-$	$Cl(D_2O)^-$	$Cl(HDO)^-$
32	$(2.6085 \pm 0.0095) \times 10^{-7}$	$(3.2352 \pm 0.0052) \times 10^{-4}$	$(1.8040 \pm 0.0036) \times 10^{-5}$
48	$(2.2828 \pm 0.0085) \times 10^{-7}$	$(3.0682 \pm 0.0050) \times 10^{-4}$	$(1.6431 \pm 0.0033) \times 10^{-5}$
64	$(2.1754 \pm 0.0082) \times 10^{-7}$	$(3.0109 \pm 0.0049) \times 10^{-4}$	$(1.5889 \pm 0.0032) \times 10^{-5}$
96	$(2.1006 \pm 0.0080) \times 10^{-7}$	$(2.9704 \pm 0.0049) \times 10^{-4}$	$(1.5508 \pm 0.0032) \times 10^{-5}$
192	$(2.0567 \pm 0.0079) \times 10^{-7}$	$(2.9462 \pm 0.0048) \times 10^{-4}$	$(1.5282 \pm 0.0032) \times 10^{-5}$
extrapolated	$(2.0424 \pm 0.0079) \times 10^{-7}$	$(2.9381 \pm 0.0048) \times 10^{-4}$	$(1.5208 \pm 0.0032) \times 10^{-5}$

TABLE 5: Vibrational−Rotational Partition Functions, $Q^{[P]}$ at 298 K, Extrapolated Values, and 2σ Uncertainties for Isotopomers of $Cl(H_2O)^-$ Obtained with the MDWX PES

P	$Cl(H_2O)^-$	$Cl(D_2O)^-$	$Cl(HDO)^-$
32	$(4.030 \pm 0.012) \times 10^{-7}$	$(4.1467 \pm 0.0060) \times 10^{-4}$	$(2.5563 \pm 0.0045) \times 10^{-5}$
48	$(3.577 \pm 0.011) \times 10^{-7}$	$(3.9556 \pm 0.0058) \times 10^{-4}$	$(2.3522 \pm 0.0042) \times 10^{-5}$
64	$(3.428 \pm 0.011) \times 10^{-7}$	$(3.8899 \pm 0.0057) \times 10^{-4}$	$(2.2829 \pm 0.0041) \times 10^{-5}$
96	$(3.323 \pm 0.011) \times 10^{-7}$	$(3.8433 \pm 0.0057) \times 10^{-4}$	$(2.2343 \pm 0.0040) \times 10^{-5}$
192	$(3.262 \pm 0.011) \times 10^{-7}$	$(3.8155 \pm 0.0056) \times 10^{-4}$	$(2.2053 \pm 0.0040) \times 10^{-5}$
extrapolated	$(3.241 \pm 0.010) \times 10^{-7}$	$(3.8063 \pm 0.0056) \times 10^{-4}$	$(2.1957 \pm 0.0040) \times 10^{-5}$

RCI) with the renormalized variant[69] of the multireference generalization[70] of the Davidson[71,72] size-extensivity correction (+Q). The reference state for the icMRCI+Q calculations is a full-valence complete active space self-consistent field (CASSCF) wave function (16 electrons in 10 active orbitals; 825 configurations) where six orbitals are frozen at their Hartree−Fock values. All correlated calculations employed frozen cores (the 1s orbital on O and the 1s, 2s, and 2p orbitals on Cl). The largest icMRCI calculation (the one with the aug-cc-pV(Q+d)Z basis) involves 3811800 contracted configurations composed of 3.8×10^8 uncontracted ones.

4. Results

Table 1 lists the parameters used for the PI calculations. Atomic masses of 1.0078250321, 2.0141017780, 15.9949146221, and 34.9688527 amu were used for H, D, O, and Cl, respectively. The domain boundaries were chosen as safe values because the sampling for this problem is well-confined by the importance functions. The width parameters of the importance sampling functions were lightly optimized; for this problem precise optimization would lead to only modest additional savings. The coordinates used in eq 15 are mass dependent, so some of the center parameters for our importance functions are also mass dependent. We have chosen to sample 10 paths per centroid for calculations on water and 20 paths per centroid for calculations on $Cl(H_2O)^-$; these values are sufficient to move the time-intensive portion of the calculation to the integration over the paths but are not so large as to lead to a substantial degradation in the sampling efficiency due to correlation.

Tables 2 and 3 list accurate vibrational−rotational partition functions calculated for the PS and RRK2 surfaces, respectively, and Tables 4, 5, and 6 list partition functions for the $Cl(H_2O)^-$ isotopomers calculated on the DWX, MDWX, and RB surfaces, respectively. The zero of energy for all partition functions is the classical minimum of the potential.

Table 7 lists equilibrium geometries for the global minimum of $Cl(H_2O)^-$ for the analytical PESs and from various electronic structure calculations. Table 8 compares harmonic frequencies for $Cl(H_2O)^-$ for the analytical PESs to those of the various electronic structure calculations. Similar comparisons for $Cl(D_2O)^-$, the two distinct minima, $[Cl\cdots HOD]^-$ and $[Cl\cdots DOH]^-$, of $Cl(HDO)^-$, and the isotopomers of water are given in Supporting Information.

Table 9 lists vibrational−rotational partition functions for the isotopomers of $Cl(H_2O)^-$ calculated by various methods. Rheinecker and Bowman[41] estimate that the $[Cl\cdots HOD]^-$ and $[Cl\cdots DOH]^-$ conformers of $Cl(HDO)^-$ have a barrier to interconversion of 631 cm^{-1}, so at room temperature $Cl(HDO)^-$ is properly regarded as a single species. In this table the PT2 and HORR calculations for $Cl(HDO)^-$ are the sum of those for

TABLE 6: Vibrational−Rotational Partition Functions, $Q^{[P]}$ at 298 K, Extrapolated Values, and 2σ Uncertainties for Isotopomers of $Cl(H_2O)^-$ Obtained with the RB PES

P	$Cl(H_2O)^-$	$Cl(D_2O)^-$	$Cl(HDO)^-$
32	$(6.533 \pm 0.020) \times 10^{-7}$	$(6.4442 \pm 0.0093) \times 10^{-4}$	$(4.022 \pm 0.012) \times 10^{-5}$
48	$(5.762 \pm 0.020) \times 10^{-7}$	$(6.1325 \pm 0.0089) \times 10^{-4}$	$(3.685 \pm 0.011) \times 10^{-5}$
64	$(5.507 \pm 0.020) \times 10^{-7}$	$(6.0253 \pm 0.0088) \times 10^{-4}$	$(3.571 \pm 0.011) \times 10^{-5}$
96	$(5.330 \pm 0.020) \times 10^{-7}$	$(5.9491 \pm 0.0087) \times 10^{-4}$	$(3.491 \pm 0.011) \times 10^{-5}$
192	$(5.225 \pm 0.020) \times 10^{-7}$	$(5.9038 \pm 0.0087) \times 10^{-4}$	$(3.443 \pm 0.011) \times 10^{-5}$
extrapolated	$(5.190 \pm 0.020) \times 10^{-7}$	$(5.8887 \pm 0.0087) \times 10^{-4}$	$(3.427 \pm 0.011) \times 10^{-5}$

TABLE 7: Equilibrium Configuration of the Global Minimum of $Cl(H_2O)^-$ As Predicted by a Variety of Methods[a]

Method	R(OH)	R(OH′)	θ(HOH′)	R(ClH)	θ(ClHO)
DWX PES	0.987	0.954	99.4	2.164	165.6
MDWX PES	0.992	0.954	99.0	2.118	167.2
RB PES	0.988	0.962	100.8	2.135	168.2
mPW1PW/aug-cc-pVTZ	0.989	0.957	101.4	2.123	168.4
MP2/aug-cc-pVTZ	0.991	0.961	100.6	2.116	168.9
MP2/aug-cc-pV(T+d)Z	0.991	0.961	100.6	2.115	168.9
MP2/aug-cc-pV(Q+d)Z	0.988	0.958	100.7	2.116	168.2
MP2/aug-cc-pV(5+d)Z	0.988	0.958	100.8	2.115	168.1
MP2/E4[b]	0.984	0.958	100.6	2.150	165.8
CCSD(T)/aug-cc-pVTZ	0.988	0.961	100.8	2.138	168.1
CCSD(T)/aug-cc-pV(T+d)Z	0.988	0.961	100.8	2.137	168.1
CCSD(T)/aug-cc-pV(Q+d)Z	0.985	0.958	100.8	2.144	167.0
icMRCI+Q/aug-cc-pVTZ	0.986	0.961	100.6	2.148	168.0
icMRCI+Q/aug-cc-pV(T+d)Z	0.986	0.961	100.6	2.148	168.0
icMRCI+Q/aug-cc-pV(Q+d)Z	0.983	0.958	100.7	2.156	167.0

[a] Distances are in angstroms and angles are in degrees; the dihedral angle is 0° in all cases. [b] MP2/E4 from ref 31, other results from present calculations.

TABLE 8: Harmonic Frequencies (in cm^{-1}) for $Cl(H_2O)^-$ for the Analytical Surfaces and Various Electronic Structure Methods

method	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
DWX PES	3925	3483	1819	404	192	817
MDWX PES	3770	3351	1730	433	221	860
RB PES	3860	3387	1710	367	202	723
mPW1PW/aug-cc-pVTZ	3922	3328	1677	368	199	750
MP2/aug-cc-pVTZ	3894	3338	1669	366	203	753
MP2/aug-cc-pV(T+d)Z	3894	3337	1669	366	203	753
MP2/aug-cc-pV(Q+d)Z	3912	3355	1674	359	202	751
MP2/aug-cc-pV(5+d)Z	3915	3355	1674	357	202	750
MP2/E4[a]	3918	3418	1685	352	194	741
CCSD(T)/aug-cc-pVTZ	3867	3390	1688	357	200	742
CCSD(T)/aug-cc-pV(T+d)Z	3867	3389	1688	359	201	743
CCSD(T)/aug-cc-pV(Q+d)Z	3888	3416	1693	349	199	736
icMRCI+Q/aug-cc-pVTZ	3871	3415	1695	357	197	740
icMRCI+Q/aug-cc-pV(T+d)Z	3871	3414	1695	357	197	740
icMRCI+Q/aug-cc-pV(Q+d)Z	3894	3444	1701	346	195	734

[a] MP2/E4 from ref 31, other results from present calculations.

the two structures $[Cl\cdots HOD]^-$ and $[Cl\cdots DOH]^-$, whereas the PI calculations for $Cl(HDO)^-$ span both conformers.

Equilibrium constants for the reaction $A + B \rightleftharpoons C + D$ may be calculated from vibrational−rotational partition functions via

$$K_{eq} = K_{trans}\frac{Q_C Q_D}{Q_A Q_B} \tag{23}$$

where the translational contribution is obtained by

$$K_{trans} = \left(\frac{M_C M_D}{M_A M_B}\right)^{3/2} \tag{24}$$

and M_X denotes the mass of species X. Table 10 gives results for K_{eq} for a variety of methods; these values include contributions from the translational degrees of freedom that are factors of 0.9022, 0.9481, and 1.0589, respectively, for reactions R1, R2, and R3. The PI results on the analytical surfaces are all calculated using partition functions for the isotopomers of water from the more accurate PS PES. Partition functions on the RRK2 PES are 5.9%, 3.1%, and 4.6% larger than those of the PS PES for H_2O, D_2O, and HDO, respectively. Thus, if we had calculated K_{eq} values using the RRK2 partition functions these would be 2.7% higher for reaction R1, 1.2% higher for reaction R2, and 1.4% lower for reaction R3. In Table 11 we consider various means of estimating the fundamental frequencies and compare these to experimental values. In Table 12 the anharmonic zero-point energies estimated by PT2 are given.

5. Discussion

5.1. Path Integral Efficiency. We can gain a rough idea of the effectiveness of the centroid energy stratification by considering the uncertainties after the initial passive stratification phase and at the end of the calculation. For the $Cl(HDO)^-$ calculation with the DWX PES, the 2σ relative uncertainty was about 20% after the initial 1 million accepted samples, and after the remaining 9 million samples were distributed with adaptively optimized stratification the 2σ relative uncertainty had dropped to about 0.21%. Because errors in Monte Carlo sampling decrease inversely with the square root of the number of samples, a similar drop in uncertainly using only passive stratification would have required about 10^{10} additional samples, or over 1000 times as many as were actually used. The time spent in the initial passive stratification phase was a little over 1% of the total time, which is about a factor of 10 less time than one would estimate based only on the percentage of samples in this phase; this is mainly because we employed a screening scheme whereby the contributions of paths with a centroid energy above 20 kcal/mol were assumed to be zero (this is a very conservative value, about 52% of the partition

TABLE 9: Vibrational-Rotational Partition Functions for Isotopomers of $Cl(H_2O)^-$ for the Analytical Surfaces and Selected Electronic Structure Methods Calculated via Path Integrals, the Rigid Rotator Harmonic Oscillator Approximation, or Second-Order Vibrational Perturbation Theory[a]

method	$Cl(H_2O)^-$	$Cl(D_2O)^-$	$Cl(HDO)^-$
DWX PES, PI	2.042×10^{-7}	2.938×10^{-4}	1.521×10^{-5}
MDWX PES, PI	3.241×10^{-7}	3.806×10^{-4}	2.196×10^{-5}
RB PES, PI	5.190×10^{-7}	5.889×10^{-4}	3.427×10^{-5}
mPW1PW/aug-cc-pVTZ, PT2	4.532×10^{-7}	5.285×10^{-4}	2.989×10^{-5}
MP2/aug-cc-pVTZ, PT2	4.710×10^{-7}	5.626×10^{-4}	3.080×10^{-5}
DWX PES, HORR	1.142×10^{-7}	1.986×10^{-4}	9.378×10^{-6}
MDWX PES, HORR	1.929×10^{-7}	2.715×10^{-4}	1.433×10^{-5}
RB PES, HORR	2.929×10^{-7}	4.055×10^{-4}	2.145×10^{-5}
mPW1PW/aug-cc-pVTZ, HORR	2.934×10^{-7}	4.039×10^{-4}	2.143×10^{-5}
MP2/aug-cc-pVTZ, HORR	3.063×10^{-7}	4.162×10^{-4}	2.223×10^{-5}
MP2/aug-cc-pV(T+d)Z, HORR	3.070×10^{-7}	4.167×10^{-4}	2.226×10^{-5}
MP2/aug-cc-pV(Q+d)Z, HORR	2.864×10^{-7}	3.978×10^{-4}	2.101×10^{-5}
MP2/aug-cc-pV(5+d)Z, HORR	2.866×10^{-7}	3.984×10^{-4}	2.103×10^{-5}
CCSD(T)/aug-cc-pVTZ, HORR	3.001×10^{-7}	4.159×10^{-4}	2.199×10^{-5}
CCSD(T)/aug-cc-pV(T+d)Z,HORR	2.980×10^{-7}	4.131×10^{-4}	2.184×10^{-5}
CCSD(T)/aug-cc-pV(Q+d)Z, HORR	2.795×10^{-7}	3.984×10^{-4}	2.076×10^{-5}
icMRCI+Q/aug-cc-pVTZ, HORR	2.830×10^{-7}	4.024×10^{-4}	2.104×10^{-5}
icMRCI+Q/aug-cc-pV(T+d)Z, HORR	2.831×10^{-7}	4.023×10^{-4}	2.103×10^{-5}
icMRCI+Q/aug-cc-pV(Q+d)Z, HORR	2.636×10^{-7}	4.060×10^{-4}	1.982×10^{-5}

[a] The $Cl(HDO)^-$ results include contributions from both conformers.

TABLE 10: K_{eq} for the Analytical Surfaces and Electronic Structure Methods Compared to Experimental Values for Reactions R1−R3[a]

method	R1	R2	R3
experiment[b]	0.76	0.64	0.84
DWX PES, PI	1.200	1.097	0.914
MDWX PES, PI	0.979	0.998	1.019
RB PES, PI	0.946	0.972	1.028
mPW1PW/aug-cc-pVTZ, PT2	0.945	0.940	0.995
MP2/aug-cc-pVTZ, PT2	1.011	0.973	0.963
DWX PES, HORR	1.212	1.105	0.911
MDWX PES, HORR	0.981	0.999	1.019
RB PES, HORR	0.965	0.985	1.021
mPW1PW/aug-cc-pVTZ, HORR	0.936	0.970	1.037
MP2/aug-cc-pVTZ, HORR	0.964	0.985	1.021
MP2/aug-cc-pV(T+d)Z, HORR	0.963	0.984	1.022
MP2/aug-cc-pV(Q+d)Z, HORR	0.960	0.983	1.023
MP2/aug-cc-pV(5+d)Z, HORR	0.957	0.981	1.025
MP2/E4, HORR[c]	0.99		
CCSD(T)/aug-cc-pVTZ, HORR	0.998	1.002	1.004
CCSD(T)/aug-cc-pV(T+d)Z,HORR	0.999	1.002	1.004
CCSD(T)/aug-cc-pV(Q+d)Z, HORR	0.997	1.001	1.004
icMRCI+Q/aug-cc-pVTZ, HORR	1.018	1.014	0.996
icMRCI+Q/aug-cc-pV(T+d)Z, HORR	1.017	1.013	0.996
icMRCI+Q/aug-cc-pV(Q+d)Z, HORR	1.069	1.010	0.945

[a] Calculations for the analytical surfaces used partition functions calculated on the PS surface for isotopomers of water. PI denotes an accurate anharmonic value calculated via path integrals; PT2 denotes an approximate result calculated from partition functions computed by second-order vibrational perturbation theory, and HORR denotes the harmonic oscillator rigid rotator approximation. [b] Reference 28 [c] MP2/E4, HORR from ref 31; other results are from present calculations.

TABLE 11: Comparison of Calculated Anharmonic Fundamental Frequencies (in cm^{-1}) to Experimental Measurements and Mean Unsigned Deviations (MUD) between Experiment and Various Theoretical Estimates

method	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	MUD
experiment[a]	3690	3130	1650		210	745	
PT2 MP2/avtz[b]	3713	3064	1652	346	198	764	24
PT2 MP2/avqz[c]	3727	3077	1661	355	211	772	26
PT2 mPW1PW/avtz[d]	3741	2993	1610	349	193	762	52
adj PT2 MP2/avtz[e]	3707	3141	1676	329	194	747	14
adj PT2 MP2/avqz[f]	3704	3138	1680	344	207	758	14
adj PT2 mPW1PW/avtz[g]	3707	3081	1626	329	192	747	22
RB PES, accurate[h]	3681	3123	1660	362	205	715	12
adjusted RB accurate[i]	3701	3143	1649	349	202	724	11

[a] Reference 30. [b] Second-order vibrational perturbation theory with MP2/aug-cc-pVTZ. [c] Second-order vibrational perturbation theory with MP2/aug-cc-pVQZ. [d] Second-order vibrational perturbation theory with mPW1PW/aug-cc-pVTZ. [e] Second-order vibrational perturbation theory with MP2/aug-cc-pVTZ adjusted by the difference between the harmonic frequencies with the CCSD(T)/aug-cc-pV(Q+d)Z and MP2/aug-cc-pVTZ methods. [f] Second-order vibrational perturbation theory with MP2/aug-cc-pVQZ adjusted by the difference between the harmonic frequencies with the CCSD(T)/aug-cc-pV(Q+d)Z and MP2/aug-cc-pVQZ methods. [g] Second-order vibrational perturbation theory with mPW1PW/aug-cc-pVTZ adjusted by the difference between the harmonic frequencies with the CCSD(T)/aug-cc-pV(Q+d)Z and mPW1PW/aug-cc-pVTZ methods. [h] Reference 41; accurate anharmonic fundamentals calculated with the RB PES. [i] The accurate fundamentals of ref 41; for the RB PES adjusted by the difference between the CCSD(T)/aug-cc-pV(Q+d)Z harmonic frequencies and the harmonic frequencies of the RB PES.

function for this calculation comes from contributions from paths with a centroid energy below 2 kcal/mol, and this percentage increases to 99% for centroid energies below 6 kcal/mol); thus, the adaptive stratification yielded a speedup of about a factor of 100 compared to passive stratification for this case. If we had carefully optimized all parameters for both a calculation with and without stratification, the advantage of the former would probably not be quite as large as the factor of 100 estimated above, but clearly energy stratification can provide very substantial improvements in efficiency.

The number of candidate samples needed to identify an acceptable centroid during the adaptive sampling phase varies significantly with the system studied; for the isotopomers of H_2O this value varied from about 19 to 62 whereas for the isotopomers of $Cl(H_2O)^-$ it varied from about 840 to 3900. These values, along with the parameters (given in Table 1) for the number of paths used at each accepted centroid, the order (P) of the path discretization, the number of centroids sampled, and the extent of screening employed, yield the number of potential evaluations needed for our algorithm.

TABLE 12: Anharmonic Zero-Point Energies Estimated with Second-Order Vibrational Perturbation Theory and either MP2 or mPW1PW with the aug-cc-pVTZ Basis Set

system	MP2	mPW1PW
$Cl(H_2O)^-$	5029	5037
$Cl(D_2O)^-$	3685	3699
$Cl^- \cdots HDO$	4398	4399
$Cl^- \cdots DHO$	4339	4353
H_2O	4621	4655
D_2O	3378	3403
HDO	4010	4035

Because the RB surface is not a global fit, energies evaluated at configurations outside its domain of validity may have spuriously low values even though accurate determination of the energy at these configurations would be high. This is a potential complication for Monte Carlo schemes such as ours that sample the PES very widely. To avoid evaluating such regions on the RB surface, every configuration where the DWX surface, which does have reasonable global behavior, predicted an energy above 80 kcal/mol was assumed to have a negligible contribution in our calculations on the RB surface; the results were quite insensitive to the value of this screening criteria.

The convergence for the partition function with respect to P is slowest for $Cl(H_2O)^-$, with the calculated values for the RB surface being 26%, 11%, 6.1%, 2.7%, and 0.7% higher than the converged result at $P = 32$, 48, 64, 96, and 192, respectively. The equilibrium constants converge significantly more rapidly with P; K_{eq} values for reaction R1 on the RB surface are 2.5%, 1.2%, 0.7%, 0.3%, and 0.07% higher than the converged result at $P = 32$, 48, 64, 96, and 192, respectively.

5.2. Electronic Structure. The inclusion of tight *d* functions on Cl in the basis set results in negligible changes in the optimized structures, and the maximum difference between the frequencies calculated by CCSD(T) with the aug-cc-pVTZ and aug-cc-pV(T+d)Z basis sets is less than 2 cm^{-1}. Similarly, the effect of multireference character seems to be quite modest, with the mean unsigned difference between the harmonic frequencies calculated by the CCSD(T) and icMRCI+Q levels of theory with the aug-cc-pV(Q+d)Z basis set being only 8 cm^{-1} and the optimized structures at these two levels of theory differing negligibly. The mean unsigned difference between harmonic frequencies at the MP2 level with the aug-cc-pV(Q+d)Z and aug-cc-pV(5+d)Z basis sets is only 1.1 cm^{-1}; this, together, with the observation that the convergence of the frequencies with the basis set size is roughly similar at the MP2 and CCSD(T) levels suggests that the harmonic force field is well converged with the aug-cc-pV(Q+d)Z basis set.

5.3. Anharmonicity Estimation and Comparisons to Experiment. For the $Cl(H_2O)^-$ isotopomer, the partition functions calculated by path integrals range from 1.68 to 1.79 times larger than the harmonic values for the same PES, whereas the vibrational perturbation theory values with the aug-cc-pVTZ basis set are both about 1.54 times as large as the harmonic values calculated at the same level of theory. Similar trends are observed for the other isotopomers, and this suggests that second-order vibrational perturbation theory systematically underestimates the vibrational−rotational partition functions for this system.

As shown in Table 11, vibrational perturbation theory based on MP2/aug-cc-pVTZ force constants gives a mean unsigned deviation (MUD) from experimental fundamental frequencies of 24 cm^{-1}, whereas vibrational perturbation theory based on mPW1PW/aug-cc-pVTZ gives a MUD of 52 cm^{-1}. Barone has demonstrated[63] that the PT2 vibrational anharmonicity corrections are relatively insensitive to the correlation treatment and basis set size but that the harmonic frequencies are quite sensitive to both; thus, he suggested that anharmonic fundamental frequencies should be adjusted by the difference between the values of the harmonic frequencies from the best available treatment and the harmonic frequencies with the electronic structure method used for the PT2 calculations. Using CCSD(T)/aug-cc-pV(Q+d)Z harmonic frequencies to adjust the PT2 fundamentals reduces the mean unsigned differences with experiment to 14 and 22 cm^{-1} for MP2/aug-cc-pVTZ and mPW1PW/aug-cc-PVTZ, respectively. These values are comparable to the MUD from experiment of 12 cm^{-1} observed by Rheinecker and Bowman[41] for accurate fundamental frequencies calculated using the MULTIMODE program[73] with the RB PES (adjusting these fundamentals by a harmonic correction leads to a slight reduction of the mean unsigned difference to 11 cm^{-1}). We also considered PT2 based MP2/aug-cc-pVQZ force constants; this yields fundamental frequencies having a MUD from experiment of 26 cm^{-1} or—after adjustment as above using the coupled cluster frequencies—a MUD from experiment of 14 cm^{-1}; these MUDs differ only slightly from the values obtained with the aug-cc-pVTZ basis set.

The anharmonic zero-point energy (ZPE) reported[41] for the RB surface for the $Cl(H_2O)^-$ isotopomer is 5024 cm^{-1}; as seen in Table 12, this agrees well with the PT2 estimates of 5029 and 5037 cm^{-1} calculated with MP2 and mPW1PW, respectively, with the aug-cc-pVTZ basis set. Good agreement is also observed between the accurate H_2O ZPE of 4638 cm^{-1} and the PT2 estimates of 4655 and 4733 cm^{-1}, calculated with MP2 and mPW1PW, respectively. The change in the ZPE for reaction R1 with MP2/aug-cc-pVTZ force constants is estimated to be -92 cm^{-1} in the harmonic limit and -101 cm^{-1} with PT2 anharmonicity, and with mPW1PW/aug-cc-pVTZ force constants the ZPE change is estimated to be -86 cm^{-1} in the harmonic limit and -87 cm^{-1} with PT2 anharmonicity. Thus, harmonic estimates of the ZPE change are quite reasonable even though the harmonic estimates of the absolute ZPEs are of low accuracy.

It is also interesting to note that using the MP2/aug-cc-pVTZ PT2 ZPE, we have $\exp(-\beta\Delta E^{ZPE}) = 1.63$, and if this value was used to estimate the vibrational contribution to the equilibrium constant and combined with translational and rotational factors of 0.9022 and 0.5535, respectively, we would obtain an estimate for K_{eq} of 0.81 which agrees poorly with the value $K_{eq} = 1.011$ obtained using the accurate PT2 vibrational−rotational partition functions. We conclude that K_{eq} is not dominated by contributions from the ZPE at this temperature.

The most striking observation concerning the K_{eq} calculations is that the experimental values differ significantly from each of the theoretical estimates; for example, Table 10 shows that the PI values calculated with the RB PES are 24%, 52%, and 22% higher than the experimental values for reactions R1, R2, and R3, respectively. Surprisingly, for each PES the PI calculations of the K_{eq} agree with the HORR calculations to within better than 2% even though anharmonicity has a large effect on the individual partition functions. The equilibrium constants calculated via PT2 all agree with HORR estimates corresponding to the same set of quadratic force constants within better than 6%. The accurate equilibrium constants for the MDWX and RB PESs all agree to within 3.5% or better, whereas the values for the DWX PES differ from those of the RB surface by from 11% to 27%; however, this is not too surprising because the DWX surface yields poor agreement with the experimental[30] frequencies as well. All of the equilibrium constants calculated by using frequencies from electronic structure calculations with the HORR approximation agree with each other to within a few percent.

6. Concluding Remarks

We have presented two modifications to our Feynman path integral algorithms for calculating accurate partition functions. The sequential sectioning method provides a simple means to generate random free-particle paths with a cost that scales as $O(P)$; compared to the bisection method, this scheme is both less expensive and more general (because it may be used for any value of P and for arbitrary time slice distributions). A stratified sampling scheme involving the energy of the path centroids was described and was observed to yield improvements in efficiency of as much as 2 orders of magnitude. Equilibrium constants for the fractionation of chloride ions in complexes with isotopomers of water were calculated for three different potential energy surfaces via PI methods. A very large discrepancy is observed between all of the results for these potential surfaces and the experimental ICR measurements. Although anharmonicity has a large effect on the partition functions, the equilibrium constants calculated with the harmonic oscillator rigid rotator approximation agree surprisingly well with the accurate calculations—to within better than 2% in all cases. A number of electronic structure calculations were also performed, some using vibrational perturbation theory estimates of the anharmonicity and others employing the harmonic approximation, in order to test the sensitivity of the results to various types of basis sets and electron correlation treatment. All of these calculations displayed good agreement with the results for the RB analytical surface; the present study therefore suggests that the RB surface and the PI partition functions calculated with it are reasonably accurate and that the experimental−theoretical discrepancy is not likely to be resolved by further refinements to the potential energy surface. In view of these findings, we suggest that additional experimental work on this system would be useful.

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Supporting Information Available: Tables of harmonic frequencies for the two isomers of $Cl(HDO)^-$, $Cl(D_2O)^-$, H_2O, HDO, and D_2O and optimized configurations for H_2O for various potential energy surfaces and methods of electronic structure theory, versions of Tables 7 and 8 with more significant figures, and a discussion of the calculation of statistical uncertainly estimates. This material is available free of charge via the Internet at http://pubs.acs.org.

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