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An Accurate Theoretical Prediction of the Zero Point Vibrational Energy of CH_5^+

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A recently developed signal processing method has been applied to a time evolved Gaussian wave packet roughly corresponding to the ground vibrational state of protonated methane at time zero. The time evolution of the wave packet was described by semiclassical initial value representation theory where classical trajectories are used to evaluate the quantum mechanical propagator, $\exp[-i\hat{H}t/\hbar]$. We show that only about 25 000 relatively short time trajectories are necessary to yield a well converged eigenvalue of the ground vibrational state. The calculations reveal an unusually large red shift of 448 cm^{-1} from the harmonic zero point level placing the ground state at 10 973 cm^{-1}, with a statistical error of ±30 cm^{-1}. These results agree remarkably well with full-dimensionality quantum mechanical calculations.

The challenge of the methonium ion (protonated methane), CH_5^+, has captured the interest of spectroscopists and theoreticians for the past few decades.[1,2] A series of high level ab initio calculations have revealed an extremely floppy molecule by identifying three unique, nearly isoenergetic structures connected by low barriers.[3,4] Furthermore, the inclusion of (harmonic) vibrational zero point energy seems to completely delocalize proton motion.[3−5] Such nature of a "fluxional proton" system may introduce strong nonadiabatic effects due to the coupling of electron and proton motions. Marx and Parrinello[6] examined this possibility by performing path integral calculations treating the electrons and the nuclei on equal footing. The quantum calculations suggested that two hydrogen groups consisting of two and three atoms centered on the carbon define two regions of vibrational density where the hydrogens freely scramble. The study also inferred a less dramatic picture of scrambling protons in the ground state, as thought before, and thus gave support to the possibility of a structured CH_5^+, consistent with the canonical picture of hypercoordinated carbocations.

If the system is indeed highly fluxional, i.e., undergoing large amplitude motion, can one expect to see an unusually large red shift in the zero point level from its harmonic value? To answer this question quantitatively, we need to perform full dimensionality quantum mechanical calculations on a potential energy surface that encompasses all the dynamically important regions in the configuration space. Until recently, most quantum mechanical methods have been limited in performance for systems of six and more atoms. In particular, basis set and discrete variable representation methods require diagonalization of prohibitively large matrices for even as few as five vibrational degrees of freedom. Other popular non basis set methods, such as path integrals and Green's function methods, have the suitable scaling properties for calculating high dimensional systems, but one faces either challenges of Monte Carlo convergence due to the fast oscillating phase, i.e., the path integral sign problem, or the construction of exact Green's function. A new study by McCoy et. al.,[7] appearing earlier in this issue, has changed the situation for CH_5^+. A high quality global potential energy surface is now available[8] and has been used for diffusion Monte Carlo calculations.[7] The authors report a value for the zero point energy that serves as a basis for comparison for the calculations presented here.

Monte Carlo based semiclassical (SC) methods, specifically the initial value representation theory (IVR),[9] have shown to be a practical alternative to quantum dynamics. At the cost of propagating classical trajectories, one has the ability of describing purely quantum effects, such as probabilities, superposition of states (interferences), tunneling, etc.[10] It has also been shown that SC-IVR, together with various integrand smoothing techniques, can be very effective in calculating time dependent correlation functions that yield accurate vibrational eigenvalues for polyatomic systems.[11]

A spectral density of molecular Hamiltonian can be written as

$$I(E) \equiv \langle \psi | \delta(E - \hat{H}) | \psi \rangle \tag{1}$$

where ψ is a conveniently chosen reference state that has an optimal overlap with the desired spectral range. If one were interested in a specific group of eigenstates, then the reference state would be chosen as close as possible to the corresponding eigenfunctions so that their "peaks" in the spectrum were dominant. Casting eq 1 in a Fourier integral form allows us to re-express the spectral density in the time domain,

$$I(E) = \frac{\mathrm{Re}}{\pi\hbar}\int_0^{\infty} \mathrm{d}t\, \mathrm{e}^{(i/\hbar)Et} c(t) \tag{2}$$

where the time dependent quantity is the autocorrelation function,

$$c(t) \equiv \langle \psi | \psi(t) \rangle = \langle \psi | \mathrm{e}^{-(i/\hbar)\hat{H}t} | \psi \rangle \tag{3}$$

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Applying the semiclassical Herman−Kluk (HK) approximation[12] to the time evolution operator, we obtain the correlation function in the following form,

$$c(t) = \frac{1}{(2\pi\hbar)^F}\int d\mathbf{p}_0 \int d\mathbf{q}_0\, C_t e^{(i/\hbar)S_t}\langle\psi|\mathbf{p}_t\mathbf{q}_t\rangle\langle\mathbf{p}_0\mathbf{q}_0|\psi\rangle \qquad (4)$$

for a system with F degrees of freedom (here, $F = 12$ vibrational modes). In the above expression $\mathbf{p}_0$ and $\mathbf{q}_0$ are the initial momenta and coordinates of classical trajectories, and $\mathbf{p}_t(\mathbf{p}_0,\mathbf{q}_0)$ and $\mathbf{q}_t(\mathbf{p}_0,\mathbf{q}_0)$ are their respective values propagated to time t along with the classical action integral, $S_t(\mathbf{p}_0,\mathbf{q}_0)$ and the Herman−Kluk preexponential factor, $C_t(\mathbf{p}_0,\mathbf{q}_0)$. The wave function for the coherent state is,

$$\langle\mathbf{q}|\mathbf{p}_t\mathbf{q}_t\rangle = \left(\frac{\gamma}{\pi}\right)^{F/4}\exp\left[-\frac{\gamma}{2}(\mathbf{q}-\mathbf{q}_t)^2 + \frac{i}{\hbar}\mathbf{p}_t(\mathbf{q}-\mathbf{q}_t)\right] \qquad (5)$$

Here γ is a diagonal matrix of Gaussian width parameters, which are determined according to practical considerations, as will be mentioned below. The essential task is to carry out the integration over the initial conditions in eq 4 via Monte Carlo sampling and to solve the classical equations of motion for each initial $(\mathbf{p}_0,\mathbf{q}_0)$ phase point (trajectory). The "effort" scales linearly with the number of degrees of freedom, and this is perhaps the main reason the SC-IVR is amenable to large scale calculations.

As was mentioned above, the choice of ψ determines the spectral shape. Because, at present, we are interested particularly in the zero point energy, i.e., the lowest energy eigenvalue, it is desirable to use for the reference state the closest possible approximation to the exact ground state. One can take the normal mode wave function at a stationary point so that

$$\langle\mathbf{q}|\psi\rangle = \left(\frac{\omega}{\pi}\right)^{F/4}\exp\left[-\frac{\omega}{2}(\mathbf{q}-\bar{\mathbf{q}})^2\right] \qquad (6)$$

where $\bar{\mathbf{q}}$ can be a local minimum or a transition state on the potential energy surface. The choice of the coherent state width parameter is simply $\gamma_j = \omega_j$ for the mass scaled normal coordinate j. It is well-known that the topology of CH_5^+ has several low energy configurations that are essentially dynamically equivalent after the inclusion of zero point motion. However, it may be advantageous to choose a configuration with most symmetry, such as a transition state structure connecting two identical minima. The C_{2v} saddle point, which is a low energy transition state between two global minimum configurations C_s, is the most suitable choice for present calculations.

Figure 1 shows the correlation function $c(t)$ computed as prescribed by eqs 4−6. One can see that the curve is well behaved at shorter times; i.e., the amplitude is smooth and remains within the physical bounds for the first twenty or so periods. The longer time dynamics introduces error that is inherent to the approximate nature of the semiclassical propagator and is practically impossible to control without performing a filtering procedure a priori. (By that we mean smoothing of the integrand in eq 4 before carrying out the phase space integration.) Such methods tend to reduce the number of trajectories required to converge the result, i.e., time signal $c(t)$ or any other physical property that can be defined using HK-IVR. However, spectral resolution remains a weak point because it is based purely on the Fourier transformation of the signal. Short signals lack resolution and longer ones are inaccurate (Figure 1). In this work, we use a much more sophisticated error reduction and noise filtering procedure that not only can achieve adequate resolution using a short time signal, which in HK-IVR is closer to convergence than a longer time one, but also requires a smaller number of initially well placed trajectories to compute the phase space integral as the short time signal has less error to average out. It is also possible to combine integrand smoothing with signal processing.

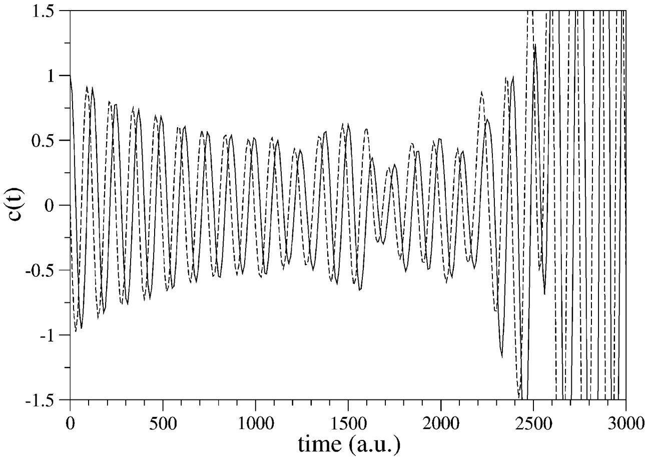

Figure 1. Real (solid) and imaginary (dash) parts of the correlation function $c(t)$ defined by eqs 4−6. The calculation was done with 25 600 trajectories sampled from a normal distribution: $\exp[-\omega\Delta\mathbf{q}^2/2]$ $\exp[-\Delta\mathbf{p}^2/2\omega]$. The signal acquires a large error shortly after $t = 2500$ au.

Here, as in the previous work, the signal is assumed to be decomposable into a sum of the true signal and the error term as[13,14]

$$c(t) = x(t) + \epsilon(t). \qquad (7)$$

Calculation of $x(t)$, given as $c(t)$, is done by employing Cadzow's method of regularization,[15,16] which in turn uses singular value decomposition (SVD) of a data matrix in which the true signal is assumed to have the following analytical form,

$$x(t) = \sum_{k=1}^{K} d_k \exp(-iE_k t) \qquad (8)$$

where E_k is the eigenvalue corresponding to the eigenfunction Ψ_k and d_k is the weight factor whose true value is $|\langle\psi|\Psi_k\rangle|^2$. The form is valid for any correlation function signal generated by quantum mechanics. SVD yields a signal much closer to $x(t)$ than the original $c(t)$. The "cleaned", here rank $K = 2$, signal is then input into a harmonic inversion (HI) program to extract the E_k and d_k parameters.

In Figure 2 one can see the singular values. The two separated points on the graph indicate that these singular values and their eigenvectors alone can be used to approximate $x(t)$. The other singular values are due to error. The gap between the two sets can be thought of as an indication that the space implied by the Hankel data matrix made from $c(t)$ can be partitioned into a (true) signal subspace with a noise subspace as its orthogonal compliment. Perturbation theory tells us that the larger the gap the less the noise space perturbs the signal space. This allows us to construct $x(t)$ from the projection of the signal state vectors taken as columns of the data matrix onto the signal subspace. The HI scheme using the rank $K = 2$ clean signal yields two complex E_k and two complex d_k parameters (E_k, d_k; $k = 1, 2$) specifying two complex Lorentzians. The weight factor of one of those Lorentzians is orders of magnitude smaller than the other's ($|d_2| \ll |d_1|$), and its width is very large, indicating that it is fitting the background seen in Figure 3. The other

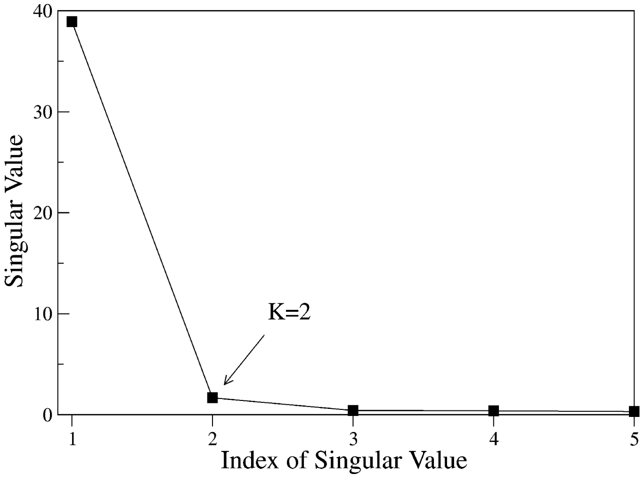

Figure 2. First five singular values of the data matrix constructed from the windowed signal. (The rest of the 120 total singular values are on the order of $10^{-3}-10^{-7}$ and are not shown.) The easily noticeable gap is an indicator that the space of only two singular values is contained in signal $c(t)$.

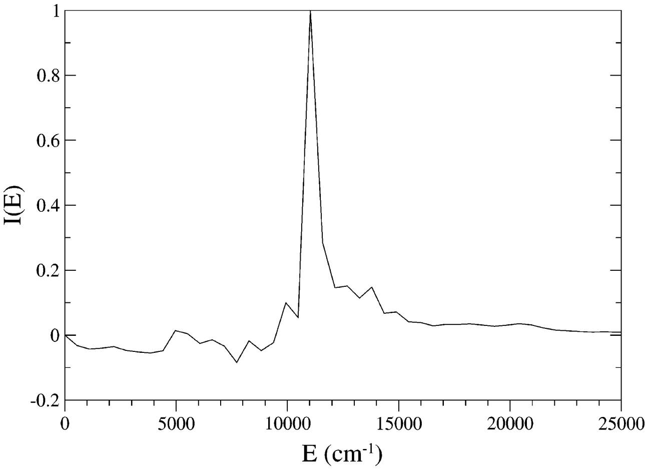

Figure 3. Fourier transform of the correlation function shown in Figure 1 on the time interval [0, 2500] au. The zero point peak is identified at 11 032 ± 552 cm^{-1}. The low resolution of the discrete Fourier transform poses severe limitations on accurate spectral analysis.

Lorentzian ($k = 1$) has a narrow width, and its position yields our result.

Our best estimate of the zero point energy of CH_5^+ is 10 973 cm^{-1}, with a statistical error of ±30 cm^{-1} based on the average of several independent signals. (Compare this value with the one from the Fourier transform: 11 032 ± 552 cm^{-1}.) This is a fairly large anharmonic correction (~3.9%) given that the harmonic zero point level at the C_s minimum is 11 421 cm^{-1}. For comparison, the zero point energy stabilization in methane, based on a calculation using a realistic potential energy surface,[17] is 127 cm^{-1}, which is merely ~1.3%. Clearly, adding a proton to methane causes strong delocalization effects in the ground vibrational state. It is thus fair to assume that anharmonicity will be even more pronounced in the excited states suggesting that quantum calculations will be extremely difficult to converge in those cases.

Besides the work of Marx and Parrinello,[6] who considered excited vibrational states implicitly by taking into account the temperature effects,[18] the ongoing work of McCoy et al.[7] has calculated the ground-state energy and properties using diffusion Monte Carlo methods. Their independent estimate of the zero point energy, for example, is ~2 cm^{-1} above the one reported here. This is an encouraging result showing that two completely different approaches lead to essentially the same conclusion for an inherently difficult system. However, to better understand the fluxional character of CH_5^+ and especially to explain the experimentally observed infrared spectrum,[19] further work needs to be done. The combination of SC-IVR and signal processing can be effectively used to extract the excited states, simply by taking different reference states in eq 6. Similarly, the infrared spectrum can be calculated given the corresponding dipole moment function. Another possibility is to examine the temperature effect on quantum mechanical expectation values of interatomic distances, bond angles, rotation constants, etc., using the global potential energy surface.

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