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LETTERS

Ab Initio Diffusion Monte Carlo Calculations of the Quantum Behavior of CH_5^+ in Full Dimensionality

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We report an ab initio calculation of the potential surface, quantum structures, and zero-point energies of CH_5^+ and $CH_2D_3^+$ in full dimensionality. This potential energy surface is a very precise fit to 20 633 ab initio energies and an even larger data set of potential gradients, obtained at the MP2/cc-pVTZ level of theory/basis. The potential, which exactly obeys the permutational symmetry of the five hydrogen atoms, is used in diffusion Monte Carlo (DMC) calculations of the fully anharmonic zero-point energies and ground-state wave functions of CH_5^+ and $CH_2D_3^+$. Bond length distributions are obtained from the DMC ground state and are compared to those resulting from classical molecular dynamics simulations, which are performed at the quantum zero-point energy for roughly 300 picoseconds.

The structure and dynamics of CH_5^+ has been a problem of long-standing interest in chemistry owing to its unusual, three-center, two-electron bonding and the very small barriers to internal scrambling of the hydrogen atoms. It is also of practical interest due to its role in interstellar and combustion chemistry. A recent, and still unassigned, spectrum of this molecule[1] in the 2750−3150 cm^{-1} region poses a major challenge to theory and computation. Several overviews and perspectives on this fascinating cation have appeared recently,[2,3] and so we do not attempt to repeat the excellent reviews and comments made there. An important outstanding issue is whether this molecule has a well-defined structure that is truly stationary or perhaps just transiently so. Some evidence that the motion is highly fluxional but with significant structure was concluded by Marx and Parrinello.[4] They used density functional theory in direct electronic-nuclear path integral calculations of the structure. The zero-point energy and ground-state wave function were not obtained in this study. In their latest perspective on the subject,[2] these authors called for a full dimensional, high quality potential energy surface and quantum calculations of the nuclear motion. In the most recent summary of the state of the art Schreiner writes “Clearly, this [the conclusions of Marx and Parinello[4] on fluxionality with some structure in a statistical sense] is an uncomfortable situation for chemists who require that a stable molecule, which CH_5^+ obviously is, ... must have [a] structure.”

These challenges to theory and computation stimulated us to develop a potential energy surface and to examine the quantum motion of the nuclei in full dimensionality. In a very recent paper[5] we reported a potential energy surface for CH_5^+, using

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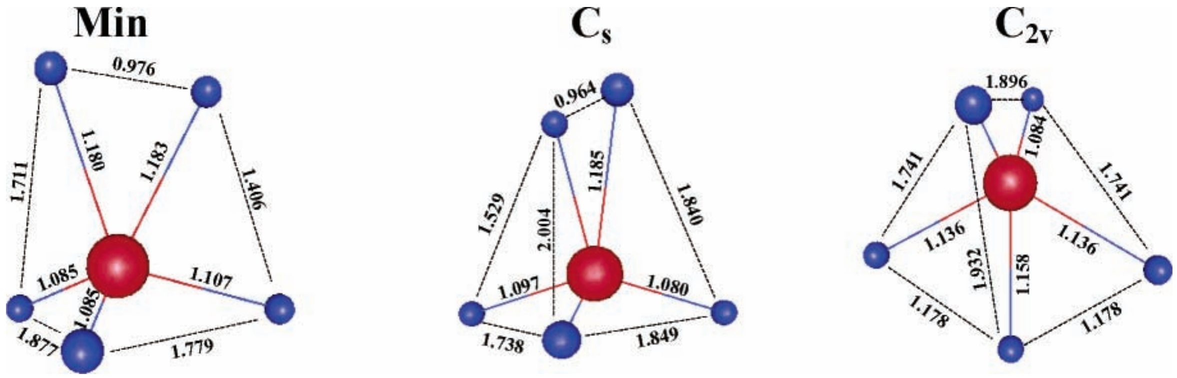

Figure 1. Structures of CH_5^+ at minimum (Min), the "rotation" (C_s) saddle point, and the "flip" (C_{2v}) saddle point. The red atom represents carbon, and the five blue atoms are the five hydrogen atoms. The atom−atom distances are reported in Å.

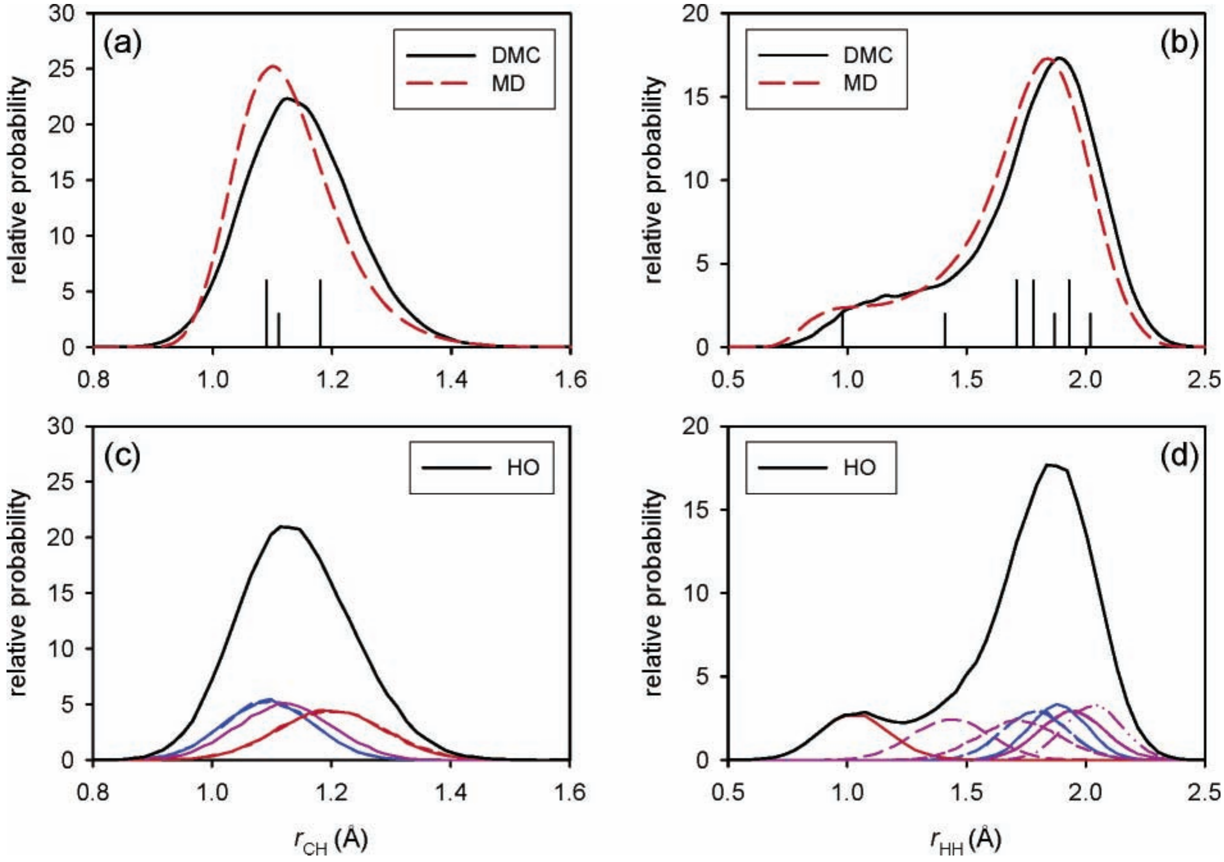

Figure 2. Plots of projections of the ground-state density onto (a) r_{CH} and (b) r_{HH}, described in the text. In all cases, solid black lines represent the DMC results, dashed red lines show the distributions from the MD simulations, and the stick heights indicate the relative frequency of a given equilibrium distance. In (c) and (d) the corresponding harmonic distributions are plotted. Here the blue, red, and purple curves provide the distributions for individual hydrogen atoms, and the black curve provides the sum of these distributions.

direct classical dynamics to generate thousands of ab initio energies and gradients, at the MP2/cc-pVTZ level of theory/basis set. We chose this level of theory and basis as a compromise between accuracy and computational efficiency. The potential fit was limited to configurations with energies up to 8000 cm^{-1} above the potential minimum. The fit to the 13 014 ab initio energies (and a much larger data set of gradients) was done in a manner that ensured that the potential is symmetric with respect to the permutation of the five hydrogen atoms. To perform diffusion Monte Carlo (DMC) calculations of the zero-point energy and ground state wave function, the potential fit had to be extended considerably to regions of configuration space sampled by the DMC wave function. This was done by adding 7619 ab initio electronic energies, obtained with MOLPRO,[6] to the previous data set and refitting the larger data set. The new fit contains 2303 coefficients and has an rms fitting error of 51.0 cm^{-1} for the entire data set. For potential values less than or equal to 20 000 cm^{-1}, the rms fitting error is 17.9 cm^{-1}. The geometries at the minimum and at the C_s and C_{2v} saddle points are fit virtually perfectly and the energies of the saddle points, 43 and 193 cm^{-1}, are within 1 cm^{-1} of the corresponding ab initio values. They also are in good accord with the best ab initio estimates of ~30 and ~287 cm^{-1}, respectively,[7] which were obtained with larger basis sets and more accurate (and much more computationally intensive) methods than are used here. The structures at the potential minimum and at these two saddle points are shown in Figure 1. As seen, the minimum energy structure can be represented by $[CH_3-H_2]^+$.

This potential energy surface was used for DMC[8-10] and standard molecular dynamics (MD) calculations. The DMC calculations provide the ground state wave function and energy

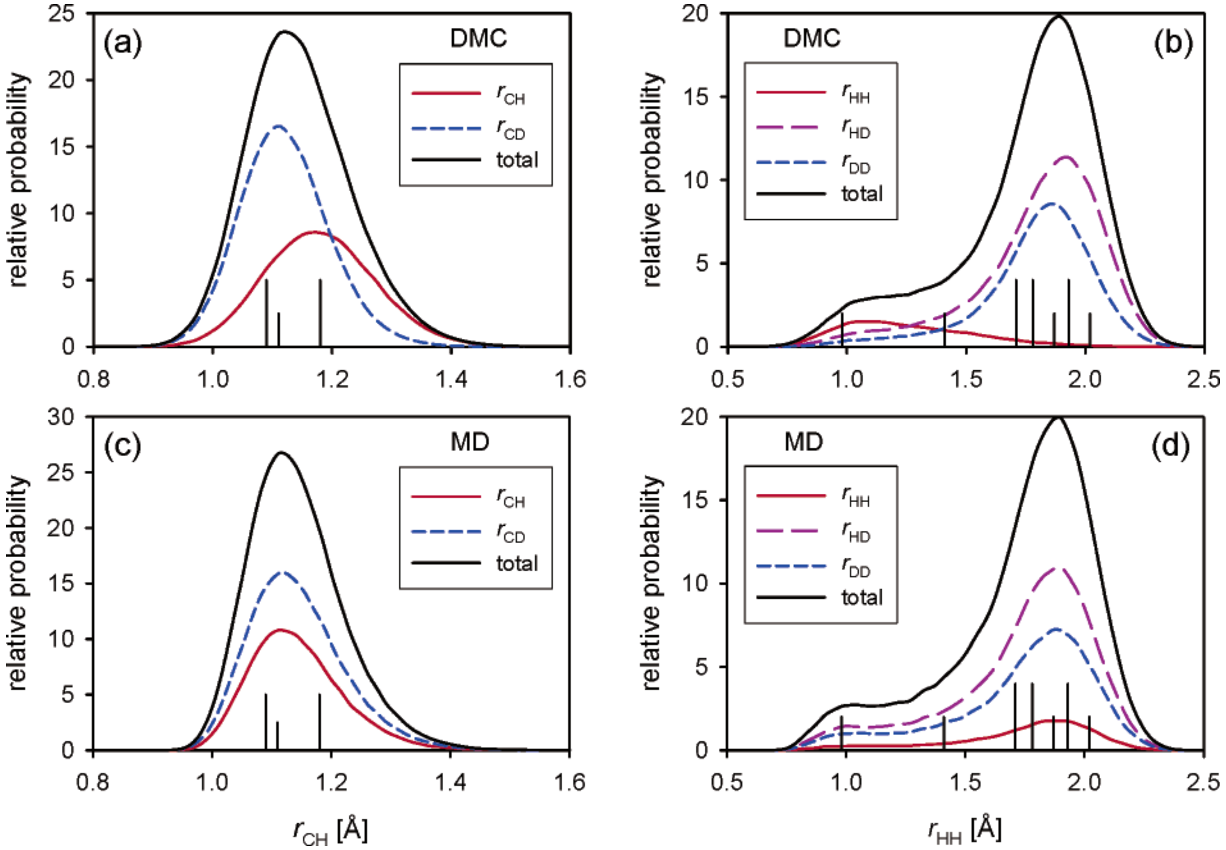

Figure 3. Plots of the distance distributions for $CH_2D_3^+$. The results from the DMC simulations are plotted in (a) and (b), and the MD results are shown in (c) and (d). Black lines provide the full distribution with solid red lines giving the distributions for r_{CH} and r_{HH}; the short-dashed, blue lines the distributions for r_{CD} and r_{DD} distances and the dashed purple lines the distributions for r_{HD}. The heights of the black vertical lines indicate the relative frequency of a given equilibrium distance.

for zero total angular momentum. Thus, this spatial wave function is correctly totally symmetric with respect to exchange of any two hydrogen atoms. Details of the DMC calculations can be found in the Supporting Information. For the MD calculations, a trajectory was initiated at the potential minimum and the initial momenta of the atoms were selected randomly, adjusted so that the total angular momentum is zero and then readjusted by a uniform constant to give a total energy equal to the DMC zero-point energy. The trajectory was propagated by a high order predictor-corrector method for roughly 300 ps and appears to have ergodically sampled the energetically accessible phase space.

For CH_5^+, we calculate a zero-point energy of 10 975(5) cm^{-1}, where the number in parentheses provides an uncertainty that is equal to one standard deviation in the DMC energy. This value can be compared to the value obtained by performing a harmonic analysis at the minimum on the surface, which gives a zero-point energy of 11 421 cm^{-1}. For the partially deuterated $CH_2D_3^+$ the DMC zero-point energy is 9148(15) cm^{-1}, whereas the corresponding harmonic values are between 9454 and 9714 cm^{-1}, depending on where the deuterium substitutions are made; the lowest value corresponds to a $[CD_3-H_2]^+$ configuration.

It is not surprising that the DMC zero-point energies are lower than the harmonic values. The lowering is 4% of the harmonic estimate, and this is roughly twice the corresponding value for CH_4,[11] which is strongly bound, but comparable to the percent lowering in the fairly floppy protonated water dimer, $H_5O_2^+$.[12] Thus, the percent lowering of the true zero-point energy is an indication of the expected delocalization/floppiness of the ground-state wave function over the multiple minima, which are separated by very low barriers.

This putative delocalization is investigated through an analysis of the distributions of all the bond lengths. Due to the high symmetry and low barriers between the 120 distinct minima on the CH_5^+ potential surface, all five CH bonds are, on average, equivalent, as are all ten HH bonds. For $CH_2D_3^+$, we can distinguish between the r_{CH} and r_{CD} distributions as well as the r_{HH}, r_{HD}, and r_{DD} distributions. Differences in the widths of these distributions compared to the corresponding distributions in CH_5^+ will reflect localization of the hydrogen and deuterium in the ground state of $CH_2D_3^+$.

We plot distributions of r_{CH} and r_{HH} from the ground-state density in Figure 2. For comparison, we also report the distributions that are obtained from the standard molecular dynamics simulations, the distributions from a harmonic ground-state density (HO), and a stick representation of the CH and HH bond lengths in the equilibrium configuration of CH_5^+. Here, the harmonic distributions are obtained using the conventional description, in which the wave function is localized in a single minimum and the potential is approximated by a quadratic expansion about this minimum. As such, we plot separate distributions for each of the CH and HH bonds, where each distribution is centered on one of the distances from the equilibrium configuration. In contrast, the MD distribution and the DMC ground state appear to be delocalized over all minima, and all of the CH and HH distance distributions are identical, providing evidence that the MD trajectory is ergodically sampling the potential.

Although the classical trajectory is delocalized over all of the equivalent minima, the distribution function for r_{HH} shows definite structure that is consistent with the picture that, on average, the ion resembles the $[CH_3-H_2]^+$ minimum energy structure, shown in Figure 1, with one HH distance that is much shorter than the other nine. The DMC radial distribution functions resemble the MD ones; however, there are quantitative differences. A similar structure was also noted by Marx and Parrinello.[2] As such, we consider the ground state of CH_5^+ as being highly delocalized in several of the twelve vibrational coordinates, including the two vibrational motions that connect the global minima to the two saddle points, shown in Figure 1, whereas the motions are localized in the majority of the CH and HH stretching vibrations.

The distributions of bond lengths become more structured and the differences between MD and DMC results become even sharper when some of the hydrogen atoms are replaced by heavier isotopes. In the discussion that follows we focus on the $CH_2D_3^+$ isotopomer, although similar behavior is seen in all four partially deuterated isotopomers of CH_5^+.[13] Based on the C_s symmetry of the equilibrium structure, there are seven minima for the $CH_2D_3^+$ system that cannot be connected by either exchange of identical atoms or reflection in the symmetry plane. Even within the Born−Oppenheimer approximation, which provides a potential surface for which all 120 potential minima are identical, the zero-point energy will depend on the locations of the hydrogen atoms.

Because the zero-point energy is still much larger than the barriers between the minima, the classical trajectory that is run at the zero-point energy samples all of the minima with equal probability. As a result, the distributions, plotted in Figure 3c,d, are nearly identical to the corresponding r_{CH} or r_{HH} distributions for CH_5^+. In contrast, the distributions that are based on the DMC ground state deviate substantially from the corresponding picture for CH_5^+. The r_{CH} and r_{CD} distributions are plotted in Figure 3a. The r_{CH} distribution is shifted to larger values of r_{CH}, whereas the r_{CD} distribution is shifted to smaller values. Even more striking is the fact that the r_{HH} distribution is peaked at the shortest values of r_{HH} and decreases monotonically with increasing r_{HH}, see Figure 3b. The r_{HD} distribution resembles the r_{HH} distribution from CH_5^+ but is shifted to larger r_{HD} values. Based on the plots in Figure 3 there is a clear difference between the quantum and classical descriptions of this ion. The DMC structure clearly favors the $[CD_3-H_2]^+$ arrangement, whereas the MD trajectory appears to ergodically sample all of the minima. Interestingly, this is the lowest energy structure, based on the harmonic zero-point energies. Despite the greater localization of the DMC ground state, it remains much more delocalized than the corresponding harmonic picture.

From the above discussion, it is clear that CH_5^+ has structure. Even in the classical description, the propensity of the hydrogen atoms in CH_5^+ to partition into one group that forms a H_2 unit and another group that forms a CH_3^+ unit is clearly seen. On the other hand, when the permutational symmetry of the ion is lowered through partial deuteration, the quantum mechanical description of the ion shows a strongly nonstatistical localization of the ion into a subset of the minima. As CH_5^+ is subjected to further studies, it will be interesting to see if reduced dimensional models or approaches that are based on a single reference geometry can describe the spectroscopy and dynamics of this ion, which clearly represents an intermediate case between the highly structured and fully fluxional limits. It will also provide a challenging system for semiclassical methods; however, recent calculations using the current potential surface look quite promising.[14]

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Supporting Information Available: Details of the fit and the DMC and MD calculations. The material is available free of charge via the Internet at http://pubs.acs.org

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