Classical and quasiclassical spectral analysis of CH_5^+ using an *ab initio* potential energy surface

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We report a potential energy surface and calculations of power spectra for CH_5^+. The potential surface is obtained by precise fitting of MP2/cc-pVTZ electronic energies and gradients, which are obtained in classical direct-dynamics calculations. The power spectra are obtained using standard microcanonical classical and novel quasiclassical calculations of the velocity autocorrelation function, from which the power spectrum is obtained in the usual way. Both calculations agree qualitatively that the overall spectrum is quite complex; however, the latter calculations indicate that some spectral features may be assignable. © *2003 American Institute of Physics.*
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The structure and dynamics of CH_5^+ is a problem of long-standing interest.[1] Numerous quantum chemical studies[2–3] have been performed to characterize the relative energetics, and, in some reports, the normal modes of the low-lying stationary points on the potential energy surface. These studies have focused on the relative energetics of the C_s(I), C_s(II), and C_{2v} isomers. The general conclusion is that while the C_s(I) structure is the global minimum, once zero-point energy is taken into account (in the harmonic approximation), there may be no barrier to complete hydrogen scrambling. Indeed, the fluxional nature of CH_5^+ has been borne out in several direct-dynamics calculations.[4,5] The most relevant ones to the present report are those of Tse *et al.*,[5] who obtained the vibrational density of states using local DFT Car-Parrinello molecular dynamics. The classical dynamics calculations were run for 6.4 picoseconds (ps) and at 300 K. The implications of the possible facile interchange of the five identical H atoms on the rotational spectrum has been analyzed in a rigid-rotor model by Bunker and co-workers.[6]

The only experimental work reported on the spectrum of CH_5^+ has been that of Oka and co-workers,[7] who measured 900 lines in the region 2770–3150 cm^{-1}. Despite the heroic efforts to measure the spectrum, it remains completely unassigned.

Detailed classical or quantum calculations of the dynamics of CH_5^+, beyond the direct-dynamics DFT calculations, have been hindered due to the lack of a potential energy surface (PES). We have obtained the first PES (and dipole moment) using extensive direct-dynamics calculations of the potential and gradient at the MP2 level of theory with cc-pVDZ and cc-pVTZ basis sets,[8] as implemented in MOLPRO.[9] Several PESs in the 15 internuclear distances (redundant internal coordinates) have been fit to these data and then used in extensive classical simulations of the dynamics. Details of these calculations and calculations of the dipole moment surface will be presented elsewhere. In this Communication, we report briefly on the PES (using data obtained with the cc-pVTZ basis) and present standard classical and novel quasiclassical calculations of the power spectra, using this new potential surface.

As noted, the new PES is based on classical direct-dynamics calculations, which were done using total energies ranging from roughly 1000 to 8000 cm^{-1} above the global minimum. These trajectories were initiated at the global minimum and run for approximately 8200 integration steps, i.e., 1 to 8 ps depending on the size of the integration time step, with the constraint of zero total angular momentum, but otherwise with a microcanonical distribution of initial momenta. The potential energy and gradient data generated from these trajectories were fit to an analytical multinomial expression, using as variables the complete set of inverse internuclear distances. A total of 4096 unique geometries were used in the fit, which has the full permutational symmetry built into the functional form. The resulting expression consists of 1912 independent terms of total degree seven or less. The dipole moment was also obtained and fit. The details of this fitting and tests of the accuracy of the fit will be

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TABLE I. Harmonic vibrational frequencies (cm^{-1}) of CH_5^+ , at the global C_s(I) minimum from MP2/ cc-pVTZ *ab initio* calculations and the new potential fit (PES).

Mode no.	Symmetry	PES	*Ab initio*
12	A''	3272.4	3272.7
11	A'	3171.0	3170.9
10	A'	3034.6	3035.4
9	A'	2718.8	2719.4
8	A'	2522.3	2522.7
7	A'	1579.4	1580.6
6	A''	1496.2	1499.0
5	A'	1473.3	1474.2
4	A''	1302.1	1301.2
3	A'	1287.3	1289.1
2	A'	744.5	748.6
1	A''	239.8	244.5

given elsewhere; however, we note that the fit reproduced the *ab initio* potential data with an rms fitting error of several wavenumbers and that properties such as relative energetics of the minimum and saddle points as well as normal mode frequencies of the three stationary points were also obtained with extremely high precision, e.g., frequencies to

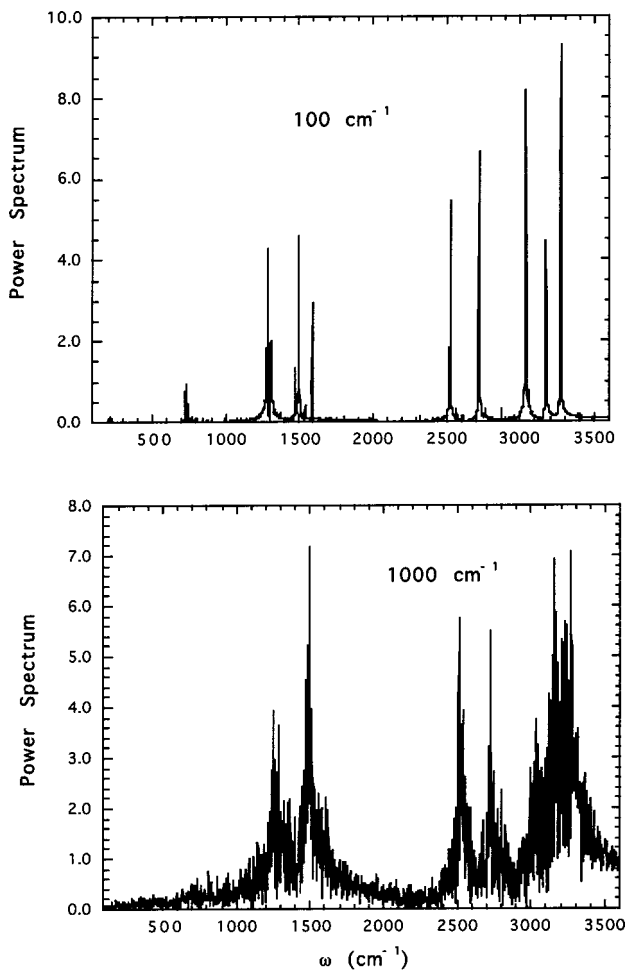

FIG. 1. Classical power spectrum for CH_5^+ obtained from the Fourier transform of the velocity correlation function averaged over ten 15.8 ps trajectories run at a fixed energy of 100 cm^{-1} (upper panel) and 1000 cm^{-1} (lower panel).

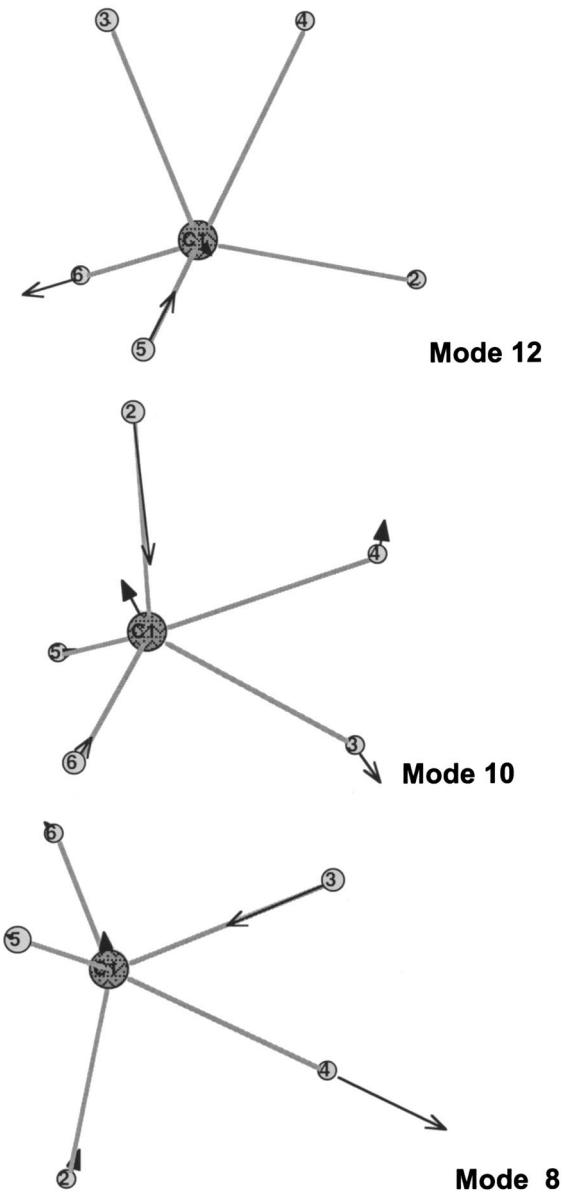

FIG. 2. Mass-scaled normal modes 12, 10, and 8 listed in Table I.

within a few wavenumbers of the *ab initio* results. A comparison of these frequencies at the global minimum is given in Table I.

This PES was used in extensive classical calculations of the dynamics, over time scales much longer than were used in the direct-dynamics calculations. The dynamics calculations were carried out as described above for the purpose of fitting. Standard power and infrared spectra were obtained (by Fourier transformation of the appropriate correlation function), as a function of total energy instead of temperature. The resulting power spectra are shown in Fig. 1 for two total energies. At the lower energy of 100 cm^{-1}, corresponding to 8.3 cm^{-1} per mode, the spectrum is quite simple and the peak positions correspond very well to the normal mode frequencies, as expected. At 1000 cm^{-1}, which corresponds to 83 cm^{-1} per mode, the spectrum is complex and cannot be simply assigned, although remnants of the most intense harmonic peaks seen in the 100 cm^{-1}-spectrum are clearly seen.

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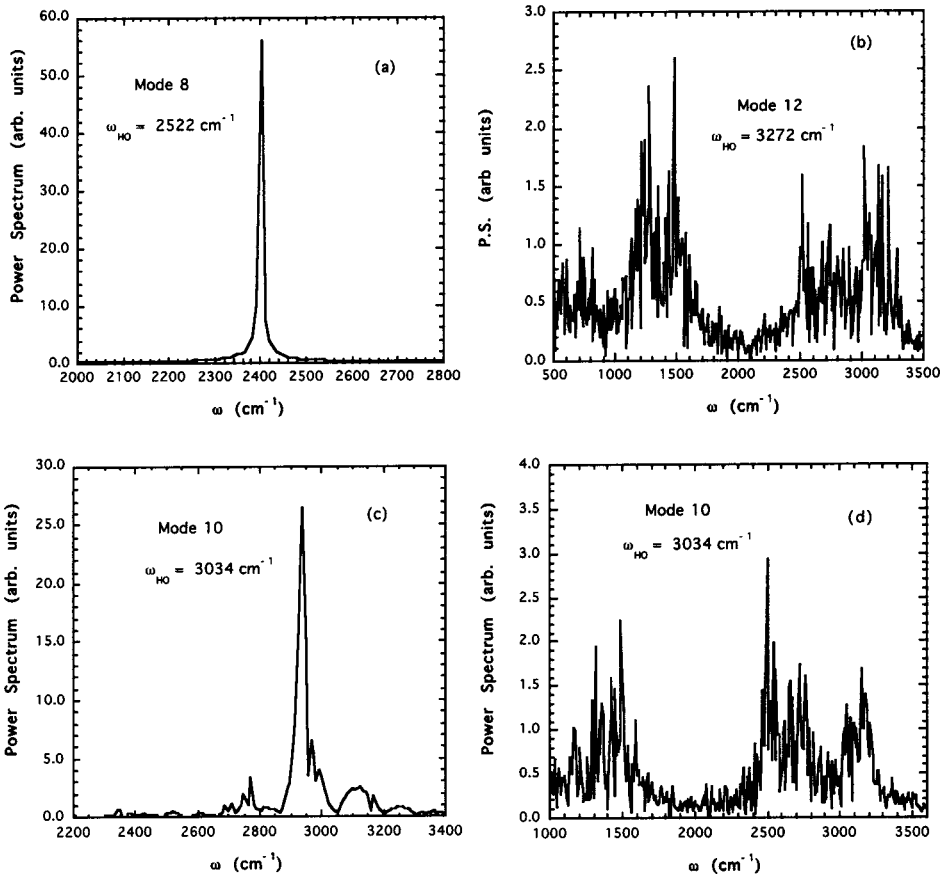

FIG. 3. Quasiclassical power spectra of CH_5^+ obtained for mode specific excitations (see text for a complete description): (a) Mode 8, (b) Mode 12, (c) Mode 10—"short time" spectrum, and (d) Mode 10—"full time" spectrum.

We have examined classical trajectories corresponding to these two energies and find, as expected, regular periodic behavior at 100 cm^{-1}, but highly fluxional, complex behavior at 1000 cm^{-1} (Mpeg movies of some trajectories can be viewed at www.emory.edu/CHEMISTRY/faculty/bowman).

These spectra, although suggestive of what is observed experimentally, are run at energies that are much below the excitation energies of the various CH-fundamentals (modes 8–12, cf. Table I) and so do not sample the anharmonic regions of the potential that are relevant to the experimental spectrum. Thus, even if the vibrational motion were quasiperiodic, significant anharmonic shifts in the peak positions would be expected in the experimental spectrum, and these shifts would not be obtained from the low energy spectra shown in Fig. 1.

We considered another approach to obtain a spectrum that is more closely related to the experimental one and alsoallows an investigation of the time evolution of mode excitation. The approach is to excite the fundamentals of the normal modes and to obtain the spectrum for each mode. To do this, we initiated trajectories by extending a normal mode to a potential value equal to the harmonic estimate of the fundamental excitation, and with initial Cartesian momenta equal to zero. The time evolution of the normal mode, the velocity autocorrelation (with $t=0$ for this purpose defined by a short time after initiation of the trajectory) and power spectrum are then determined. We refer to this approach and the resulting spectrum as *quasiclassical*, in analogy with the terminology used in gas-phase reaction dynamics. Further, in order to investigate the time evolution of the resulting spectrum, we calculated the power spectrum using different time-segments. We report results here for three high frequency normal modes: modes 8, 10, and 12 listed in Table I and shown in Fig. 2. For these modes, the velocity autocorrelation function was obtained over a total time of 15.8 ps. Four time segments of duration 3.96 ps were used to obtain the spectrum; the first time-segment is from 0 to 3.96 ps, segment two from 3.96 to 7.92 ps, etc. Before presenting some selected results, we note that inspection of the trajectories formodes 10 and 12 revealed that the motion was regular up to times 3.5 and 0.5 ps, respectively. By contrast, mode 8 remained regular over the full time of 15.8 ps. We obtained the power spectrum corresponding to the short-time dynamics by simply evaluating the Fourier transform of the velocity autocorrelation function for times between zero and t_R; the power spectrum over the full time was also obtained and the results are shown in Fig. 3. The spectrum for mode 8 (obtained over the full time 15.8 ps) is quite simple, with a peak that is red-shifted from the harmonic frequency by 122 cm^{-1}. The spectrum of mode 12 is highly complex with huge red-shifts and some blueshifts. In particular, the appearance of spectral features below 2000 cm^{-1} can be attributed to the rapid coupling of the original CH-stretching normal mode to motions more closely related to isomerization, i.e., bending or rocking. Two spectra are shown for mode 10, one obtained over the first 3.5 ps (where the motion is regular) and the other over the full 15.8 ps. As seen the "short-time" spectrum is fairly clean with a prominent peak, which is

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red-shifted by roughly $100\,cm^{-1}$ from the harmonic frequency. The fully resolved spectrum in panel (d) is highly complex and shows some bi- or tri-modality, with peaks with large redshifts, but also with some blueshifted peaks. Again, the spectrum demonstrates the coupling of the original vibrational motion with other vibrational modes as well as motions more closely attributable to isomerization.

The present results agree qualitatively with the general conclusions that CH_5^+ is highly fluxional and has a complex spectrum. However, the results for mode 8 suggest that regular motion may exist, and thus the complex spectrum may have some simple, assignable features. (Similar behavior was also found for mode 6.) This conclusion must be regarded as somewhat speculative because it is based on classical dynamics. Another caveat is the assumption of an initial structure localized at the global minimum. There is some support of the assumption of an initial state characterized by the equilibrium structure, based on the 0 K quantum calculations of the structure of CH_5^+ by Marx and Parrinello.[4(b)] Also, in preliminary DMC calculations using the present PES, McCoy[10] has estimated the quantum zero-point energy to be roughly $500\,cm^{-1}$ below the harmonic estimate and finds expectation values of HH distances that suggest a zero-point structure that is close to the structure of the global minimum. With the availability of the new PES, we plan to investigate quantum and semiclassical approaches to the spectrum dynamics in the future.

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