

Deuteration Effects on the Structure and Infrared Spectrum of CH_5^+

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CH_5^+ has been of considerable interest in recent years. This is based on its importance in interstellar chemistry¹ as well as its potential interest in combustion chemistry. It also represents the simplest of Olah's carbocations.² From a fundamental perspective, it allows us to address the issue of experimental signatures of large amplitude motions. These features of CH_5^+ have made it a subject of a number of experimental, theoretical, and computational studies.^{3–15}

The structures, symmetries, and energies of the minimum and two low-lying saddle points of CH_5^+ , obtained from a full-dimensional potential energy surface that is based on CCSD(T)/aug-cc-pVTZ electronic energies,¹³ are shown in Figure 1. In earlier work, using a slightly lower level of electronic structure theory, we showed that the ground state wave function is fully delocalized over all 120 equivalent minima, the $C_s(\text{I})$ structure in Figure 1, and has substantial amplitude at all three stationary points.¹⁰ In a related study, we investigated the CH_2D_3^+ and found that the ground state wave function was localized, with 85% of the probability amplitude being in the minima in which the hydrogen atoms were in positions a and b or in b and c in Figure 1.¹¹ This contrasts with the classical statistical expectation, where 10% of the probability amplitude would be in each of these minima. Similar quantum localization was observed in earlier path integral studies of CH_4D^+ and CHD_4^+ ⁹ and in spectroscopic studies of $\text{CH}_5^+(\text{H}_2)_n$.⁴

Recent analysis of the low⁵ and high¹⁴ resolution spectra of CH_5^+ has indicated that features at a resolution as high as 10 cm^{-1} , full-width half-maximum (fwhm), can be interpreted in terms of excitations of specific CH stretching or HCH bending vibrations of CH_5^+ about its C_{2v} saddle point structure.¹⁴ Experimental investigations are being extended to include CD_5^+ , CH_4D^+ , and CHD_4^+ .¹⁵ The anticipation of these spectra motivated us to investigate how the localization caused by deuteration will be reflected in the spectra of these species.

There are five bonding sites for the hydrogen atom in the equilibrium structure of CH_5^+ , labeled a–e in Figure 1, and only sites d and e can be related by symmetry. We have shown¹⁰ that, when a classical trajectory is run at an energy that is higher than the saddle points in Figure 1, CH_5^+ samples all of the minima with equal probability, independent of the extent of deuteration. This is not the case for quantum mechanical descriptions.^{9,11} On the basis of an analysis of the Diffusion Monte Carlo (DMC)¹⁶ wave functions for CH_4D^+ , there is 75% probability that the deuterium will be in position d or e: 17, 5, and 2% for positions c, a, and b, respectively. For CHD_4^+ , there is 55% probability for the hydrogen being in position b: 35, 8, and 2% in position a, c, and d or e. This degree of localization of the deuterium atoms reflects the fact that the CH stretch frequencies depend on the bonding position of the hydrogen atom, with the frequencies for positions a and b being the lowest, and d and e being the highest.

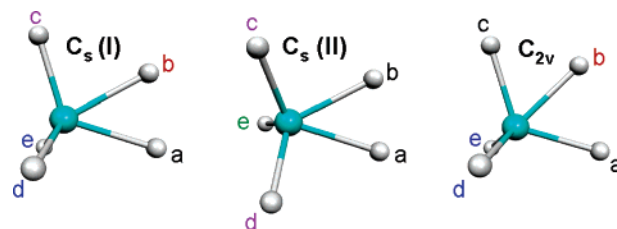


Figure 1. Structures of the three low-lying stationary points on the CH_5^+ potential surface. The hydrogen atoms are labeled a–e with the labels for equivalent hydrogen atoms given in the same color. In all cases, a and b label the hydrogen atoms in the H_2 subunit, hydrogen atoms c–e are in the CH_3^+ subunit. Here $C_s(\text{I})$ represents the minimum energy configuration. On the basis of the potential surface used for this study, the $C_s(\text{II})$ and C_{2v} configurations are both saddle points and are 29 and 341 cm^{-1} above the minimum energy configuration, respectively. While a–e labels have been placed on all three renderings of CH_5^+ , in the text, we use these labels to describe the closest $C_s(\text{I})$ minimum to a particular configuration of the ion.

While these predictions are interesting, they raise the question of the experimental consequences of this quantum localization. To investigate this, we use two approaches to obtain the infrared (IR) spectra of selected isotopologs of CH_5^+ . In each approach, spectra are calculated at stationary points, weighted by the DMC probability amplitudes at these stationary points, and then summed to give the final spectrum. In one approach, the spectra at all stationary points and all distinct bonding sites are obtained in the harmonic approximation. In the second, higher level, approach, we performed vibrational configuration–interaction (VCI) calculations of the spectra using the program MULTIMODE.¹⁷ Harmonic analysis provides a simple treatment of molecular vibrations, but it suffers from the lack of inclusion of anharmonicities or contributions to the spectrum from overtone or combination bands, which will be particularly important below $\sim 1000\text{ cm}^{-1}$. In contrast, the VCI calculations can be made to be exact, but in practice, this is intractable computationally. We find that we can correct for this by taking the appropriate average over the spectra calculated at the various stationary points.¹⁴ Owing to the much larger computational effort required to perform each of the VCI calculations, compared to harmonic ones, the VCI calculations were performed at only the stationary points and bonding sites that had relative probabilities larger than 0.1.

We recently demonstrated that both approaches reproduce the experimental spectra for CH_5^+ .¹⁴ Here we present the results of calculations of the IR spectra of CH_4D^+ , CHD_4^+ , and CD_5^+ . For the earlier and the present work, we use fits to potential and dipole moment surfaces, calculated at the CCSD(T)/aug-cc-pVTZ and MP2/cc-pVTZ level of theory/basis set, respectively. These surfaces have been described in detail elsewhere.^{10,13} In Figure 2, we plot the spectra for CH_5^+ , CH_4D^+ , CHD_4^+ , and CD_5^+ , obtained by the two approaches. We convolute the calculated spectra by a Gaussian, $\text{fwhm} = 200\text{ cm}^{-1}$, to roughly agree with the resolution of the experimental laser-induced reaction (LIR) spectrum for CH_5^+ .⁵

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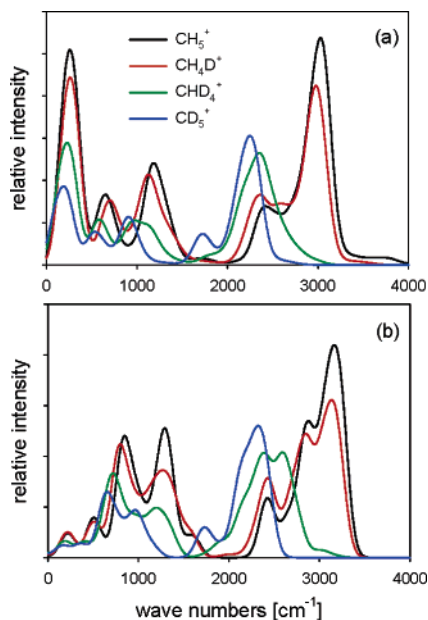


Figure 2. Spectra for isotopologs of CH_5^+ obtained from (a) VCI and (b) harmonic calculations. Differences below 1000 cm^{-1} reflect lack of anharmonicities and contributions from overtones and combination bands in the harmonic spectrum.

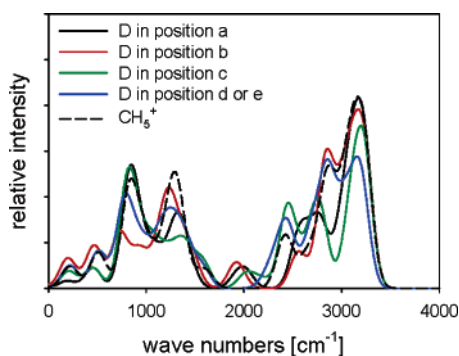


Figure 3. Weighted harmonic spectra for CH_4D^+ obtained for the four possible deuterium substitutions.

While there are quantitative differences between the spectra obtained from harmonic and the VCI calculations, the trends, discussed below, are robust. Specifically, in the CH or CD stretch region of CH_4D^+ , between 2000 and 3200 cm^{-1} , we note a red-shift in the CH stretch peak compared to CH_5^+ . To understand the source of this red-shift, we consider the harmonic spectra that correspond to the four bonding sites of the deuterium atom in the $C_s(I)$ minimum, plotted in Figure 3. Here, we use the weights for the three stationary points that were obtained for CH_5^+ , rather than the weights for CH_4D^+ , as the weights for CH_4D^+ also contain information about the differences in the populations at the different minima. As seen, only when the deuterium is put into position d or e is the high frequency band red-shifted. From the DMC studies, we find that more than 75% of the ground state amplitude corresponds to the deuterium being in one of these positions. Hence, the red-shift of the CH stretch band reflects the quantum localization of the deuterium in position d or e, which has the effect of lowering the highest CH stretch frequency upon deuteration. In addition, both the harmonic and VCI spectra show little intensity in the 1800 –

2000 cm^{-1} region. This gap is only seen in the spectrum in Figure 3 in which the deuterium is in position d or e. Finally, we find a small red-shift of the feature at 1200 cm^{-1} . All of the above predictions are consistent with preliminary reports of the LIR spectrum for this species.¹⁵

A similar analysis has been performed for CHD_4^+ . We observe little intensity in the spectral region of the prominent peak in CH_5^+ . In addition, the shape of the feature in the CH/CD stretch region differs from what is seen in the other three species. These reflect the less than 200 cm^{-1} difference between the frequency the CH stretch and the highest frequency CD stretch when the hydrogen atom is in position a or b in this isotopomer.

Finally, the spectrum for CD_5^+ closely resembles that of CH_5^+ , albeit shifted to lower frequency. This is not at all surprising since all of the vibrations involve CH/CD stretches or HCH/DHD bends so the increase in the masses of all of the hydrogen atoms by a constant factor should, to lowest order, simply scale the spectrum by a factor of $1/\sqrt{2}$.

In summary, we use two approaches to calculate the spectra of deuterated analogues to CH_5^+ at various stationary points on the potential surface. The resulting spectra are weighted by the probability amplitudes at these stationary points, obtained by DMC calculations. We find that the predicted spectra for CH_4D^+ and CHD_4^+ both contain features associated with the single D or H atom being preferentially located in one of the bonding sites, shown in Figure 1. At this stage, we await experimental verification of this form of quantum localization in these deuterated species.

Acknowledgment. A.B.M. and J.M.B. thank the National Science Foundation for financial support under Grants CHE-0200968/CHE-0515627 (A.B.M.) and CHE-0446527 (J.M.B.). X.H. and J.M.B. also thank the Office of Naval Research for financial support (N00014-01-0235, N00014-05-0460) and a DURIP grant for computational resources. We also thank Professor David J. Nesbitt and his group for discussions of the spectroscopy of CH_5^+ .

Supporting Information Available: Descriptions of the DMC and VCI and harmonic calculations; DMC weights used in this work; an analysis of the spectrum of CHD_4^+ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA057514O