SPECTRAL SIGNATURES OF LARGE AMPLITUDE MOTIONS IN CH_5^+

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The vibrational spectrum of CH_5^+ has been of long-standing interest, although the high resolution remains unassigned.[a] The past year has seen significant activity and progress, with the reports of the low-resolution LIR spectrum of Asvany *et. al*[b] and the high resolution, rotationally resolved spectrum of Savage, Dong and Nesbitt.[c] Motivated by these reports, we have used the DMC probability amplitudes to evaluate spectra that are convolutions of the spectra that are obtained at distinct stationary points. We also evaluate the vibrationally averaged rotational constants. The results for CH_5^+ and its five isotoplogues will be reported. Excellent agreement with the reported spectra down to resolutions of 10 cm^{-1} are obtained. Based on this, we assign the gross features in the low and high resolution CH_5^+ spectra. We also investigated the expected shifts in the spectral features and show that there should be evidence of localization of the deuterium atoms in the mixed isotoplogues. For these studies, we employed fully *ab initio* potential surfaces, recently reported by Jin, *et al.*[d]

[a] E. T. White, J. Tang and T. Oka, Science, 284, 135 (1999).
[b] O. Asvany, P. Kumar, B. Redlich, I. Hegemann, S. Schelmmer and D. Marx, Science, 309, 1219 (2005)
[c] X. Huang, J. M. Bowman, A. B. McCoy, L. M. Johnson, C. Savage, F. Dong and D. J. Nesbitt, Science, 311, 60 (2006)
[d] Z. Jin, B. J. Braams , and J. M. Bowman, J. Phys. Chem. A, 110, 1569 (2006).