Analysis of Rotationally Excited States of Deuterated CH_5^+ Using Diffusion Monte Carlo

Jason E. Ford, Anne B. McCoy

Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH 43210

Introduction

- Spectroscopy, the study of interactions of light and matter, is used to determine the presence and certain properties of atoms and molecules in the interstellar medium.
- It is possible to calculate the spectra of molecules based on simplified theories. For larger and more complicated molecules, the calculated spectra based on these simple models frequently do not line up with experimentally measured spectra.
- Floppy molecules, those that exhibit large amplitude motions in the ground state, present such a challenge for theoretical and computational studies. The prototypical floppy molecule, CH_5^+, is no exception; this polyatomic ion can be seen below.
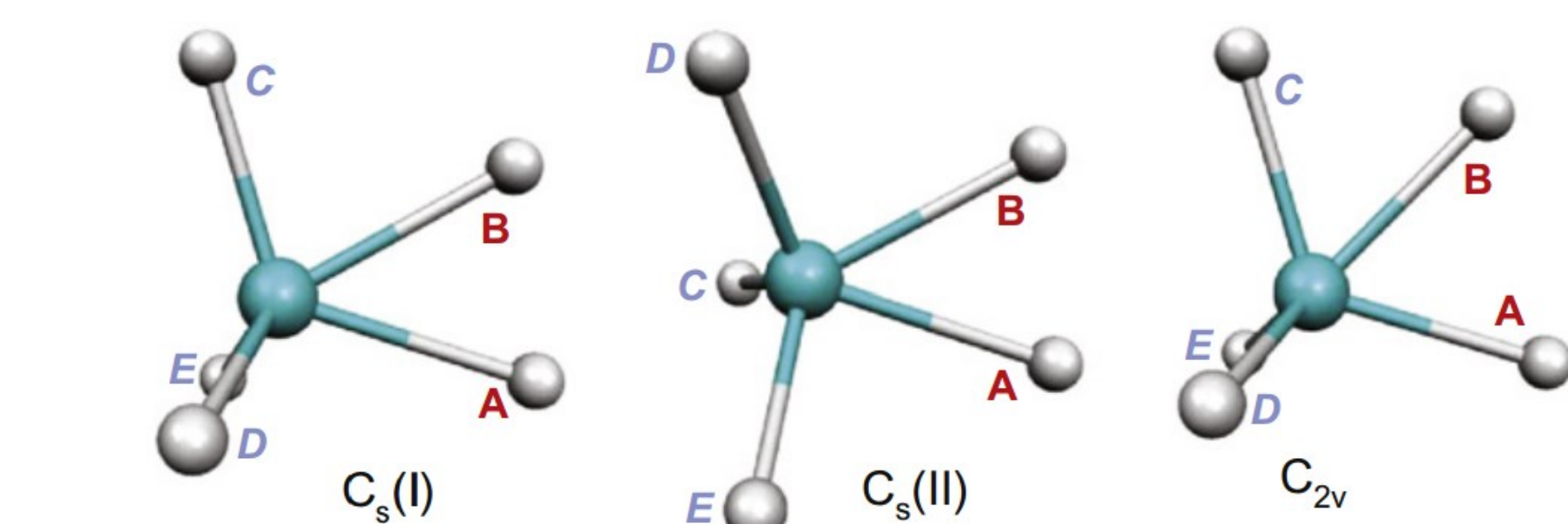

Figure 1: Geometries sampled by CH_5^+ in its ground state

- This ion and its deuterated isotopologues have many equivalent energetic minima. Transition state geometries connecting these minima lie below the zero point energy. This leads to delocalization of hydrogen atoms about the central carbon atom, preventing the calculation of spectral line frequencies with simple theories.
- More complex theories such as diffusion Monte Carlo may help in understanding the fine details that have yet to be understood in the spectra taken of these molecular ions.
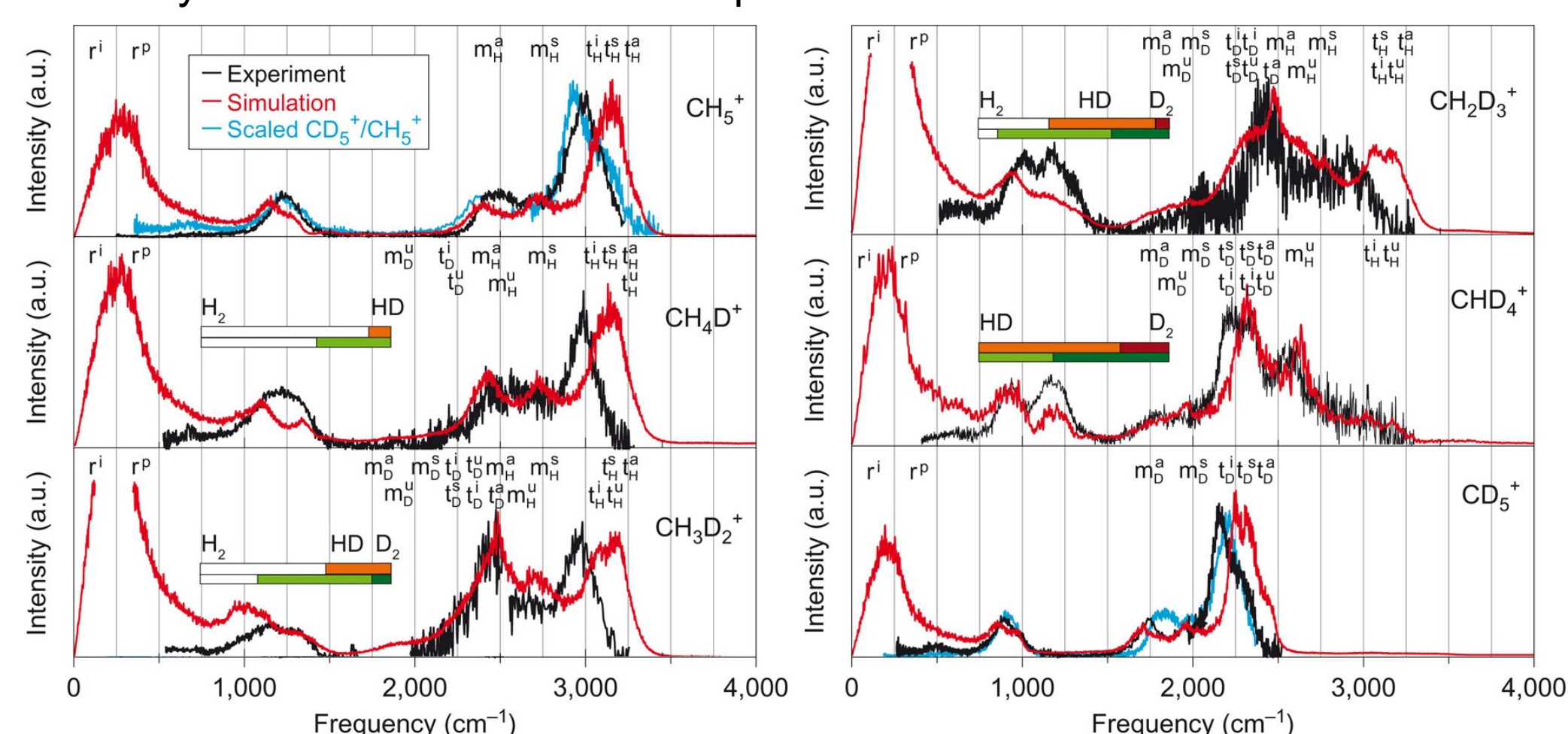

Figure 2: Experimental vs. previously simulated spectra of CH_5^+ and isotopologues

Schlemmer, Stephan et al. "Quantum-induced symmetry breaking explains infrared spectra of CH5+ isotopologues". *Nature Chemistry* **2**, 298–302 (2010).

Methodology - Diffusion Monte Carlo (DMC)

- Diffusion Monte Carlo (DMC) methodology is employed to calculate the ground state properties of CH_5^+. DMC works based on the isomorphism of time-dependent Schrödinger equation in imaginary time $\tau = it/\hbar$ with the diffusion equation modified by a first order rate term, $-kC$.

$-i\hbar \dfrac{\partial \psi}{\partial t} = \dfrac{\hbar^2}{2m}\dfrac{\partial^2 \psi}{\partial x^2} - V(x)\psi$	$\dfrac{\partial C}{\partial t} = D\dfrac{\partial^2 C}{\partial x^2}$
Time-dependent Schrödinger equation	Diffusion equation
$\dfrac{\partial \psi}{\partial \tau} = \dfrac{\hbar^2}{2m}\dfrac{\partial^2 \psi}{\partial x^2} - V(x)\psi$	$\dfrac{\partial C}{\partial t} = D\dfrac{\partial^2 C}{\partial x^2} - kC$
Schrödinger equation in imaginary time	Modified diffusion equation

- In order to build a simulation out of this idea, we first express the wave function by an ensemble of N_{walker} δ-functions:

$$\langle \vec{R}|\Psi(\tau)\rangle = \sum_{n=1}^{N_{walker}} W_n(\tau)\,\delta^{3N}\left(\vec{R} - \vec{R}_n(\tau)\right)$$

Methodology Continued

- These δ-functions are referred to as walkers; they represent a specific molecular geometry in configuration space, $R_n(\tau)$, and each have an associated weight W_n. This ensemble evolves according to the split operator approximation with a reference energy added:

$$|\Psi(\tau+\delta\tau)\rangle \approx e^{-(\hat{V}-E_{ref}(\tau))\delta\tau}e^{-\hat{T}\delta\tau}|\Psi(\tau)\rangle$$

- The reference energy, E_{ref}, which becomes the ground state energy of the system as the ensemble reaches equilibrium, is defined:

$$E_{ref}(\tau) = \bar{V}(\tau) - \alpha\frac{W_{tot}(\tau) - W_{tot}(0)}{W_{tot}(0)}$$

- The walkers are first acted on by the kinetic energy part of the propagator causing each atom to change position by a random amount based on a Gaussian distribution of width $\sqrt{\delta\tau/m_k}$, where m_k is the mass of the atom.
- Potential energy is then evaluated followed by reassignment of weight based on:

$$W_n(\tau+\delta\tau) = \exp\left[-\left(V\left(\vec{R}_n(\tau+\delta\tau)\right) - E_{ref}(\tau)\right)\right]W_n(\tau)$$

- This reduces the contribution to the wavefunction from walkers that have higher than average potential energies and increases the contribution from walkers with lower than average potential energies.
- The addition of rotational state vectors to each walker allows for the possibility of rotational excitation, and is given by:

$$\langle \vec{R}|\Psi(\tau)\rangle = \sum_{n=1}^{N_{walker}} W_n(\tau)\,\delta^{3N}\left(\vec{R} - \vec{R}_n(\tau)\right)|\Phi_{n,J}(\tau)\rangle$$

with

$$|\Phi_{n,J}(\tau)\rangle = \sum_{K=-J}^{J} C_{n,J,K}(\tau)|J,K\rangle$$

- Where J is the rotational angular momentum being calculated and K is the projection of the rotational angular momentum onto a given axis, the z-axis in this case.
- The propagator was modified so these state vectors evolve as:

$$|\Psi(\tau+\delta\tau)\rangle \approx e^{-(\hat{V}-E_{ref}(\tau))\delta\tau}e^{-\hat{h}_{rot}\delta\tau}e^{-\hat{T}\delta\tau}|\Psi(\tau)\rangle$$

with

$$\hat{h}_{rot}\left(\vec{R}\right) = \frac{1}{2}\sum_{\alpha,\beta}\hat{J}_\alpha I_{\alpha,\beta}^{-1}\left(\vec{R}\right)\hat{J}_\beta$$

- The state vector coefficients are then updated after the action of the kinetic energy part of the propagator according to first order time-dependent perturbation theory

$$C_{n,J,K}(\tau+\delta\tau) = C_{n,J,K}(\tau) - \delta\tau\sum_{K'=-J}^{J} C_{n,J,K'}\left\langle J,K\left|\hat{h}_{rot}\left(\vec{R}_n(\tau+\delta\tau)\right)\right|J,K'\right\rangle$$

- The state vector is then normalized and used to calculate the rotational energies

$$E_{rot}\left(\vec{R}_n(\tau+\delta\tau)\right) = \left\langle \Phi_{n,J}(\tau+\delta\tau)\left|\hat{h}_{rot}\left(\vec{R}_n(\tau+\delta\tau)\right)\right|\Phi_{n,J}(\tau+\delta\tau)\right\rangle$$

- This rotational energy is then added to the potential energy in evaluating E_{ref} and in updating the weights of walkers.
- The DMC code was then modified by dressing each walker with an array of N_{state} rotational state vectors, allowing simultaneous calculations of N_{state} rotational states, and greatly reducing the total calculation time required.

$$\left\langle \vec{R}\middle|\Psi(\tau)\right\rangle = \sum_{n=1}^{N_{walker}}\left(\vec{R}-\vec{R}_n(\tau)\right)\begin{pmatrix} W_n^{(1)}(\tau)\left|0,0\right\rangle \\ W_n^{(2)}(\tau)\left|\Phi_{n,J}^{(2)}(\tau)\right\rangle \\ W_n^{(3)}(\tau)\left|\Phi_{n,J}^{(3)}(\tau)\right\rangle \\ \vdots \\ W_n^{(N_{state})}(\tau)\left|\Phi_{n,J_{max}}^{(N_{state})}(\tau)\right\rangle \end{pmatrix}$$

- This requires that the walkers have associated weights for each rotational state, and that E_{ref} be replaced by a vector of length N_{state}. Other calculations remain the same, simply using the weight and reference and energy associated with each state.
- Feedback eventually leads to equilibration, where the elements of E_{ref} provide energies of the state, while the wavefunction is given by the distribution of walkers. Probability distributions can be produced by descendant weighting.

Results

J	$E_{0,DMC}$	$E_{0,RR}$	$E_{2,DMC}$	$E_{2,RR}$	$E_{3,DMC}$	$E_{3,RR}$
0	10920 ± 7	—	9699 ± 8	—	9097 ± 10	—
1	7.70 ± 0.19	7.71	5.42 ± 0.09	5.49	4.87 ± 0.05	4.88
1	7.77 ± 0.11	7.76	5.64 ± 0.10	5.74	4.89 ± 0.07	4.94
1	7.77 ± 0.15	7.90	5.88 ± 0.12	6.46	5.00 ± 0.02	5.11
2	23.15 ± 0.54	23.12	16.15 ± 0.21	16.45	14.50 ± 0.16	14.53
2	23.19 ± 0.39	23.12	16.33 ± 0.28	16.51	14.75 ± 0.21	14.58
2	23.20 ± 0.43	23.23	17.17 ± 0.25	16.94	14.83 ± 0.16	14.87
2	23.30 ± 0.42	23.33	17.38 ± 0.30	17.48	14.83 ± 0.14	14.94
2	23.35 ± 0.47	23.56	17.69 ± 0.39	18.65	14.89 ± 0.15	15.17
3	46.35 ± 1.10	46.18	31.73 ± 0.44	32.72	29.03 ± 0.36	28.95
3	46.36 ± 1.07	46.19	31.82 ± 0.53	32.77	29.22 ± 0.24	28.97
3	46.38 ± 0.34	46.40	34.23 ± 0.39	33.61	29.40 ± 0.20	29.52
3	46.42 ± 0.85	46.44	34.39 ± 0.64	33.93	29.57 ± 0.36	29.59
3	46.54 ± 0.79	46.51	34.65 ± 0.56	34.18	29.60 ± 0.42	29.85
3	46.59 ± 0.44	46.69	34.86 ± 0.52	35.18	29.91 ± 0.36	29.93
3	46.62 ± 1.04	47.02	35.46 ± 0.86	36.82	29.91 ± 0.36	30.22

Table 1: Energies (cm^{-1}) ordered from lowest to highest, subscript of E gives the number of deuterium atoms in the calculation and calculation type. $J = 0$ denotes ZPE.

ABC	% CH_4D^+	% $CH_3D_2^+$	% $CH_2D_3^+$	% CHD_4^+
HHH	0.75	0.42	—	—
HHD	0.18	0.39	0.64	—
HDH	0.02	0.04	< 0.01	—
DHH	0.05	0.12	0.24	—
HDD	—	0.01	0.09	0.35
DHD	—	< 0.01	< 0.01	0.54
DDH	—	< 0.01	0.01	0.08
DDD	—	—	< 0.01	0.03

Table 2: Probabilities of a given combination of hydrogen or deuterium atoms occupying the A, B, and C positions of Figure 1 are shown.
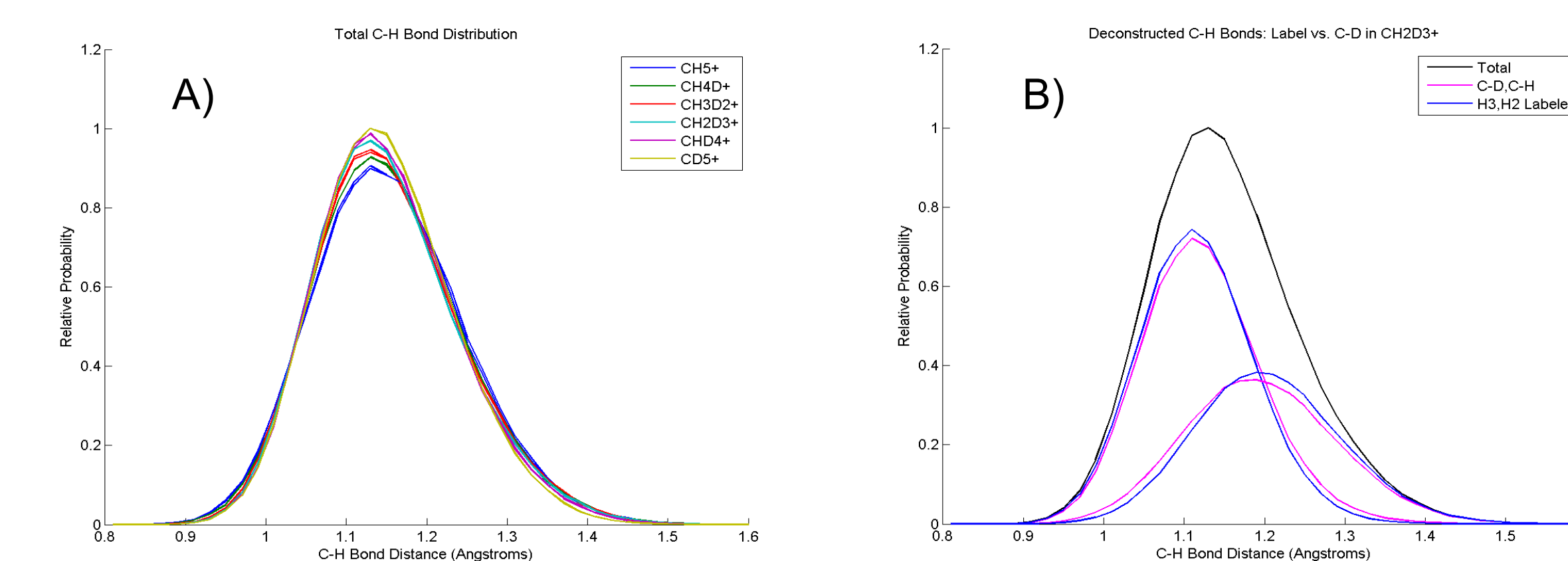

Figure 3: Projections of the wavefunction.
A) Total C—H bond length distribution with all isotopologues at ground and $J=10$ states.
B) Probability of C—H/C—D bond length vs. bond length of labeled positions.

Conclusion

- The energies of CH_5^+ and its isotopologues very closely follow those of the asymmetric top rigid rotor. The wavefunctions change very little with rotational excitation up to J=10. This is likely due to the relatively small amount of energy which is being introduced to the system when compared to the ground state energy.
- Deuterium atoms localize to the H_3 subunit of the CH_5^+ isotopologues.
- Currently, vibrational excitation is being explored so that it may be introduced concurrently with rotational excitation. Initial testing has begun with H_2D^+ as a model system.

Acknowledgments