SUPPORTING INFORMATION: Guided Diffusion Monte Carlo: A Method for Studying Molecules and Ions That Display Large Amplitude Vibrational Motions

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Supporting Information

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- Table S10: Convergence of Zero-Point Energy for Deuterated Analogues of CH_5^+ in cm^{-1} from Figure S3

DVR calculation of the wave functions for the CH and OH stretches

To obtain the trial wave function for the CH stretch used in this study, we performed a one-dimensional scan of the potential energy along this coordinate, constraining all of the other bond lengths and HCH angles to their values in the minimum energy structure. For these calculations, we used the potential of Jin *et al.*[1] For this scan, we evaluated the potential at 5000 CH bond lengths ranging from 0.21 to 3.18 Å. This provided the potential function for a one-dimensional discrete variable representation (DVR) calculation of the ground state wave function.[2] Similar calculations were performed to obtain the other CH wave functions and vibrational frequencies reported in Figures 4 and S2 and Table S5.

A similar approach was taken to obtain the OH stretch wave function for the OH stretch in water. For these calculations, we use the water potential developed by Partridge and Schwenke.[3] The scan included 500 OH bond lengths ranging from 0.26 to 2.11 Å. These potential evaluations were then used in a one-dimensional DVR calculation to generate the ground state wave function for the OH stretch used in the study.[2]

Calculation of $r_{\mathrm{OH}}^{\mathrm{max}}$ and σ_{OH} for $\mathbf{H^+(H_2O)_3}$ and $\mathbf{H^+(H_2O)_4}$

Starting from the equilibrium structure, we performed two-dimensional potential energy scans in the hydrogen-bonded OH stretch coordinate (r_{OH}) and the corresponding OO stretch (R_{OO}) using the potential energy surface that was used in this study. The hydrogen atom was constrained to lie on the OO axis.

The R_{OO} scans ranged from 2.17 to 3.55 Å and 2.24 to 3.62 Å for $H^+(H_2O)_3$ and $H^+(H_2O)_4$ respectively. At each of the 50 R_{OO} values, we evaluated the potential at 2000 values of r_{OH}, ranging from 0.56 to 1.67 Å and 0.53 to 1.64 Å for $H^+(H_2O)_3$ and $H^+(H_2O)_4$ respectively. The potential evaluations at the r_{OH} scan points were then used in a one-dimensional DVR

calculation to generate the ground state wave function as a function of the OH bond length for each value of R_{OO}.[2] Using these ground state wave functions, we then calculated the standard deviation σ_{OH} and the value of r_{OH} at which the maximum amplitude of the wave function occurred, which is referred to as $r_{\mathrm{OH}}^{\mathrm{max}}$ throughout the discussion.

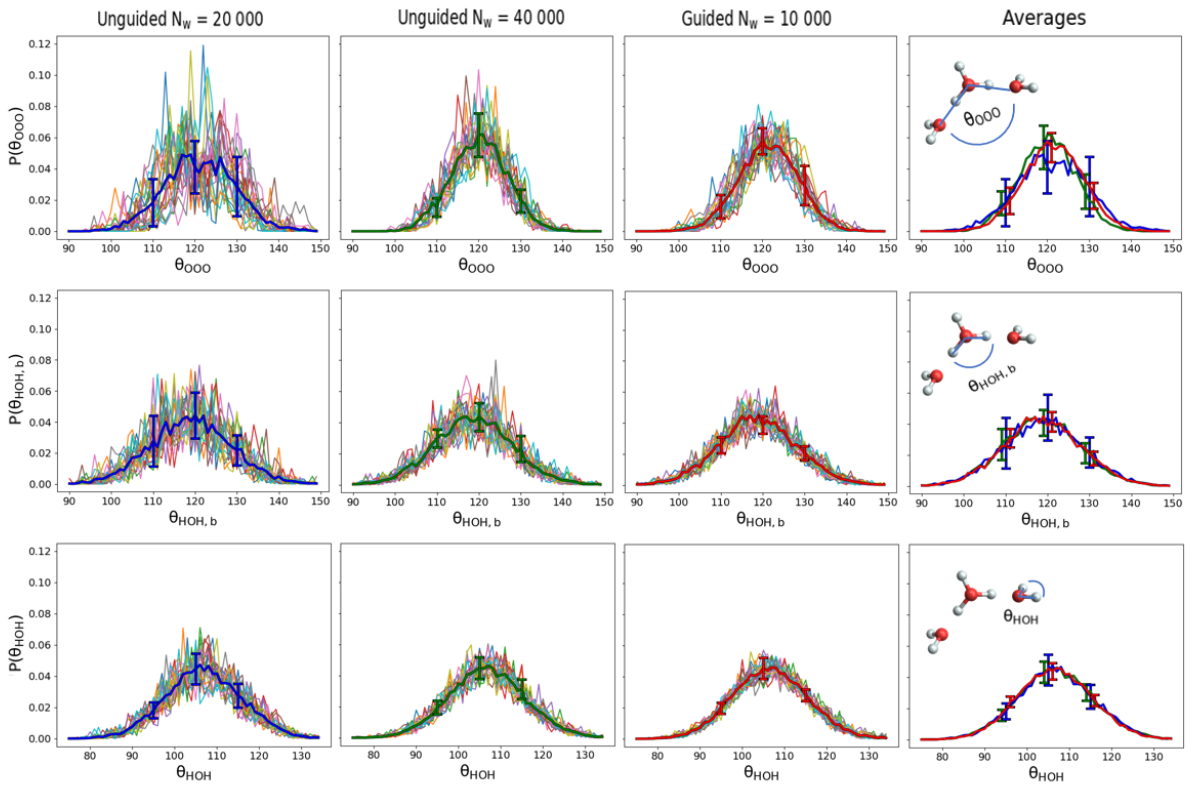

Figure S1: Projections of the ground state probability amplitude onto the OOO angle, θ_{OOO}, the bound HOH angle, θ_{HOH_b}, and the outer HOH angle, θ_{HOH}, in $H^+(H_2O)_3$. Twenty projections are shown using the unguided approach with 20 000 walkers, the unguided approach with 40 000 walkers, and the guided approach based on the OH stretches of the outer water molecules and unbound OH bonds in the hydronium core as well as the HOH angles in the outer water molecules with 10 000 walkers. The thicker lines show the average of these 20 projections with standard deviations when θ_{OOO} or $\theta_{\mathrm{HOH}_b} = 110°$, 120°, and 130° and when $\theta_{\mathrm{HOH}} = 95°$, 105°, and 115°. The last column shows the averages of these projections in the same plot to directly compare the various methods.

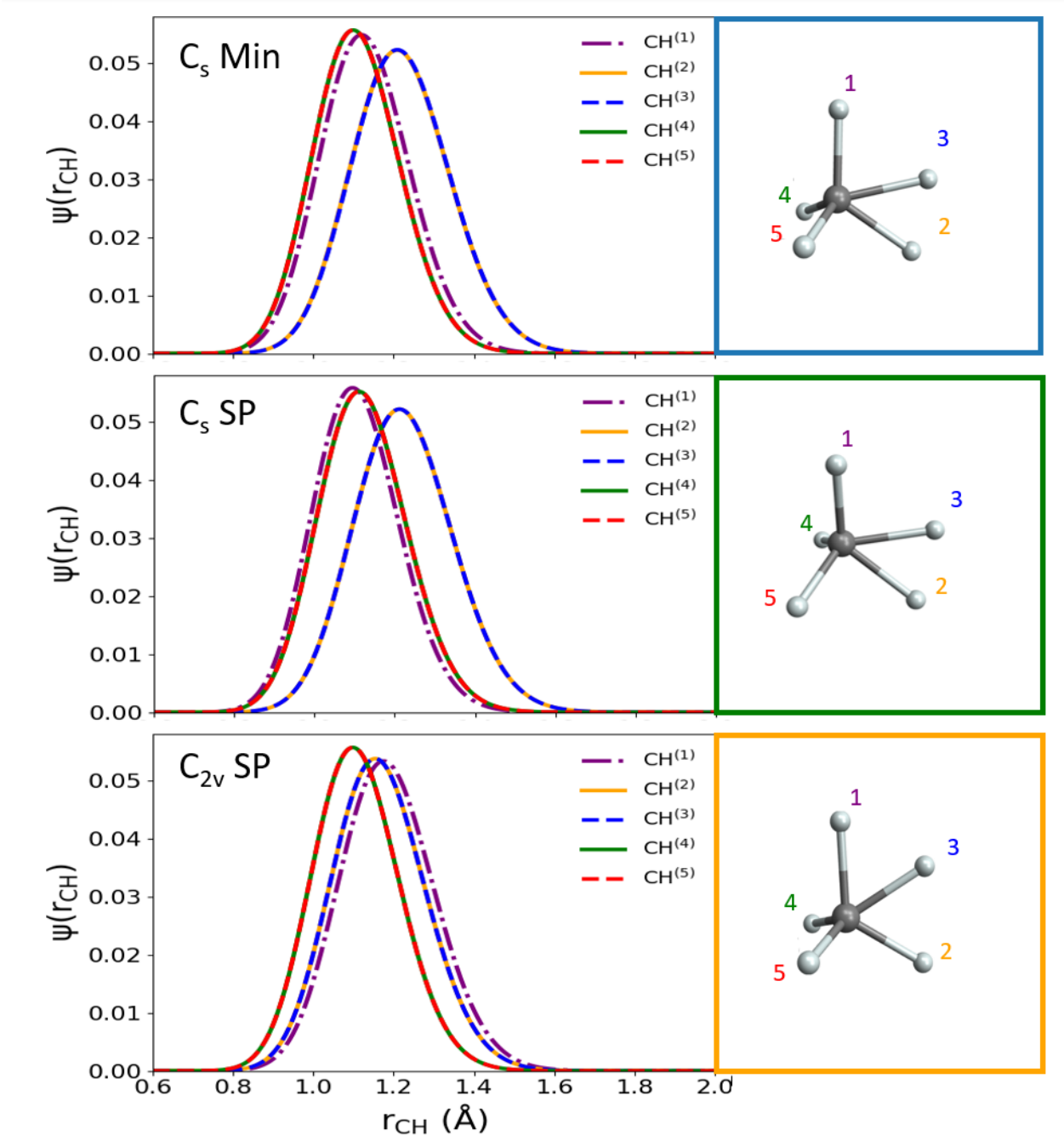

Figure S2: Ground state wave functions for CH stretches evaluated at the C_s minimum energy geometry, the C_s saddle point geometry, and the C_{2v} saddle point geometry of CH_5^+. The associated frequencies of these stretches are provided in Table S5.

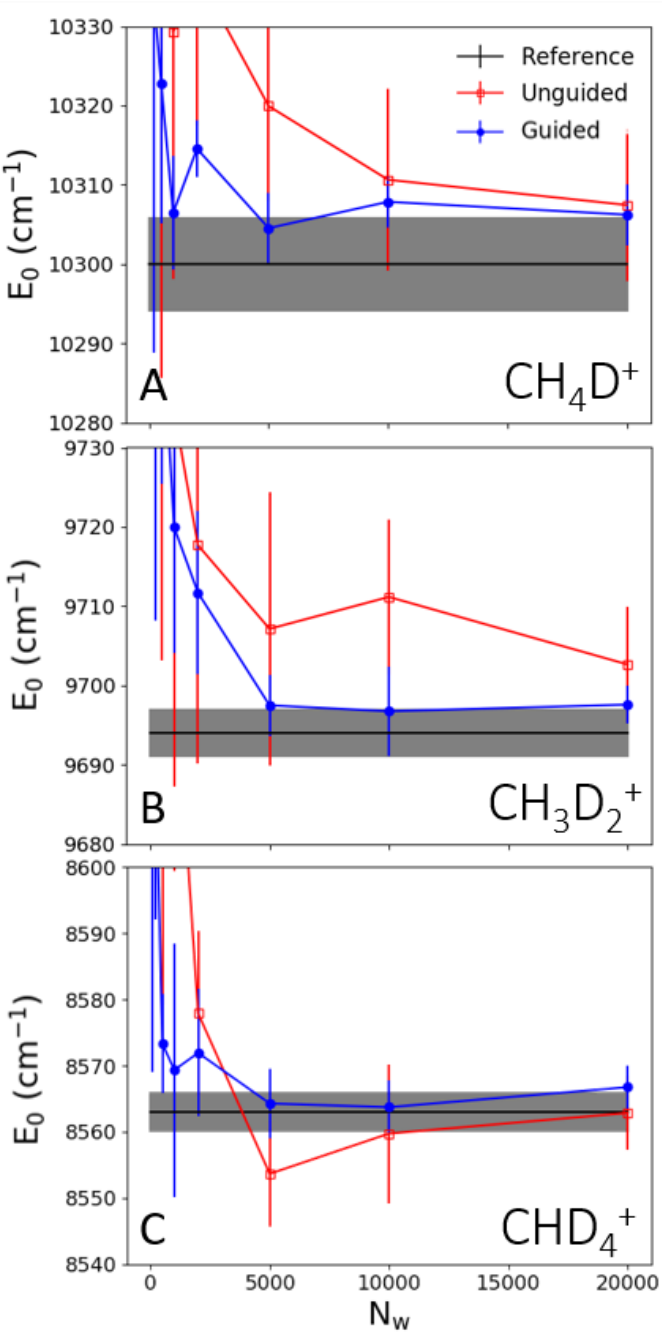

Figure S3: Calculated zero-point energies for (A) CH_4D^+, (B) $CH_3D_2^+$, and (C) CHD_4^+ plotted as functions of the number of walkers used in the simulation (N_W) for unguided (blue) and guided (red) DMC simulations. The black lines are the previously reported values of these zero-point energies, and the grey shading indicates their reported uncertainties.[1] The energies used to generate these plots are also provided in Table S10.

Table S1: Convergence of Zero-Point Energy for H_3O^+ in cm^{-1} from Figure 1

N_W	Guided(water)[a]	Guided(H_3O^+)[b]	Unguided
100	7467 (17)	7459 (26)	7535 (47)
200	7459 (8)	7475 (9)	7508 (30)
500	7457 (8)	7454 (11)	7458 (17)
1000	7455 (4)	7455 (8)	7467 (17)
2000	7457 (5)	7454 (5)	7465 (10)
5000	7453 (3)	7453 (2)	7460 (10)
10000	7455 (1)	7454 (1)	7454 (5)
20 000[c,d,e]	-	-	7456 (5)

[a] Guiding function using OH stretch wave functions from an isolated water molecule.

[b] Guiding function using OH stretch wave functions from an isolated hydronium molecule.

[c] Previous literature value based on 20 000 walkers and $\Delta\tau = 1$ a.u. is 7453 (2) cm^{-1}.[4]

[d] Unguided energy based on 20 000 walkers and $\Delta\tau = 10$ a.u., averaged over 15 000 time steps (150 000 a.u.) is 7448 (1) cm^{-1}.

[e] Unguided energy based on 20 000 walkers and $\Delta\tau = 10$ a.u., averaged over 15 000 a.u. is 7449 (3) cm^{-1}.

Table S2: Convergence of Zero-Point Energy for $H^+(H_2O)_2$ in cm^{-1} from Figure 1

N_W	Guided[a]	Unguided
100	12 463 (82)	12 872 (306)
200	12 431 (28)	12 767 (141)
500	12 379 (16)	12 489 (56)
1000	-	12 430 (43)
2000	12 379 (10)	12 427 (40)
5000	12 375 (7)	12 391 (20)
10 000	-	12 371 (14)
20 000[b,c]	-	12 371 (5)

[a] Guiding function using OH stretch wave functions from an isolated water molecule and harmonic HOH bend wave functions.

[b] Unguided energy based on 20 000 walkers and $\Delta\tau = 10$ a.u., averaged over 15 000 time steps (150 000 a.u.) is 12 362 (4) cm^{-1}.

[c] Unguided energy based on 20 000 walkers and $\Delta\tau = 10$ a.u., averaged over 15 000 a.u. is 12 358 (6) cm^{-1}.

Table S3: Convergence of Zero-Point Energy for $H^+(H_2O)_3$ in cm^{-1} from Figure 1

N_W	Guided ($H^+(H_2O)_3$)[a]	Guided (water)[b]	Guided ($H^+(H_2O)_4$)[c]	Unguided
2000	18018 (45)	18021 (33)	18035 (43)	-
5000	18009 (16)	18006 (18)	18011 (9)	-
10000	17997 (12)	17998 (8)	17996 (6)	18033 (11)
15000	18003 (7)	18000 (10)	18004 (6)	-
20000[d,e]	18000 (10)	18002 (4)	17998 (8)	18018 (18)
30000	17999 (3)	18004 (6)	-	18015 (19)
40000	-	-	-	18009 (8)
50000	-	-	-	18007 (11)
100000	-	-	-	18005 (6)

[a] Guiding function using OH stretch wave functions from an isolated water molecule and harmonic HOH bend wave functions with the shared proton stretch described using the $H^+(H_2O)_3$ parameters from Figure 3.

[b] Guiding function using OH stretch wave functions from an isolated water molecule and harmonic HOH bend wave functions.

[c] Guiding function using OH stretch wave functions from an isolated water molecule and harmonic HOH bend wave functions with the shared proton stretch described using the $H^+(H_2O)_4$ parameters from Figure 3.

[d] Unguided energy based on 20 000 walkers and $\Delta\tau = 10$ a.u., averaged over 15 000 time steps (150 000 a.u.) is 18 004 (6) cm^{-1}.

[e] Unguided energy based on 20 000 walkers and $\Delta\tau = 10$ a.u., averaged over 15 000 a.u. is 18 006 (18) cm^{-1}.

Table S4: Convergence of Zero-Point Energy for $H^+(H_2O)_4$ in cm^{-1} from Figure 1

N_W	Guided ($H^+(H_2O)_4$)[a]	Guided (water)[b]	Guided ($H^+(H_2O)_3$)[c]	Unguided[d]	Unguided[e]
2000	23 501 (63)	23 481 (55)	23 474 (36)	-	-
5000	23 424 (8)	23 429 (20)	23 429 (38)	-	-
10 000	23 401 (24)	23 422 (18)	23 417 (34)	23 478 (36)	23 482 (27)
15 000	23 418 (11)	23 416 (7)	23 403 (18)	-	-
20 000	23 407 (18)	23 401 (21)	23 399 (9)	23 412 (76)	23 441 (8)
30 000	23 398 (18)	23 409 (6)	-	23 453 (24)	-
40 000	23 397 (8)	-	-	23 409 (23)	23 415 (6)
50 000	-	-	-	23 440 (21)	23 409 (12)
60 000	-	-	-	-	23 397 (5)
75 000	-	-	-	23 421 (19)	23 397 (4)[f]
100 000	-	-	-	23 421 (10)	-

[a] Guiding function using OH stretch wave functions from an isolated water molecule and harmonic HOH bend wave functions with the shared proton stretch described using the $H^+(H_2O)_4$ parameters from Figure 3.

[b] Guiding function using OH stretch wave functions from an isolated water molecule and harmonic HOH bend wave functions.

[c] Guiding function using OH stretch wave functions from an isolated water molecule and harmonic HOH bend wave functions with the shared proton stretch described using the $H^+(H_2O)_3$ parameters from Figure 3.

[d] Based on $\Delta\tau = 1$ a.u., averaged over 15 000 a.u.

[e] Based on $\Delta\tau = 10$ a.u., and averaging over 15 000 time steps (150 000 a.u.).

[f] Unguided energy based on 20 000 walkers and $\Delta\tau = 10$ a.u., averaged over 15 000 a.u. is 23 414 (15).

Table S5: Frequencies and Equilibrium Bond Lengths in CH_5^+

C_s Min		
CH	$\nu_{CH}^{(i)}$ $(cm^{-1})^a$	$r_{CH,e}^{(i)}$ $(Å)^b$
1	2896.28	1.1076
2	2383.95	1.1966
3	2393.78	1.1971
4	3069.90	1.0881
5	3069.90	1.0881
C_s SP		
CH	$\nu_{CH}^{(i)}$ $(cm^{-1})^a$	$r_{CH,e}^{(i)}$ $(Å)^b$
1	3110.05	1.0842
2	2373.51	1.1996
3	2373.51	1.1996
4	2968.06	1.0991
5	2968.06	1.0991
C_{2v} SP		
CH	$\nu_{CH}^{(i)}$ $(cm^{-1})^a$	$r_{CH,e}^{(i)}$ $(Å)^b$
1	2587.22	1.1626
2	2671.41	1.1414
3	2671.41	1.1414
4	3073.04	1.0870
5	3073.04	1.0870

[a] Frequency of the CH stretch based on a DVR calculation.[2]

[b] Equilibrium bond length.

Table S6: HH Distances and Standard Deviations for the Minimum Energy Structure of CH_5^+

atom	$H^{(1)}$	$H^{(2)}$	$H^{(3)}$	$H^{(4)}$	$H^{(5)}$	σ $(Å)^a$	$\overline{\sigma}$ $(Å)^b$	$r_{CH,e}$ $(Å)^c$
$H^{(1)}$	-	2.0367	1.4413	1.7912	1.7912	0.2449	0.1023	1.1076
$H^{(2)}$	2.0367	-	0.9521	1.7182	1.7182	0.4613	0.1910	1.1966
$H^{(3)}$	1.4413	0.9521	-	1.9428	1.9428	0.4748	0.1983	1.1971
$H^{(4)}$	1.7912	1.7182	1.9428	-	1.8789	0.0985	0.0458	1.0881
$H^{(5)}$	1.7912	1.7182	1.9428	1.8789	-	0.0985	0.0458	1.0881

[a] Standard deviation of the four H-H distances.

[b] Normalized standard deviation among the four H-H distances obtained by scaling the CH bond lengths to 1 a_0.

[c] Equilibrium bond length.

Table S7: HH Distances and Standard Deviations for the C_s Saddle Point Structure of CH_5^+

atom	$H^{(1)}$	$H^{(2)}$	$H^{(3)}$	$H^{(4)}$	$H^{(5)}$	σ (Å)^a	$\overline{\sigma}$ (Å)^b	$r_{CH,e}$ (Å)^c
$H^{(1)}$	-	1.8471	1.8471	1.8527	1.8527	0.0033	0.0214	1.0842
$H^{(2)}$	1.8471	-	0.9444	2.0141	1.5485	0.4706	0.1956	1.1996
$H^{(3)}$	1.8471	0.9444	-	1.5485	2.0141	0.4706	0.1956	1.1996
$H^{(4)}$	1.8527	2.0141	1.5485	-	1.7564	0.1946	0.0825	1.0991
$H^{(5)}$	1.8527	1.5485	2.0141	1.7564	-	0.1946	0.0825	1.0991

[a] Standard deviation of the four H-H distances.

[b] Normalized standard deviation among the four H-H distances obtained by scaling the CH bond lengths to 1 a_0.

[c] Equilibrium bond length.

Table S8: HH Distances and Standard Deviations Among the C_{2v} Saddle Point Structure of CH_5^+

atom	$H^{(1)}$	$H^{(2)}$	$H^{(3)}$	$H^{(4)}$	$H^{(5)}$	σ (Å)^a	$\overline{\sigma}$ (Å)^b	$r_{CH,e}$ (Å)^c
$H^{(1)}$	-	1.1785	1.1785	1.9383	1.9383	0.4387	0.1852	1.1626
$H^{(2)}$	1.1785	-	2.0065	1.7485	1.7485	0.3498	0.1454	1.1414
$H^{(3)}$	1.1785	2.0065	-	1.7485	1.7485	0.3498	0.1454	1.1414
$H^{(4)}$	1.9383	1.7485	1.7485	-	1.9021	0.1002	0.0446	1.0870
$H^{(5)}$	1.9383	1.7485	1.7485	1.9021	-	0.1002	0.0446	1.0870

[a] Standard deviation of the four H-H distances.

[b] Normalized standard deviation among the four H-H distances obtained by scaling the CH bond lengths to 1 a_0.

[c] Equilibrium bond length.

Table S9: Convergence of Zero-Point Energy for Deuterated Analogues of CH_5^+ in cm^{-1} Also Plotted in Figure 6

CH_5^+		
N_W	Guided	Unguided
100	10 949 (40)	11 228 (142)
200	10 924 (21)	11 096 (30)
500	10 922 (16)	10 971 (33)
1000	10 918 (19)	10 981 (25)
2000	10 920 (5)	10 930 (26)
5000	10 918 (6)	10 932 (8)
10 000	10 919 (2)	10 924 (7)
20 000	10 917 (4)	10 918 (7)
Reference[a]	10 917 (3)	
CD_5^+		
N_W	Guided	Unguided
100	8101 (45)	8332 (88)
200	8076 (29)	8158 (22)
500	8052 (22)	8071 (27)
1000	8052 (13)	8062 (7)
2000	8050 (15)	8061 (20)
5000	8044 (3)	8047 (16)
10 000	8045 (6)	8045 (8)
20 000	8042 (2)	8045 (8)
Reference[a]	8044 (2)	
$CH_2D_3^+$		
N_W	Guided	Unguided
100	9219 (56)	9488 (111)
200	9186 (62)	9299 (83)
500	9114 (15)	9167 (52)
1000	9105 (9)	9184 (73)
2000	9098 (10)	9126 (30)
5000	9101 (3)	9118 (38)
10 000	9096 (4)	9111 (7)
20 000	9097 (3)	9101 (8)
Reference[a]		9097 (6)

[a] Based on an unguided simulation with 20 000 walkers and $\Delta\tau = 10$ a.u.[1]

Table S10: Convergence of Zero-Point Energy for Deuterated Analogues of CH_5^+ in cm^{-1} Also Plotted in Figure S3

CH_4D^+		
N_W	Guided	Unguided
100	10 397 (61)	10 620 (78)
200	10 334 (50)	10 461 (49)
500	10 323 (20)	10 372 (97)
1000	10 306 (8)	10 329 (35)
2000	10 315 (4)	10 337 (21)
5000	10 305 (5)	10 320 (13)
10 000	10 308 (4)	10 311 (13)
20 000	10 306 (4)	10 307 (11)
Reference[a]	10 300 (6)	
$CH_3D_2^+$		
N_W	Guided	Unguided
100	9804 (77)	10058 (84)
200	9754 (51)	9927 (71)
500	9746 (23)	9751 (53)
1000	9720 (18)	9735 (53)
2000	9712 (12)	9718 (31)
5000	9697 (4)	9707 (19)
10 000	9697 (6)	9711 (11)
20 000	9698 (3)	9703 (8)
Reference[a]		9694 (3)
CHD_4^+		
N_W	Guided	Unguided
100	8618 (54)	8852 (155)
200	8619 (30)	8745 (76)
500	8573 (8)	8646 (75)
1000	8569 (21)	8632 (36)
2000	8572 (11)	8578 (14)
5000	8564 (6)	8554 (9)
10 000	8564 (5)	8560 (12)
20 000	8567 (4)	8563 (6)
Reference[a]		8563 (3)

[a] Based on an unguided simulation with 20 000 walkers and $\Delta\tau = 10$ a.u.[1]

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