

Ab Initio Calculation of the Rotational Spectrum of CH₅⁺ and CD₅⁺

Allan L. L. East, M. Kolbuszewski, and P. R. Bunker*

Steacie Institute for Molecular Sciences, National Research Council of Canada,
Ottawa, Ontario, Canada K1A 0R6

Received: February 5, 1997; In Final Form: May 2, 1997[⊗]

The highly flexible CH₅⁺ molecular ion has been shown by *ab initio* calculations to have 120 symmetrically equivalent minima of C_s symmetry in its ground electronic state. Each minimum has the structure of a hydrogen molecule bound to the apex of a CH₃⁺ pyramid, with the hydrogen molecule approximately perpendicular to the C₃ axis. Complete proton rearrangement, making all minima accessible to each other, is possible as a result of two large-amplitude internal motions: an internal rotation about the C₃ axis with an *ab initio* barrier of 30 cm⁻¹ and an internal flip motion with an *ab initio* barrier of 300 cm⁻¹ that exchanges protons between the H₂ and CH₃⁺ groups. We calculate the structure of the J = 2 ← 1, and 1 ← 0 rotational transitions for CH₅⁺ and CD₅⁺. The calculation proceeds in two stages. The first stage involves calculating rotation–torsion energies, and the second stage involves a matrix diagonalization to include the flip tunneling. In the first stage the rotation–torsion energies are calculated using the exact rotation–torsion Hamiltonian with a fully relaxed *ab initio* minimum energy path for internal rotation. The rotation–torsion energy levels and the final proton rearrangement energies that we obtain here are significantly different from those obtained earlier by us using the approximate precessing-internal-rotor Hamiltonian of X.-Q. Tan and D. W. Pratt [*J. Chem. Phys.* **1994**, *100*, 7061] that they developed for application to *p*-toluidine. This is partly because the angle of tilt between the precessing C₃ axis of the CH₃⁺ internal rotor and the C₂ axis of the CH₂ frame is too large for the approximate precessing-internal-rotor Hamiltonian to be appropriate and partly because the CH₃⁺ group significantly distorts as it internally rotates. In the final calculation we include the contribution to the torsional barrier from the zero point energies of the other (high-frequency) vibrations, the effect of centrifugal distortion, and the effect of second-order rotation–vibration interactions (i.e. the α constants).

I. Introduction

In two recent papers we have calculated the expected positions of the proton rearrangement energy levels of the highly flexible CH₅⁺ molecular ion using *ab initio* potential energy surfaces.^{1,2} The *ab initio* equilibrium structure is that of a hydrogen molecule bound to the apex of a pyramidal CH₃⁺ group, with the H₂ group approximately perpendicular to the C₃ axis of the CH₃⁺ group (see Figure 1). There is facile internal rotation and an internal flip tunneling motion through the C_{2v} structure shown in Figure 2 that exchanges protons between the H₂ and CH₃⁺ groups (see refs 1–3 and references cited therein). There are 120 symmetrically equivalent minima on the potential surface, and they are all accessible to each other through the torsion and flip motions; complete rearrangement of the five protons occurs. The most accurate *ab initio* torsional barrier is 30 cm⁻¹, and the *ab initio* flip barrier^{2,3} is 300 cm⁻¹, on the vibrationless potential.

In the earlier work^{1,2} we used the approximate precessing-internal-rotor Hamiltonian of Tan and Pratt.⁴ This Hamiltonian becomes less precise as the angle of tilt between the precessing internal-rotation C₃ axis and the C₂ axis of the framework becomes larger. It was designed by Tan and Pratt for application to molecules such as *p*-toluidine in which the tilt angle is small. We have developed the exact rotation–torsion Hamiltonian,⁵ which can allow for full geometrical relaxations along a minimum energy path for the torsional mode, and we use this Hamiltonian here with such a path.

The calculation of the proton rearrangement energy levels proceeds in two stages. In the first stage an *ab initio* minimum energy path is determined for the nuclei as a function of the

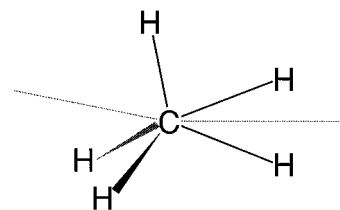


Figure 1. Equilibrium structure of CH₅⁺ showing the tilt between the internal-rotation C₃ axis and the C₂ axis of the C_{2v} framework.

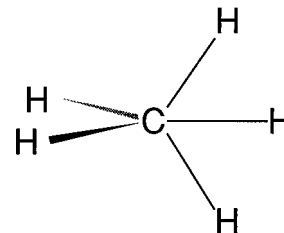


Figure 2. C_{2v} saddle point involved in the flip motion.

internal-rotation parameter τ (see section II) and used with the exact rotation–torsion Hamiltonian⁵ to obtain the rotation–torsion energy levels (section III). There are significant changes to previous predictions, and this is mainly because the tilt angle of the internal-rotation axis is large (about 14°; see Figure 1); as a result of the large tilt angle the Tan and Pratt Hamiltonian (used previously) is not appropriate. In the second stage of the calculation, a matrix involving all 120 symmetrically equivalent minima is set up to include the flip tunneling for each rotational state (section IV); this is an approximate “high-barrier” treatment as discussed in section III of ref 2. From these calculated energies we predict the proton rearrangement fine structure for the J = 2 ← 1 and 1 ← 0 rotational transitions centered around

[⊗] Abstract published in *Advance ACS Abstracts*, July 1, 1997.

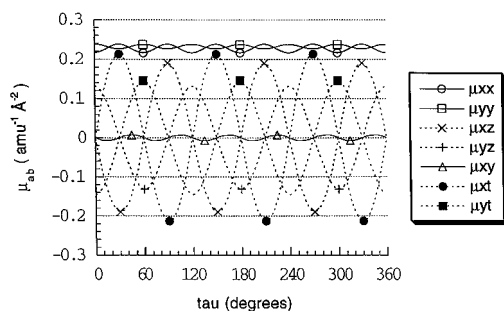


Figure 3. Variation of the μ matrix elements with τ .

450 and 225 GHz, respectively. Our final predictions include the effect of the zero point motions of the high-frequency vibrations on the torsional barrier and geometrical structure and the effect of centrifugal distortion. Results for CD₅⁺ are also reported.

We hope that these results will be of help in the search for the as yet unknown spectrum of the CH₅⁺ molecular ion.

II. *Ab Initio* Calculation of the Internal-Rotation Minimum Energy Path

In order to calculate the rotation–torsion energies, we must first determine by *ab initio* methods the geometrical changes and potential energy along the internal-rotation minimum energy path (MEP). We define the torsional angle τ as

$$\tau = (\tau_3 + \tau_4 + \tau_5 - 2\pi)/3 \quad (1)$$

where the τ_i are the dihedral angles of each of the three C–H_{*i*} bonds ($i = 3, 4, \text{ or } 5$) of the CH₃⁺ group relative to the f -H₁ axis of the H₂ group, and f is the center of mass of the H₂ group. In an initial *ab initio* calculation of the internal-rotation MEP the geometry was fully optimized at 13 values of the angle τ_3 . The calculation was performed using the MP2 method with a 6-311++G(2df,2p) basis set (84 atomic orbital functions); this was denoted level I in ref 2. The program system⁶ Gaussian 92 was used in the calculation.

The bond length parameters that vary along the MEP are as follows: r_i , the three CH bond lengths of the CH₃⁺ group ($i = 3-5$); R , the distance R between the C atom and the center of mass of the H₂ group; and r_{HH} , the HH bond length in the H₂ group. The bond angle parameters are the three angles α_i between the CH_{*i*} bonds of the CH₃⁺ group and the C– f axis, the three dihedral angles τ_i , and the angle λ of the HH bond relative to the C– f axis. The variations of these MP2 parameters with τ were accurately fitted by the following analytical functions (where bond lengths are in angstroms and bond angles are in degrees):

$$r_3 = 1.0907 + 0.0123 \cos(2\tau) + 0.0018 \cos(4\tau) \quad (2)$$

$$\alpha_3 = 106.16 - 4.74 \cos(2\tau) - 0.71 \cos(4\tau) \quad (3)$$

$$\tau_3 = \tau + 6.40 \sin(2\tau) - 0.45 \sin(4\tau) \quad (4)$$

$$R = 1.0814 - 0.0023 \cos(6\tau) \quad (5)$$

$$r_{\text{HH}} = 0.9614 + 0.0044 \cos(6\tau) \quad (6)$$

$$\lambda = 90.00 + 0.17 \cos(3\tau) \quad (7)$$

For r_4 , α_4 , and τ_4 , we replace τ by $\tau - 120^\circ$ in the expressions

TABLE 1: Rotation–Torsion Energies (cm⁻¹) Relative to $K_i = 0$ for $J = 0$

K_i	symmetry ^a	CH ₅ ⁺			CD ₅ ⁺
		MP2 ^b	CCSD(T) ^b	CCSD(T) ^c	CCSD(T) ^d
6	A' ₁	1227.459	1314.635	1315.232	672.966
6	A'' ₂	1227.508	1314.658	1315.047	672.503
5	E''	852.471	912.998	913.576	467.593
4	E'	545.687	584.419	585.264	300.096
3	A'' ₂	313.989	335.858	346.134	183.282
3	A'' ₁	299.821	321.531	311.809	153.630
2	E'	136.310	145.998	145.703	74.132
1	E''	34.084	36.505	36.459	18.581
0	A' ₁	(15.083 ^e)	(15.043 ^e)	(34.835 ^e)	(29.545 ^e)

^a In the G_{12} group. ^b Using the pure *ab initio* torsional barrier of 30 cm^{-1} . ^c Using the ZPE corrected torsional barrier of 70 cm^{-1} for CH₅⁺. ^d Using the ZPE corrected torsional barrier of 60 cm^{-1} for CD₅⁺. ^e Torsional zero point energy.

for r_3 , α_3 , and τ_3 given above. For r_5 , α_5 , and τ_5 , we replace τ by $\tau + 120^\circ$ in the expressions for r_3 , α_3 , and τ_3 given above.

From the results in eqs 2–7 we see that only a few parameters are needed to describe the variation of the bond lengths and bond angles along the torsional MEP. This means that only the optimized structures at equilibrium and at the saddle point ($\tau = 30^\circ$) are needed to specify this path. These two optimized structures have been determined at a higher level of *ab initio* theory (CCSD(T)/TZ2P + f) in ref 3, and we can therefore use these results to determine better bond length and bond angle functions. The corresponding CCSD(T) expressions are

$$r_3 = 1.0937 + 0.0110 \cos(2\tau) + 0.0014 \cos(4\tau) \quad (8)$$

$$\alpha_3 = 105.78 - 4.11 \cos(2\tau) - 0.55 \cos(4\tau) \quad (9)$$

$$\tau_3 = \tau + 5.65 \sin(2\tau) - 0.34 \sin(4\tau) \quad (10)$$

$$R = 1.1017 - 0.0016 \cos(6\tau) \quad (11)$$

$$r_{\text{HH}} = 0.9424 + 0.0028 \cos(6\tau) \quad (12)$$

$$\lambda = 90.00 + 0.08 \cos(3\tau) \quad (13)$$

The additional level of correlation in the higher level of theory improves most notably the geometry of the three center bond, i.e., the values of R and r_{HH} . The torsional barrier is taken as 30 cm^{-1} from ref 3 (see also ref 2).

Careful analysis of the internal-rotation motion of the CH₃⁺ group along the MEP shows it to be well-described as being a motion about a precessing internal rotation axis, just as envisaged by Tan and Pratt⁴ for *p*-toluidine, with an angle of tilt that is roughly constant. The angle of tilt θ is defined as the angle between the top axis (which points from the center of mass of the three protons to the center of mass of the CH₃⁺ group) and the frame axis (which points from the center of mass of the CH₃⁺ group to the center of mass of the H₂ group). If these two axes are coaxial, then $\theta = 0^\circ$. Fitting to our *ab initio* MP2 minimum energy path, we find that θ is given by (in degrees)

$$\theta = 13.43 + 1.19 \cos(6\tau) \quad (14)$$

Fitting to the *ab initio* CCSD(T) minimum energy path, we find that θ is given by (in degrees)

$$\theta = 12.17 + 0.89 \cos(6\tau) \quad (15)$$

In ref 5 we use the Tan and Pratt Hamiltonian with a tilt angle of 13.43°. The energies obtained are compared there with those obtained using our exact Hamiltonian with the same tilt

TABLE 2: Rotation–Torsion Energies (cm⁻¹) Relative to $J = K_i = 0$ for $J = 1$

<i>K</i>	<i>K_i</i>	symmetry ^a	CH ₅ ⁺			CD ₅ ⁺	
			MP2 ^b	CCSD(T) ^b	CCSD(T) ^c	CCSD(T) ^d	
1	3	A' ₂	521.880	559.499	560.419	287.261	
		A' ₁	161.354	171.471	171.112	87.064	
		A' ₁	521.876	559.494	560.404	287.248	
	2	A' ₂	161.324	171.447	171.078	87.042	
		E''	290.219	311.161	307.147	153.106	
		E''	50.981	53.576	53.517	27.267	
	1	E'	128.787	137.876	137.636	69.932	
		E'	8.755	8.671	8.671	4.372	
	0	A'' ₁	34.791	36.870	36.835	18.687	
		A'' ₂	34.602	36.684	36.648	18.592	
	0	3	A'' ₁	321.592	343.335	353.611	187.071
			A'' ₂	307.437	329.017	319.296	157.423
E'		143.919	153.480	153.185	77.923		
E''		41.693	43.987	43.941	22.373		
1		E''	7.610	7.482	7.482	3.791	
		A' ₂					

^a In the *G*₁₂ group. ^b Using the pure *ab initio* torsional barrier of 30 cm⁻¹. ^c Using the ZPE corrected torsional barrier of 70 cm⁻¹ for CH₅⁺. ^d Using the ZPE corrected torsional barrier of 60 cm⁻¹ for CD₅⁺.

TABLE 3: Rotation–Torsion Energies (cm⁻¹) Relative to $J = K_i = 0$ for $J = 2$

<i>K</i>	<i>K_i</i>	symmetry ^a	CH ₅ ⁺			CCSD(T) ^d	
			MP2 ^b	CCSD(T) ^b	CCSD(T) ^c	CCSD(T) ^d	
2	3	A'' ₁	798.440	856.186	856.798	438.007	
		A'' ₂	77.780	80.508	80.434	40.903	
		A'' ₂	798.440	856.186	856.798	438.007	
	2	A'' ₁	77.780	80.508	80.434	40.903	
		E'	507.976	544.439	545.445	279.407	
		E'	27.410	27.202	27.200	13.698	
	1	E''	284.935	304.977	302.916	152.215	
		E''	45.205	46.904	46.878	23.648	
	1	0	A' ₁	131.164	139.613	139.416	70.669
			A' ₂	131.163	139.613	139.416	70.668
		3	A' ₁	537.103	574.467	575.396	294.856
			A' ₂	176.603	186.459	186.109	94.668
A' ₂			537.091	574.453	575.353	294.817	
2		A' ₁	176.514	186.387	186.009	94.603	
	E''	305.443	326.127	322.117	160.692		
1	E''	66.201	68.540	68.482	34.849		
	E'	144.008	152.841	152.601	77.515		
	E'	23.974	23.634	23.634	11.955		
0	0	A'' ₂	50.197	52.018	51.984	26.365	
		A'' ₁	49.631	51.460	51.425	26.078	
	3	A'' ₂	336.798	358.289	368.566	194.649	
		A'' ₁	322.670	343.991	334.269	165.010	
		E'	159.139	168.444	168.150	85.506	
	1	E''	56.916	58.955	58.909	29.957	
A' ₁		22.828	22.445	22.445	11.373		

^a In the *G*₁₂ group. ^b Using the pure *ab initio* torsional barrier of 30 cm⁻¹. ^c Using the ZPE corrected torsional barrier of 70 cm⁻¹ for CH₅⁺. ^d Using the ZPE corrected torsional barrier of 60 cm⁻¹ for CD₅⁺.

angle and all other bond angles and bond lengths fixed at the mean MP2 values. It is shown in ref 5 that this is much too large a tilt angle for the approximations made in deriving the Tan and Pratt Hamiltonian to be valid. The MEP involves not only internal rotation about a precessing axis but also changes in the bond lengths and angles with torsional angle. In the next section we see that these distortions have a significant effect on the rotation–torsion energies.

III. Rotation–Torsional Energy Level Calculation

The rotation–torsion energy levels are calculated using the Hamiltonian and computer program described in ref 5. To do this, we need the elements of the 4 × 4 extended moment of inertia matrix **I** given in eqs 5–8 of ref 5, and these can be determined from the expressions for the Cartesian coordinates of the atoms. From the results in eqs 2–13 above we can obtain analytical expressions, at both the MP2 and CCSD(T) levels, for the Cartesian coordinates of the atoms as functions of τ .

We choose the molecule–fixed axes, with origin at the molecular center of mass, to be fixed to the CH₂ frame with the *z*-axis parallel to the axis that points from the carbon atom to the center of mass of the H₂ group, and the *yz*-plane parallel to the CH₂ plane. Numerically inverting the **I** matrix, we obtain the elements of the μ matrix that we use in the quantum mechanical Hamiltonian (see eqs 1–4 of ref 5) at any desired value of τ . All but three of the μ matrix elements are plotted as functions of τ in Figure 3 for the CCSD(T) level of theory; the elements μ_{zz} , and $\mu_{\tau\tau}$, and $\mu_{z\tau}$ (not plotted) have mean values of +1.97, +2.17, and -1.92 amu⁻¹ Å⁻², respectively, with variations of up to ±0.08 amu⁻¹ Å⁻² with τ .

The rotation–torsion energy levels are calculated using a combination of numerical integration and matrix diagonalization. The Numerov–Cooley method is used to integrate the $J = 0$ Schrödinger equation, with a grid size of 0.05°. This gives the $J = 0$ energies for the torsional states, and it gives the torsional wavefunctions in numerical form. The free internal rotor

TABLE 4: Rotation–Torsion Energies (cm⁻¹) relative to $J = K_i = 0$ for $J = 3$

K	K _i	symmetry ^a	CH ₅ ⁺			CD ₅ ⁺	
			MP2 ^b	CCSD(T) ^b	CCSD(T) ^c	CCSD(T) ^d	
3	3	A' ₁	1136.847	1219.005	1219.520	622.732	
		A' ₂	55.965	55.593	55.588	27.977	
		A' ₂	1136.847	1219.005	1219.520	622.732	
	2	A' ₁	A' ₁	55.965	55.593	55.588	27.977
			E''	786.277	842.571	843.204	430.654
		E''	65.617	66.894	66.875	33.610	
	1	E'	E'	503.983	539.248	540.379	276.571
			E'	143.439	151.209	151.047	76.347
	0	A'' ₁	A'' ₁	289.226	308.330	307.017	154.698
			A'' ₂	289.226	308.330	307.017	154.698
		A'' ₂	A'' ₂	821.269	878.632	879.243	449.380
			A'' ₁	100.611	102.955	102.881	52.278
A'' ₁		A'' ₁	821.269	878.632	879.243	449.380	
		A'' ₂	100.610	102.955	102.881	52.277	
2	2	E'	530.805	566.885	567.890	290.779	
		E'	50.236	49.645	49.644	25.071	
	1	E''	E''	307.769	327.426	325.368	163.593
			E''	68.011	69.329	69.303	35.011
	0	A' ₂	A' ₂	153.999	162.064	161.868	82.045
			A' ₁	153.995	162.060	161.864	82.043
	3	A' ₂	A' ₂	559.938	596.920	597.863	306.248
			A' ₁	199.477	208.941	208.607	106.076
		A' ₁	A' ₁	559.913	596.891	597.777	306.170
			A' ₂	199.299	208.798	208.407	105.944
		E''	E''	328.278	348.578	344.572	172.071
			E''	89.035	90.991	90.933	46.225
1	E'	E'	166.840	175.289	175.050	88.890	
		E'	46.799	46.077	46.077	23.327	
	A'' ₁	A'' ₁	73.305	74.740	74.707	37.881	
		A'' ₂	72.174	73.625	73.589	37.307	
	A'' ₁	A'' ₁	359.607	380.721	390.998	206.015	
		A'' ₂	345.519	366.451	356.730	176.391	
0	E'	E'	181.970	190.891	190.598	96.881	
		E''	79.762	81.416	81.371	41.339	
	A' ₂	A' ₂	45.653	44.887	44.888	22.745	
		A' ₁	45.653	44.887	44.888	22.745	

^a In the G_{12} group. ^b Using the pure *ab initio* torsional barrier of 30 cm⁻¹. ^c Using the ZPE corrected torsional barrier of 70 cm⁻¹ for CH₅⁺. ^d Using the ZPE corrected torsional barrier of 60 cm⁻¹ for CD₅⁺.

torsional quantum number is k_i , with $K_i = |k_i|$, and we can label the states using this quantum number. For each J value greater than 0 we set up a basis set of products of $2K_i^{\max} + 1$ torsional functions (as $k_i = -K_i^{\max}, -K_i^{\max} + 1, \dots, +K_i^{\max}$, where the maximum K_i value, K_i^{\max} , is chosen to ensure satisfactory convergence) with $2J + 1$ symmetric top rotational wavefunctions (as $k = -J, -J + 1, \dots, +J$) and diagonalize the full rotation–torsion Hamiltonian. This is described in detail in ref 5. We have chosen $K_i^{\max} = 12$ for the calculations involving $0 < J < 4$. Tests with $K_i^{\max} = 9$ and 15 shows that the results we obtain are converged to much better than 0.001 cm⁻¹.

The results for J less than 4 are given in Tables 1–4, where we label states using (J, K, K_i) , and we add G_{12} symmetries. In the G_{12} group the statistical weights for CH₅⁺ are $A'_1(4), A'_2(4), E'(4), A''_1(12), A''_2(12)$, and $E''(12)$. The statistical weights for CD₅⁺ are $A'_1(66), A'_2(66), E'(96), A''_1(33), A''_2(33)$, and $E''(48)$. The best results in Tables 1–4 are those obtained using the CCSD(T) minimum energy path and a torsional barrier corrected for the torsional variation of the zero point energies (ZPE) of the eleven other (high-frequency) vibrations; the ZPE corrected torsional barrier is estimated to be 70 cm⁻¹ for CH₅⁺ and 60 cm⁻¹ for CD₅⁺, on the basis of our scaled MP2/6-311++G-(2df,2p) harmonic frequencies.

Comparing the results obtained here with those obtained using the Tan and Pratt Hamiltonian⁴ that are given in the final column of Tables 2–4 in ref 1, we see that there are very significant differences. As discussed in ref 5, an important contribution to this difference is the use of the Tan and Pratt Hamiltonian in a situation for which it is inappropriate because of the large

value of the angle of tilt in CH₅⁺. We see that the $J = 1 \leftarrow 0$ wavenumbers are close to $2\bar{B}$. The results we obtain here using the MP2 minimum energy path for $J = 0$ and 1 can be compared to those given in column 1 of Table 3 of ref 5, where we use the exact rotation–torsion Hamiltonian and an internal rotation path having a precessing CH₃⁺ internal rotor with a fixed tilt angle of 13.43°, with no variation in the bond lengths and angles as τ changes. The differences are due to the significant deformation in the CH₃⁺ group as it internally rotates.

IV. Effect of the Flip Tunneling

To include the effect of the flip tunneling, we use the *ab initio* MEP and potential energy surface determined in ref 2 and the high-barrier matrix technique as described in section III of ref 2. The matrix technique is an approximation that we can justify since the splitting caused by the flip motion is small (see ref 2). For each (J, K) state we have a stack of K_i energies. We focus on the lowest four energies, i.e., those having $K_i = 0, 1, 2$, and 3(lower), where the $K_i = 1$ and 2 levels are doubly degenerate. For each (J, K) state we set up a 6×6 matrix with matrix elements chosen to generate these four lowest torsional energies and construct a 120×120 matrix with 20 of these 6×6 matrices along the diagonal. Off-diagonal matrix elements having the value -0.69 cm⁻¹ for CH₅⁺ and -0.039 cm⁻¹ for CD₅⁺ (determined in ref 2) are placed to link each of the minima that are connected by the flip tunneling. There are 60 connections in all between the 120 minima. Diagonalizing this matrix gives the lowest 120 torsion–flip (or proton rearrangement) levels belonging to that particular (J, K) state.

TABLE 5: CH₅⁺ Proton Rearrangement Energy Levels for $K = 0$

K_i	$J = 2$		$J = 1$		$J = 0$		
	E/cm^{-1}	$\Gamma(\text{sw})^a$	E/cm^{-1}	$\Gamma(\text{sw})$	E/cm^{-1}	$\Gamma(\text{sw})$	
3(lower)	335.196	$H_2^-(2)$	320.223	$H_2^+(2)$	312.736	$H_2^-(2)$	
	335.196	$I^+(0)$	320.223	$I^-(0)$	312.736	$I^+(0)$	
	334.849	$G_2^-(4)$	319.876	$G_2^+(4)$	312.389	$G_2^-(4)$	
	334.617	$G_1^+(0)$	319.644	$G_1^-(0)$	312.157	$G_1^+(0)$	
	334.269	$A_2^-(6)$	319.296	$A_2^+(6)$	311.809	$A_2^-(6)$	
2	169.537	$G_1^-(0)$	154.572	$G_1^+(0)$	147.090	$G_1^-(0)$	
	169.194	$H_2^+(2)$	154.229	$H_2^-(2)$	146.747	$H_2^+(2)$	
	169.191	$I^+(0)$	154.226	$I^-(0)$	146.744	$I^+(0)$	
	168.963	$I^-(0)$	153.998	$I^+(0)$	146.516	$I^-(0)$	
	168.613	$G_1^+(0)$	153.648	$G_1^-(0)$	146.166	$G_1^+(0)$	
	168.500	$H_1^-(0)$	153.535	$H_1^+(0)$	146.053	$H_1^-(0)$	
	168.495	$H_2^-(2)$	153.530	$H_2^+(2)$	146.048	$H_2^-(2)$	
	168.267	$H_1^+(0)$	153.302	$H_1^-(0)$	145.820	$H_1^+(0)$	
	1	60.296	$G_2^+(4)$	45.328	$G_2^-(4)$	37.846	$G_2^+(4)$
		59.952	$I^-(0)$	44.984	$I^+(0)$	37.502	$I^-(0)$
59.946		$H_1^-(0)$	44.978	$H_1^+(0)$	37.496	$H_1^-(0)$	
59.715		$I^+(0)$	44.474	$I^-(0)$	37.265	$I^+(0)$	
59.375		$G_2^-(4)$	44.407	$G_2^+(4)$	36.925	$G_2^-(4)$	
59.264		$H_1^+(0)$	44.296	$H_1^-(0)$	36.814	$H_1^+(0)$	
59.253		$H_2^+(2)$	44.285	$H_2^-(2)$	36.803	$H_2^+(2)$	
59.024		$H_2^-(2)$	44.056	$H_2^+(2)$	36.574	$H_2^-(2)$	
0		23.364	$I^-(0)$	8.401	$I^+(0)$	0.919	$I^-(0)$
		23.360	$H_1^+(0)$	8.397	$H_1^-(0)$	0.915	$H_1^+(0)$
	23.021	$G_1^+(0)$	8.058	$G_1^-(0)$	0.576	$G_1^+(0)$	
	22.787	$G_2^-(4)$	7.824	$G_2^+(4)$	0.342	$G_2^-(4)$	
	22.445	$A_1^+(0)$	7.482	$A_1^-(0)$	0.000	$A_1^+(0)$	

^a Symmetry in G_{240} and statistical weight.

The high-barrier approximation that we use means that we are neglecting flip tunneling interactions between the lowest four torsional states and higher torsional states, as well as neglecting flip tunneling interactions between states having different K values.

The energies obtained using the CCSD(T) minimum energy path and the ZPE corrected torsional barriers are given in Tables 5 and 6 for CH₅⁺ and Table 8 for CD₅⁺. In the tables the symmetries in the G_{240} molecular symmetry group and the corresponding nuclear spin statistical weights, appropriate when complete hydrogen rearrangement is feasible, are given (see ref 2 for details). States with statistical weight zero are missing; more than half the rotational levels are missing for CH₅⁺. In Table 7 we give the energies of the lowest level of each symmetry for CH₅⁺. The calculated $J = 2 \leftarrow 1$ and $1 \leftarrow 0$ transition wavenumbers, using $\Delta K = \Delta K_i = 0$ selection rules, are given in Tables 9 and 10 for the $K = 0$ states of CH₅⁺ and CD₅⁺, respectively. The effect of the flip tunneling on these rotational transition wavenumbers is negligible to within 0.001 cm⁻¹.

V. Summary and Discussion

Calculating the *ab initio* minimum energy path and potential energy for the internal rotation motion in CH₅⁺, and using the exact rotation–torsion Hamiltonian developed in ref 5, we have obtained rotation–torsion energy levels for the internal rotation of the CH₃⁺ group in the CH₅⁺ molecular ion. This internal rotation motion is hindered by a six-fold barrier with an *ab initio* barrier height of 30 cm⁻¹. The motion is about a C_3 axis that precesses about the molecule-fixed z -axis, exactly as envisaged by Tan and Pratt⁴ in *p*-toluidine. However, in CH₅⁺ there is also a significant distortion of the CH₃⁺ group as it internally rotates, which affects the rotation–torsion energies. Further, there is an internal flip tunneling motion that interchanges a CH₃⁺ and an H₂ proton, which when included with the torsional

TABLE 6: CH₅⁺ Proton Rearrangement Energy Levels for $J = K = 1$

K_i	$K = 1(\text{lower})$		$K = 1(\text{upper})$		
	E/cm^{-1}	$\Gamma(\text{sw})^a$	E/cm^{-1}	$\Gamma(\text{sw})$	
3(lower)	172.006	$H_1^-(0)$	172.044	$I^-(0)$	
	172.006	$I^+(0)$	172.038	$H_1^+(0)$	
	171.659	$G_1(0)$	171.700	$G_1^+(0)$	
	171.428	$G_2^+(4)$	171.459	$G_2^-(4)$	
	171.078	$A_1^-(0)$	171.112	$A_1^+(0)$	
2	54.904	$G_2^-(4)$	308.534	$G_2^+(4)$	
	54.565	$H_1^+(0)$	308.190	$I^-(0)$	
	54.561	$I^+(0)$	308.190	$H_1^-(0)$	
	54.346	$I^-(0)$	307.958	$I^+(0)$	
	53.994	$G_2^+(4)$	307.612	$G_2^-(4)$	
	53.872	$H_2^-(2)$	307.496	$H_1^+(0)$	
	53.862	$H_1^-(0)$	307.496	$H_2^+(2)$	
	53.640	$H_2^+(2)$	307.263	$H_2^-(2)$	
	1	10.058	$G_1^+(0)$	139.023	$G_1^-(0)$
		9.703	$H_2^-(2)$	138.677	$I^+(0)$
9.701		$I^-(0)$	138.674	$H_2^+(2)$	
9.474		$I^+(0)$	138.436	$I^-(0)$	
9.126		$G_1^-(0)$	138.092	$G_1^+(0)$	
9.010		$H_1^+(0)$	137.986	$H_2^-(2)$	
9.006		$H_2^+(2)$	137.981	$H_1^-(0)$	
8.785		$H_1^-(0)$	137.748	$H_1^+(0)$	
0		37.577	$H_2^+(2)$	37.757	$I^+(0)$
		37.563	$I^-(0)$	37.756	$H_2^-(2)$
	37.209	$G_2^+(4)$	37.411	$G_2^-(4)$	
	36.999	$G_1^-(0)$	37.179	$G_1^+(0)$	
	36.648	$A_2^+(6)$	36.835	$A_2^-(6)$	

^a Symmetry in G_{240} and statistical weight.

tunneling, makes all 120 symmetrically equivalent minima accessible and allows complete proton rearrangement. We have calculated the effect of this flip tunneling on the energy levels and find that it has a very small effect on the rotational transition frequencies since the upper and lower states of the rotational

TABLE 7: Lowest Energy Level of Each Symmetry for CH₅⁺

$\Gamma(\text{sw})^a$	E/cm^{-1}	$[K_i, J, K]$	$\Gamma(\text{sw})^a$	E/cm^{-1}	$[K_i, J, K]$
$A_1^+(0)$	0.000	[0,0,0]	$A_1^-(0)$	7.482	[0,1,0]
$A_1^+(6)$	36.648	[0,1,1(lower)]	$A_2^-(6)$	36.835	[0,1,1(upper)]
$G_1^+(0)$	0.576	[0,0,0]	$G_1^-(0)$	8.058	[0,1,0]
$G_2^+(4)$	7.824	[0,1,0]	$G_2^-(4)$	0.342	[0,0,0]
$H_1^+(0)$	0.915	[0,0,0]	$H_1^-(0)$	8.397	[0,1,0]
$H_2^+(2)$	9.006	[1,1,1(lower)]	$H_2^-(2)$	9.703	[1,1,1(lower)]
$I^+(0)$	8.401	[0,1,0]	$I^-(0)$	0.919	[0,0,0]

^a Symmetry in G_{240} and statistical weight.**TABLE 8: CD₅⁺ Deuteron Rearrangement Energy Levels for $K = 0$**

K_i	$J = 2$		$J = 1$		$J = 0$		
	E/cm^{-1}	$\Gamma(\text{sw})^a$	E/cm^{-1}	$\Gamma(\text{sw})$	E/cm^{-1}	$\Gamma(\text{sw})$	
3(lower)	165.062	$H_2^-(3)$	157.475	$H_2^+(3)$	153.682	$H_2^-(3)$	
	165.062	$I^+(6)$	157.475	$I^-(6)$	153.682	$I^+(6)$	
	165.042	$G_2^-(0)$	157.455	$G_2^+(0)$	153.662	$G_2^-(0)$	
	165.029	$G_1^+(24)$	157.442	$G_1^-(24)$	153.649	$G_1^+(24)$	
	165.010	$A_2^-(0)$	157.423	$A_2^+(0)$	153.630	$A_2^-(0)$	
2	85.584	$G_1^-(24)$	78.001	$G_1^+(24)$	74.210	$G_1^-(24)$	
	85.564	$H_2^+(3)$	77.981	$H_2^-(3)$	74.190	$H_2^+(3)$	
	85.564	$I^+(6)$	77.981	$I^-(6)$	74.190	$I^+(6)$	
	85.551	$I^-(6)$	77.968	$I^+(6)$	74.177	$I^-(6)$	
	85.532	$G_1^+(24)$	77.949	$G_1^-(24)$	74.158	$G_1^+(24)$	
	85.525	$H_1^-(15)$	77.942	$H_1^+(15)$	74.151	$H_1^-(15)$	
	85.525	$H_2^-(3)$	77.942	$H_2^+(3)$	74.151	$H_2^-(3)$	
	85.512	$H_1^+(15)$	77.929	$H_1^-(15)$	74.138	$H_1^+(15)$	
	1	30.035	$G_2^+(0)$	22.451	$G_2^-(0)$	18.659	$G_2^+(0)$
		30.015	$I^-(6)$	22.431	$I^+(6)$	18.639	$I^-(6)$
30.015		$H_1^-(15)$	22.431	$H_1^+(15)$	18.639	$H_1^-(15)$	
30.002		$I^+(6)$	22.418	$I^-(6)$	18.626	$I^+(6)$	
29.983		$G_2^-(0)$	22.399	$G_2^+(0)$	18.607	$G_2^-(0)$	
29.976		$H_1^+(15)$	22.392	$H_1^-(15)$	18.600	$H_1^+(15)$	
29.976		$H_2^+(3)$	22.392	$H_2^-(3)$	18.600	$H_2^+(3)$	
29.963		$H_2^-(3)$	22.379	$H_2^+(3)$	18.587	$H_2^-(3)$	
0		11.425	$I^-(6)$	3.843	$I^+(6)$	0.052	$I^-(6)$
		11.425	$H_1^+(15)$	3.843	$H_1^-(15)$	0.052	$H_1^+(15)$
	11.405	$G_1^+(24)$	3.823	$G_1^-(24)$	0.032	$G_1^+(24)$	
	11.392	$G_2^-(0)$	3.810	$G_2^+(0)$	0.019	$G_2^-(0)$	
	11.373	$A_1^+(21)$	3.791	$A_1^-(21)$	0.0	$A_1^+(21)$	

^a Symmetry in G_{240} and statistical weight.**TABLE 9: CH₅⁺ CCSD(T)^a Wavenumbers (cm⁻¹) for the $J = 2 \leftarrow 1$ and $1 \leftarrow 0$ Rotational Transitions with $K = 0$**

K_i	$J = 2 \leftarrow 1$	$J = 1 \leftarrow 0$	K_i	$J = 2 \leftarrow 1$	$J = 1 \leftarrow 0$
3(upper)	14.954	7.477	1	14.968	7.482
3(lower)	14.973	7.487	0	14.963	7.482
2	14.965	7.482			

^a Using the ZPE corrected torsional barrier of 70 cm⁻¹.**TABLE 10: CD₅⁺ CCSD(T)^a Wavenumbers (cm⁻¹) for the $J = 2 \leftarrow 1$ and $1 \leftarrow 0$ Rotational Transitions with $K = 0$**

K_i	$J = 2 \leftarrow 1$	$J = 1 \leftarrow 0$	K_i	$J = 2 \leftarrow 1$	$J = 1 \leftarrow 0$
3(upper)	7.578	3.789	1	7.584	3.791
3(lower)	7.587	3.793	0	7.582	3.791
2	7.583	3.791			

^a Using the ZPE corrected torsional barrier of 60 cm⁻¹.

transitions have very similar splitting patterns. In Tables 9 and 10 we give the calculated $J = 2 \leftarrow 1$ and $1 \leftarrow 0$ transition wavenumbers for the $K = 0$ states. Our results are very different from those that we obtained before,^{1,2} since we no longer make the approximations of the model Hamiltonian from ref 4, which is only valid for small angles of tilt of the C_3 axis and further assumes that there is no distortion of the rigid CH₃⁺ group as it internally rotates.

The results presented in Tables 5–10 neglect rotation–

vibration interactions involving the other (high-frequency) vibrations. There are two effects that we should allow for: the difference between \bar{B}_0 and \bar{B}_e caused by second order rotation–vibration interaction (i.e., the α constants) and centrifugal distortion. We calculate the α constants and the centrifugal distortion constants with the ANHARM program⁸ using standard expressions,⁹ employing equilibrium-structure molecular constants computed at the MP2/6-311++G(2df,2p) level of *ab initio* theory.¹⁰ By summing the $\alpha/2$ values for the 11 modes (excepting the torsional mode) we determine that

$$\bar{B}_0 = 0.9995\bar{B}_e \quad (16)$$

We also determine that $D_J = 0.000\,063\text{ cm}^{-1}$.

Using eq 16 to scale the rotational transition wavenumbers and including the effect of D_J , we obtain the results for CH₅⁺ presented in Table 11; these represent our final predictions. The rotational transitions could have observable splittings of the order of 1 MHz from the flip tunneling,² and the statistical weights given in Tables 5 and 6 will help in their characterization for CH₅⁺. The flip tunneling causes energy level splittings (rather than rotational transition splittings) that may be observable in the rotation–vibration spectrum of CH₅⁺ and CD₅⁺; the energies and statistical weights given in Tables 5, 6, and 8 could be useful in this case.

TABLE 11: CH₅⁺ CCSD(T) Wavenumbers (cm⁻¹) for the $J = 2 \leftarrow 1$ and $1 \leftarrow 0$ Rotational Transitions with $K = 0$, after Correcting for the Effects of D_J and the α Constants

K_i	$J = 2 \leftarrow 1$	$J = 1 \leftarrow 0$	K_i	$J = 2 \leftarrow 1$	$J = 1 \leftarrow 0$
3(upper)	14.945	7.473	1	14.959	7.478
3(lower)	14.964	7.483	0	14.954	7.478
2	14.956	7.478			

Very recently, a new *ab initio* investigation of CH₅⁺ has been published,¹¹ and it is suggested that the zero point energies of the high-frequency vibrations could eliminate the barrier for the flip (through the C_{2v} conformation shown in Figure 2) on the “effective” potential surface for fluxional motion. If we consider the fluxional motion in this molecule to be two-dimensional (involving the torsion and the flip), then we can use the harmonic frequencies for the other 10 vibrational modes³ to estimate the zero point energy corrections at the two C_s and one C_{2v} stationary points. Using the harmonic frequencies, we determine that the zero point corrected barrier between the two C_s structures is reduced from 30 to 1 cm⁻¹ and that the barrier between the equilibrium C_s structure and the C_{2v} structure is reduced from 300 to 170 cm⁻¹. However, the 10-mode zero point energy is of the order of 10 000 cm⁻¹ at all geometries, and thus the anharmonicity correction to the harmonic zero point energy will be of the order of the corrections we are seeking to calculate. Hence, it is not yet clear by how much the zero point energy in the other 10 modes will change the effective potential for the torsion–flip motion. This makes it even more necessary to try to locate experimentally the pattern of the lower energy levels. By comparison with the predictions of this paper one will be able to see if the zero point energy variation is important.

Acknowledgment. We are grateful to Drs. J. K. G. Watson and Per Jensen for critically reading the manuscript.

References and Notes

- (1) Bunker, P. R. *J. Mol. Spectrosc.* **1996**, *176*, 297.
- (2) Kolbuszewski, M.; Bunker, P. R. *J. Chem. Phys.* **1996**, *105*, 3649.
- (3) Schreiner, P. R.; Kim, S.-J.; Schaefer, H. F.; Schleyer, P. v. R. *J. Chem. Phys.* **1993**, *99*, 3716.
- (4) Tan, X.-Q.; Pratt, D. W. *J. Chem. Phys.* **1994**, *100*, 7061.
- (5) East, A. L. L.; Bunker, P. R. *J. Mol. Spectrosc.* **1997**, *183*, 157.
- (6) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*; Gaussian Inc.: Pittsburgh, PA, 1992.
- (7) Herzberg, G. *Molecular Spectra and Molecular Structure, Vol. I. Spectra of Diatomic Molecules*; Krieger: Malabar, FL, 1989.
- (8) Clabo, D. A.; Allen, W. D.; Remington, R. B.; Yamaguchi, Y.; Schaefer, H. F. *Chem. Phys.* **1988**, *123*, 187.
- (9) Papoušek, D.; Aliev, M. R. *Molecular Vibrational Rotational Spectra*; Academia: Prague, 1982.
- (10) For the calculation of the α_i constants the required third derivatives of the energy with respect to internal coordinates were computed from analytical second derivatives. To do this, the second derivatives were determined at 20 locations displaced about the equilibrium geometry. The displacements were taken along symmetrized internal coordinates in increments of 0.001 Å and 0.002 rad for linear and angular coordinates, respectively. Two resonant Coriolis interactions were detected which vitiate the use of the perturbation theory expressions for the individual α_i constants. However, the sum of the α_i constants for B and C , which is all we need, is unaffected by these resonances.
- (11) Müller, H.; Kutzelnigg, W.; Noga, J.; Klopper, W. *J. Chem. Phys.* **1997**, *106*, 1863.