

A General Rotation–Contortion Hamiltonian with Structure Relaxation: Application to the Precessing Internal Rotor Model

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A general computer program has been written to compute rotation–contortion energy levels, using the semirigid-bender structure-relaxation Hamiltonian, for any molecule having one large amplitude (contortional) degree of freedom. In an application it is necessary to input the contortional potential energy function and the expressions for the molecule fixed *xyz* coordinates of the nuclei as functions of the contortional coordinate. The contortional coordinate can be of any type, such as an internal rotation, an inversion, or a bend, but the boundary conditions in the numerical integration part of the program must be chosen appropriately; these boundary conditions are in a separate subroutine. The code is applied to the model of a tilted and precessing internally rotating CH_3^+ group in protonated methane, CH_5^+ . From the results we can determine quantitatively the effect of the approximations present in the Hamiltonian of X-Q. Tan and D. W. Pratt [*J. Chem. Phys.* **100**, 7061–7067 (1994)] when the angle of tilt of the internal rotation axis becomes large.

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I. INTRODUCTION

In a study of *p*-toluidene, Tan and Pratt (1) developed an approximate rotation–torsion Hamiltonian for a methyl internal rotor attached to a C_{2v} frame. This Hamiltonian describes the methyl internal rotor as rigidly rotating about a tilted and precessing internal rotation axis, where the axis of internal rotation precesses at three times the rate of the internal rotation. This nicely models the form of some extra symmetry allowed terms that were introduced by Sørensen (2) in the rotation–torsion Hamiltonian of nitromethane. Recently Sørensen (3) considered the problem further, using perturbation theory to allow for full structural relaxation in these terms. In Refs. (4, 5) the rotation–torsion energy levels involving the torsion of the CH_3^+ group in the CH_5^+ molecular ion were calculated using the Hamiltonian of Ref. (1). In these calculations the angle of tilt for the CH_3^+ group was taken from *ab initio* results (6), and at 14° it is much larger than that envisaged by Tan and Pratt when they developed their model. It is thus necessary to test the applicability of the model when the tilt angle is large.

In the present paper we first discuss the general rotation–contortion Hamiltonian, and the structure of the computer program that we have written to diagonalize it. The program is applicable to the calculation of the rotation–contortion energies of any molecule that has one large amplitude vibrational degree of freedom, and such problems have been considered before (most recently by Makarewicz (7) who quoted an extensive list of references to earlier work). We use the program to calculate the rotation–torsion energies for CH_5^+ . We model the nuclear coordinates as analytic functions of the torsional angle and the tilt angle so that the C_3

axis of the CH_3^+ group precesses at three times the rate of the internal rotation of the CH_3^+ group and so that there is a constant angle of tilt. We compare the exact rotation–torsion energies obtained with those obtained using the Hamiltonian of Ref. (1) and find that the error in the latter is significant for large values of the tilt angle.

II. THE CALCULATION OF ROTATION–CONTORTION ENERGIES

We consider a molecule with one low-frequency large amplitude internal contortion mode τ , and we adiabatically separate it from the other “fast” vibrational degrees of freedom. The electronic and “fast” vibrations contribute together to provide the effective contortional potential function $V(\tau)$. The four-dimensional Hamiltonian for rotation and τ motion can be written as (8)

$$\hat{H} = \hat{H}^{\text{rot}} + \hat{H}^{\text{rot},\tau} + \hat{H}^\tau, \quad [1]$$

where

$$\hat{H}^{\text{rot}} = (1/2) \sum_{\alpha,\beta=\text{xyz}} \mu_{\alpha\beta} \hat{J}_\alpha \hat{J}_\beta, \quad [2]$$

$$\hat{H}^{\text{rot},\tau} = (1/2) \sum_{\alpha=\text{xyz}} \{ [\hat{J}_\tau, \mu_{\alpha\tau}] \hat{J}_\alpha + \mu_{\alpha\tau} (\hat{J}_\alpha \hat{J}_\tau + \hat{J}_\tau \hat{J}_\alpha) \}, \quad [3]$$

and

$$\begin{aligned} \hat{H}^\tau = & (1/2) \mu_{\tau\tau} \hat{J}_\tau^2 + (1/2) [\hat{J}_\tau, \mu_{\tau\tau}] \hat{J}_\tau \\ & + (1/2) \mu^{1/4} [\hat{J}_\tau, \mu_{\tau\tau} \mu^{-1/2} [\hat{J}_\tau, \mu^{1/4}]] + V(\tau). \end{aligned} \quad [4]$$

In Eqs. [2] to [4] \hat{J}_x , \hat{J}_y , and \hat{J}_z are the components of the total angular momentum operator along molecule fixed axes, $\hat{J}_\tau = -i\hbar \partial/\partial\tau$ is the torsional angular momentum operator, μ is the determinant of the 4×4 matrix $\boldsymbol{\mu}$, and the matrix $\boldsymbol{\mu}$ is the inverse of the generalized 4×4 moment of inertia matrix \mathbf{I} . The elements of the 4×4 matrix \mathbf{I} are (8)

$$I_{\alpha\alpha} = \sum_i m_i (a_{i\beta}^2 + a_{i\gamma}^2), \quad [5]$$

$$I_{\alpha\beta} = - \sum_i m_i a_{i\alpha} a_{i\beta}, \quad [6]$$

$$I_{\tau\tau} = \sum_i m_i (a_{ix}^{\prime 2} + a_{iy}^{\prime 2} + a_{iz}^{\prime 2}), \quad [7]$$

and

$$I_{\alpha\tau} = - \sum_i m_i (a_{i\gamma} a'_{i\beta} - a_{i\beta} a'_{i\gamma}), \quad [8]$$

where m_i is the mass of the i th nucleus, $a_{i\alpha}$ is the Cartesian coordinate of the i th nucleus along the α molecule-fixed axis, $a'_{i\alpha}$ is the partial derivative of this coordinate with respect to τ , and $[\alpha\beta\gamma]$ must be chosen in cyclic order from $[xyz]$. Each element of \mathbf{I} , and hence of $\boldsymbol{\mu}$, can be nonzero and τ -dependent. The computation of the rotation–contortion energies involves three stages: (1) setting up \mathbf{I} and $V(\tau)$, (2) calculating the eigenvalues and numerical eigenfunctions of \hat{H}^τ , and (3) diagonalizing the full Hamiltonian \hat{H} .

II.1. The Elements of the Matrix \mathbf{I}

The elements of the matrix \mathbf{I} are molecule specific and are calculated from the expressions for the $a_{i\alpha}$ and $a'_{i\alpha}$ using Eqs. [5] to [8]. Thus the initial step is to define how the molecule fixed xyz axes are attached to the molecule and to determine the expressions for the $a_{i\alpha}$. Once the elements of the 4×4 matrix \mathbf{I} are set up and the potential function provided, the rest of the calculation can proceed. It is best to use analytical expressions for the Cartesian derivatives $a'_{i\alpha}$ needed in the calculation of some of the elements of \mathbf{I} in order to maintain precision; this is because numerical differentiation of the elements of $\boldsymbol{\mu} = \mathbf{I}^{-1}$ is performed later.

Due to the “brute-force” way we diagonalize the Hamiltonian the motivation for the choice of the axis system can be different from the customary one of trying to eliminate off-diagonal elements of \mathbf{I} . Rather than having to choose from among the PAM, IAM, or Hougen’s RAM systems (9, 10) to simplify the \mathbf{I} matrix, and subsequent Hamiltonian expression, one is free to choose the axes for other reasons, such as ease in obtaining functions for the Cartesian coordinates of the atoms. For a molecule with an internal rotor attached to a “frame” the axes can be tied to the frame or to the internal rotor, or to any intermediate position. The same energies will be obtained (and this provides a check

on the program), although the level of convergence achieved with a given size of basis set will change.

II.2. Determining the Eigenvalues and Eigenfunctions of \hat{H}^τ

The formulas of Ref. (8) were developed for triatomic molecules using molecule fixed axes oriented so that $I_{x\tau} = I_{y\tau} = I_{z\tau} = 0$. In the general case Eq. [4] for \hat{H}^τ reduces to

$$\hat{H}^\tau = - \frac{\hbar^2}{2} \left\{ \mu_{\tau\tau} \frac{\partial^2}{\partial\tau^2} + \left(\frac{\partial\mu_{\tau\tau}}{\partial\tau} \right) \frac{\partial}{\partial\tau} + \mu^{1/4} \left[\frac{\partial}{\partial\tau} \mu_{\tau\tau} \mu^{-1/2} \left(\frac{\partial}{\partial\tau} \mu^{1/4} \right) \right] \right\} + V(\tau) \quad [9]$$

which is the same as Eq. [39] in Ref. (8) except that $1/I_{\tau\tau}^0$ has been replaced by $\mu_{\tau\tau}$. The eigenfunctions of this one-dimensional Hamiltonian are determined numerically using a generalized Numerov–Cooley (11) procedure.

The Numerov–Cooley procedure can be generalized to solve differential equations of the type

$$P''(\tau) = G(\tau, E)P(\tau), \quad [10]$$

where $P''(\tau)$ is the second derivative with respect to τ of the function $P(\tau)$, E is an eigenvalue, and $G(\tau, E)$ is a function of τ and of E . We use the recursion formula

$$Y_{i+1} = 2Y_i - Y_{i-1} + (\Delta\tau)^2 G_i P_i, \quad [11]$$

where $Y_i = [1 - (1/12)(\Delta\tau)^2 G_i] P_i$, i is shorthand for the i th value of the coordinate τ , and $\Delta\tau$ is the grid size. The energy correction DE for the iterating (initially guessed) energy eigenvalue E is given by

$$DE = \frac{(-Y_{m-1} + 2Y_m - Y_{m+1})/(\Delta\tau)^2 + G_m P_m}{\sum_{i=1}^n (-\partial G/\partial E)_i P_i^2}, \quad [12]$$

where m is the grid point label of the meeting point of the forward and backward integrations and n is the number of evenly spaced points chosen along the coordinate τ . If we put

$$P(\tau) = N\psi(\tau)\sqrt{g(\tau)}, \quad [13]$$

where $\psi(\tau)$ is the normalized eigenfunction of \hat{H}^τ , $g(\tau) = (1/2)\hbar^2\mu_{\tau\tau}$, and N is a constant, then $P(\tau)$ satisfies Eq. [10], the generalized Numerov–Cooley problem, with

$$G(\tau, E) = f_1(\tau) + [V(\tau) - E]/g(\tau), \quad [14]$$

where

$$f_1(\tau) = \text{aux}''(\tau)/\text{aux}(\tau), \quad [15]$$

$$\text{aux}(\tau) = \mu_{\tau\tau}^{1/2} \mu^{-1/4}, \quad [16]$$

and

$$N = \sqrt{\sum_{i=1}^n (-\partial G/\partial E)_i P_i^2}. \quad [17]$$

This looks quite similar to Eqs. [41]–[43] of Ref. (8) but is more general. In our code, $\text{aux}''(\tau)$, the double differentiation of $\text{aux}(\tau)$ with respect to τ , is determined numerically so as not to be molecule-dependent. Boundary conditions for the Numerov–Cooley algorithm are kept in a separate subroutine, and are dependent upon the type of contortion (inversion, bending, internal rotation, etc.).

For an internally rotating molecule the resulting energy levels will correspond to $J = 0$ levels regardless of how the Cartesian axes are fixed to the molecule, as long as the molecule undergoes one complete internal rotation as τ advances by 2π , and $a_{i\alpha}(2\pi) = a_{i\alpha}(0)$ for all nuclear coordinates.

II.3. Diagonalizing the Rotation–Contortion Hamiltonian \hat{H}

Having obtained the contortion wavefunctions $\psi(\tau)$ in numerical form, we multiply them by a complete set of appropriate linear combinations of symmetric top rotational basis functions $|J, k, 0\rangle$ (we need only consider the $M_J = 0$ functions for calculations in free space; see Eq. (8-111) of Ref. (13)) to form a basis set for diagonalizing the full rotation–contortion Hamiltonian. We use the following linear combinations of symmetric top functions (with $K = |k|$), as devised by Szalay and Lane (12), in order that all matrix elements be real.

$$|J, 0\rangle = |J, 0, 0\rangle, \quad [18]$$

$$|J, K\rangle = -(1/\sqrt{2})(|J, K, 0\rangle + (-1)^K |J, -K, 0\rangle), \quad [19]$$

and

$$|J, -K\rangle = (i/\sqrt{2})[|J, -K, 0\rangle - (-1)^K |J, K, 0\rangle], \quad [20]$$

where $K = 1, 2, \dots, J$. If we let $|p\rangle$ represent the p th product of numerical contortion function $|m_p\rangle$ with Szalay-Lane basis function $|J_p K_p\rangle$, and let $|q\rangle$ represent the q th product, then the (pq) th matrix element of the Hamiltonian can be written as

$$H_{pq} = H_{pq}^{\text{rot}} + H_{pq}^{\text{rot},\tau} + H_{pq}^{\tau}, \quad [21]$$

where

$$H_{pq}^{\text{rot}} = (1/2) \sum_{\alpha,\beta=xyz} \langle m_p | \mu_{\alpha\beta} | m_q \rangle \langle J_p K_p | \hat{J}_\alpha \hat{J}_\beta | J_q K_q \rangle, \quad [22]$$

$$H_{pq}^{\text{rot},\tau} = -(1/2) i\hbar \sum_{\alpha=xyz} (\langle m_p | \mu'_{\alpha\tau} | m_q \rangle + 2 \langle m_p | \mu_{\alpha\tau} | m'_q \rangle) \langle J_p K_p | \hat{J}_\alpha | J_q K_q \rangle, \quad [23]$$

and

$$H_{pq}^{\tau} = \delta_{pq} \epsilon_{m_p}^{\tau}. \quad [24]$$

The primes refer to partial differentiation with respect to τ , δ_{pq} is the Kronecker delta, and $\epsilon_{m_p}^{\tau}$ is the eigenvalue of \hat{H}^{τ} associated with the contortion function $|m_p\rangle$. The partial differentiations are performed numerically. These formula require two different kinds of integrals: those over τ (done quite acceptably with Simpson's Rule) and those over the rotational degrees of freedom. Since the Szalay-Lane functions are expressed as linear combinations of symmetric top eigenfunctions, we need expressions for matrix elements of \hat{J}_x , \hat{J}_y , and \hat{J}_z in the symmetric top basis. These can be derived from the matrix elements in Table 8-1 of Ref. (13), using $\hat{J}_x = (\hat{J}_m^+ + \hat{J}_m^-)/2$ and $\hat{J}_y = (\hat{J}_m^+ - \hat{J}_m^-)/(2i)$. Note that these are components of the total angular momentum along molecule-fixed axes.

III. APPLICATION TO CH₃⁺

We apply the Hamiltonian and computer program to the calculation of the rotation–torsion energy levels of the CH₃⁺ molecular ion modeling it as having a tilted and precessing (and rigidly C_{3v}) CH₃⁺ internal rotor. As in Ref. (1) we model the precession of the C₃ axis of the CH₃⁺ group as taking place at three times the speed of the internal rotation. To implement the program we must first define the molecule-fixed axes and then determine the expressions for the Cartesian coordinates of the nuclei. We must also define the torsional potential energy function, and we use a simple cosine function with a barrier of 30 cm⁻¹ (4, 5) in all the calculations presented here.

The frame protons are labeled 1 and 2, and the top protons are labeled 3, 4, and 5 in a clockwise sense when viewed from the frame (see Fig. 1). The center of mass of the H₂ frame is labeled f , the center of mass of the CH₃⁺ top is labeled t , and the center of mass of the entire molecule is labeled 0. We define the molecule fixed xyz axes to have origin at 0 and to be tied to the frame; the z axis points from t to f , the y axis is in the plane of the frame with H₁ having positive y value, and the x axis is such that the axes are right handed. The tilt angle θ is the

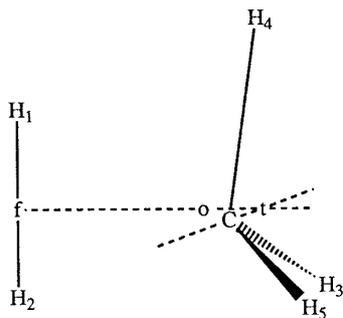


FIG. 1. The atom labeling convention. The configuration shown here has $\tau = 120^\circ$.

angle between the $t \rightarrow C$ axis and the $t \rightarrow f$ axis. We tie right handed $x'y'z'$ axes to the CH_3^+ top with z' being the $t \rightarrow C$ axis and y' being in the $\text{H}_3\text{C}t$ plane with H_3 having a positive y' coordinate. The orientation of the $x'y'z'$ axes relative to the xyz axes is given by the Euler angles θ (the angle of tilt), ϕ , and χ . When $\theta = 0$ the torsional angle τ is the angle measured in a right handed sense about the $z' = z$ axis from the yz plane to the $y'z'$ plane, and $\tau = \phi + \chi$. For $\theta \neq 0$ the appropriately precessing internal rotation motion is achieved by taking $\phi = (3\tau - \pi/2)$ and $\chi = (-2\tau + \pi/2)$ which retains $\tau = \phi + \chi$. In our Hamiltonian θ is fixed and τ is the dynamical variable. Using the direction cosine matrix with these expressions for the Euler angles ϕ and χ in terms of τ we obtain the analytic expressions for the nuclear coordinates to be as given in Table 1. The expressions given in Table 1 involve the following τ -independent geometrical factors,

$$\begin{aligned}
 q_1 &= r_{\text{CH}} \sin(\pi - \alpha_{\text{T}}) \\
 q_2 &= [m_{\text{C}} / (3m_{\text{H}} + m_{\text{C}})] r_{\text{CH}} \cos(\pi - \alpha_{\text{T}}) \\
 q_3 &= [3m_{\text{H}} / (3m_{\text{H}} + m_{\text{C}})] r_{\text{CH}} \cos(\pi - \alpha_{\text{T}}) \\
 q_4 &= [2m_{\text{H}} / (5m_{\text{H}} + m_{\text{C}})] R \\
 q_5 &= [(3m_{\text{H}} + m_{\text{C}}) / (5m_{\text{H}} + m_{\text{C}})] R \\
 q_6 &= r_{\text{XH}} \sin(\alpha_{\text{F}}) \\
 q_7 &= r_{\text{XH}} \cos(\alpha_{\text{F}}),
 \end{aligned} \tag{25}$$

where m_{H} and m_{C} are the atomic masses, R is the distance between the centers-of-mass of the top and frame, r_{CH} is the C-H bond distance in the top, r_{XH} is half the H-H distance in the frame, α_{T} is the angle between the $C \rightarrow \text{H}$ bonds of the top and the $t \rightarrow C$ axis, and α_{F} is the angle between the $\text{H}_2 \rightarrow \text{H}_1$ bond of the frame and the z axis. From *ab initio* calculations (14), we take $R = 1.1425 \text{ \AA}$, $r_{\text{CH}} = 1.0907 \text{ \AA}$, $r_{\text{XH}} = 0.4807 \text{ \AA}$, $\alpha_{\text{T}} = 106.16^\circ$, and $\alpha_{\text{F}} = 90^\circ$, from which the q_i values quoted in Table 1 are obtained. The expressions given in Table 1 are such that

TABLE 1
The Cartesian Coordinates for the Precessing Internal Rotor Model of CH_3^+

| Coordinate | Function ^a |
|----------------|--------------------------------------------------------------------------------------|
| x_{C} | $q_3 \sin\theta \sin 3\tau$ |
| x_1 | 0 |
| x_2 | 0 |
| x_3 | $-q_1[\sin\tau + \cos 2\tau \sin 3\tau(\cos\theta - 1)] - q_2 \sin 3\tau \sin\theta$ |
| x_4 | $x_3(\tau = \tau - 2\pi/3)$ |
| x_5 | $x_3(\tau = \tau + 2\pi/3)$ |
| y_{C} | $-q_3 \sin\theta \cos 3\tau$ |
| y_1 | q_6 |
| y_2 | $-q_6$ |
| y_3 | $q_1[\cos\tau + \cos 2\tau \cos 3\tau(\cos\theta - 1)] + q_2 \cos 3\tau \sin\theta$ |
| y_4 | $y_3(\tau = \tau - 2\pi/3)$ |
| y_5 | $y_3(\tau = \tau + 2\pi/3)$ |
| z_{C} | $-q_4 + q_3 \cos\theta$ |
| z_1 | $q_5 + q_7$ |
| z_2 | $q_5 - q_7$ |
| z_3 | $-q_4 - q_2 \cos\theta + q_1 \cos 2\tau \sin\theta$ |
| z_4 | $z_3(\tau = \tau - 2\pi/3)$ |
| z_5 | $z_3(\tau = \tau + 2\pi/3)$ |

^a The q_i parameters are defined in Eq.[25] and have the values (in \AA):

$$q_1=1.0476, q_2=0.2425, q_3=0.0611, q_4=0.1352, q_5=1.0073, q_6=0.4807, q_7=0.0.$$

the CH_3^+ group remains with fixed and equal CH bond lengths and HCH bond angles, and the C_3 axis precesses around the z axis at three times the rate of internal rotation and tilted at a constant angle θ from the z axis. The expressions for the coordinates of the nuclei in the top could be used for any molecule having a tilted and precessing CH_3 rotor attached to a frame.

IV. RESULTS AND DISCUSSION

The coefficients of \hat{J}_τ^2 , \hat{J}_z^2 , \hat{J}_y^2 , \hat{J}_x^2 and $\hat{J}_z \hat{J}_\tau$ are $\mu_{\tau\tau}/2$, $\mu_{zz}/2$, $\mu_{yy}/2$, $\mu_{xx}/2$, and $\mu_{z\tau}$, respectively. In the Tan and Pratt Hamiltonian (1) these coefficients are called F , A_{F} , B , C , and $-2A_{\text{F}} \cos\theta$ respectively, and the parameters F , A_{F} , B , and C are taken to be independent of θ and τ . Table 2 shows these calculated Hamiltonian coefficients for five tilt angles, from 0° to 13.43° (the latter being the average *ab initio* tilt angle for CH_5^+ (14)), at the $\tau = 0^\circ$ (a minimum in V) and $\tau = 30^\circ$ (a maximum in V) positions. The data show a dramatic decrease in the magnitudes of $\mu_{\tau\tau}$, μ_{zz} , and $\mu_{z\tau}$ as the tilt angle is increased, and the neglect of this dependence is a serious error if the tilt angle is not negligible.

Also worthy of note is the importance of some other coupling terms. The choice of principal axes for the molecule-fixed xyz axis system (i.e., PAM) does not remove the $\hat{J}_\alpha \hat{J}_\beta$ terms from the rotation-contortion Hamiltonian, because of contributions from $I_{\alpha\tau}$ elements. There is perhaps a (τ -dependent) coordinate transformation (as Tan

TABLE 2

The Coefficients (in cm^{-1}) of J_τ^2 , J_z^2 , J_y^2 , J_x^2 and $\hat{J}_z\hat{J}_\tau$ as Functions of the Tilt Angle θ and Torsional Angle τ

| τ^a | θ^a | $\mu_{\tau\tau}/2$ | $\mu_{zz}/2$ | $\mu_{yy}/2$ | $\mu_{xx}/2$ | $\mu_{z\tau}$ |
|----------|------------|--------------------|--------------|--------------|--------------|---------------|
| 0 | 0.00 | 41.274 | 36.194 | 4.012 | 3.612 | -72.387 |
| | 1.00 | 41.134 | 36.096 | 4.021 | 3.612 | -72.152 |
| | 5.00 | 38.038 | 33.922 | 4.215 | 3.612 | -66.939 |
| | 10.00 | 30.745 | 28.799 | 4.644 | 3.612 | -54.638 |
| | 13.43 | 25.450 | 25.075 | 4.918 | 3.612 | -45.678 |
| 30 | 0.00 | 41.274 | 36.194 | 4.012 | 3.612 | -72.387 |
| | 1.00 | 41.125 | 36.088 | 4.012 | 3.619 | -72.135 |
| | 5.00 | 37.841 | 33.753 | 4.012 | 3.775 | -66.574 |
| | 10.00 | 30.250 | 28.355 | 4.012 | 4.116 | -53.701 |
| | 13.43 | 24.861 | 24.523 | 4.012 | 4.329 | -44.538 |

^a In degrees.

TABLE 4

The Wavenumbers (in cm^{-1}) of the $J = 2 \leftarrow 1$ and $1 \leftarrow 0$ Rotational Transitions with $K = 0$

| Transition | K_i^a | $\theta = 0^\circ$ | $\theta = 1^\circ$ | $\theta = 5^\circ$ | $\theta = 10^\circ$ | $\theta = 13.43^\circ$ |
|--------------------|---------|--------------------|--------------------|--------------------|---------------------|------------------------|
| $J=2 \leftarrow 1$ | 3 | 15.2487 | 15.2490 | 15.2559 | 15.2774 | 15.3000 |
| | 3 | 15.2488 | 15.2490 | 15.2547 | 15.2723 | 15.2909 |
| | 2 | 15.2493 | 15.2496 | 15.2560 | 15.2758 | 15.2967 |
| | 1 | 15.2633 | 15.2635 | 15.2694 | 15.2860 | 15.3010 |
| | 0 | 15.2447 | 15.2449 | 15.2506 | 15.2680 | 15.2858 |
| $J=1 \leftarrow 0$ | 3 | 7.6242 | 7.6243 | 7.6278 | 7.6385 | 7.6498 |
| | 3 | 7.6242 | 7.6243 | 7.6271 | 7.6358 | 7.6450 |
| | 2 | 7.6242 | 7.6243 | 7.6275 | 7.6373 | 7.6476 |
| | 1 | 7.6242 | 7.6243 | 7.6264 | 7.6315 | 7.6348 |
| | 0 | 7.6242 | 7.6243 | 7.6273 | 7.6364 | 7.6457 |

^a K_i is the absolute value of the torsional quantum number k_i .

and Pratt (1) suggest) other than the PAM that can remove the $\hat{J}_\alpha\hat{J}_\beta$ terms, although $\hat{J}_\alpha\hat{J}_\tau$ terms will remain.

The calculated energies are given in Table 3 for the precessing internal rotor model for the CH_5^+ molecular ion, with tilt angle $\theta = 0^\circ$ and 13.43° , using both our exact rotation-torsion Hamiltonian and the Hamiltonian of Ref. (1). For $\theta = 0^\circ$ the results are the same, but for $\theta =$

TABLE 3

The Rotation-Torsion Energy Levels (in cm^{-1}) Obtained for $J = 0$ and 1 for Two Values of the Tilt Angle θ

| J | K | K_i^a | symmetry | $E(\theta = 13.43^\circ)^b$ | $E(\theta = 13.43^\circ)^c$ | $E(\theta = 0^\circ)^{b,c}$ | | |
|------------------|-----|---------|----------|-----------------------------|-----------------------------|-----------------------------|----------|----------|
| 1 | 1 | 3 | A_2' | 389.0681 | 620.4904 | 628.8307 | | |
| | | | A_1' | 120.3022 | 200.1676 | 194.2418 | | |
| | | | A_1' | 389.0898 | 620.4791 | 628.8169 | | |
| | | | A_2' | 120.2586 | 202.5466 | 194.2280 | | |
| | | | E'' | 216.7447 | 343.4118 | 349.0246 | | |
| | 1 | 2 | 1 | E'' | 39.3642 | 65.6608 | 60.3151 | |
| | | | | E' | 98.0165 | 150.3791 | 153.6190 | |
| | | | | E' | 8.6434 | 10.7067 | 8.8921 | |
| | | | | 0 | A_1'' | 28.4059 | 39.4210 | 40.1989 |
| | | | | | A_2'' | 28.0098 | 39.1936 | 39.7985 |
| 1 | 0 | 3 | A_1'' | 241.6747 | 384.5233 | 386.6481 | | |
| | | | A_2'' | 226.5395 | 369.3830 | 371.6482 | | |
| | | | E' | 108.1532 | 170.5159 | 172.6602 | | |
| | | | 1 | E'' | 32.7707 | 45.7522 | 48.8889 | |
| | | | 0 | A_2' | 7.6457 | 5.2323 | 7.6242 | |
| | 0 | 0 | 3 | A_2'' | 234.0248 | 379.0239 | 379.0239 | |
| | | | | A_1'' | 218.8945 | 364.0240 | 364.0240 | |
| | | | | 2 | E' | 100.5056 | 165.0360 | 165.0360 |
| | | | | 1 | E'' | 25.1359 | 41.2647 | 41.2647 |
| | | | | 0 | A_2' | 0.0000 | 0.0000 | 0.0000 |
| ZPE ^d | | | | 14.9175 | 14.9243 | 14.9243 | | |

^a K_i is the absolute value of the torsional quantum number k_i .

^b Energies calculated using the exact rotation-torsion Hamiltonian.

^c Energies calculated using the Hamiltonian of Ref.(1).

^d Zero-point energy of the torsional mode.

13.43° there are large differences, and the energies of the approximate Hamiltonian are spaced much wider with increasing K_i . In the calculation using the Hamiltonian of Ref. (1) the values for F , A_F , B , and C correspond to values of $\mu_{\tau\tau}/2$, $\mu_{zz}/2$, $\mu_{yy}/2$, and $\mu_{xx}/2$, respectively, for $\theta = \tau = 0^\circ$. It is interesting to note that using the exact Hamiltonian the energy of the levels having $J = 1, 2, 3, \dots$ with $K = K_i = 0$ are only slightly affected when the tilt angle is changed from 0° to 13.43° as one would expect (since the distance between the centers of mass of the top and frame are unaffected by the angle of tilt and it is this distance which largely governs the values of the $K = K_i = 0$ energies), whereas using the Hamiltonian of Ref. (1) they are strongly shifted (5).

Some $K = 0$, $J = 2 \leftarrow 1$ and $1 \leftarrow 0$ transition energies are listed in Table 4 for CH_5^+ using several different tilt angles computed using our general Hamiltonian. The incorporation of a precessing tilt in the methyl group has the effect of splitting these transitions by 0.01 to 0.02 cm^{-1} , and of shifting them to higher wavenumber by 0.02 to 0.06 cm^{-1} .

In a following paper (14) we apply the general rotation-contortion Hamiltonian to the calculation of the rotation-torsion energy levels of CH_5^+ using a full *ab initio* minimum energy path in which all bond lengths and angles are allowed to vary as the molecule internally rotates. The energies obtained are very different from those obtained earlier (4, 5), partly because the earlier work uses the approximate rotation-torsion Hamiltonian of Ref. (1), which is not appropriate when the tilt angle is large, and partly because the CH_3^+ group distorts as it internally rotates.

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