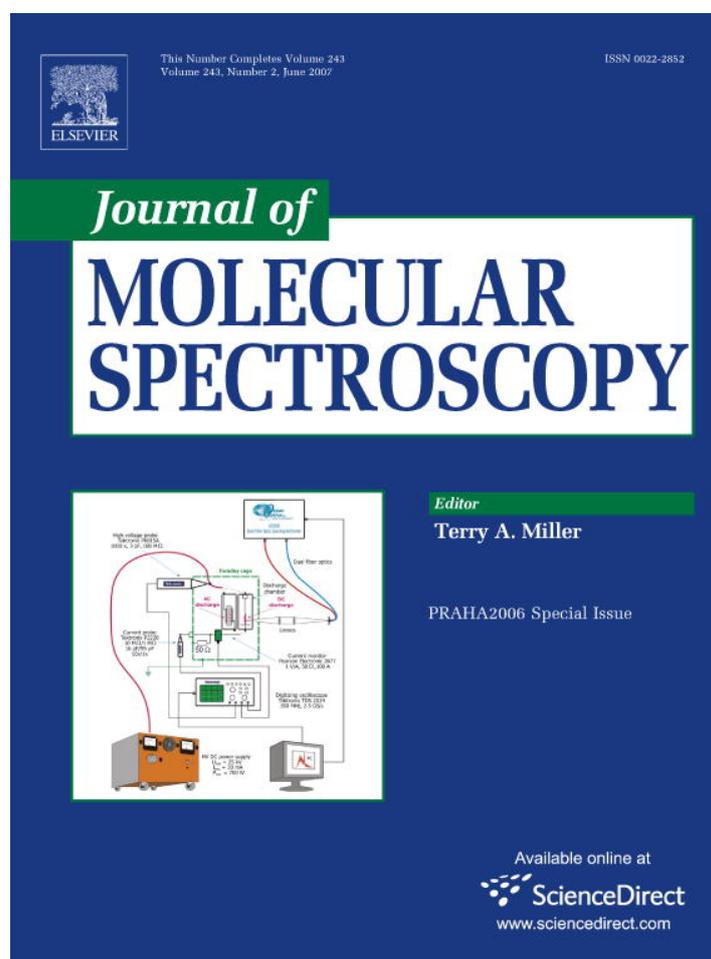


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Reanalysis of the microwave absorption spectrum of dimethyl methylphosphonate and its internal rotation problem [☆]

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Abstract

The Fourier transform microwave spectrum of dimethyl methylphosphonate studied by us previously is reanalyzed here to obtain more physically reasonable parameters describing the various Coriolis-like couplings between overall rotation and internal rotation of the two methoxy methyl tops. In particular, we use exactly the same frequencies and spectral assignments as in our previous study, but the least squares fit is started from a rather different set of initial molecular parameters and is carried out with a slightly smaller set of adjustable parameters. The standard deviation of the fit is not significantly changed, but convergence to a rather different minimum in parameter space is obtained. This new minimum does not change the three rotational constants significantly, but values for the 12 Coriolis coupling constants are dramatically rearranged, so that parameters arising from coupling between the two internal rotation motions are greatly reduced in magnitude. These new Coriolis constants bring the derived direction cosines for the methoxy methyl groups in the principal axis system into much better agreement with ab initio predictions. We have used our new parameters to derive internal rotation barrier heights for the two methyl groups of 280 and 188 cm⁻¹.

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1. Introduction

A few years ago we used a group-theoretical formalism [1] to carry out an apparently satisfactory global fit of the microwave spectrum of dimethyl methylphosphonate (DMMP) [2]. At that time we also gave an interpretation of the physical meaning of various parameters obtained from the analysis. Recently, however, we found that our reported values [2] for the Coriolis-like parameters are physically unreasonable, since they require a coupling between the two methoxy methyl groups that seems unacceptably large.

In the present work, we reanalyze the same spectral data treated in our previous study [2], using the same spectral

assignments, but using a different set of initial molecular parameters to start the least-squares fit. Using our newly obtained Coriolis-like parameters, we derive direction cosines for the methyl tops in much better agreement with ab initio predictions, and thus go on to make estimates for the internal rotation barrier heights.

2. Spectral data, line assignments, effective Hamiltonian and tunneling matrix elements

The spectral data and line assignments in the present study are the same as those given in Table 4 of Ref. [2]. The form of the effective Hamiltonian and expressions for the tunneling matrix elements used in the global fit are the same as those given in Eqs. (1)–(21) of Ref. [2]. The set of adjustable parameters used in the present fit, however, is somewhat different from that given in Table 3 of Ref. [2].

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3. Least squares global analysis

The essential difference between the previous and the present global analysis consists of starting the fit with a quite different set of initial values for the tunneling matrix elements related to the Coriolis-like coefficients q , s , and t in Eq. (1) of Ref. [2]. In the present analysis large initial values were given only to the $1 \rightarrow 4$ and $1 \rightarrow 6$ tunneling matrix elements (q_4 , q_6 , s_4 , s_6 , t_4 and t_6) of the coefficients q , s , and t , which correspond (see Table 1 of Ref. [1]) to individual one-top internal-rotation tunnelings (i.e., to motions where one top is stationary while the other rotates). In the previous analysis large initial values were given to the individual one-top internal-rotation parameters mentioned above, but were also given to the $1 \rightarrow 2$ and $1 \rightarrow 5$ tunneling matrix elements of q , s , and t , which correspond (see Table 1 of Ref. [1]) to simultaneous internal-rotation tunnelings of both methyl groups (i.e., to geared and antigeared motions). Such a set of large initial values is less natural, since it implies that coupling between the two rather distant methyl groups is strong enough to make concerted internal rotations as probable as individual internal rotations.

Molecular parameters from the present reanalysis, which was carried out for 609 transitions and 45 adjustable parameters and resulted in a root-mean-square (rms) deviation of 0.0065 MHz, are given in Table 1. This table also shows for comparison the molecular parameters obtained from the previous fit [2] of the same 609 transitions to 54 adjustable parameters, which gave an rms deviation of 0.0080 MHz. It is seen from Table 1 that the present Coriolis-like parameters corresponding to simultaneous internal-rotation tunnelings of the two methyl groups are negligibly small, which is very different from the previous result. On the other hand, many parameters other than the Coriolis-like parameters are nearly the same as those obtained in the previous study.

4. Estimate of barrier heights to internal rotation

The estimation of barrier heights from a multidimensional tunneling formalism is not straightforward, because in general neither the exact path length nor the exact amount of mass involved is known for motion along the tunneling paths chosen by the molecule. For methyl-top internal rotations the situation is in principle simpler, since one can assume to a reasonable approximation that: (i) the tunneling path consists of a rotation around a fixed axis of the methyl top against the rest of the molecule, and (ii) the moment of inertia of the methyl group about its threefold axis as well as the moments of inertia of the rest of the molecule do not vary during the internal rotation motion. With these assumptions, we combine the present tunneling parameters with the ab initio structural data given in Ref. [3] to derive internal rotation barrier heights as shown below.

The first step is to transform the Coriolis-like parameters along the x , y , z axes in the present global fit to those

Table 1

Molecular parameters (MHz) of dimethyl methylphosphonate obtained from the present reanalysis

Par ^a	This work ^b	Ref. [2] ^b
h_{10}	-0.1558(30)	-0.1548(39)
h_{12}	-0.0825(29)	-0.0845(38)
h_{16}	-1.64515(77)	-1.64873(93)
A_1	2816.794(74)	2818.968(88)
A_4	0.87530(18)	
A_5	-0.000601(73)	
A_6	0.110738(79)	0.110430(93)
A_{16}	-0.001429(98)	
B_1	1976.91(51)	1978.049(36)
B_2	-0.000367(22)	
B_4	0.24038(31)	0.22371(14)
B_6	0.11645(20)	0.115959(45)
B_{12}		-0.001701(70)
B_{16}	-0.00259(24)	0.00265(23)
C_1	1618.83(51)	1615.513(81)
C_2	-0.000235(23)	
C_4	0.07758(29)	0.96834(36)
C_6	0.00622(20)	0.006810(39)
C_{10}		-0.00252(26)
C_{12}		0.00210(26)
C_{16}		0.00087(19)
D_{ab1}	-77.87(78)	-73.90(20)
D_{bc1}	-20.5(45)	
D_{ac1}	-60.7(12)	37.3(15)
D_{ac4}		12.16(38)
Δ_{J1}	0.0009692(20)	0.0009697(24)
Δ_{J4}	0.0000112(13)	0.0000119(16)
Δ_{JK1}	-0.004033(12)	-0.003994(15)
Δ_{JK4}	0.0000551(68)	0.0000483(90)
Δ_{JK10}		0.0000253(79)
Δ_{K1}	0.007862(39)	0.007789(50)
Δ_{K4}		-0.000087(31)
Δ_{K10}		-0.000076(19)
Δ_{K16}		0.000138(12)
δ_{J1}	0.0004179(19)	0.0004161(16)
q_2	0.00274(18)	39.9923(47)
q_4	69.416(11)	29.508(28)
q_5	0.01432(32)	-1.3695(42)
q_6	9.5955(14)	50.1265(46)
q_{10}^c	0.00623(16)	0.00430(19)
q_{J2}		-0.003597(28)
q_{J4}	-0.007361(29)	-0.002866(25)
q_{J6}	-0.001139(20)	-0.00283(15)
q_{K4}	0.002453(87)	
q_{K6}		-0.00315(28)
s_2		11.832(11)
s_4	15.34(29)	-10.1034(96)
s_5	-0.0222(33)	-15.2159(53)
s_6	-11.926(41)	6.993(14)
s_{J6}		-0.00158(25)
s_{K6}		-0.0218(13)
t_2	0.00488(20)	2.715(72)
t_4	-23.01(19)	-17.497(44)
t_5		1.7210(29)
t_6	3.23(15)	2.210(78)
t_{10}	-0.00193(11)	-0.00279(14)
t_{J4}	0.000661(13)	0.000215(15)
t_{J6}	0.000076(13)	

(continued on next page)

Table 1 (continued)

Par ^a	This work ^b	Ref. [2] ^b
t_{K2}		−0.00216(39)
t_{K4}	0.01539(16)	0.01589(19)
t_{K5}		−0.00152(38)
t_{K6}	−0.00312(17)	−0.00257(38)

^a See Ref. [2] for the parameter notation and meaning.

^b Numbers in parentheses are one standard uncertainty (1σ) in units of the least significant digit, as obtained from the least squares fitting (type A uncertainty [4]).

^c q_{10} here actually represents $q_{10} + q_{12}$.

along the a , b , c principal axes. This step is required because, as discussed in Section 3 of Ref. [2], an axis system was chosen for the fits which allowed maximum use of group-theoretical symmetry arguments to eliminate many symmetry-forbidden operators from the fitting Hamiltonian. As one consequence of this axis choice, however, the present global fit Hamiltonian contains nonzero contributions to all three off-diagonal terms in the quadratic angular momentum expression, i.e., contains terms like $D_{zx}(J_z J_x + J_x J_z)$, whose coefficients are treated as adjustable parameters in the least squares fits. It can be shown that vectors in the two axis systems are related by the transformation

$$\begin{bmatrix} q'_i \\ s'_i \\ t'_i \end{bmatrix} = T^{-1} \begin{bmatrix} q_i \\ s_i \\ t_i \end{bmatrix}, \quad (1)$$

where the subscript $i = 2, 4, 5$, and 6 indicates one of the four internal rotation tunneling paths, and T is a 3×3 rotation matrix defined by

$$T^{-1} \begin{bmatrix} A_1 & D_{ab1} & D_{ac1} \\ D_{ab1} & B_1 & D_{bc1} \\ D_{ac1} & D_{bc1} & C_1 \end{bmatrix} T = \begin{bmatrix} A'_1 & 0 & 0 \\ 0 & B'_1 & 0 \\ 0 & 0 & C'_1 \end{bmatrix}, \quad (2)$$

where primed quantities in Eqs. (1) and (2) represent parameters expressed in the principal axis system, while unprimed quantities represent parameters taken directly from the fit (i.e., from Table 1). The transformed Coriolis-like parameters obtained from this procedure are given in Table 2.

To estimate internal rotation barrier heights, we relate the rotated Coriolis tunneling parameters in Table 2 to properties of a hypothetical two-top internal-rotation problem, using the following arguments: (i) DMMP actually tunnels between pairs of 18 distinct frameworks (see Table 1 of Ref. [1]), but half of these tunnelings involve intramolecular motions that result in an exchange of roles for the two inequivalent methoxy groups. We are interested here in

Table 2
Coriolis-like parameters transformed to the principal axis system (MHz) using Eqs. (1) and (2)

q'_2	0.00249	s'_2	−0.00012	t'_2	0.00501
q'_4	68.788	s'_4	22.91	t'_4	−18.08
q'_5	0.01625	s'_5	−0.0208	t'_5	−0.00073
q'_6	10.4616	s'_6	−11.256	t'_6	2.93

interpreting only parameters that involve purely torsional tunneling, i.e., only parameters that involve tunneling between 9 distinct frameworks. (ii) Tunneling from framework 1 to each of the other frameworks in DMMP is treated as an independent motion in the present formalism, in the sense that each tunneling parameter has only one path subscript, and the parameters do not occur as products in the Hamiltonian matrix. (iii) It thus seems reasonable to compare our $1 \rightarrow 2, 4, 5$, and 6 tunneling parameters with results from a traditional two-top internal-rotation problem, where the other large-amplitude motions of DMMP, i.e., the $1 \rightarrow 10, 11, 12, 16, 17$, and 18 tunneling motions, are totally absent. Since the 9 frameworks accessed by internal rotation in DMMP do not involve any group-theoretical exchange of the two methyl tops, these tops must be taken as inequivalent in the traditional problem. Also, in agreement with our chemical intuition, we further simplify the two-top Hamiltonian by removing all top–top interactions from the potential energy expression.

A derivation of the torsion–rotation Hamiltonian for two equivalent methyl tops ($i = 1, 2$) is given in Wollrab [5]. For the present problem, we modify the torsion–rotation Hamiltonian given in Eq. (7) of Ref. [6] for the two inequivalent methyl tops in *N*-methylacetamide,

$$\begin{aligned} H = & AJ_a^2 + BJ_b^2 + CJ_c^2 \\ & + F_1(p_1 - \pi_1)^2 + F_2(p_2 - \pi_2)^2 + F_{12}[(p_1 - \pi_1)(p_2 - \pi_2) \\ & + (p_2 - \pi_2)(p_1 - \pi_1)] + (1/2)V_1(1 - \cos 3\tau_1) \\ & + (1/2)V_2(1 - \cos 3\tau_2), \end{aligned} \quad (3)$$

as follows: (i) top–top potential-energy interactions are removed, (ii) the zeros of τ_1 and τ_2 are chosen to eliminate $\sin 3\tau_1$ and $\sin 3\tau_2$ terms (though higher-order sine terms cannot be eliminated without postulating more symmetry than DMMP actually has), and (iii) the c -axis components of the Coriolis interaction (which are symmetry-allowed in DMMP) are added, so that the analogs of Eqs. (8) of Ref. [6] become here

$$\begin{aligned} \pi_1 = & \rho_{1a}J_a + \rho_{1b}J_b + \rho_{1c}J_c \\ \pi_2 = & \rho_{2a}J_a + \rho_{2b}J_b + \rho_{2c}J_c \end{aligned} \quad (4)$$

with

$$\begin{aligned} \rho_{1\beta} = & \lambda_{1\beta}I_1/I_\beta \\ \rho_{2\beta} = & \lambda_{2\beta}I_2/I_\beta. \end{aligned} \quad (5)$$

The notation in Eqs. (3)–(5) is relatively standard [5]: A , B , and C are asymmetric-top rotational constants; J_a , J_b , and J_c are components of the total angular momentum along the principal axes; F_1 , F_2 , and F_{12} are the torsional kinetic energy coefficients; p_1 and p_2 are the torsional angular momentum operators conjugate to the torsional angles τ_1 and τ_2 ; V_1 and V_2 are the two different torsional barrier heights; π_1 and π_2 are torsion–rotation Coriolis coupling terms; the $\lambda_{i\beta}$ (for $i = 1, 2$; $\beta = a, b, c$) are direction cosines between the symmetry axis of top i and

the principal axes of the molecule; I_i is the moment of inertia of top i about its symmetry axis; and I_β (for $\beta = a, b, c$) is one of the principal moments of inertia of the whole molecule.

The permutation-inversion (PI) group of DMMP is one of the G_{18} groups, and in particular is one with a rather complicated set of separably and nonseparably degenerate symmetry species [1,2]. The PI group for the Hamiltonian in Eq. (3) is G_9 (note that $\tau_1, \tau_2 \rightarrow -\tau_1, -\tau_2$ is not a symmetry operation), which also involves separably degenerate species. Fortunately, it is not necessary to deal with most of the subtleties of these PI groups, because tunneling parameters in the present formalism are defined by expressions like Eq. (13) of [2], and it is only necessary to relate frameworks 1 and n in such expressions to their analogs in the formalism associated with Eq. (3).

We can now take expectation values of appropriate operators in Eq. (3) to derive the following twelve equations relating quantities in Table 2 with those in Eqs. (3) and (4):

$$\begin{aligned}
 \sqrt{3}(+q'_2 + q'_5 - q'_6) &= -(2F_1\rho_{1z} + 2F_{12}\rho_{2z})\langle E_1|p_1|E_1\rangle - (2F_2\rho_{2z} + 2F_{12}\rho_{1z})\langle E_1|p_2|E_1\rangle \\
 \sqrt{3}(+q'_2 + q'_4 - q'_5) &= -(2F_1\rho_{1z} + 2F_{12}\rho_{2z})\langle E_2|p_1|E_2\rangle - (2F_2\rho_{2z} + 2F_{12}\rho_{1z})\langle E_2|p_2|E_2\rangle \\
 \sqrt{3}(-q'_4 - q'_5 - q'_6) &= -(2F_1\rho_{1z} + 2F_{12}\rho_{2z})\langle E_3|p_1|E_3\rangle - (2F_2\rho_{2z} + 2F_{12}\rho_{1z})\langle E_3|p_2|E_3\rangle \\
 \sqrt{3}(-q'_2 + q'_4 - q'_6) &= -(2F_1\rho_{1z} + 2F_{12}\rho_{2z})\langle E_4|p_1|E_4\rangle - (2F_2\rho_{2z} + 2F_{12}\rho_{1z})\langle E_4|p_2|E_4\rangle \\
 \sqrt{3}(+s'_2 + s'_5 - s'_6) &= -(2F_1\rho_{1x} + 2F_{12}\rho_{2x})\langle E_1|p_1|E_1\rangle - (2F_2\rho_{2x} + 2F_{12}\rho_{1x})\langle E_1|p_2|E_1\rangle \\
 \sqrt{3}(+s'_2 + s'_4 - s'_5) &= -(2F_1\rho_{1x} + 2F_{12}\rho_{2x})\langle E_2|p_1|E_2\rangle - (2F_2\rho_{2x} + 2F_{12}\rho_{1x})\langle E_2|p_2|E_2\rangle \\
 \sqrt{3}(-s'_4 - s'_5 - s'_6) &= -(2F_1\rho_{1x} + 2F_{12}\rho_{2x})\langle E_3|p_1|E_3\rangle - (2F_2\rho_{2x} + 2F_{12}\rho_{1x})\langle E_3|p_2|E_3\rangle \\
 \sqrt{3}(-s'_2 + s'_4 - s'_6) &= -(2F_1\rho_{1x} + 2F_{12}\rho_{2x})\langle E_4|p_1|E_4\rangle - (2F_2\rho_{2x} + 2F_{12}\rho_{1x})\langle E_4|p_2|E_4\rangle \\
 \sqrt{3}(+t'_2 + t'_5 - t'_6) &= -(2F_1\rho_{1y} + 2F_{12}\rho_{2y})\langle E_1|p_1|E_1\rangle - (2F_2\rho_{2y} + 2F_{12}\rho_{1y})\langle E_1|p_2|E_1\rangle \\
 \sqrt{3}(+t'_2 + t'_4 - t'_5) &= -(2F_1\rho_{1y} + 2F_{12}\rho_{2y})\langle E_2|p_1|E_2\rangle - (2F_2\rho_{2y} + 2F_{12}\rho_{1y})\langle E_2|p_2|E_2\rangle \\
 \sqrt{3}(-t'_4 - t'_5 - t'_6) &= -(2F_1\rho_{1y} + 2F_{12}\rho_{2y})\langle E_3|p_1|E_3\rangle - (2F_2\rho_{2y} + 2F_{12}\rho_{1y})\langle E_3|p_2|E_3\rangle \\
 \sqrt{3}(-t'_2 + t'_4 - t'_6) &= -(2F_1\rho_{1y} + 2F_{12}\rho_{2y})\langle E_4|p_1|E_4\rangle - (2F_2\rho_{2y} + 2F_{12}\rho_{1y})\langle E_4|p_2|E_4\rangle,
 \end{aligned}
 \tag{6}$$

where the axis choice is $z = a$, $x = b$, and $y = c$. In agreement with the form of the tunneling basis functions, which are products of a purely (large and small amplitude) vibrational framework function $|n\rangle$ and a symmetric top rotational function $|J, K\rangle$ (see Eqs. (9) of Ref. [2]), the $|E_{1,2,3,4}\rangle$ functions appearing in the matrix elements on the right of Eqs. (6) must be taken to be torsional eigenfunctions calculated using the pure torsional Hamiltonian obtained from Eqs. (3) and (4) by setting $J_a = J_b = J_c = 0$. The symmetry species E_1, E_2, E_3 , and E_4 labeling these eigenfunctions represent the four separably doubly degenerate symmetry species in the two-top internal-rotation problem described by the PI group G_9 . They can be defined by noting that: (i) the E_1, E_2, E_3 , and E_4 functions are invariant to (456), (123), (123)(456), and (123)(465), respectively (see Table 1 of Ref. [6]), (ii) the E_1, E_2, E_3 , and E_4 functions correspond to framework basis functions

with coefficients in the $n = 1-9$ positions as given for the species $G_{\text{sep}}(1)_{-a}$, $G_{\text{sep}}(2)_{+b}$, $E_{1\text{sep}+}$ or $E_{2\text{sep}+}$, and $-(1/\sqrt{2})E(1)_b - (i/\sqrt{2})E(1)_a$ or $(1/\sqrt{2})E(2)_a - (i/\sqrt{2})E(2)_b$, respectively, in Tables 1 and 2 of [2] (note that the E_3 and E_4 coefficients generated in this way must be renormalized by multiplying by $\sqrt{2}$), and (iii) correct signs can be obtained in the matrix elements on the right of Eqs. (6) by using free-rotor basis functions characterized by the m_1, m_2 modulo 3 values specified for E_1, E_2, E_3 , and E_4 on p. 33 of [6] in a calculation using the pure torsional Hamiltonian obtained from Eq. (3).

Eqs. (6) represent 12 equations, with 12 numerical values from Table 2 on the left and 14 unknowns on the right, i.e., the $3F$'s, $2V$'s, $5I$'s, and two unit vectors λ from Eqs. (3)–(5). To solve these equations, some of the unknowns must obviously be fixed. We chose to fix the following structural parameters to values obtained from the ab initio molecular structure shown in Table 5 of Ref. [3]:

$$\begin{aligned}
 F_1 &= 5.4178 \text{ cm}^{-1}, \quad F_2 = 5.4424 \text{ cm}^{-1}, \quad F_{12} = -0.01673 \text{ cm}^{-1} \\
 I_1 &= 3.1546 \text{ u}\text{\AA}^2, \quad I_2 = 3.1474 \text{ u}\text{\AA}^2.
 \end{aligned}
 \tag{7}$$

For consistency with our other labeling conventions, we define top 1 to contain hydrogens 14, 15, 16, and top 2 to contain hydrogens 8, 9, 10 in Table 5 of [3]. For computational simplicity we define each top axis to be the perpendicular to the plane of the three hydrogens at their center of mass. Imposition of the conditions in Eqs. (7) is in fact equivalent to fixing the three F 's and two of the five I 's. The other three I 's, i.e., I_a, I_b , and I_c , were fixed to values obtained from the observed rotational constants A'_1, B'_1 , and C'_1 of Eq. (2). Using the quantities on the left of Eqs. (6) as “observed values” and using the pure torsional Hamiltonian from Eq. (3) to calculate the expectation values of p_1 and p_2 appearing on the right in Eqs. (6), we obtained the following values for the unknown parameters V_1, V_2 ,

Table 3
Reproducibility of input data in the least squares analysis deriving internal rotation barrier heights from Eqs. (6)

	Obs (MHz)	o-c (MHz)
$3^{1/2}(+q'_2 + q'_5 - q'_6)$	-18.088	0.038
$3^{1/2}(+q'_2 + q'_4 - q'_5)$	119.120	-0.027
$3^{1/2}(-q'_4 - q'_5 - q'_6)$	-137.292	-0.032
$3^{1/2}(-q'_2 + q'_4 - q'_6)$	101.019	-0.005
$3^{1/2}(+s'_2 + s'_5 - s'_6)$	19.460	-0.035
$3^{1/2}(+s'_2 + s'_4 - s'_5)$	39.715	0.039
$3^{1/2}(-s'_4 - s'_5 - s'_6)$	-20.147	0.037
$3^{1/2}(-s'_2 + s'_4 - s'_6)$	59.175	-0.002
$3^{1/2}(+t'_2 + t'_5 - t'_6)$	-5.076	0.006
$3^{1/2}(+t'_2 + t'_4 - t'_5)$	-31.301	0.009
$3^{1/2}(-t'_4 - t'_5 - t'_6)$	26.229	0.001
$3^{1/2}(-t'_2 + t'_4 - t'_6)$	-36.402	-0.008

and λ_{ix} ($i = 1, 2$; $\alpha = a, b, c$) from a least squares analysis with 12 observed values and six parameters (since $|\lambda_1| = |\lambda_2| = 1$):

$$V_1 = 279.82(6) \text{ cm}^{-1}, \quad V_2 = 188.11(1) \text{ cm}^{-1}$$

$$[\lambda_{1a}, \lambda_{1b}; \lambda_{1c}] = [0.5255(6), -0.8107(4); 0.2582]$$

$$[\lambda_{2a}, \lambda_{2b}; \lambda_{2c}] = [-0.8334(1), -0.3979(2); 0.3836]. \quad (8)$$

Numbers in parentheses are one standard uncertainty ($k = 1$, type A [4]), as obtained from the least squares analysis, and apply to the last digit of the parameters. (The λ_c components were calculated from the two fitted components after the fit was completed.) The reproducibility of the “observed values” in the least squares analysis carried out above is shown in Table 3.

Support for the present results in Eqs. (8) is given by a comparison with ab initio barriers taken from Table 1 and ab initio direction cosines calculated from Table 5 of Ref. [3]

$$V_1 = 426 \text{ cm}^{-1}, \quad V_2 = 281 \text{ cm}^{-1}$$

$$[\lambda_{1a}, \lambda_{1b}, \lambda_{1c}]_{\text{ab initio}} = [0.5205, 0.8206, -0.2361]$$

$$[\lambda_{2a}, \lambda_{2b}, \lambda_{2c}]_{\text{ab initio}} = [-0.8506, 0.3894, -0.3533], \quad (9)$$

where the difference in sign for the b and c components in Eqs. (8) and (9) arises from the fact that our (implicit) axis choice and the explicit choice of Ref. [3] differ by a C_2 about the a axis.

We note in passing, that almost the same results as in Eqs. (8) are obtained when we treat the two one-top problems independently, i.e., when we neglect (i.e., set to zero in the fit) the small quantities F_{12} , q_2 , q_5 , s_2 , s_5 , t_2 , and t_5 representing coupling between the two methyl groups. This independent-top approximation also gives torsional wavefunctions for the right of Eqs. (6) which are the products of one-top functions of the form $E_1 = E_+A$, $E_2 = AE_+$, $E_3 = E_+E_-$, and $E_4 = E_+E_+$. These products can be used to show that there is only one independent matrix element for each of the operators p_1 and p_2 , a result which leads in turn to a qualitative explanation for some of the sum and difference regularities that can be found in Table 3, and

to greatly simplified logic in relating the top 1 and top 2 labels in the ab initio and fitting procedures.

5. Discussion

We reanalyzed the DMMP FTMW spectrum for essentially two reasons: (i) from an intuitive point of view, the Coriolis-like parameters obtained previously seemed physically unreasonable, since parameters corresponding to the coupled geared and antigeared tunnelings of the two methyl groups were abnormally large in magnitude, and (ii) making the quite reasonable assumptions necessary to convert these Coriolis parameters into structural information yielded directions for the methyl top symmetry axes at variance with the ab initio predictions [3]. Both of these difficulties disappeared after the present reanalysis.

The question arises, however, of what went wrong initially. We believe that our first fit converged to a “false minimum” in parameter space, but that the existence of this false minimum is not a random event, but is instead connected somehow to a number of sign ambiguities present in the fit. Evidence for this conclusion came initially from the observations that: (i) the magnitudes of the linear combinations of quantities on the left hand side of Eqs. (6), after they are rotated into the principal axis system, differ by only a few percent between the previous fit and the present fit (these two fits use slightly different sets of fitting parameters), but (ii) the signs of the fourth, sixth, and ninth linear combinations in Eqs. (6) and the sign of D_{ac1} in Table 1 are opposite in the two fits. (The sign change of D_{bc1} is ambiguous, because its value is zero in the fit of Ref. [2].) Further experimentation then showed that one can arbitrarily change the sign of some other sets of linear combinations on the left of Eqs. (6) (keeping, for simplicity, the signs of D_{ab1} , D_{bc1} , and D_{ac1} constant) and still get a fit of exactly the same quality as the present fit, even though such a change in sign leads to very different values for the individual parameters in the linear combinations of Eqs. (6).

We have not examined this matter in detail, but one can try to imagine an explanation for the existence of multiple sign possibilities by considering the simple case where only the internal rotations of the methyl groups occur (i.e., no methyl-group exchange tunneling occurs), and where the PAM axis system is used. For this case, the dominant contributions to the torsion-rotation Coriolis splittings of states with E_1 , E_2 , E_3 , and E_4 symmetry in a near symmetric top will come from the linear combinations of $q_{1,2,3,4}$ terms shown in Eqs. (6). Experimentally, the magnitudes of these splittings are measurable quantities, but their signs are not (in the sense of whether positive or negative K corresponds to the lower component, for example). The analogous linear combinations of s and t terms in Eqs. (6) also affect these observed splittings, but their contributions have essentially the form of a second-order perturbation correction, which again allows magnitudes, but not signs, to be determined. If this thinking is correct, then it will always

be necessary in tunneling treatments of multi-top problems to use structural information from ab initio calculations (or from chemical intuition) to fix approximate magnitudes and signs for the initial guesses of quantities on the left of Eqs. (6) before beginning the least squares procedure.

References

- [1] N. Ohashi, J.T. Hougen, *J. Mol. Spectrosc.* 211 (2002) 119–126.
- [2] N. Ohashi, J. Pyka, G. Yu. Golubiatnikov, J.T. Hougen, R.D. Suenram, F.J. Lovas, A. Lesarri, Y. Kawashima, *J. Mol. Spectrosc.* 218 (2003) 114–126.
- [3] R.D. Suenram, F.J. Lovas, D.F. Plusquellic, A. Lesarri, Y. Kawashima, J.O. Jensen, A.C. Samuels, *J. Mol. Spectrosc.* 211 (2002) 110–118.
- [4] B.E. Taylor, C.E. Kuyatt, Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results, NIST Technical Note 1297, 1994, <<http://physics.nist.gov/cuu/Uncertainty/index.html>>.
- [5] J.E. Wollrab, *Rotational Spectra and Molecular Structure*, Academic Press, New York, 1967. Comparison of Eqs. (6-25), (6-93) and (6-211) indicates that a factor of two is missing before the Coriolis terms in Eq. (6-211) in this reference.
- [6] N. Ohashi, J.T. Hougen, R.D. Suenram, F.J. Lovas, Y. Kawashima, M. Fujitake, J. Pyka, *J. Mol. Spectrosc.* 227 (2004) 28–42.