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A new torsion–rotation fitting program for molecules with a sixfold barrier: Application to the microwave spectrum of toluene

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ABSTRACT

A new program is described for fitting rotation–torsion energy levels in molecules like toluene, in which the frame (C_6H_5) has C_{2v} symmetry and the methyl top has C_{3v} symmetry, i.e., for molecules where the internal rotation barrier is expanded in $\cos 6n\alpha$, where α is the internal rotation angle and $n = 1,2,\ldots$. The program is based on the theoretical framework developed by Sørensen and Pedersen in their application of the Longuet-Higgins permutation-inversion group G_{12} to the microwave spectrum of CH_3NO_2. It is specifically designed for sixfold barrier molecules, and allows the user to select almost any symmetry-allowed torsion–rotation term for inclusion in the fitting Hamiltonian. This program leads to a very successful fit of transitions in the microwave spectrum of toluene characterized by $J \leqslant 30$, $K_a \leqslant 12$, and by the free-rotor quantum number $|m| \leqslant 3$. In these fits we included both published and rather extensive unpublished new measurements, for which fits using other torsion–rotation programs have not been very successful. The fit presented here uses 28 parameters to give an overall standard deviation of 7.4 kHz for 372 line frequencies, and results in a much improved value for the sixfold barrier for toluene, $V_6 = 13.832068(3)$ cal mol^{-1}.

1. Introduction

Most torsion–rotation fitting programs consider an expansion of the internal rotation barrier in $\cos 3n\alpha$, where α is the internal rotation angle and $n = 1, 2, \ldots$, since such an expansion applies to the large class of molecules (like acetaldehyde) where the frame (CHO) has a plane of symmetry. In this paper we are concerned with molecules like toluene ($CH_3C_6H_5$), where the frame (C_6H_5) has C_{2v} symmetry, and the internal rotation barrier requires an expansion in $\cos 6n\alpha$.

Wilson, Lin, and Lide wrote an early paper [1] on the group theoretical considerations necessary for treating a molecule like CH_3BF_2 under the assumption of a rigid top and rigid frame, and came to the conclusion that a group of order 24 was appropriate. Nearly a decade later, Longuet-Higgins showed in his paper introducing the concept of permutation-inversion (PI) groups [2] that the correct group to use for this molecule is only of order 12 if the top and frame are allowed to undergo structural distortions during the internal rotation process. Sørensen and Pedersen used Longuet-Higgins' ideas to develop the theoretical expressions and computer program necessary for fitting the microwave spectrum of CH_3NO_2 [3], and also confirmed the correctness of Longuet-Higgins' PI group G_{12}. Much later these ideas were used as the starting point for treatments of the infrared spectrum of CH_3CH_2 [4] and the $S_1 \leftarrow S_0$ electronic spectra of *p*-toluidene [5] and toluene [6,7].

In this paper we closely follow the approach of [3] to develop a new computer program for fitting torsion–rotation levels in molecules with a C_{3v} top and a C_{2v} frame (and therefore, a sixfold barrier), which allows the user to select essentially any symmetry-allowed torsion–rotation term for inclusion in the fitting Hamiltonian. We then apply this program to fit a relatively large data set containing old and new measurements of the microwave spectrum of toluene.

Toluene was chosen for the first application of the program since published and rather extensive unpublished data are available, and since fits of these data using other torsion–rotation programs available have not been very successful to date. Toluene is a prolate asymmetric top with $\kappa = -0.59$, and can be considered as a prototype for molecules with nearly free internal rotation of a methyl top with a sixfold barrier. The molecular structure, axis system, and atom numbering used in the present work are shown in Fig. 1.

The microwave spectrum of toluene was the subject of several previous investigations [8–11]. In the seminal study for this molecule, Rudolph et al. [8] assigned several low-*J* transitions in the

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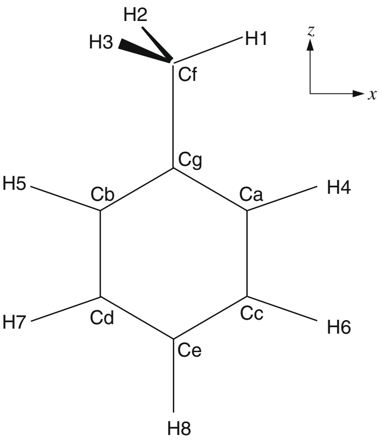

Fig. 1. Schematic illustration of the molecular structure of toluene, showing also the orientation of the axis system and the atom numbering used here. The coordinate system used to define the quantities $\mathbf{a}_i^0$ in Eqs. (1)–(3) has its origin at C_f, so that the phenyl group has both an xz and a yz plane of symmetry. For positive V_6 and a sixfold potential of the form $(1/2)V_6(1 - \cos 6\alpha)$ the six equivalent minima resulting from internal rotation of the methyl group will correspond to coplanar orientation of the symmetry plane of the methyl group and the plane of the phenyl ring, with one methyl proton in the plane of the ring. Alternatively, for a sixfold potential of form $(1/2)V_6(1 + \cos 6\alpha)$ and again a positive V_6, the equilibrium configuration will correspond to a perpendicular relative orientation of the methyl group symmetry plane and the ring plane, i.e., the equilibrium configuration will be that given by ab initio calculations and laser fluorescence experiments (see text).

$m = 0$ and $m = 3$ internal rotation states and measured the dipole moment. Most importantly they derived the much cited value $V_6 = 13.94 \pm 0.1$ cal/mol = 4.88(3) cm^{-1} for the sixfold internal rotation barrier. It should be noted, however, that their value was determined from analysis of a specific splitting affecting $m = 3$, $K = 1$ lines in the spectrum and was based on only two pairs of such lines identified in the spectrum. Their results were supplemented later by results for the deuterated [9] and the ^{13}C [9,10] isotopologues that allowed determination of the partial molecular geometry of toluene. In the most recent study of the rotational spectrum of toluene, the frequency ranges from 3.5 to 26.5 GHz and 160 to 330 GHz were investigated with four different spectrometers [11]. In that study an analysis of the ground state ($m = 0$) rotational spectrum of toluene was performed up to rather high values of $J \leqslant 92$. Previous microwave spectroscopic work on toluene has thus resulted in: a data set covering frequency ranges from 3.5 to 26.5 GHz and 160 to 330 GHz; a determination of the barrier height, partial geometry, and dipole moment; and a rather complete analysis of the rotational spectrum of the $m = 0$ internal rotation state.

The next natural step in studying the toluene spectrum was to try to analyze the rotational spectrum of $m \neq 0$ states ($m = 1$, 2, and 3), lines of which were clearly present in records obtained in the latest study [11]. Such an attempt was made by two of us (Z.K. and H.M.) using the XIAM [12] and SPFIT [13,14] programs. Although these programs allowed making assignments, which in the majority of cases were confirmed by further analysis using the new program described below, our $m \neq 0$ data could not be fit to experimental error using either of the two programs.

In the present study we have fit within experimental error a data set of 372 transitions with $J \leqslant 30$ belonging to $m = 0$, 1, 2, 3, and -3 states using 28 parameters, which gave an overall standard deviation of 7.4 kHz. Because of the considerable gap between 26.5 and 160 GHz in the frequency range covered to date, we decided to limit ourselves to $J \leqslant 30$ transitions, which constrained us to measurements made in the frequency range from 3.5 to 26.5 GHz. In the future we plan to supplement the presently available data set by measurements in the 50–150 GHz frequency range, which will permit us to go smoothly in J assignments from the lower frequency range to higher frequencies. We note in passing that addition to the fit of high-J transitions already fitted in [11] for the $m = 0$ state does not pose any problem for the new program.

The rest of the paper is organized as follows. In Section 2 we review the group theoretical ideas necessary to take advantage of the symmetry of this molecule. In Section 3 we give a brief description of the structure of the computer fitting program. Experimental details and the data set treated here are described in Section 4. Section 5 discusses qualitative understanding of the torsion–rotation levels in toluene and Section 6 gives the fitting results and describes possible future work on this molecule.

2. Group theory

This section presents many of the ideas in [3], using in places, however, somewhat different language and/or a somewhat different level of detail.

2.1. Permutation-inversion group and coordinate transformations

At equilibrium, toluene belongs to the point group C_s, but as is now well known, when internal rotation of the methyl group against the phenyl frame is considered, it becomes necessary to use the permutation-inversion (PI) group G_{12} shown in Table 1, where the atom labels in Fig. 1 are used to indicate the permutation cycles. In addition, we use in Table 1 the shorthand notation (ab) to represent the full set of eight permuted atoms in the phenyl frame: $(ab)(cd)(45)(67)$.

To set up symmetrized basis set functions and to determine symmetry-allowed terms in the Hamiltonian operator, it is necessary to apply these PI group operations to functions of the torsional angle α and/or the three rotational angles χ,θ,ϕ. For this purpose, we consider the usual [16] equation connecting laboratory-fixed Cartesian coordinates $\mathbf{R}_i$ for each atom to the center of mass $\mathbf{R}$, to the direction cosine matrix $\mathrm{S}^{-1}(\chi,\theta,\phi)$ relating the laboratory-fixed X,Y,Z axes to the molecule-fixed x,y,z axes, and to a second direction cosine matrix $\mathrm{S}_i^{-1}(\alpha,0,0)$ describing rotation of the methyl group,

$$\mathbf{R}_i = \mathbf{R} + \mathrm{S}^{-1}(\chi,\theta,\phi)\left[\mathrm{S}_i^{-1}(\alpha,0,0)\mathbf{a}_i^0 - \mathbf{A}(\alpha)\right]. \tag{1}$$

We define $\mathrm{S}_i^{-1}(\alpha,0,0)$ to be the identity matrix for $i \neq 1$, 2, or 3, so that a change in the internal rotation angle α does not affect the

Table 1
Character table for the permutation-inversion group[a] G_{12} appropriate for toluene when internal rotation of the methyl group is feasible (see Fig. 1).

	E 1 [d]	(ab)(123) 2[d]	(123) 2[d]	(ab)[b] 1[d]	(23)* 3[d]	(ab)(23)* 3[d]	stat. wt.[c]
A_1	1	1	1	1	1	1	5
A_2	1	1	1	1	−1	−1	5
B_1	1	−1	1	−1	1	−1	3
B_2	1	−1	1	−1	−1	1	3
E_1	2	1	−1	−2	0	0	3
E_2	2	−1	−1	2	0	0	5
	E	C_{2z}	E	C_{2z}	C_{2y}	C_{2x}	Equivalent rotation[e]

[a] This PI group is isomorphic to the point groups C_{6v}, D_{3d}, and D_6. Here we use a notation that emphasizes the isomorphism with C_{6v}.

[b] (ab) in this table is a shorthand notation for the set of four permutations (ab)(cd)(45)(67) in Fig. 1.

[c] This column gives the nuclear statistical weights for torsion–rotation levels of the species indicated, for isotopically normal toluene, i.e., for $^{12}C_7{}^1H_8$.

[d] These integers indicate the number of elements in each class. The classes of order 2 contain the element shown and its inverse. The classes of order 3 contain the element shown and two others obtained by replacing (23) by (12) and (13).

[e] As defined in [15]. See also Table 2 here.