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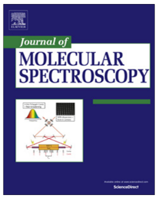

Reanalysis of the ground and three torsional excited states of *trans*-ethyl methyl ether by using an IAM-like tunneling matrix formalism

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ABSTRACT

The *trans*-ethyl methyl ether has two inequivalent methyl internal rotors and shows tunneling splittings of maximum up to five components. However, the barrier of these two internal rotation potentials were relatively high and the five components were not resolved in the ground state microwave spectra. In this study, well-resolved Fourier transform microwave ground state spectrum was measured for the first time to resolve the five components. The ground state microwave spectra were reanalyzed based on these new measurements and the additional millimeter-wave spectra as well as those studied previously by Fuchs et al. Ninety Fourier transform microwave spectral lines were assigned to 107 transitions in the ground state and 3508 conventional microwave absorption lines were assigned up to $K_a = 16$ of the ground state, including all 707 lines reported by Fuchs et al. In addition, 10 transitions were observed by the double resonance experiment. They were least-squares-analyzed by the use of an internal axis method (IAM)-like tunneling matrix formalism based on an extended permutation-inversion group theoretical idea. Twenty-two molecular parameters composed of rotational constants, centrifugal distortion constants, internal rotation parameters and internal rotation tunneling parameters were determined for the ground state. The microwave spectra in the three torsionally excited states, that is, the $v_{28} = 1$ C–CH$_3$ torsional state, the $v_{29} = 1$ O–CH$_3$ torsional state and the $v_{30} = 1$ skeletal torsional state, were also reanalyzed by using the IAM-like tunneling matrix formalism and somewhat extended line assignments.

1. Introduction

The *trans*-ethyl methyl ether molecule ($CH_3CH_2OCH_3$), which was tentatively identified in Orion KL [1], is interesting in the spectroscopic viewpoint since it has three low-frequency torsional vibrations, that is, two inequivalent methyl internal rotations (=methyl torsions) and a skeletal torsion. The couplings among these three vibrational modes produce somewhat strange internal-rotation tunneling splitting patterns in the pure rotational absorption spectrum in its torsionally excited states. In our previous studies, the pure rotational microwave spectrum in the first skeletal torsional ($v_{30} = 1$) [2], the first O–CH$_3$ torsional ($v_{29} = 1$) [3], and the first C–CH$_3$ ($v_{28} = 1$) torsional [4] states were studied and molecular parameters for these states were determined by the use of the tunneling matrix formalism (TMF) [5], which we call the *simple* tunneling matrix formalism hereafter in this paper in order to discriminate it from the IAM-like tunneling matrix formalism used in the present analyses. Through these studies, information on interactions among the two methyl internal rotations and the skeletal torsion was obtained [4]. On the other hand, as for rotational spectra in its ground vibrational state, Hayashi et al. reported results on molecular constants, dipole moment, molecular structure and the internal rotation barrier heights (1154 cm^{-1} and 891 cm^{-1} for the C–CH$_3$ and the O–CH$_3$ internal rotations, respectively) from analyses of the microwave spectra of normal species and many isotopologues up to 34 GHz [6,7]. Fuchs et al. [8] extended the measurement of the normal species up to 350 GHz and analyzed the spectrum using the effective rotational Hamiltonian (ERHAM) method developed by Groner [9]. Independently, Tsunekawa et al. reported pure-rotational transitions in the ground state in the 24–110 GHz frequency range, which exhibited only splittings due to the O–CH$_3$ torsion and were least-squares analyzed by using an ordinary asymmetric rotor Hamiltonian [10]. A spectral atlas of about 21,000 lines up to 200 GHz was prepared by them at the same time [11].

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Considering the fact (i) that in the studies so far made for the ground state of the *trans*-methyl ethyl ether, the C–CH_3 internal rotation tunneling splitting, which is much smaller than the O–CH_3 internal rotation splitting, was not fully resolved for most of the rotational transitions, (ii) assignments of transitions with K_a larger than 6 were given rarely, we decided to carry out a further investigation of the ground state. Thus, the main purposes of this study are

(i) to show well resolved tunneling splitting patterns in the vibrational ground state produced by the two CH_3 internal rotations by using the pulsed nozzle jet Fourier transform microwave method,
(ii) to apply an IAM-like tunneling matrix formalism based on an extended permutation-inversion group theoretical idea to the analysis of spectra for the ground state and the torsionally excited state as well,
(iii) to serve the present results for astronomical observations.

The outline of the present formalism is shown in the next section. The theoretical method reformulated in the present paper is similar to those developed by Groner [9,12]. This formalism was used in the previous analysis of the *trans*-methyl ethyl ether molecule [8]. However, our formalism described in the Theory section adopted the extended permutation-inversion group theory developed by Hougen and DeKoven [13] explicitly. The results obtained by analyzing the *trans*-ethyl methyl ether data based on the present formalism are reported and discussed.

2. Theory

In the present study, the spectral analysis is made by using the formalism constructed on the basis of the extended permutation-inversion group [13] which was made in the spectrum analysis of the methylamine molecule [14,15] with two types of large amplitude motion, that is, the methyl internal rotation and the amino wagging vibration. The outline of the theory will be given below.

(i) Coordinate system

An important point in our formalism is to start from the coordinate system. The laboratory-fixed atom position vectors $\mathbf{R}_i$ in the *trans*-ethyl methyl ether molecule are expressed as follows:

$$\begin{aligned}
\mathbf{R}_i &= \mathbf{R} + S^{-1}(\chi,\theta,\phi)\mathbf{a}_i^{ref},\\
\mathbf{a}_i^{ref} &= S^{-1}(-\rho_{1z}\alpha_1 - \rho_{2z}\alpha_2,0,0)\\
&\quad\times[S^{-1}(0,\theta_{PAMj},0)S^{-1}(\alpha_j,0,0)S^{-1}(0,-\theta_{PAMj},0)(\mathbf{a}_i - \mathbf{A}_j) + \mathbf{A}_j],\\
&\quad(\text{for hydrogens in the } j'\text{th methyl top},\ j=1,2),\\
\mathbf{a}_i^{ref} &= S^{-1}(-\rho_{1z}\alpha_1 - \rho_{2z}\alpha_2,0,0)\mathbf{a}_i,\ (\text{for other atoms}).
\end{aligned} \tag{1}$$

In this paper, only the methyl internal rotations are treated as the intra-molecular motions and the other small-amplitude vibrations are neglected. In Eq. (1), $\mathbf{R}$ denotes the position vector of the molecular center of mass, $\mathbf{a}_i$ represents the equilibrium position vector for the i-th atom with the vector components given in the PAM axis system, and $\mathbf{A}_j$ (j = 1, 2) is the position vector for the center of mass of top j. Four rotation matrices $S^{-1}(\chi,\theta,\phi)$, $S^{-1}(\alpha_j,0,0)$, $S^{-1}(0,\theta_{PAMj},0)$, and $S^{-1}(-\rho_1\alpha_{1z} - \rho_{2z}\alpha_2,0,0)$ are defined as follows:

$S^{-1}(\chi,\theta,\phi)$: 3×3 matrix representing the overall rotation of the molecule with Eulerian angles χ, θ, and ϕ,

$S^{-1}(\alpha_j,0,0)(j=1,2)$: 3×3 matrix representing the internal rotation of methyl top j through an angle α_j about its C_3 axis,

$S^{-1}(0,\theta_{PAMj},0)(j=1,2)$: 3×3 constant matrix used for transforming the C_3 axis of methyl top j to the z-axis of the PAM coordinate,

$S^{-1}(-\rho_{1z}\alpha_1 - \rho_{2z}\alpha_2,0,0)$: 3×3 matrix used to cancel the angular momentum z-component generated during the internal rotation(s) of the methyl top(s). By having introduced this 3x3 matrix, we call the present coordinate system described in Eq. (1) an IAM-like system.

Parameters $\rho_{kz}(k=1,2)$ appearing in $S^{-1}(-\rho_{1z}\alpha_1 - \rho_{2z}\alpha_2,0,0)$ are given by

$$\rho_{kz} = \frac{\lambda_{kz}I_k}{I_z},(k=1,2) \tag{2}$$

where I_z is the principal moment of inertia of the molecule about the PAM z-axis, I_k is the moment of inertia of the kth methyl top about its C_3 axis, and λ_{kz} is the z-component of direction cosines of the symmetry axis of the kth methyl top.

(ii) Transformations of the variables in Eq. (1)

In Table 1, transformations of the variables in Eq. (1) under generating operations of the permutation-inversion group G_{18} for the *trans*-ethyl methyl ether molecule are given, whose character table is given in Table 1 in the previous paper [3]. The numbers 1, 2, 3 denote the protons in the O-methyl group (=top 1), and 4, 5, 6 are the protons in the C-methyl group, while 7 and 8 denote two hydrogen atoms in the CH_2 group (=top 2). The operations (123), (456), and (23)(56)(78)* are feasible operations corresponding to the 120° internal rotation of the O–CH_3 top and the C–CH_3 top, and the reflection in the plane of symmetry, respectively. Note that as seen in Table 1, $(123)^3 \neq e$ and $(456)^3 \neq e$ (e: identity operation) except for special cases.

(iii) Introduction of an extended permutation-inversion group

To avoid the inconvenience of $(123)^3 \neq e$ and $(456)^3 \neq e$, we replace parameters ρ_{1z} and ρ_{2z} by

$$\rho_{1z} \to p/m, \quad \rho_{2z} \to q/n, \tag{3}$$

where p, m, q, n are integers, and in place of α_1 and α_2 we use β_1 and β_2 defined as

$$\beta_1 = \alpha_1/m, \quad \beta_2 = \alpha_2/n. \tag{4}$$

Defining a, b, and c as group operations in the (χ, θ, ϕ, β_1, β_2) space corresponding to (123), (456) and (23)(56)(78)* respectively, makes

$$a^{3m} = b^{3n} = c^2 = e. \tag{5}$$

Operations a, b and c are the generating operations of the extended permutation-inversion group ${G_{18}}^{mn}$ of the permutation-inversion group G_{18}.

Table 1
Transformations of the variables in Eq. (1) under generating operations of the G_{18} group.

	R	χ, θ, ϕ	α_1	α_2
(123)	**R**	$\chi + (2/3)\ \pi\rho_{1z}$, θ, ϕ	$\alpha_1 + (2/3)\pi$	α_2
(456)	**R**	$\chi + (2/3)\ \pi\rho_{2z}$, θ, ϕ	α_1	$\alpha_2 + (2/3)\pi$
(23)(56)(78)*	−**R**	$\pi - \chi$, $\pi - \theta$, $\pi + \phi$	$-\alpha_1$	$-\alpha_2$

The * represents the inversion of all particle positions. The numbers 1–8 represent protons in the molecule. See text for detail.