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Analysis and fit of the high-resolution spectrum of the $\tilde{A}^1A_u$–$\tilde{X}^1A_g$ LIF spectrum of the two-equivalent-top molecule biacetyl

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ABSTRACT

The jet-cooled laser-induced visible fluorescence excitation spectrum of the $\tilde{A}\ ^1A_u\ (S_1)$– $\tilde{X}\ ^1A_g\ (S_0)$ transition in biacetyl ($CH_3—C(=O)—C(=O)—CH_3$) exhibits a long progression in the torsional vibrations of the two equivalent methyl tops in this molecule, whose structure has previously been described and qualitatively understood using local mode ideas applied to the two equivalent methyl rotor torsions together with the G_{36} symmetry species A_1, A_2, A_3, A_4, E_1, E_2, E_3, E_4, and G. In the present rotational analysis, we have assigned a G_{36} symmetry species, two local-mode torsional quantum numbers, and the usual three asymmetric rotor quantum numbers J_{KaKc} to the upper and lower torsion–rotation levels involved in the observed transitions, relying heavily on comparison of quantum-beat patterns to determine transitions with a common upper state. These torsion–rotation transitions were then globally fit using a two-equivalent-top computer program, which was written in the principal axis system of the molecule and which uses a free-rotor basis set for each top, a symmetric-top basis set for the rotational functions, and a single-step diagonalization procedure. We can fit 411 lines involving 16 torsional sublevels from states with zero to three quanta of torsional excitation in the excited electronic state, using 24 parameters to obtain a standard deviation of 0.0045 cm^{-1}, which is quite satisfactory, but inclusion in the fit of 440 transitions from all 17 rotationally assigned torsional levels increases the standard deviation by some 25%. The present fit gives a value of V_3 = 238 cm^{-1} for the threefold barrier height in the excited electronic state, in reasonable agreement with earlier studies.

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1. Introduction

This is the third in a series of papers on the laser-induced fluorescence (LIF) excitation spectrum of the $\tilde{A}^1A_u(S_1)$– $\tilde{X}^1A_g(S_0)$ electronic transition of biacetyl ($CH_3—C(=O)—C(=O)—CH_3$). In the first paper [1] experimental details and rotational analyses using an asymmetric-rotor Hamiltonian for the seven lowest-lying bands in the upper state torsional progression were reported. In the second paper [2], a quantitative fit of 15 torsional band centers in the $\tilde{A}^1A_u(S_1)$ upper electronic state to a two-equivalent-rotor torsional Hamiltonian was carried out, and the positions of the levels were discussed qualitatively in terms of a local-mode model. The reader is referred to those two papers for a more extensive introduction to the problem and for references to earlier work.

This paper is concerned with a global least-squares fit of rotational energy levels belonging to various torsional sublevels in the $\tilde{A}^1A_u(S_1)$ electronic state, using a two-equivalent-top torsion–rotation Hamiltonian based on the G_{36} permutation–inversion group. This G_{36} Hamiltonian is quite similar to the two-inequivalent-top Hamiltonian based on the G_{18} permutation–inversion group used previously to carry out a rotational fit to the microwave spectrum of the closely related molecule *N*-methylacetamide ($CH_3—C(=O)—N(—H)—CH_3$) [3].

Our global fits have been relatively successful, in the sense that overall standard deviations of the fits are within a factor of two or three of the estimated experimental measurement uncertainty. Nevertheless, a fit to 415 rotational transitions from 16 torsional sublevels using 24 parameters (different from the fit cited in the abstract), gives a root-mean-square (rms) residual of 0.0049 cm^{-1}, while attempts to fit 440 rotational transitions from all 17 torsional sublevels having rotational assignments lead to a significant increase in the rms residual to 0.0057 cm^{-1}, indicating that some unexplained difficulties remain.

The rest of this paper contains the following parts. We briefly review the G_{36} group theory needed to classify torsion–rotation states in this molecule in Section 2, and discuss the form of the torsion–rotation Hamiltonian in Section 3. We discuss the data set in Section 4 and the results of our least-squares fits in Section 5.

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2. Group theory

Biacetyl has C_{2h} point-group symmetry at equilibrium, but, as discussed by Senent et al. [4], it belongs to the permutation–inversion (PI) group G_{36} when internal rotations of the two methyl groups are considered. We use here the atom numbering scheme shown in Fig. 1 and the species notation and character table given by Nelson and Klemperer in their study of the ammonia dimer [5], which can also be found in our first paper in this series [1].

The precise relations between the G_{36} PI operations and the transformations of variables in the torsion–rotation wavefunctions are determined here, as usual, by first setting up an algebraic relation between the laboratory-fixed coordinates and a somewhat idealized set of molecule-fixed coordinates that preserve the essential symmetry of the problem:

$$\boldsymbol{R}_i = \boldsymbol{R} + S^{-1}(\chi,\theta,\phi)S^{-1}(0,\theta_{\mathrm{PAM}},0)\boldsymbol{a_i}(\alpha_1,\alpha_2), \tag{1}$$

where

$$\begin{aligned} &\boldsymbol{a}_i(\alpha_1,\alpha_2) = \boldsymbol{a}_i^0 \quad \text{for } i = a-f \\ &\boldsymbol{a}_i(\alpha_1,\alpha_2) = [S^{-1}(+\alpha_1,0,0)(\boldsymbol{a}_i^0 - \boldsymbol{a}_{Ca}^0) + \boldsymbol{a}_{Ca}^0] \quad \text{for } i = 1-3 \\ &\boldsymbol{a}_i(\alpha_1,\alpha_2) = [S^{-1}(-\alpha_2,0,0)(\boldsymbol{a}_i^0 - \boldsymbol{a}_{Cb}^0) + \boldsymbol{a}_{Cb}^0] \quad \text{for } i = 4-6 \end{aligned} \tag{2}$$

In Eq. (1), the $\boldsymbol{R}_i$ on the left represent 3×1 vectors containing laboratory-fixed Cartesian coordinates for the atoms i = 1–6 and a–f of the molecule, as labeled in Fig. 1. On the right, $\boldsymbol{R}$ represents a 3×1 vector containing the laboratory-fixed Cartesian coordinates of the center of mass of the molecule; $S^{-1}(\chi, \theta, \phi)$ represents the 3×3 direction cosine matrix between the laboratory-fixed and molecule-fixed axes, as defined using the Euler angle conventions of [6]; the $\boldsymbol{a}_i(\alpha_1, \alpha_2)$ represent 3×1 vectors containing the molecule-fixed Cartesian coordinates of the atoms, defined as functions of the internal rotation angles α_1 and α_2 in Eq. (2); and the constant matrix $S^{-1}(0, \theta_{\mathrm{PAM}}, 0)$ rotates the whole molecule about the y axis into a "torsion–rotation principal axis system" (see Section 5). In Eq. (2), the constant vectors $\boldsymbol{a}_i^0$ represent the set of "initial atom positions" given in Table 1, where the C_3 axes of the methyl tops are parallel to the molecule-fixed z axis and point towards the C_c or C_d carbon atoms to which they are bonded; the matrices $S^{-1}(+\alpha_1, 0, 0)$ and $S^{-1}(-\alpha_2, 0, 0)$ carry out the internal rotation of each methyl group about its C_3 axis, according to its own torsional angle. (We note in passing that constant matrices of the form $S^{-1}(0, \pm\theta_{\mathrm{top}}, 0)$ could be introduced to rotate the two methyl top C_3 axes symmetrically away from the z axis, but this small correction does not change the symmetry properties of the coordinates, so it will not be described here.)

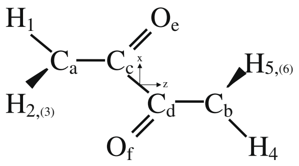

Fig. 1. Atom numbering scheme for biacetyl adopted in this work. All atoms lie in the plane of the paper, except for H_2 and H_5, which are above the plane, and H_3 and H_6, which are below the plane of the paper and completely eclipsed by H_2 and H_5, respectively, in the view shown in this figure. The x and z axes chosen are shown by arrows.

Table 1
Schematic values for the coordinates[a] $\boldsymbol{a}_i^0$ used in the idealized structure of Eq. (2).

Atom[b]	a_x^0	a_y^0	a_z^0	Atom[b]	a_x^0	a_y^0	a_z^0
C_a	$+x_a$	0	$-z_a$	H_1	$+x_a + x_1$	0	$-z_1$
C_c	$+x_a$	0	$-z_c$	H_2	$+x_a - x_1/2$	$+x_1\sqrt{3}/2$	$-z_1$
O_e	$+x_e$	0	$+z_e$	H_3	$+x_a - x_1/2$	$-x_1\sqrt{3}/2$	$-z_1$

[a] The quantities x_a, x_e, x_1 and z_a, z_c, z_e, z_1 are all taken to be positive.

[b] Because of the center of symmetry in biacetyl, $\boldsymbol{a}_i^0 = -\boldsymbol{a}_j^0$ for the atom pairs (i, j) = (1, 4), (2, 6), (3, 5), (a, b), (c, d), and (e, f), using the atom labels shown in Fig. 1.

Table 2
Transformation properties of the molecule-fixed coordinates in Eqs. (1) and (2) corresponding to the indicated permutation–inversion (PI) operations[a] of the G_{36} group with the atom numbering in Fig. 1.

PI operation[a]	c-o-m[b]	Euler angles[c]	Torsional angles[d]	
E	$+\boldsymbol{R}$	χ, θ, ϕ	α_1	α_2
$A = (123)$	$+\boldsymbol{R}$	χ, θ, ϕ	$\alpha_1 + 2\pi/3$	α_2
$B = (456)$	$+\boldsymbol{R}$	χ, θ, ϕ	α_1	$\alpha_2 + 2\pi/3$
$C = (14)(25)(36)(ab)(cd)(ef)$	$+\boldsymbol{R}$	$\pi - \chi, \pi - \theta, \pi + \phi$	α_2	α_1
$D = (23)(56)^*$	$-\boldsymbol{R}$	$\pi - \chi, \pi - \theta, \pi + \phi$	$-\alpha_1$	$-\alpha_2$

[a] The operations A, B, C, D are generators for G_{36}.

[b] The center-of-mass vector in laboratory-fixed Cartesian coordinates.

[c] The rotational variables occurring in the direction cosine matrix $S^{-1}(\chi, \theta, \phi)$ of Eq. (1).

[d] Each torsional angle governs the internal rotation of one methyl top (see Eq. (2)).

Table 2 gives coordinate transformations for the generators of G_{36}. It can be shown that substitution into the right of Eqs. (1) and (2) of the coordinate changes specified in a given row on the right of Table 2 yields on the left of Eq. (1) the PI transformation given on the left of that row in Table 2. For example, working through the substitutions in the last of Eq. (3) yields the PI operation on the left of Eq. (3):

$$\begin{aligned} &(142\,635)(ab)(cd)(ef)* \\ &\quad f(\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3,\boldsymbol{R}_4,\boldsymbol{R}_5,\boldsymbol{R}_6,\boldsymbol{R}_a,\boldsymbol{R}_b,\boldsymbol{R}_c,\boldsymbol{R}_d,\boldsymbol{R}_e,\boldsymbol{R}_f) \\ &\quad = f(-\boldsymbol{R}_4,-\boldsymbol{R}_6,-\boldsymbol{R}_5,-\boldsymbol{R}_2,-\boldsymbol{R}_1,-\boldsymbol{R}_3,-\boldsymbol{R}_b,-\boldsymbol{R}_a,-\boldsymbol{R}_d,-\boldsymbol{R}_c,-\boldsymbol{R}_f,-\boldsymbol{R}_e) \\ &\quad = ACD\,f(\boldsymbol{R},\chi,\theta,\phi,\alpha_1,\alpha_2) = f(-\boldsymbol{R},\chi,\theta,\phi,-\alpha_2,-\alpha_1-2\pi/3) \end{aligned} \tag{3}$$

It can also be seen that the transformation properties in Table 2 are consistent with those described in Eqs. (3)–(5) of our earlier work [2], if we make the identifications α_1, α_2 here = θ_1, θ_2 there. The information in Table 1 of [1] and Table 2 can be used to determine the symmetry species of the torsional basis functions shown in Table 2 of [2] and the rotational basis functions [7] shown in Table 3.

3. Torsion–rotation Hamiltonian operator

The torsion–rotation Hamiltonian operator for the $\tilde{A}^1A_u(S_1)$ excited electronic state of biacetyl is similar to that used previously for the ground electronic state of N-methylacetamide [3], except that some parameter pairs must be set equal to each other because of the higher symmetry of biacetyl. Also, a number of centrifugal distortion terms that were determinable in the microwave study of [3], but are not determinable in the visible study here, are not explicitly shown in the Hamiltonian of Eq. (4). Similarly, higher-

Table 3
G_{36} symmetry species Γ[a] for linear combinations of the symmetric-top rotational basis functions $|K, J, M\rangle$.

Γ	Rotational function	Γ	Rotational function
A_1	$\lvert K = 0, J = \text{even}, M\rangle$	A_1	$[\lvert K, J, M\rangle + (-1)^{J-K}\lvert -K, J, M\rangle]/\sqrt{2}$
A_2	$\lvert K = 0, J = \text{odd}, M\rangle$	A_2	$[\lvert K, J, M\rangle - (-1)^{J-K}\lvert -K, J, M\rangle]/\sqrt{2}$

[a] Γ is the symmetry species in G_{36} (see Table 1 of [1]) to which the indicated rotational wavefunction belongs, using Euler angle transformations from Table 2 and transformation properties for symmetric top functions from [7].

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