

A fitting program for molecules with two equivalent methyl tops and  $C_{2v}$  point-group symmetry at equilibrium: Application to existing microwave, millimeter, and sub-millimeter wave measurements of acetone

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At the present time three related programs are available on Z. Kisiel's PROSPE website. The program BELGI-Cs fits spectra of molecules with one methyl rotor, a three-fold barrier, and a plane of symmetry at equilibrium. The program BELGI-C<sub>1</sub> fits spectra of molecules with one methyl rotor, a three-fold barrier, and no symmetry at equilibrium. The program RAM36 was designed specifically to fit spectra of molecules with one methyl rotor, a six-fold barrier, and a plane of symmetry at equilibrium, but it can also be applied to molecules with a three-fold barrier. The recently completed program BELGI-Cs-2Tops, which is not yet on PROSPE, fits spectra of molecules with two inequivalent methyl rotors having different three-fold barriers, and a plane of symmetry at equilibrium.

The program described in the present talk is called PAM\_C2v\_2tops, and is designed for fitting high-resolution torsion-rotation spectra of molecules with two equivalent methyl rotors and  $C_{2v}$  symmetry at equilibrium, such as acetone [(CH<sub>3</sub>)<sub>2</sub>CO]. PAM\_C2v\_2tops is closely related group-theoretically to a program written by N. Ohashi, and used for a treatment of the electronic spectrum of biacetyl [CH<sub>3</sub>-C(=O)-C(=O)-CH<sub>3</sub>], a molecule with two equivalent rotors, but having a  $C_{2h}$  equilibrium structure.

The permutation-inversion (PI) group for acetone and related molecules is  $G_{36}$  (which also happens to be the PI group for biacetyl and dimethylacetylene, even though they belong to very different point groups at equilibrium). Since  $G_{36}$  applied to various molecules is discussed in the well-known book by Bunker and Jensen, we will not present group-theoretical details in this talk. To construct the Hamiltonian in the computer program for fitting microwave data, we considered torsional, rotational, and torsion-rotation operators depending on only five variables, namely the two large-amplitude-motion (LAM) torsional angles used to describe internal rotation of each methyl top, and the three Eulerian angles used to describe overall rotation of the asymmetric-rotor molecule. PI group theory is needed to insure that all terms occurring in the fitting Hamiltonian are allowed by symmetry. This checking for correct symmetry of individual terms is in fact done by a checking algorithm in the program. In addition, all terms in the Hamiltonian are checked to insure that they are Hermitian and invariant to time reversal.

The structure of the present program, PAM\_C2v\_2tops, is very similar to that of RAM36. Briefly, a general expression for the Hamiltonian to be used in the fitting procedure is written as

$$\begin{aligned}
 H = & (1/4) \sum_{knpqr1r2s1s2t1t2} B_{knpqr1r2s1s2t1t2} \\
 & \times \{ J_z^{2k} J_x^n J_y^p J_z^q [ p_A^{r1} p_B^{r2} \cos(3s_1\alpha_A) \cos(3s_2\alpha_B) \sin(3t_1\alpha_A) \sin(3t_2\alpha_B) \\
 & + (-1)^{(p+q)} p_B^{r1} p_A^{r2} \cos(3s_1\alpha_B) \cos(3s_2\alpha_A) \sin(3t_1\alpha_B) \sin(3t_2\alpha_A) ] \\
 & + [ (-1)^{(p+q)} \sin(3t_2\alpha_A) \sin(3t_1\alpha_B) \cos(3s_2\alpha_A) \cos(3s_1\alpha_B) p_A^{r2} p_B^{r1} \\
 & + \sin(3t_2\alpha_B) \sin(3t_1\alpha_A) \cos(3s_2\alpha_B) \cos(3s_1\alpha_A) p_B^{r2} p_A^{r1} ] J_y^q J_x^p J_z^n J_z^{2k} \},
 \end{aligned}$$

where the  $B$ 's are fitting parameters, the quantities in square brackets are quantum mechanical operators in the usual notation, and subscripts A and B denote the two methyl tops. Since all possible terms provided by this Hamiltonian will automatically be Hermitian, the program checks only to see if the terms requested by the user (as input to the program via the integers  $k, n, p, q, r_1, r_2, s_1, s_2, t_1$  and  $t_2$ ) are totally symmetric in  $G_{36}$  and invariant to time reversal. The program uses the principal axis method and a two-step diagonalization procedure.

As a first application, the program was used to carry out a weighted least-squares fit of the 1720 microwave, millimeter-wave, and sub-millimeter-wave line frequencies of acetone that are available in the extensive acetone data set collected together in a series of papers by P. Groner et al. in the literature. This literature data set contains rotational transitions within the ground state and within the fundamental torsional states of  $\nu_{12}$  and  $\nu_{17}$ , with  $J$  values up to 60, 38, 31 and  $K_a$  up to 30, 16, 8 respectively. In the present fit we have chosen to restrict the maximum value of  $J$  to 38 for the following reasons: (i) A fit to experimental measurement error of such a data set clearly demonstrates the capabilities of the new program. (ii) A fit with  $J \leq 38$  includes all the  $\nu_{12}$  and  $\nu_{17}$  transitions in the literature that gave significant fitting problems there. (iii) Based on a few remeasurements using the Kharkov spectrometer, we suspect that measurement error bars on some of the higher- $J$  measurements may be too optimistic by a factor of two or so. (iv) Higher- $J$  fits require significantly more time per iteration, and a significantly larger search in parameter space. Primarily because of (iii), we prefer to postpone any attempts to obtain a good fit for the full  $J \leq 60$  data set until a remeasurement campaign can be carried out. (We have, however, carried out exploratory fits of the  $J \leq 60$  data set in the literature.)

A fit achieving a weighted root-mean-square (wrms) deviation of 0.93 for 1720 microwave and 13 FIR line frequencies with 40 parameters included in the model was chosen as our "best fit" for a MS recently submitted to J. Mol. Spectrosc. The final fit converged perfectly in all three senses: (i) the relative change in the wrms deviation of the fit at the last iteration is less than  $10^{-10}$ ; (ii) the corrections to the parameter values generated at the last iteration are less than  $10^{-5}$  of the calculated parameter confidence intervals; (iii) the changes generated at the last iteration in the calculated frequencies are less than 1 kHz even for the vibrational FIR transitions. Essentially because of computer limitations in the past, previous literature fits of this data treated the individual torsional states separately, without explicitly introducing a potential function. Our combined fit provides significant improvement in rms deviations for rotational transitions all three torsional states (changing in a number of cases from MHz residuals to kHz residuals).

A large number of individual-top parameters and top-top interaction parameters have been well determined in the present work, but the lower-order torsional parameters frequently disagree within their standard deviations with those reported in the literature. We believe these differences arise because of a slightly different choice of higher-order interaction terms in the various models. The present fit is characterized by a ratio of 43 lines per adjustable parameter, which we feel is quite satisfactory. This ratio represents a factor of two improvement over the ratio of 19 lines/parameter obtained from the separate-torsional-state fits in the literature. It can also be compared with the ratio of 43 lines/parameter obtained in Kharkov for a preliminary fit of a data set with  $J \leq 60$  and a weighted rms of 1.19. As another measure of the quality of the model, we find a ratio  $40/3 = 13.3$  parameters per  $(\nu_{12}, \nu_{17}) = (0,0), (1,0),$  and  $(0,1)$  torsional state.