ANALYSIS AND FIT OF THE HIGH-RESOLUTION VISIBLE SPECTRUM OF THE TWO-EQUIVALENT-TOP MOLECULE BIACETYL

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The $A^1A_u(S_1) - X^1A_g(S_0)$ LIF spectrum of biacetyl ($CH_3C(=O)C(=O)CH_3$) shows a long progression in the torsional vibrations of the two methyl tops. The S_1 torsional level pattern can be qualitatively understood[a] using local mode ideas applied to the two equivalent methyl rotors and symmetry ideas from the PI group G_{36}. For the present rotational analysis, we assigned a G_{36} symmetry species, two local-mode torsional quantum numbers, and rotational quantum numbers $J_{Ka,Kc}$ to each observed torsion-rotation level. Transitions were globally fit with a two-equivalent-top computer program, which uses the molecular principal axis system, a free-rotor basis set for each top, a symmetric-top basis set for the rotational functions, and a single-step diagonalization procedure. The program is similar to our two-inequivalent-top program for N-methylacetamide.[b] Last year, we refit 179 previously published[c] rotational lines involving 7 torsional tunneling sublevels with zero or one quantum of torsional excitation in the S_1 state of biacetyl, using 14 parameters (5 for S_0, 9 for S_1) to obtain a standard deviation of 0.0041 cm^{-1}. We have now extended that fit by adding 131 unpublished lines involving 5 tunneling sublevels with two quanta of torsional excitation, using 19 parameters to obtain a standard deviation of 0.0040 cm^{-1}. Including transitions with still higher torsional excitation leads to a degraded standard deviation. We thus suspect that a number of higher-order terms describing top-top-overall-rotation interactions are missing from the present model, but the possibility of misassignments in the higher-energy regions must also be considered.

[a] C.-L. Huang, C.-L. Liu, C.-K. Ni, and J. T. Hougen, J. Mol. Spectrosc. **233**, 122-132 (2005).
[b] N. Ohashi, J. T. Hougen, R. D. Suenram, F. J. Lovas, Y. Kawashima, M. Fujitake, and J. Pyka, J. Mol. Spectrosc. **227**, 28-42 (2004).
[c] C.-L. Huang, H.-H. Liu, C.-L. Liu, A. H. Kung, and C.-K. Ni, J. Chem. Phys. **117**, 5165-5173 (2002).