

ROTATIONAL AND FINE STRUCTURE OF PSEUDO-JAHN-TELLER MOLECULES WITH C_1 SYMMETRY

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It has been found in our previous works that rotational and fine-structure analysis of spectra involving nearly degenerate electronic states may aid in interpretation and analysis of the vibronic structure, specifically in the case of pseudo-Jahn-Teller (pJT) molecules with C_s symmetry. The spectral analysis of pJT derivatives (isopropoxy^a and cyclohexoxy^b) of a prototypical JT molecule (the methoxy radical) allowed for quantitative determination of various contributions to the energy separation between the nearly degenerate electronic states, including the relativistic spin-orbit (SO) effect, the electrostatic interaction, and their zero-point energy difference. These states are coupled by SO and Coriolis interactions, which can also be determined accurately in rotational and fine structure analysis. Most recently, the spectroscopic model for rotational analysis of pJT molecules has been extended for analysis of molecules with C_1 symmetry, i.e., no symmetry. This model includes the six independently determinable components of the spin-rotation (SR) tensor and the three components of the SO and Coriolis interactions. It has been employed to simulate and fit high-resolution laser-induced fluorescence (LIF) spectra of jet-cooled alkoxy radicals with C_1 symmetry, including the 2-hexoxy and the 2-pentoxy radicals, as well as previously recorded LIF spectrum of the trans-conformer (defined by its OCCC dihedral angle) of the 2-butoxy radical.^c Although the LIF spectra can be reproduced by using either the SR constants or SO and Coriolis constants, the latter simulation offers results that are physically more meaningful whereas the SR constants have to be regarded as effective constants. Furthermore, we will review the SO and Coriolis constants of alkoxy radicals that have been investigated, starting from the well-studied methoxy radical (CH_3O).

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^cL. Stakhursky, L. Zu, J. Liu, and T. A. Miller, *J. Chem. Phys.* 125, 094316 (2006)