EFFECTS OF ASYMMETRIC DEUTERATION ON THE ROTATIONAL LEVEL STRUCTURE OF JAHN-TELLER ACTIVE METHOXY RADICALS

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Recently the high resolution microwave, LIF and SEP spectra of the methoxy isotopologues of the C_{3v} symmetry, $^{12}CH_3O$, $^{12}CD_3O$, and $^{13}CH_3O$ have been analyzed[b,c]. The data were globally fit to the effective rotational Hamiltonian (ERH), and the physical interpretation of its parameters has been given. In the present work we extend the studies of the rotationally resolved spectra of this Jahn-Teller active species to its asymmetrically substituted isotopologues. In these molecules the electronic wavefunction retains its threefold symmetry. Although the vibrational modes are no longer degenerate, the asymmetry induced by deuteration can be treated as a perturbation and the molecule can still be analyzed using theory similar to that which has been employed for the symmetric isotopologues. For this analysis we have used the ERH derived[d] for the internal axis system (IAS), whose $z-$axis is parallel to the C-O bond. The form of the ERH has been extended to include the effects of the Jahn-Teller distortion on the rotational and spin-rotational Hamiltonian in IAS axis system with a nondiagonal rotational tensor. The microwave, LIF and SEP transitions were globally fit to the extended form of the ERH. The resulting parameters are compared to the corresponding values derived from the parameters of the symmetric species using the isotopic relationships. For the most signidicant parameters, the first and the second order contributions are calculated. The results of this analysis will be presented.

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