THE EFFECT OF TORSION - VIBRATION COUPLINGS ON THE ν_9 AND ν_1 BANDS IN THE $CH_3OO\cdot$ RADICAL

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There are three CH stretch modes in the $CH_3OO\cdot$, namely the totally symmetric stretch, ν_2, the out-of-phase symmetric stretch, ν_1, and the antisymmetric stretch, ν_9. However, only two strong partially rotationally resolved vibrational transitions are observed in the CH stretch region of the infrared spectrum of $CH_3OO\cdot$. Moreover, the Q-branches of both bands are significantly broader than the simulations using an asymmetric rigid rotor model. Previously, the rotational contour of the ν_2 band in the experimental spectrum has been simulated by considering the fundamental as well as sequence band transitions involving torsionally excited levels populated at room temperature[a]. Using a four dimension Hamiltonian that involves the three CH stretches and the CH_3 torsion, the torsional sequence bands of the ν_2 stretch were calculated to be slightly shifted from the origin band as a result of the couplings between the CH stretches and CH_3 torsion which are particularly large due to an accidental degeneracy between the combination level involving the ν_2 stretch and n quanta in the CH_3 torsion and the combination level involving the ν_1 or ν_9 stretch and $n-1$ quanta in the CH_3 torsion. In this study we focus on the part of $CH_3OO\cdot$ vibrational spectrum containing the ν_1 and ν_9 bands. Along with the 4-dimensional Hamiltonian which was used to simulate the spectra in the ν_2 region, we analyze the effect of torsion-stretch couplings on the ν_1 and ν_9 bands based on the model developed by Hougen[b] to describe methanol. To account for the accidental degeneracies in CH_3OO, we extend the previous model to include the combination levels involving the ν_2 stretch and the CH_3 torsion. Unlike the torsional sequence bands and fundamental of ν_2, the tunneling splittings of the torsional sequence bands and fundamentals of ν_1 and ν_9 have different signs, which results in the weak intensity of ν_1 fundamental and broadening in the rotational contour of the torsional sequence bands of ν_9.The simulation of the ν_9 and ν_1 bands including the torsional sequence bands using the parameters which are consistent with the ones used in the simulation of the ν_2 band is in good agreement with the experimental spectrum.

[a] K.-H. Hsu, Y.-H. Huang, Y.-P. Lee, M. Huang, T. A. Miller and A. B. McCoy *J. Phys. Chem. A*, 2016, 120 (27), 4827

[b] J.-T. Hougen *J. Mol. Spec.*, 2001, 207, 60