TORSION - VIBRATION COUPLINGS IN THE $CH_3OO\cdot$ RADICAL

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A partially rotationally resolved infrared spectrum of $CH_3OO\cdot$ in the CH stretch region has been reported[a]. The rotational contour of the ν_2 CH stretch band in the experimental spectrum can be simulated with an asymmetric rotor model. The simulation shows good agreement with the experimental spectrum except that the broadening of the Q-branch in the experimental spectrum remains unexplained. This broadening is likely due to the sequence band transitions from the torsionally excited levels populated at room temperature to combination levels involving the CH stretch and the same number of torsional quanta. A four dimension model involving three CH stretches and the CH_3 torsion is applied to the $CH_3OO\cdot$ radical to obtain the frequencies and intensities of the vibrational transitions in the CH stretch region. Based on these calculations, the torsional sequence bands are calculated to be slightly shifted from the origin band, because of the couplings between the CH stretches and CH_3 torsion, thereby causing the apparent broadening observed for the ν_2 fundamental. Due to the accidental degeneracy of two different CH stretch and CH_3 torsion combination levels which differ by one quantum in the torsional excitation, the frequencies of the torsional sequence bands will be very sensitive to details of the potential, which makes the shifts difficult to precisely predict with electronic structure calculations. Complementary analyses are now underway for the other two CH stretch vibrational bands, ν_1 and ν_9.

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