THEORY OF ODD TORSIONAL TRANSITIONS IN THE $V-N$ RESONANCE RAMAN SPECTRUM OF ETHYLENE

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The $V-N$ resonance Raman spectrum of ethylene[a] shows a long progression in even quanta of the ground-state torsional mode $\nu_4''(a_u)$. Bands approximately midway between the even quanta have been assigned[b] to transitions to odd quanta of ν_4''. Such transitions are forbidden according to the usual $g \not\leftrightarrow u$ selection rule of Raman spectroscopy. Here we consider the theory of the intensity of such transitions allowing for the fact that the excited state is twisted by 90° at equilibrium, using Hougen's double group theory[c]. From approximate one-dimensional torsional potentials of the V and N electronic states, it is shown that good qualitative agreement between observed and calculated intensities is obtained. The electronic transition moment is assumed to be proportional to $\cos\theta$, where θ is the torsional angle, but the calculated relative intensities are not sensitive to the precise torsional dependence. More detailed theory will require consideration of the avoided crossing affecting the V state[d].

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