GAS PHASE RAMAN SPECTRA OF BUTADIENE AND BUTADIENE-d_6 AND THE INTERNAL ROTATION POTENTIAL ENERGY FUNCTION

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The Raman spectrum of butadiene has been previously reported by Carreira [a] and by Engeln and co-workers [b]. Both studies reported a series of bands corresponding to double quantum jumps of ν_{13}, the internal rotation vibration, of the trans rotamer. Both studies also reported weaker bands assigned to the higher energy conformer. Carriera assigned these to the cis form while Engeln assigned them to the gauche form. Recent high level calculations by Feller and Craig [c] also assign the higher energy form as gauche. In the present study we report the gas phase Raman spectrum of butadiene and its d_6 isotopomer at both 25°C and 260°C. Several new spectral features in the 330 to 210 cm^{-1} region were observed and the effect of heating on the band intensities was studied. In addition, combination bands were observed in the 630 to 690 cm^{-1} ($\nu_{12} + \nu_{13}$) and 1130 to 1180 cm^{-1} ($\nu_{10} + \nu_{13}$) regions. A periodic potential energy function with V_1, V_2, V_3, V_4, and V_6 terms was utilized to fit the data. This function was compared to the results from previous work and to the theoretical calculation.

[a] L. Carreira, J. Phys. Chem. 62, 3851 (1975).
[b] R. Engeln, D. Consalvo, and J. Reuss, J. Chem. Phys. 160, 427 (1992).
[c] D. Feller and N. C. Craig, J. Phys. Chem. 113, 1601 (2009).