EFFECT OF STRUCTURE AND CONFORMATION ON RAMAN TRACE SCATTERING INTENSITIES IN HYDROCARBONS

KATHLEEN M. GOUGH, JASON R. DWYER, and TED GAWLIK , *Department of Chemistry, University of Manitoba, Winnipeg, MB, Canada R3T 2N2*.

The *ab initio* (HF/D95**) optimized geometries and equilibrium molecular polarizabilities have been obtained for thirty-five hydrocarbons: all-*trans* straight chain alkanes to C_{15}, as well as C_{25}, *iso*-butane, six cyclo- and methylcycloalkanes, eight bicycloalkanes, four propellanes and a tetracyclane. The derivative of the molecular polarizability associated with the stretch of a single CH bond has been calculated for each unique CH. In contrast to expectations of the bond polarizability model, there is considerable variation in the magnitude of the derivatives, ranging from a high of 1.38 x 10^{-30} Cm/V for the bridgehead CH bond in bicyclo[1.1.1]pentane to a low of 0.908 x 10^{-30} Cm/V for a methylene CH in bicyclo[3.3.1]nonane. These differences would result in a factor of 2.3 difference in the Raman scattering intensity for the respective CH stretching vibrations. Principal factors governing the magnitude of the derivative are identified as: location, alignment, group strain and steric hindrance. Averaging of competing effects is also inferred. Derivatives for some of the CC bonds have also been calculated. Implications for the prediction and interpretation of Raman scattering intensities are discussed. [a]

[a] K. M. Gough and J. R. Dwyer, *J. Phys. Chem.* in press.