

UV RESONANCE RAMAN ENHANCEMENT: FROM SMALL MOLECULES TO PROTEINS

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Our recent extension of Raman spectroscopy into the UV spectral region¹ from 200 to 400 nm has demonstrated the utility of resonance Raman enhancement studies as an important physical technique to explore excited state structure. The selectivity of resonance excitation in the UV permits studies of aromatic chromophores in complex environments. Analytically and biophysically important examples include studies of polycyclic aromatic hydrocarbons in coal liquids^{2,3} and aromatic amino acids in proteins.⁴ UV Raman measurements of condensed phase samples avoid the fluorescence interferences that often fatally degrade the signal-to-noise ratios of spectra obtained with visible wavelength excitation.⁵

We will discuss Raman cross section studies of a series of small molecules which are useful as internal standards for Raman spectral studies. We have developed a new technique⁶ to measure the dispersion of the absolute Raman cross section between 210 and 800 nm and have measured the cross sections of molecules such as CH_3CN , H_2O , acetone, SO_4 , ClO_4 , and NO_3 . The preresonance dispersion of the cross section of these species (except for NO_3) appears to be dominated by states in the far, far UV. In contrast, the preresonance Raman dispersion of NO_3 , acetamide, and N-methyl acetamide is dominated by the 180-200 nm transitions.⁷ These observations question the existence of discrete valence electronic transitions in the vacuum UV in condensed phase samples.

We examined resonance enhancement in both gas phase and condensed⁸ phase benzene. For excitation between 215 and 250 nm the symmetric ring breathing 992 cm^{-1} vibration derives enhancement mainly from the B_{1u}/E_{1u} states with little evidence of enhancement from the B_{2u} transition. In contrast, in the gas phase the smaller homogeneous linewidth of the vibronic components of the B_{2u} transition results in enhancement with exact resonance.

Both resonance Raman and single vibrational level fluorescence (SVL) are observed for excitation in the vibronic components of the gas phase benzene B_{2u} transition. These phenomena have been differentiated by the fact that Raman intensity must add at the amplitude level to any preresonance enhancement, while SVL adds at the intensity level because it occurs from a state which has dephased by a T_2 process from the virtual intermediate state.

We will also discuss the selection of vibrational modes enhanced by the UV transitions of substituted benzene derivatives including the aromatic amino acids. We will relate the observed cross sections to those observed for the aromatic amino acids as side chains in proteins. The utility of the use of Raman cross sections as probes of protein structure will be discussed.

We will also examine Raman excitation profiles of polycyclic aromatic hydrocarbons such as pyrene and relate the excitation profiles to the underlying vibronic structure..

References

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