

THEORETICAL INVESTIGATION OF ANHARMONIC EFFECTS OBSERVED IN THE INFRARED SPECTRA OF THE FORMALDEHYDE CATION AND ITS HYDROXYMETHYLENE ISOMER

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Formaldehyde is the smallest organic molecule and is a prime candidate for a thorough investigation regarding the anharmonic approximations made in computationally modeling its infrared spectrum. Mass-selected ion spectroscopy was used to detect mass 30 cations which include of HCOH^+ and CH_2O^+ . In order to elucidate the differences between the structures of these isomers, infrared spectroscopy was performed on the mass 30 cations using Ar predissociation. Interestingly, several additional spectral features are observed that cannot be explained by the fundamental OH and CH stretch vibrations alone. By including anharmonic coupling between OH and CH stretching and various overtones and combination bands involving lower frequency vibrations, we are able to identify how specific modes couple and lead to the experimentally observed spectral features. We combine straight-forward, *ab initio* calculations of the anharmonic frequencies of the mass 30 cations with higher order, adiabatic approximations and Fermi resonance models. By including anharmonic effects we are able to confirm that the isomers of the $\text{CH}_2\text{O}^+\cdot\text{Ar}$ system have substantially different, and thus distinguishable, IR spectra and that many of the features can only be explained with anharmonic treatments.