UBIQUITOUS INTERSTELLAR MOLECULES WITH RADICALLY DIFFERENT CATION STRUCTURES: INFRARED SPECTROSCOPY OF FORMALDEHYDE AND METHANOL CATIONS

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Formaldehyde and methanol are detected in interstellar and circumstellar sources by rotational transitions resulting from their well-known structures. For the radical cations with nominal formulas $[C, H_2, O]^+$ and $[C, H_4, O]^+$, no such measurements have been made in interstellar sources or in the laboratory to our knowledge. We measured the infrared spectrum of both radical cations in the gas phase using infrared photodissociation spectroscopy and found structures that differ drastically from the neutral closed shell species. For the case of $[C, H_2, O]^+$, formaldehyde cation CH_2O^+ and hydroxymethylene cation $CHOH^+$ are predicted to be minima with only 5 kcal/mol difference in stability. We see evidence for two isomers in the infrared spectrum and investigate the effects of the argon tag on these small (four atoms) radical cations. For the mass 32 cation $[C, H_4, O]^+$, theory predicts the methyleneoxonium cation $CH_2OH_2^+$ to be about 15 kcal/mol more stable than the methanol cation CH_3OH^+. We present definitive assignments of vibrational features to these two isomers of the mass 32 cation. We discuss the kinetic trapping occurring in the ion source that produce the thermodynamically unfavorable CH_3OH^+ simultaneously with the lowest energy structure, $CH_2OH_2^+$. The application of our findings to astrochemistry is discussed.