

Direct Optical Measurements of C₃H₄⁺ and C₃H₃⁺ Cations in Solid Ar

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C₃H₄⁺ and C₃H₃⁺ ions are important in many diverse applications and fields, such as flame and combustion processes, and planetary and interstellar chemistry. They are commonly observed fragments in the combustion of hydrocarbons and are proposed as reactants in the synthesis of cumulenenic and cyclic hydrocarbons in interstellar medium through ion–molecule reactions. C₃H₃⁺ ions have also been detected in the tail of Halley’s comet.

We produced allene cations (H₂C₃H₂⁺) in solid Ar via electron bombardment (200 eV) of an allene/Ar matrix sample during matrix deposition. Subsequently, we irradiated the matrix sample with 365-nm light, which resulted in isomerization from allene cations to propyne cations (H₃C₃H⁺) in the solid Ar. The IR absorption features of the both cations were recorded and assigned based on the theoretical prediction, D-isotopic substitution, and photochemical behaviors [1]. In the meanwhile, we also recorded UV absorption spectra of this sample and an intense vibrationally resolved progression in the spectral region of 266–237 nm was assigned to the $A^2E \leftarrow X^2E$ electronic transition of allene cations, and the torsional mode is dominant in this progression. Moreover, although the strong absorption of neutral allene appeared in the spectral region at wavelengths shorter than 225 nm, the weak absorption of allene cations corresponding to the $B^2A_1 \leftarrow X^2E$ transition was extracted from the difference spectrum recorded after photolysis at 385 nm [2].

In separate experiments, we subjected propyne/Ar matrix samples to electron bombardment at 200 or 2000 eV, followed by deposition at 8 K. Allene cations also were found to be dominant for low-energy bombardment, similar to the case in previous allene experiments. This suggests that the loss of H atoms from the two precursors might be inhibited due to the rapid excess energy quenching after bombardment. In contrast, several H-degradation species including propargyl cations (H₂C₃H⁺) were formed in the high-energy bombardment experiment [3]. This study confirmed the assignment of the ν_5 mode at 1140.6 cm⁻¹ which was reported discrepantly in previous IRPD [4] and VMI-PE [5] measurements. In addition, the IR absorption of the ν_{11} mode was observed for the first time. The “true” experimental relative IR intensities of the observed vibrational modes of the cation were also determined.

References

- [1] M.-C. Liu, S.-C. Chen, T.-P. Huang, C.-H. Chen, H.-F. Chen, & Y.-J. Wu, *J. Phys. Chem. Lett.* **6**, 3185-3189 (2015).
- [2] C.-H. Chin, M.-Y. Lin, T.-P. Huang, & Y.-J. Wu, *Spectrochim. Acta A* **196**, 233-237 (2018).
- [3] C.-H. Chin, M.-Y. Lin, T.-P. Huang, P.-Z. Wu, & Y.-J. Wu, *Sci. Rep.* (2018) accepted
- [4] A. M. Ricks, G. E. Douberly, P. v. R. Schleyer, & M. A. Duncan, *J. Chem. Phys.* **132**, 051101 (2010).
- [5] H. Gao, Z. Lu, L. Yang, J. Zhou, & C. Y. Ng, *J. Chem. Phys.* **137**, 161101 (2012).