Electronic spectroscopy of bare and hydrogenated carbon cluster isomers

S,J,P. Marlton, [1]* C. Liu, [1] J,T. Buntine, [1] P. Watkins, [1] & E,J. Bieske. [1]
*presenting author
[1] smarlton@unimelb.edu.au, School of Chemistry, University of Melbourne, 3010 Parkville, Victoria, Australia

The importance of bare and hydrogenated carbon clusters in combustion and in the chemistry of interstellar space has motivated numerous spectroscopic studies, most of which have focused on smaller neutral and charged clusters with fewer than 10 carbon atoms and on the C_{60} and C_{70} fullerenes.[1,2] Recently, we have obtained electronic spectra of bare and hydrogenated carbon cation clusters containing between up to 36 carbon atoms.[3] Spectroscopically interrogating carbonaceous molecules containing more than 10 carbon atoms is complicated by the coexistence of different isomers possessing unique spectroscopic properties. To address this issue, we have developed an apparatus that allows formation and selection by ion mobility of a particular $C_xH_y^+$ isomer population, which is incarcerated in a cryogenically cooled ion trap and subjected to tunable radiation.[4] Resonant excitation of an electronic transition leads to cluster fragmentation, which when monitored as a function of wavelength yields an action spectrum. We have used this approach to obtain electronic spectra for monocyclic C_n^+ clusters with $12\leq n \leq 36$, which exhibit sharp transitions that progressively shift to longer wavelength with increasing cluster size. The photodissociation products provide evidence of a photoisomerization pathways that convert rings into fullerenes. The photodissociation pathways that connect highly unsaturated carbon clusters with PAHs were also interrogated by ionizing and photodissociating neutral pyrene vapor in the ion source and spectroscopically probing the photodissociation products. The photodissociation products of pyrene are $C_xH_y^+$ clusters with diverse size and shape, each of which can be selected by their ion mobility arrival time and their mass to charge ratio. Pyrene photoproducts include highly unsaturated $C_{(2n+1)}H_3^+$ clusters and $C_{(2n+1)}H^+$ clusters. $C_{(2n+1)}H^+$ clusters are shown to exist as linear and cyclic isomers that have distinct electronic spectra.[5] These results illustrate how different $C_xH_y^+$ cluster isomers may form, dissociate, and isomerise in interstellar space, and provide spectroscopic fingerprints to aid their astronomical detection.

References:

1. Jochnowitz, E.B. and Maier, J.P., Electronic spectroscopy of carbon chains. *Molecular Physics*, **106**, 2093-2106 (2008)
2. Campbell, E.K., Holz, M., Gerlich, D. and Maier, J.P., Laboratory confirmation of C_{60}^+ as the carrier of two diffuse interstellar bands. *Nature*, **523**, 322–323 (2015).
3. Buntine, J.T., Cotter, M.I., Jacovella, U., Liu, C., Watkins, P., Carrascosa, E., Bull, J.N., Weston, L., Muller, G., Scholz, M.S. and Bieske, E.J., Electronic spectra of positively charged carbon clusters—C_{2n}^+(n=6–14). *The Journal of Chemical Physics*, **155**, 214302 (2021).
4. Buntine, J.T., Carrascosa, E., Bull, J.N., Jacovella, U., Cotter, M.I., Watkins, P., Liu, C., Scholz, M.S., Adamson, B.D., Marlton, S.J. and Bieske, E.J., An ion mobility mass spectrometer coupled with a cryogenic ion trap for recording electronic spectra of charged, isomer-selected clusters. *Review of Scientific Instruments*, **93**, 043201–043209 (2022)
5. Marlton, S.J., Buntine, J.T., Liu, C., Watkins, P., Jacovella, U., Carrascosa, E., Bull, J.N. and Bieske, E.J., Disentangling Electronic Spectra of Linear and Cyclic Hydrogenated Carbon Cluster Cations, $C_{2n+1}H^+$ (n= 3–10). *The Journal of Physical Chemistry A*, **126**, 6678-6685 (2022)