Gas-phase luminescence of complex molecular ions

M. H. Stockett1*

¹Department of Physics, Stockholm University, Sweden *Corresponding author e-mail address: Mark.Stockett@fysik.su.se

Molecular luminescence phenomena occur at wavelengths from the optical to the far infrared, and over timescales ranging from nanoseconds to seconds. Luminescence of *e.g.* Polycyclic Aromatic Hydrocarbons (PAHs) has been invoked to explain a variety of astronomical observations, most notably the ubiquitous Aromatic Infrared Bands [1]. The competition between radiative cooling and destructive photoprocessing may help shape the fate of large carbonaceous molecules in space. In this review lecture, I will give an overview of the experimental techniques which are being developed to observe and characterize the luminescence of complex molecular ions in the gas phase.

Fluorescence spectroscopy is emerging as a powerful complement to the established techniques of gas-phase ion spectroscopy such as photodissociation. The current state of the art relies on radio frequency ion traps coupled to optical spectrographs [2], and is delivering deep insights into the intrinsic photophysics of *e.g.* ionic biochromophores [3]. While most experiments to date have focused on highly fluorescent dyes, the sensitivity of these methods is now approaching that required for the more demanding cases of PAH and fullerene ions, which have much lower fluorescence quantum yields.

In order to investigate processes occurring on longer timescales (> 1 µs), ions must be isolated in a collision-free environment. For example, using electrostatic ion storage rings and beam traps, recurrent (Poincaré) fluorescence has recently been observed indirectly for PAH cations [4] and directly for carbon chain anions [5]. The advent of a new generation of cryogenic electrostatic storage devices has extended the timescales over which infrared emission rates can be tracked by several orders of magnitude [6].

Finally, a prospective view will be given on upcoming advances in the growing field of gasphase luminescence spectroscopy of complex molecular ions. The future is bright!

Acknowledgments: This work has the support of the Swedish Research Council, the Knut and Alice Wallenberg Foundation, the Carl Trygger Foundation, and the Swedish Foundation for International Cooperation in Research and Higher Education.

References

- [1] A. G. G. M. Tielens, Annu Rev Astron Astrophys 2008, 46, 289.
- [2] M. H. Stockett et al. Rev Sci Instrum 2017, 87, 053103.
- [3] L. Giacomozzi et al. J Chem Phys 2018, 148, 214309.
- [4] S. Martin et al. Phys Rev Lett 2014, 110, 063003.
- [5] Y. Ebara et al. Phys Rev Lett 2016, 117, 133004.
- [6] K. Hansen et al. *Phys Rev A* 2017, 95, 022511.