SPECTROSCOPY OF DIAMONDOID CATIONS

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Diamondoids are a class of aliphatic hydrocarbon molecules arranged in cage-like structures and serve as a link between small cyclic hydrocarbons and bulk nanodiamonds. They are well-known for their interesting optical properties, as they typically exhibit large optical band gaps of around 6 eV or higher. Their radical cations, however, are predicted to have electronic transitions in the visible range and, due to their favorable structural and optical properties, may be viable candidates as carriers of the diffuse interstellar bands. To test this hypothesis, we present here the electronic spectra of the simplest diamondoid cations, adamantane [1] and diamantane [2], recorded in a cryogenic ion trap (BerlinTrap) [3]. Despite low ion temperatures below 20 K, these optical spectra show rather broad absorptions in the whole optical range (from near infrared to ultraviolet), arising from rich vibronic activity (Franck-Condon congestion) and/or short excited state lifetime. To explore the effects of functionalization and modification of the diamondoid cage, we characterized also the optical spectra of N-substituted adamantanes, namely 1-cyanoadamantane and urotropine. While substitution with the CN group has limited impact on the optical response [4], the modification of the diamondoid cage by replacing all four CH groups by isoelectronic N atoms results in a highly-resolved vibronic spectrum. The optical spectra of the diamondoid cations and their derivatives are obtained by photodissociation of mass-selected ions in a cryogenic ion trap (held at 5 K) coupled to an electron ionization source and a quadrupole/time-of-flight tandem mass spectrometer [1,2]. The experimental results are compared to our photoelectron spectra measured in a hemispherical analyser using He(I) radiation and time-dependent DFT calculations.

[1] A. Guenther et al., 2017, JMolSpec, 332, 8.
[2] P.B. Crandall et al., 2020, ApJL, 900, L20.
[3] P.B. Crandall et al., 2022, ApJ, 940, 104.
[4] P.B. Crandall et al. 2023, submitted.