

Electronic Spectroscopy of Protonated and Hydrogenated Coronene in Solid *Para*-Hydrogen

Weber, I.,^{1*} Lee, Y.-P.²

¹ iweber@nycu.edu.tw, Department of Applied Chemistry, National Yang-Ming Chiao-Tung University, Hsinchu 300093, Taiwan.

² Department of Applied Chemistry, National Yang-Ming Chiao-Tung University, Hsinchu 300093, Taiwan and Center for Emergent Functional Matter Science, National Yang-Ming Chiao-Tung University, Hsinchu 300093, Taiwan.

Although well over 500 diffuse interstellar bands (DIB) have been identified up to today, their carrier molecules remain mostly elusive: only the buckminsterfullerene cation C_{60}^+ has been confirmed as the carrier of five DIB in the near IR.¹ The most promising candidates considered include polycyclic aromatic hydrocarbons (PAH) and their cationic, protonated and hydrogenated derivatives; however, low-temperature gas-phase electronic absorption spectra of these molecules are rarely available.

Solid *para*-hydrogen (*para*-H₂) has frequently been employed as a matrix host to record IR absorption spectra of protonated and hydrogenated PAH, which can be conveniently prepared by H⁺-transfer reaction with H₃⁺ generated by electron bombardment during deposition. As a quantum solid, *para*-H₂ is soft and can thus provide a homogenous environment leading to only small matrix shifts. Over the past years, we have studied the dispersed fluorescence and fluorescence excitation spectra of several neutral, protonated, and hydrogenated PAH and PANH ($N_C < 42$) and found consistent but comparably small red shifts (40–110 cm⁻¹) with respect to literature gas-phase spectra.

Here, we present the dispersed fluorescence and fluorescence excitation spectra of coronene (C₂₄H₁₂) and its most stable protonated (1-H⁺C₂₄H₁₂) and hydrogenated (1-HC₂₄H₁₂) isomers. Upon deposition of C₂₄H₁₂ and *para*-H₂ under electron bombardment, we observed two distinct emission systems with strong origin bands at ~14335 and ~12820 cm⁻¹, which we assign to 1-H⁺C₂₄H₁₂ and 1-HC₂₄H₁₂, respectively, based on lowest-energy transition energies predicted by TD-DFT calculations (716.51 nm for 1-H⁺C₂₄H₁₂ and 753.45 nm for 1-HC₂₄H₁₂) and the reasonable agreement of the experimental spectra with simulated emission spectra. For the S_1 – S_0 transition of 1-H⁺C₂₄H₁₂, our data indicates a red shift of ~40 cm⁻¹ relative to the gas-phase² due to the *para*-H₂ environment, consistent with our results for other PAH. Protonation and hydrogenation lead to a significant redshift compared to the parent C₂₄H₁₂ (S_1 – S_0 at ~23720 cm⁻¹ in *para*-H₂) and a shortening in radiative lifetimes. Detailed assignments for the dispersed fluorescence and fluorescence excitation spectra are derived, illustrating the impact of symmetry breaking due to hydrogenation and protonation, and a comparison to available literature data from cryogenic ion-trap² and Ne matrix isolation^{3,4} experiments is provided. The dispersed fluorescence spectrum of 1-HC₂₄H₁₂ has not been reported previously.

¹ Campbell, E.K.; Holz, M.; Gerlich, D.; Maier, J. P. Laboratory confirmation of C₆₀⁺ as the carrier of two diffuse interstellar bands. *Nature* **2015**, 523, 322.

² Rice, C. A.; Hardy, F. X.; Gause, O.; Maier, J. P. (1) ¹A'←X ¹A' electronic transition of protonated coronene at 15 K. *J. Chem. Phys. Lett.* **2014**, 5, 942.

³ Garkusha, I.; Fulara, J.; Sarre, P. J.; Maier, J. P. Electronic absorption spectra of protonated pyrene and coronene in Ne matrices. *J. Phys. Chem. A* **2011**, 115, 10972.

⁴ Garkusha, I.; Fulara, J.; Maier, J. P. Fluorescence of protonated pyrene and coronene in neon matrices. *J. Mol. Struct.* **2012**, 1025, 147.