

Electronic Spectroscopy of Polycyclic Aromatic Hydrocarbons in solid *para*-Hydrogen

I. Weber¹ and Y.-P. Lee^{1,2}

¹Dept. Applied Chemistry and Center for Emergent Functional Matter Science, National Yang-Ming Chiao Tung University, Taiwan

²Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Taiwan

Polycyclic aromatic hydrocarbons (PAH) and their heteroatom-substituted, protonated, hydrogenated, and cationic derivatives are commonly considered as the carriers of the unidentified infrared (UIR) bands and as promising candidates for the carriers of the diffuse interstellar bands (DIB), [1] absorption bands in the UV/VIS to near-IR region. However, despite the large number of known DIB (well over 200 up to today), only the buckminsterfullerene cation C_{60}^+ has been confirmed as the carrier of two DIB at 9577.5 and 9632.7 Å on the basis of its laboratory spectrum. [2,3]

Para-hydrogen (*p*-H₂) has frequently been employed as a matrix host for IR spectroscopy of PAH, PANH, and their protonated and hydrogenated derivatives; the IR absorption spectra exhibit only small shifts relative to the gas-phase, in line with the “softness” of solid *p*-H₂. Over the past years, we have recorded the dispersed fluorescence and fluorescence excitation spectra of various PAH with 10 to 42 carbon atoms as well as a small number of protonated and hydrogenated PAH and PANH, to assess the properties of *p*-H₂ as a matrix host for electronic spectroscopy and its potential to provide laboratory reference spectra for comparison to observations. We find a generally good agreement with previously literature data, indicating a rather small but consistent redshift of $<100\text{ cm}^{-1}$ relative to the gas phase due to the matrix environment.

In our contribution, we discuss advantages and disadvantages of *p*-H₂ as a matrix host for electronic spectroscopy by providing experimental data and spectra simulated based on quantum-chemical calculations for three examples: the 1-hydronaphthyl radical (1-C₁₀H₉), which has been extensively studied in the gas phase and in solid Ne, and the two large PAH *peri*-hexabenzocoronene (*peri*-HBC, C₄₂H₁₈) and ovalene (C₃₂H₁₄). Our work on 1-C₁₀H₉ demonstrates the good agreement of the *p*-H₂ data with previous work and the comparably easy accessibility of hydrogenated (and protonated) PAH in *p*-H₂, but also shows the stronger influence of *p*-H₂ on spectral line positions compared to Ne. We observed the D_1 - D_0 origin at 18881 cm^{-1} giving a matrix shift of 68 cm^{-1} ; for Ne, a blue shift of $\sim 13\text{ cm}^{-1}$ can be inferred from the work of Garkusha et al. [4] *Peri*-HBC has rarely been studied before. We provide a first full assignment of the vibrational structure of the fluorescence emission and excitation spectra centered around the S_1 - S_0 origin band located $\sim 22075\text{ cm}^{-1}$ in solid *p*-H₂. Ovalene has been discussed as potential DIB carrier and a system exhibiting anomalous fluorescence from higher excited singlet states. Combining experiment and theory, we found, however, that the lowest excited singlet state (S_1) was previously assigned erroneously; we report the fluorescence emission and excitation spectra as well as fluorescence lifetimes of the true S_1 state.

References

- [1] A. G. G. M. Tielens, 2008, Ann. Rev. Astron. Astrophys. 46, 289.
- [2] E. K. Campbell, M. Holz, P. & J. P. Maier, 2015, Nature 523, 322.
- [3] E. K. Campbell, M. Holz, J. P. Maier, P. Gerlich, G. A. H. Walker & D. Bohlender, 2016, ApJ 822, 17.
- [4] I. Garkusha, A. Nagy, J. Fulara, M. F. Rode, A. L. Sobolewski & J. P. Maier, 2013, JPCA 117, 351.