Applications of *para*-hydrogen matrix spectroscopy

Lee, Yuan-Pern[1,2]*
[1]Department of Applied Chemistry and Institute of Molecular Science, National Yang Ming Chiao Tung University, Hsinchu 300093, Taiwan
[2] Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu 300093, Taiwan
Email: yplee@nycu.edu.tw

With its unique properties associated with quantum solid, *para*-hydrogen (p-H_2) matrix isolation has facilitated several applications unachievable with noble-gas matrix isolation techniques.[1]

We performed electron bombardment on p-H_2 during deposition to produce H_3^+; H_3^+ readily transfers a proton to polycyclic aromatic hydrocarbons (PAH) to form protonated PAH, possible carriers of unidentified IR emission in astronomy. Some protonated species became neutralized to form mono-hydrogenated PAH. Examples include protonated and hydrogenated glycine, phenanthrene ($C_{14}H_{10}$) and phenanthridine ($HC_{13}H_9N$), and CH_5^+.

We also utilized several novel methods to generate H atoms for reactions in darkness; H can efficiently tunnel through solid p-H_2 via H−H bond breaking and formation to efficiently move next to the reactant for reaction; even when a barrier exists, the tunneling reaction might take place. One method for the generation of H atoms is to add trace Cl_2 in the matrix and photodissociate it at 365 nm to generate Cl atoms; subsequent IR irradiation activates Cl + H_2 ($v = 1$) → HCl + H to generate H atoms. Another method is to photolyze H_2O_2 near 250 nm to form OH, which reacts with H_2 to form H_2O + H via tunneling; in darkness, this tunneling reaction can generate H atoms slowly and continuously, causing more significant H reactions in darkness than the first method. The experiment of H + methylamine using H_2O_2 showed that the H-abstraction proceeded much further to form HCN, as compared with that using Cl_2. In addition to the production of various isomers of hydrogenated species via H addition, such as H + PAH to form HPAH, we found that the H abstraction plays important roles in astrochemistry. Furthermore, the coupling of H abstraction and H addition (i.e. H + H → H_2) enables endothermic reactions such as isomerization and fragmentation to occur in darkness. These results introduce new concept in astrochemistry.[2] Examples include H + glycolaldehyde, alanine, and glycolamide.

Finally, we will present the electronic transitions of PAH in p-H_2. With the unique properties of matrix isolation, we found misassignments of some reported transitions and new transitions. We also found consistent matrix shifts for PAH in solid p-H_2, indicating the possibility to use spectra in p-H_2 to help the identification of defuse interstellar bands (DIB). Examples include transitions of hexabenzocoronene, ovalene, isoquinoline, and their derivatives.

References

[1] Tsuge, M; Lee, Y.-P. *in Molecular and Laser Spectroscopy*, Gupta, V. P.; Ozaki, Y. Eds., Elsevier: Amsterdam, Netherlands, **2020**, *Vol. 2*, 167−215.
[2] Haupa, K. A.; Joshi, P. R.; Lee, Y.-P. *J. Chin. Chem. Soc.* **2022**, *69*, 1159−1173.