

Some applications of *para*-hydrogen matrix isolation

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Para-hydrogen (*p*-H₂) matrix isolation has emerged as a wonderful technique for various applications in free-radical spectroscopy, atmospheric chemistry, and astrochemistry because of the unique characteristics associated with this quantum solid.^{1,2} We present four types of applications using *p*-H₂ in this talk.

(1) Production of free radicals upon photolysis— Because of the diminished cage effect, production of atoms or radicals and their secondary reactions upon photolysis *in situ* becomes feasible in solid *p*-H₂. We produced Br *in situ* to react with C₆H₆ upon photolysis of a Br₂/C₆H₆/*p*-H₂ matrix at 3.2 K. Unlike the η_1 -C₆H₆Cl σ -complex, the observed infrared spectrum indicates that η_1 -C₆H₆Br is an open-form π -complex. Furthermore, according to IR spectrum, the benzene ring appears to perform a bevel-gear type rotation with respect to Br.

(2) Production of protonated and hydrogenated species— The IR spectra of 1-quinolinium cation (C₉H₇NH⁺) and 1-quinolinyl radical (C₉H₇NH), produced upon electron bombardment during deposition of a mixture of quinoline (C₉H₇N) and *p*-H₂ at 3.2 K, indicate that the protonation and hydrogenation occur mainly at the N-atom site. Additional experiments on irradiation of C₉H₇N/Cl₂/*p*-H₂ matrices at 365 nm were performed to induce the reaction H + C₉H₇N. We identified, in addition to C₉H₇NH, four radicals (3-, 4-, 7-, and 8-HC₉H₇N) with hydrogenation at the C-atom site.³

(3) New concept of hydrogen reactions in astrochemistry—Hydrogen reactions play important roles in astrochemistry; H + methylamine (CH₃NH₂) serves as a good example.⁴ We performed this reaction in solid *p*-H₂ and observed IR spectra of •CH₂NH₂ and CH₂NH on irradiation and when the matrix was maintained in darkness. Observation of IR spectrum of •CH₂NH₂ clearly indicates that •CH₂NH₂, a precursor of glycine, can be formed from H + CH₃NH₂ in dark interstellar clouds. The observed dual-cycle mechanism containing two H-abstraction and H-addition steps chemically connects CH₃NH₂ and CH₂NH and explains their quasi-equilibrium. We performed also reactions of H atoms with *trans*-NMF in *p*-H₂ at 3.3 K and found that isomer *cis*-NMF, which has higher energy, increased continuously in darkness; H addition to CH₃NCO produced only *cis*-radicals that led to *cis*-NMF. Furthermore, H-atom-induced fragmentation in darkness by breaking the C–C bond provides links between NMF and HCNO/CH₂NH.

(4) Small shift in laser-induced fluorescence— We report infrared, fluorescence excitation, and dispersed fluorescence spectra of sumanene (C₂₁H₁₂), a bowl-shaped polycyclic aromatic hydrocarbon (PAH) and a fragment of C₆₀, isolated in solid *p*-H₂. We found a rather small matrix shift of 57 cm⁻¹ for the S₁–S₀ electronic transition origin located at 27888 cm⁻¹.

¹ Tsuge, M.; Tseng, C.-Y.; Lee, Y.-P., Spectroscopy of prospective interstellar ions and radicals isolated in *para*-hydrogen matrices. *Phys. Chem. Chem. Phys.* **2018**, *20*, 5344–5358.

² Tsuge, M.; Lee, Y.-P. Spectroscopy of Molecules Confined in Solid Para-Hydrogen, in Gupta, V. P.; Ozaki, Y., eds., *Molecular and Laser Spectroscopy*, vol. 2, Elsevier: Amsterdam, Netherlands, **2020**, pp 167–215.

³ Tseng, C.-Y.; Wu, Y.-J.; Lee, Y.-P., Infrared spectra of 1-quinolinium (C₉H₇NH⁺) cation and quinolinyl radicals (C₉H₇NH and 3-, 4-, 7-, 8-HC₉H₇N) isolated in solid *para*-hydrogen, *J. Phys. Chem. A* **2022**, *126*, 2361–2372.

⁴ Joshi, P. R.; Lee, Y.-P., A chemical link between methylamine and methylene imine and implications for interstellar glycine formation, *Comms. Chem.* **2022**, *5*, 62.