

## Some applications of *para*-hydrogen matrix isolation

Lee, Yuan-Pern\*

[yplee@nycu.edu.tw](mailto:yplee@nycu.edu.tw), Department of Applied Chemistry, National Yang Ming Chiao Tung University, Taiwan

Para-hydrogen (*p*-H<sub>2</sub>) 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.<sup>1,2</sup> We present four types of applications using *p*-H<sub>2</sub> 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*-H<sub>2</sub>. We produced Br *in situ* to react with C<sub>6</sub>H<sub>6</sub> upon photolysis of a Br<sub>2</sub>/C<sub>6</sub>H<sub>6</sub>/*p*-H<sub>2</sub> matrix at 3.2 K. Unlike the η<sub>1</sub>-C<sub>6</sub>H<sub>6</sub>Cl σ-complex, the observed infrared spectrum indicates that η<sub>1</sub>-C<sub>6</sub>H<sub>6</sub>Br 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 (C<sub>9</sub>H<sub>7</sub>NH<sup>+</sup>) and 1-quinolinyl radical (C<sub>9</sub>H<sub>7</sub>NH), produced upon electron bombardment during deposition of a mixture of quinoline (C<sub>9</sub>H<sub>7</sub>N) and *p*-H<sub>2</sub> at 3.2 K, indicate that the protonation and hydrogenation occur mainly at the N-atom site. Additional experiments on irradiation of C<sub>9</sub>H<sub>7</sub>N/Cl<sub>2</sub>/*p*-H<sub>2</sub> matrices at 365 nm were performed to induce the reaction H + C<sub>9</sub>H<sub>7</sub>N. We identified, in addition to C<sub>9</sub>H<sub>7</sub>NH, four radicals (3-, 4-, 7-, and 8-HC<sub>9</sub>H<sub>7</sub>N) with hydrogenation at the C-atom site.<sup>3</sup>

**(3) New concept of hydrogen reactions in astrochemistry**—Hydrogen reactions play important roles in astrochemistry; H + methylamine (CH<sub>3</sub>NH<sub>2</sub>) serves as a good example.<sup>4</sup> We performed this reaction in solid *p*-H<sub>2</sub> and observed IR spectra of •CH<sub>2</sub>NH<sub>2</sub> and CH<sub>2</sub>NH on irradiation and when the matrix was maintained in darkness. Observation of IR spectrum of •CH<sub>2</sub>NH<sub>2</sub> clearly indicates that •CH<sub>2</sub>NH<sub>2</sub>, a precursor of glycine, can be formed from H + CH<sub>3</sub>NH<sub>2</sub> in dark interstellar clouds. The observed dual-cycle mechanism containing two H-abstraction and H-addition steps chemically connects CH<sub>3</sub>NH<sub>2</sub> and CH<sub>2</sub>NH and explains their quasi-equilibrium. We performed also reactions of H atoms with *trans*-NMF in *p*-H<sub>2</sub> at 3.3 K and found that isomer *cis*-NMF, which has higher energy, increased continuously in darkness; H addition to CH<sub>3</sub>NCO 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/CH<sub>2</sub>NH.

**(4) Small shift in laser-induced fluorescence**— We report infrared, fluorescence excitation, and dispersed fluorescence spectra of sumanene (C<sub>21</sub>H<sub>12</sub>), a bowl-shaped polycyclic aromatic hydrocarbon (PAH) and a fragment of C<sub>60</sub>, isolated in solid *p*-H<sub>2</sub>. We found a rather small matrix shift of 57 cm<sup>-1</sup> for the S<sub>1</sub>–S<sub>0</sub> electronic transition origin located at 27888 cm<sup>-1</sup>.

<sup>1</sup> 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.

<sup>2</sup> 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.

<sup>3</sup> Tseng, C.-Y.; Wu, Y.-J.; Lee, Y.-P., Infrared spectra of 1-quinolinium (C<sub>9</sub>H<sub>7</sub>NH<sup>+</sup>) cation and quinolinyl radicals (C<sub>9</sub>H<sub>7</sub>NH and 3-, 4-, 7-, 8-HC<sub>9</sub>H<sub>7</sub>N) isolated in solid *para*-hydrogen, *J. Phys. Chem. A* **2022**, *126*, 2361–2372.

<sup>4</sup> 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.