

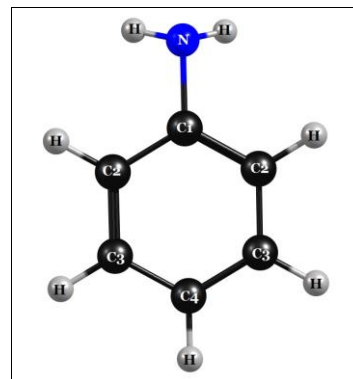
Infrared spectra of protonated aniline in solid *para*-hydrogen

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Aniline is a prototypical aromatic amine. It contains two types of basic centers that can accept an approaching proton, namely the amino group and the aromatic ring. The alkaline properties of aniline in solution result from the stabilization of the nitrogen-protonated form when solvated. However, the site of protonation in gaseous aniline is unclear [1]. Previously, the studies on protonated aniline in the gas phase are mainly based on mass spectrometry and thus provide only indirect, and sometimes ambiguous, information about the preferred protonation site of aniline [2]. Therefore, understanding the protonation site of aniline without solvent is desirable.



A new method for investigating the IR spectra of protonated species and their neutral counterparts was developed in our laboratory using electron bombardment during deposition of a gaseous mixture of *para*-hydrogen (*p*-H₂) matrix host containing a small proportion of guest molecules. This method produces mainly protonated parent molecules and corresponding neutrals without fragmentation; the IR spectra show true absorption intensity with small linewidths, excellent signal-to-noise ratio, and wide spectral coverage [3].

We applied this technique to investigate the IR spectrum of protonated aniline in a solid *p*-H₂ matrix. We grouped spectral lines into various species according to their behaviors after maintaining in darkness and upon secondary photolysis; the assignments were derived on comparison with quantum-chemical calculations using the B3LYP/CC-pVTZ method. The results indicate that three protonated isomers are observed: protonation on carbon 2 (absorption lines at 3479.0, 3391.8, 1666.7, 1503.9, 1451.8, 1418.9, 1341.5, 1188.1, 776.7 and 736.3 cm⁻¹), on carbon 4 (absorption lines at 3482.5, 3395.2, 1669.0, 1523.1, 1337.1, 1197.5, 886.4, 884.1 and 816.8 cm⁻¹), and on the nitrogen atom (absorption lines at 3302.8, 3278.8 and 3236.0 cm⁻¹); the numbering of the carbon atoms is shown in the Figure.

[1] F. M. Pasker, N. Solcà and O. Dopfer, J. Phys. Chem. A. 110, 12793 (2006).

[2] M. J. Nold and C. Wesdemiotis, J. Mass. Spectrom. 31, 1169 (1996).

[3] M. Bahou, P. Das, Y. -F. Lee, Y. -J. Wu and Y. -P. Lee, *Phys. Chem. Chem. Phys.* 16, 2200 (2014).