ANALYSIS AND MODELING OF THE THRESHOLD PHOTOELECTRON SPECTRUM OF SiH_2 WITH MCTDH

N. L. CHEN, B. GANS, S. BOYÉ-PÉRONNE, L. H. COUDERT, *Inst. des Sciences Moléculaires d'Orsay, Univ. Paris-Saclay - CNRS, Orsay, France*; **J.-C. LOISON**, *Institut des Sciences Moléculaires, Université de Bordeaux, Bordeaux, France*; **G. A. GARCIA, S. HARTWEG**, *DESIRS beamline, Synchrotron SOLEIL, Gif-sur-Yvette, France*

Although the ground $\widetilde{X}\,^1A_1$ electronic state of silylene SiH_2 is fairly well characterized,[1] fewer results are available about its first excited triplet $\tilde{a}\,^3B_1$ electronic state and about its cationic species SiH_2^+. The ground electronic state of the latter is split into bent $\widetilde{X}^+\,^2A_1$ and linear $\widetilde{A}^+\,^2B_1$ electronic states by the Renner-Teller coupling.[2]

Threshold photoelectron (TPE) spectroscopy has been used to spectroscopically study the cationic species SiH_2^+ of silylene produced through successive H atom abstractions induced by fluorine atoms in gaseous silane. The TPE spectrum, recorded at Synchrotron SOLEIL from 7.5 to 11.5 eV using VUV synchrotron radiation, displays several sharp features and was modeled using wavepacket propagation.[3] ωB97-XD *ab initio* calculations were carried out using cc-PVTZ correlation-consistent basis set functions to retrieve 3-D potential energy surfaces for the various electronic states. The ground electronic state of the neutral (cation) is characterized by an equilibrium bond length and a bond angle of 1.516 Å and 92.2° (1.474 Å and 121°). The MCTDH method[4] was first used to obtain the 3-D vibrational wavefunctions of the neutral species $\widetilde{X}\,^1A_1$ and $\tilde{a}\,^3B_1$ electronic states using propagation in negative imaginary time. The wavefunctions thus obtained were then time-propagated in the potential energy surfaces of the coupled electronic states of the cationic species using also MCTDH.[3,4] The threshold photoelectron spectrum was at last computed as the Fourier transform of the auto-correlation function.

In the poster, the results of the rovibronic energy calculations will be reported and the experimental TPE spectrum will be compared to the theoretical one. The importance of the Renner-Teller coupling will be assessed and the vibrational temperature which best reproduces the experimental spectrum will be evaluated.

[1] Clark, Ownes, Tennyson, and Yurchenko, *J. Quant. Spec. Rad. Transf.* **246** (2020) 106929

[2] Gu, Huang, Kong, and Liu, *J. Mol. Struct. (Theochm)* **253** (1992) 217

[3] Viel, Eisfeld, Evenhuis, and Manthe, *Chem. Phys.* **347** (2008) 331; and Eroms, Jungen, and Meyer, *J. Phys. Chem. A* **114** (2010) 9893

[4] Beck, Jäckle, Worth, and Meyer, *Phys. Rep.* **324** (2000) 1; and Meyer, Graham, and Worth, *Theor. Chem. Acc.* **109** (2003) 251

p-number: p067 **Submitted on Sun, 11 Jun 2023 07:24:09 +0200**