THE THRESHOLD PHOTOELECTRON SPECTRUM OF SiH$_2$ AS MODELED WITH MCTDH

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Although the ground $\widetilde{X}\,^1A_1$ electronic state of silylene SiH$_2$ is fairly well characterized,[a] 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 $\widetilde{A}^+\,^2B_1$ doublet electronic states by the Renner-Teller coupling.[b]

Threshold photoelectron (TPE) spectroscopy has been used to obtain spectroscopic information about the cationic species SiH$_2^+$ of silylene and about the first excited triplet electronic state of neutral SiH$_2$. 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.[c] ωB97XD *ab initio* calculations were carried out using cc-PVTZ correlation-consistent basis set functions to retrieve 3-D potential energy surfaces for the four electronic states involved in the TPE spectrum. The MCTDH method[d] 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.[c,d] The photoionisation cross-section was at last computed as the Fourier transform of the auto-correlation function.

In the talk, the results of the rovibronic energies calculation 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.

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

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

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

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