GENERAL METHOD FOR CALCULATION OF PREDISSOCIATION LIFETIMES OF ROVIBRONIC STATES IN DIATOMIC MOLECULES

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We present a new method for computing predissociation lifetimes for open-shell diatomic molecules. The method is based on the working photodissociation approach by Pezzella et al. (2021)[1] and applied to the three diatomics molecules, sulfur monohydride (SH), sulfur mono-deuteride (SD), and the hydroxyl radical (OH), each in the first excited $A^2\Sigma^+$ electronic state.

Predissociation of bound rovibronic states arises through the presence of locally crossing continuum states where they interact through coupling such as spin-orbit. Because of these couplings, decay of bound rovibronic states into the continuum will prematurely dissociate the molecule, providing a source of broadening for these bound energy levels.

Continuum states are treated as bound states in our variational nuclear motion code Duo[2] by imposing an infinite potential energy barrier in the potential energy curves (PECs) at a given internuclear distance R_c. The variation of R_c enables the sampling of a range of continuum states, giving a series of crossings between (quasi) bound states and continuum states. These crossings will resonate with the bound level, inducing a broadening that can be extracted by inspecting the energy distribution of the state with increasing box size. From this broadening width we are then able to extract spin-orbit induced predissociation lifetimes through the energy-time uncertainty relation. Results have good agreement with available experimental data. A parallelised code, **binSLT**, has been developed to automate this process and will be available on the ExoMol GitHub.

The analysis of the predissociation of effects in the SH and SD molecules was conducted in collaboration with secondary school students under the ORBYTS[3] out-

[1] 10.1039/D1CP02162A M. Pezzella, S. N. Yurchenko, J. Tennyson, A method for calculating temperature-dependent photodissociation cross sections and rates, *Phys. Chem. Chem. Phys.*, **23**, 16390-16400 (2021)

[2] 10.1016/j.cpc.2015.12.021 S.N. Yurchenko, L. Lodi, J. Tennyson, and A.V. Stolyarov, Duo: A general program for calculating spectra of diatomic molecules, *Comput. Phys. Commun.*, **202**, 262 (2016)

[3] Outreach programme ORBYTS website: https://www.orbyts.org/

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