# Time-independent approach for fine-structure calculations in electronic spectra

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Extraterrestrial and interstellar bodies contain molecules that are either unstable, or require experimental conditions hiding the fine-structure through thermal or collision broadening. For diatomic molecules, we can perform the quantum-exact calculations of spectra based on time-independent Schrödinger equation and R-matrix propagation of time-independent wavefunctions across the global potential energy curves for all discrete vibrational and rotational states and a combination of R-matrix and S-matrix theories for the continuum region.

We present the fine-structure spectra for sulfur dimer and its isotopologues[1] – a part of Archean Earth, Venus, Io, and other extraterrestrial atmospheres. The mass-independent isotopic fractionation for molecules with low density-of-states can be evaluated in the fine-structure spectra as a result of the anharmonicity of the potential curves. The potential energy curves and transition dipole moments are calculated at MRCI-F12/aug-cc-pVQZ level at full valence active space; absorption spectra are calculated for two lowest electronic states with an allowed transition from the ground state ($X^3\Sigma_g^-$) – $B''^3\Pi_u$ and $B^3\Sigma_u^-$.

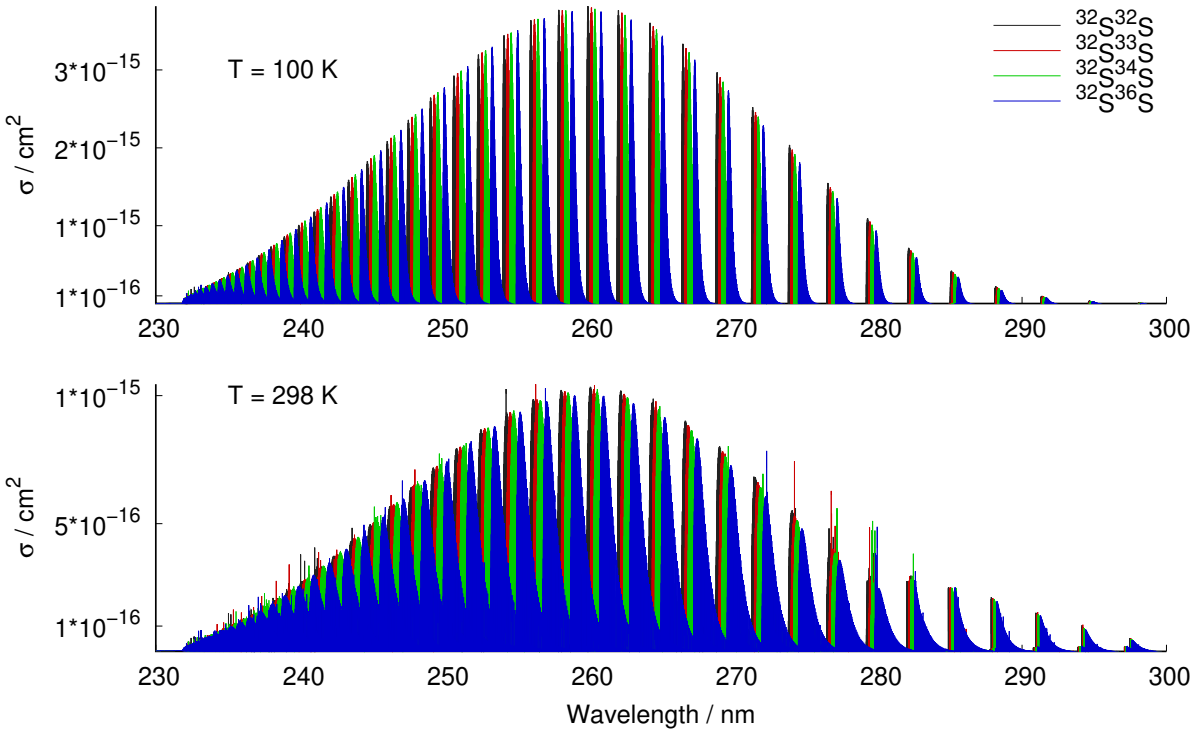


**Figure 1:** Fine-structure spectra of $S_2$ and it's isotopologues for excitation to $B^3\Sigma_u^-$ state.

## References

[1] Karolis Sarka, Sebastian O Danielache, Alexey Kondorskiy, and Shinkoh Nanbu. Theoretical study of electronic properties and isotope effects in the uv absorption spectrum of disulfur. *Chemical Physics*, 516:108–115, 2019.