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Poster

First-principles calculations of pressure broadening for the case of N₂-perturbed 118 GHz fine-structure line in O₂(X³Σ_g⁻)

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Because of its high molecular abundance in Earth's atmosphere, nitrogen N₂ plays a prominent role in perturbing the shape of the spectral distribution of radiation emitted or absorbed by other molecular species present. Of particular importance are its interactions with the molecular oxygen O₂, which is the second most abundant constituent of our planet's atmosphere. The oxygen spectral bands formed by transitions to its excited electronic states, such as the A- and B-band, are studied extensively due to their application in, e.g., the determination of cloud-top heights and coverage, optical thickness of aerosols, concentration of the pollutant gases such as CO₂, and monitoring of the greenhouse gases and vegetation fluorescence.

Many such applications involve also purely rotational transitions occurring within the ground electronic (and vibrational) ³Σ_g⁻ term of O₂. Due to spin-spin interactions of the two unpaired valence electrons in this state, the rotational levels (labeled necessarily with odd quantum numbers) are split into a triplet of fine-structure sub-levels, the transitions between which result in the presence of a strong 60-GHz spectral band and a single isolated line at about 118 GHz. These spectral features have been studied extensively due to their applications in remote sensing and temperature profiling.

Here we report the results of the first fully quantum calculations of O₂-N₂ scattering and its influence on the pressure broadening of the single 118 GHz fine-structure line in the ground-state oxygen.¹ Our fully *ab initio* approach is based on the new potential energy surface for O₂-N₂, calculated using the explicitly correlated unrestricted coupled-cluster theory with all electrons correlated and extrapolated to the complete basis set limit. In our approach we make use of the angular momentum recoupling methods,^{2,3} which allow for expressing the total S-matrix as a linear combination of the spin-free S-matrices. We include the speed-dependence of the broadening parameter in our calculations and obtain a good agreement with the experimental data. Our study is the first step toward the accurate theoretical study of collisional perturbations of the fine structure and rotational lines of O₂(X³Σ_g⁻) due to molecular species of atmospheric importance, such as N₂. Such investigations are of great importance for studies of the Earth's atmosphere and remote sensing applications, and populating spectroscopic databases such as HITRAN or GEISA.

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