COLLISION-INDUCED EFFECTS IN THE FINE-STRUCTURE RESOLVED SPECTRA OF ATMOSPHERIC OXYGEN FROM FIRST PRINCIPLES: THE EFFECT OF O_2-N_2 SCATTERING

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The properties of our planet's atmosphere are derived from models which are mostly based on remote-sensing data. A detailed knowledge of spectra of various chemical compounds making up the terrestrial atmosphere is therefore crucial for understanding the various ongoing kinetic and dynamic processes. As these compounds are not isolated, intermolecular interactions involving most abundant atmospheric constituents – N_2 ($\sim 78\%$) and O_2 ($\sim 21\%$) – may affect the shapes of the spectra under consideration. In this context, oxygen spectra are of particular interest. O_2 is a prominent example of a diatomic molecule with a $^3\Sigma$ ground-electronic term, and fine-structure resolved transitions involving this term have a wide range of applicability – from monitoring the plant vegetation status on the Earth's surface, to the quantification of the pollutant concentration in the atmosphere [*J. Quant. Spectrosc. Radiat. Transf.* **186**, 118 (2017)].

Here, we consider the effect of O_2-N_2 collisions on the shape of the oxygen spectral lines from the theoretical point of view. Utilizing the exact close-coupling approach, we calculate the relevant scattering amplitudes based on the *ab initio* intermolecular potential energy surfaces (PESs). We account for the non-zero spin of the $X^3\Sigma_g^-$ term of O_2 by performing a unitary transformation on the spin-free S-matrix, which allows us to compute the line shape parameters for the fine-structure resolved transitions in O_2 immersed in the bath of N_2. Having successfully tested our methodology against the experimental data in our previous study of the 118 GHz fine-structure transition in $O_2(X^3\Sigma_g^-)$ [*J. Chem. Phys.* **155**, 124307 (2021)], we apply it to the problem of N_2-perturbed lines in the oxygen A-band (i.e., electronic transition $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$). This problem is more challenging as it requires the use of two PESs in the scattering calculations. The PESs used in this study were constructed automatically using the `AUTOSURF` code [*J. Chem. Inf. Model.* **59**, 262 (2018)].