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Synopsis We demonstrate the results of the first *ab initio* investigation of the line-shape parameters for two molecular systems important for atmospheric studies: CO-N_2 and O_2-N_2. We provide the pressure broadening and shift coefficients with their speed dependencies for purely rotational lines, calculated from highly accurate potential energy surfaces with the close-coupling scheme. This is the first, fully quantum approach to the problem of determination of the spectral line shapes for the systems important for terrestrial atmospheric measurements.

The reduction of systematic errors in the atmospheric measurements of the Earth requires careful treatment of effects perturbing the shapes of the spectral lines. The accuracy of the classical or semi-classical calculations of the line-shape parameters is not always satisfactory. However, fully quantum calculations of the pressure broadening and shift coefficients for the helium-perturbed H_2 system resulted in a very good agreement with experimental data [1].

We present the results of the investigation of the line-shape parameters for two atmospheric systems based on *ab initio* quantum-scattering calculations. The first one is the nitrogen-perturbed CO molecule, for which we investigated the R(0) purely rotational line. We use the most accurate potential energy surfaces (PESs), calculated by means of the state-of-the-art quantum chemistry methods [2, 3, 4]. The PESs are expanded over bispherical harmonics leading to 205 radial coupling terms. The close-coupling equations are solved for a wide range of kinetic energies. The generalized spectroscopic cross sections, obtained from the scattering matrices, lead to the first-ever pressure broadening and shift coefficients for the CO-N_2 system, calculated using the fully quantum approach.

The second system is the nitrogen-perturbed oxygen. We use the four-dimensional PES [5], which is also expanded over the bispherical harmonics, leading to 85 radial coupling terms. The same methodology is used to obtain the generalized spectroscopic cross sections from the close-coupling equations and the scattering matrix. This is the first *ab initio* investigation of the line-shape parameters in the O_2-N_2 system. The data provided through the investigation of both systems can be used for populating the HITRAN database [6].

References

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