Ab initio molecular dynamic simulations of line-mixing effects in CO_2 infrared and Raman bands.

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Ab initio calculations of the shapes of pure CO_2 infrared and Raman bands under conditions for which line-mixing effects are important have been performed using requantized Classical Molecular Dynamics Simulations [1]. This approach provides the auto-correlation functions of the dipole vector and isotropic polarizability whose Fourier-Laplace transforms yield the corresponding spectra. For that, the classical equations of dynamics are solved for each molecule among several millions treated as linear rigid rotors and interacting through an anisotropic intermolecular potential. Two of the approximations used in the previous studies [1] have been corrected, allowing the consideration of line-mixing effects without use of *any* adjusted parameters. The comparisons between calculated and experimental spectra [2,3] under various conditions of pressure and temperature demonstrate the quality of the theoretical model. This opens promising perspectives for first principle *ab initio* predictions of line-mixing effects in absorption and scattering spectra of various systems involving linear molecules.

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[3] B. Lavorel, G. Millot, R. Saint-Loup, H. Berger, L. Bonamy, J. Bonamy, and D. Robert, *J. Chem. Phys.* **1990**, *93*, 2176.