Temperature variations of the CO_2 interaction-induced rototranslational absorption derived from CCSD(T) potential energy and induced dipole moment surfaces

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Interaction-induced absorption in highly symmetrical molecules is known to be responsible for about 5% of the total energy budget of the Earth's atmosphere [1] and is much more important in the spectral ranges of atmospheric windows. Accurate modeling of bimolecular absorption in the carbon dioxide is also of particular value for paleoclimate simulations in the early Earth's, Mars and Venus atmospheres.

Present paper focuses on the first-principles calculations relevant to rototranslational induced absorption band in CO_2. This band was studied previously both theoretically and experimentally (see e.g. [2,3] and references therein). Theoretical simulation of bimolecular absorption requires the knowledge of both potential energy and induced dipole moment surfaces (PES and IDS) and accuracy of the simulation is known to be sensitive to the quality of PES and IDS. Among previous *ab initio* calculations of the CO_2-CO_2 PES the most reliable is that from Bukowski et al. [4] who have used SAPT method. In contrast to PES, the IDS in a CO_2-CO_2 pair was never studied using *ab initio* methods. Previous simulations of the CO_2 FIR absorption were based on the long-range approximation of the IDS [2,3], which may diverge at small intermolecular separations. The quality of the long range approximation can be verified using accurate contemporary *ab initio* methods.

This paper presents results of new extensive *ab initio* study of the CO_2-CO_2 PES and IDS. The PES was calculated using CCSD(T)-F12a/aug-cc-pVTZ method on a grid of more than 19000 intermolecular configurations. The obtained PES at the global minimum is 33cm^{-1} deeper than that of Bukowski et al. [4]. Global fit of the PES was made through expansion in a spherical harmonics series. The quality of obtained PES was verified by virtue of the second virial coefficient calculation, which showed good agreement with experimental data. Also bound states of the CO_2-CO_2 dimer were calculated using coupled-states approach. The IDS was calculated using CCSD(T)/aug-cc-pVTZ method on a grid of approximately 1300 geometries and it was found to be in good agreement with the long-range approximation at intermolecular separations in excess of 8 Bohr. Temperature variations of the first spectral moment in rototranslational induced CO_2 spectrum were calculated and compared with experimental data.

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