Infrared absorption by pure CO_2 near 3300cm^{-1}: measurements of collisional broadening and shift coefficients and analysis of line-mixing effects at subatmospheric pressures

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The atmosphere of Venus is probed in the 2.2–4.3 μm region [1] by the SOIR (*Solar Occultation in the InfraRed*) instrument onboard the ESA Venus Express spacecraft [2]. As carbon dioxide is the predominant species in this atmosphere, reliable retrievals of concentrations of atmospheric species from SOIR spectra require an accurate knowledge of CO_2 broadening and shift coefficients. The present work is focused on the determination of these coefficients for the self-broadening case and for one of $^{12}C^{16}O_2$ bands detectable by the SOIR instrument, namely the 21102–00001 band located near 3340 cm^{-1}.

Pure CO_2 spectra were recorded using a Bruker IFS120HR Fourier transform spectrometer with an absorption path length of 55 m, at total pressures between 48 and 820 hPa and at a temperature of 294 K. Collisional self-broadening and self-shift coefficients were measured using a multi-spectrum non-linear least squares fitting procedure employing the standard Voigt profile model [3]. A preliminary analysis of the results showed the need to account for Dicke narrowing at the lowest pressure and to include the influence of line mixing effects for overlapped lines. The potential influence of speed-dependence effects on isolated line shapes is investigated.

Line-broadening coefficients for isolated lines, line-mixing Rosenkranz-profile coefficients for Q-branch transitions as well as transmittance for P-Q-R manifolds at various pressures were also computed using a theoretical approach of Energy-Corrected Sudden type for the relaxation matrix. This approach, non-Markovian in its general formulation, is characterized by the use of a non-conventional symmetric metric in the Liouville space and by an automatic satisfaction of the basic relations (detailed balance, sum rules) issued from first principles. Recently adopted to the case of infrared absorption of linear molecules with stretching and bending modes [4] and tested on high-density CO_2 absorption bands influenced by Coriolis interactions [5], this method is now tested for the case of subatmospheric pressures, where the line shapes become sensitive to Doppler broadening and collisional narrowing effects.

The obtained experimental and theoretical results agree very satisfactorily. Some conclusions drawn for CO_2-CO_2 spectra open new perspectives for improvements of the theoretical line-mixing modelling.

[1] A.C. Vandaele, M. De Mazière *et al.*, *J. Geophys. Res.* 113 (**2008**) E00B23.
[2] D. Nevejans, E. Neefs *et al.*, *Appl. Opt.* 45 (**2006**) 5191-5206.
[3] M. Tudorie, T. Földes, A.C. Vandaele, J. Vander Auwera, *JQSRT* 113 (**2012**) 1092-1101.
[4] J. Buldyreva, L. Daneshvar, *J. Chem. Phys.* (to be published).
[5] N.N. Filippov, R.E. Asfin, T.N. Sinyakova, I.M. Grigoriev, T.M. Petrova, A.M. Solodov, A.A. Solodov, J. Buldyreva, *PCCP* **2013** (in press); DOI:10.1039/C3CP50279A.