Experimental studies, line-shape analysis and theoretical modelling of broadening coefficients for $CH_3{}^{35}Cl$-CO_2 submillimeter transitions

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Methyl chloride is well known as the most abundant halocarbon in the Earth's atmosphere and the main source of stratospheric chlorine atoms involved in the chemical reactions of ozone layer depletion. Its spectroscopic parameters for perturbation by main terrestrial-atmosphere gases have been very intensively studied over last two years (updated line positions and intensities [1] as well as N_2-, O_2-, air- and self-broadening coefficients [2-5]). In the present work we extend the analysis to the case of the most important "minor" constituent – carbon dioxide.

Rotational transitions $J, K \rightarrow J+1, K$ for the $CH_3{}^{35}Cl$-CO_2 system are recorded at room temperature 296 ±1 K in the frequency interval 186–901 GHz (1.6–0.3 mm) for J = 6 → 7 (186 GHz), 10 → 11 (292 GHz), 17 → 18 (478 GHz), 22 → 23 (610 GHz), 31 → 32 (848 GHz), 33 → 34 (901 GHz) and K = 0–6, using the based on solid-state devices frequency-multiplication chain (150–990 GHz) of the Laboratory PhLAM (Lille). Their line-shape analysis is performed with various (Voigt, Galatry, Speed-dependent Voigt) profile models in order to probe the velocity-dependence effects. Like the situation previously observed for the case of collisions with O_2 [3], physically meaningful line-broadening (and line-narrowing) parameters are obtained for the Speed-dependent Voigt profile. Final results are however reported for the traditional Voigt-profile as well, since this model still continues to be used in atmospheric applications and the coherence between the line-shape parameters and the shape model is crucial for the reliability of the simulated atmospheric spectra.

The J- and K-dependences of the experimentally determined pressure-broadening coefficients are further compared to their theoretical predictions obtained by the semi-empirical approach [6]. The use of this method seems to be preferable since the polyatomic structure of the perturber risks to compromise the reliability of the atom-atom potential model employed in the semi-classical treatment. The semi-empirical parameters deduced by fitting to some experimental points lead to a good agreement of the recalculated collisional line widths with the experimental ones and enable extensive calculations for enlarged intervals of quantum numbers as well as for other (rovibrational) bands.

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