Temperature dependence of CH_3Cl self-broadening coefficients

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Methyl chloride is mostly of natural origins and is known as the principal source of chlorine in the terrestrial atmosphere. Chlorine-containing gases catalytically destroy stratospheric ozone and have, therefore, a great impact on the environment. Methyl chloride (vib)rotational lines in the terrestrial atmosphere spectra are broadened, first of all, by the main atmospheric constituents — nitrogen and oxygen. However, the case of self-broadening is also important because of high values of half-widths and significant contributions to the atmospheric absorption spectra.

In this work theoretical values of $CH_3{}^{35}Cl$-$CH_3{}^{35}Cl$ line broadening coefficients at room temperature (296 K) are first compared for two different approaches: 1) the semi-classical approach of Robert-Bonamy type involving exact classical trajectories (RBE) [1] and a rigorous treatment of the active molecule as a symmetric top [2]; 2) the semi-empirical approach [3] especially developed for strongly interacting molecules with high values of dipole moments. The semi-classical calculations, like the CH_3Br case [4], generally strongly overestimate the self-broadening and result in a good overall agreement with the experimental data if an artificial cut-off procedure is applied to the maximal value of the intermolecular distance accounted for ($r \leq 22$Å) [5]. However, with the cut-off procedure, they allow predictions for higher than experimentally observed values of the rotational number K, providing thus "experimental" points for fitting the semi-empirical parameters for large K intervals. The semi-empirical calculations give a coherent prediction of J- and K-dependences of self-broadened CH_3Cl lines for all experimentally observed transitions at room temperature and enable computing for other temperatures, for which a very limited number of experimental data is available.

In the final step, semi-empirical calculations of methyl chloride self-broadening coefficients and of their temperature dependences are performed for wide ranges of rotational quantum numbers ($0 \leq J \leq 70$, $0 \leq K \leq 20$) requested by atmospheric applications. The model parameters, adjusted at room temperature to experimental values of the ν_1 band for $K \leq 7$ and to semi-classical calculations for $8 \leq K \leq 20$, allow reproducing of all experimental data available in the literature even at the low temperature of 200 K. The computed values can be therefore considered as reliable and worthy of use in spectroscopic databases. Moreover, because of the insignificant vibrational dependence of CH_3Cl self-broadening coefficients, the calculated values can be safely used for different vibrational bands.

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