NON-LTE SPECTROSCOPY OF METHANE RECORDED IN A HYPERSONIC FLOW

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Laboratory spectroscopic data is essential for the modeling of hot exoplanet atmospheres, since molecules such as methane, a major component of hot-Jupiter-type exoplanet atmospheres, have a complex vibrational energy structure that makes computational predictions difficult at high temperatures for ro-vibrational transitions involving highly excited vibrational sates. To better inform line lists used in radiative transfer modelling, the ro-vibrational spectrum of methane has been recorded in the tetradecad region between 1.7 and 1.65 μm (5880-6060 cm^{-1}) through non-local thermodynamic equilibrium (non-LTE) cavity ringdown spectroscopy (CRDS)[1]. Non-LTE conditions, characterized by a low rotational temperature (39 K) and a high vibrational temperature (up to 1130 K), have been obtained by hypersonic expansion of a pre-heated mixture of argon and methane in a contoured Laval nozzle. The high vibrational temperature increases the intensity of new hot bands, while the very low rotational temperature greatly simplifies their rotational structure, thus facilitating their identification. A close comparison of the recorded CRDS data to the TheoReTS database reveals both inefficient vibrational relaxation between polyads and efficient vibrational relaxation between vibrational states forming a polyad. These effects result in an overpopulation of the lowest vibrational energy level of each polyad, an effect not widely currently incorporated in non-LTE radiative transfer models. A series of new hot band transitions originating from the pentad and octad polyads were assigned and are provided as a line list for use in future databases[2].

[1] doi:10.1063/5.0003886, E. Dudás *et al.*, J. Chem. Phys., 152, 134201 (2020).
[2] doi:10.1016/j.icarus.2022.115421, E. Dudás *et al.*, Icarus, 394, 115421 (2023).