New investigation of the $v_3$ band of $^{12}$CH$_4$ through the analysis of the high temperature infrared emission spectra

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Abstract

The $v_3$ C-H stretching region of methane is being re-investigated using high temperature (620 – 1715 K) emission spectra recorded in Rennes under Doppler limited resolution (0.008 cm$^{-1}$). This work follows our recent global analysis of the dyad system $\Delta n = \pm 1$ (1000 – 1500 cm$^{-1}$)[1]. Thanks to high temperature emission spectra of the pentad system ($\Delta n = a2$) observed in the spectral region 2600-3300 cm$^{-1}$, new assignments of vibration-rotation methane line positions have been achieved successfully. In particular, rotational assignments in the cold band (Pentad – GS) and in the related hot band (Octad – Dyad) were extended up to $J = 30$ and 27, respectively. In addition, 1525 new transitions belonging to the Tetradecad – Pentad hot band system were assigned for the first time, up to $J_{\text{max}} = 28$. The effective global model used to deal with the new assignments is developed to the 6th order for the first three polyads up to the Pentad, and to the 5th order for both the Octad and the Tetradecad. 1306 effective parameters were fitted with a dimension less standard deviation $\sigma = 2.64$. The mean root square deviations $d_{\text{RMS}}$ obtained are $4.18 \times 10^{-3}$ cm$^{-1}$ for the Pentad – GS cold band, $2.40 \times 10^{-3}$ cm$^{-1}$ for the Octad – Dyad, and $1.43 \times 10^{-3}$ cm$^{-1}$ for the Pentad – Tetradecad. This study is part of the ANR e-PYTHEAS project [2] aiming to model opacities of hot atmospheres, such as those of hot-jupiter type exoplanets.

Experiment

Hot emission spectra of methane have been recorded using the Bruker IFS 125 HR Fourier Transform spectrometer coupled to a High Enthalpy Source (HES) developed by R. Georges and Coworkers at the IPR–Rennes laboratory [3,4]. Six high-resolution (0.008 cm$^{-1}$) emission spectra were recorded in the spectral region (2600-3300 cm$^{-1}$) under various experimental conditions of heating and methane flow given in Table 1. A small fraction (0.1 slm) of CO was injected simultaneously with methane for helping temperature determination. Obtained spectra are illustrated in Figure 1.

The Pentad of methane $^{12}$CH$_4$

Methane ($^{12}$CH$_4$) is a tetradecad polyad for the type E, it has four nodal models:

- $v_1$ = 2485 cm$^{-1}$, $e_1$ = 651.3 cm$^{-1}$, $J = 10$
- $v_2$ = 2196 cm$^{-1}$, $e_2$ = 1533.3 cm$^{-1}$, $J = 13$
- $v_3$ = 1904 cm$^{-1}$, $e_3$ = 930.49 cm$^{-1}$, $J = 12$
- $v_4$ = 1310 cm$^{-1}$, $e_4$ = 1290 cm$^{-1}$, $J = 13$

The most efficient way to construct operators and basis functions is to use the irreducible tensors $\chi_{\text{ir}}$ [8-11].

Vibrational-rotation operators are constructed by further couplings to $\gamma$.

Effective parameters $\tilde{A}_{\text{eff}}(J, \gamma)$ are dilated with $\chi_{\text{ir}}$ (Table 2).

Table 2: Number of parameters in the effective Hamiltonians for the different orders. Numbers in parentheses indicate the number of shifted parameters in each case. $\tilde{A}_{\text{eff}}(J, \gamma)$ are dilated with $\chi_{\text{ir}}$ (Table 2).

Global analysis

294 very high-accuracy transitions (RMS) published by Amyay et al. [12] were added to bring additional constraints to the model.

Obtained parameters in the cold band are mostly belonging to the $v_3$ vibronic states.

The performance of a simultaneous analysis of the GS (the Dyad, the Pentad, the Octad and the Tetradac).

The total number of fitted transitions: 1306. The mean root square deviations $d_{\text{RMS}}$ obtained are $4.18 \times 10^{-3}$ cm$^{-1}$ for the Pentad – GS cold band, $2.40 \times 10^{-3}$ cm$^{-1}$ for the Octad – Dyad, and $1.43 \times 10^{-3}$ cm$^{-1}$ for the Pentad – Tetradecad.

Conclusions

Successful re-investigation of the $v_3$ C-H stretching region of the high temperature emission spectra recorded in Rennes between 2600 and 3300 cm$^{-1}$.

This work improves the global model in the pentad region including the cold and the corresponding hot bands with the same polyad selection rules ($\Delta n = a2$).

467 transitions have been assigned up to $J_{\text{max}} = 28$ and up to the Tetradecad (1600 cm$^{-1}$). These data were included in our database and fitted together using 1306 effective parameter with a dimension less standard deviation $2.64$.

The global limitation is extended to the 6th order in the case of the pentad.

Local perturbations at high values are also observed revealing the important Coriolis interaction between $v_3$ and $v_4$.

References:


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