



Study of the ν_3 band of $^{12}\text{CD}_4$: Line position analysis and unambiguous fit of q^2J^4 terms



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ABSTRACT

We report the analysis of $^{12}\text{CD}_4$ line positions from high-resolution rovibrational spectra, including accurate lines in the region $2160\text{--}2360\text{ cm}^{-1}$. In this analysis, 181 data points are fitted using an effective Hamiltonian expanded up to the sixth order for the ν_3 fundamental band. For the assignments and analysis, we use the SPVIEW and XTDS software programs that implement the tensorial formalism developed in the Dijon group for tetrahedral molecules. Experimental transitions are assigned up to $J \leq 15$ for the ν_3 cold band. Among the 37 parameters of the effective Hamiltonian for the ν_3 fundamental band (of which 10 are relative to the Ground State (GS or P_0), and 27 are relative to ν_3), 22 relative to ν_3 were fitted. The 32 parameters for ν_3 allow very good simulations to be made. For this study, a total of 181 line positions were used in the least squares adjustment characterized by the root mean square deviation d_{RMS} for line positions: $1.196 \times 10^{-3}\text{ cm}^{-1}$. On the basis of our set of 181 fits of experimental data for ν_3 of $^{12}\text{CD}_4$, the ambiguity of effective Hamiltonians for triply degenerate F_2 states of tetrahedral molecules is verified. It is shown that, in agreement with theory, any of q^2J^4 -type parameters cannot be determined from experimental data in a unique way, and these parameters cannot be considered as spectroscopic constants.

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1. Introduction

Valentin et al. [1] have recorded and analyzed the wave numbers of rovibrational transitions between the Ground State (GS or P_0) and the Dyad (ν_2, ν_4) or P_1 of the molecule $^{12}\text{CD}_4$, and Poussiguet et al. [2] have recorded and analyzed the wave numbers of rovibrational transitions between the GS and the Pentad ($2\nu_4, \nu_2 + \nu_4, \nu_1, 2\nu_2, \nu_3$) or P_2 .

Recently, and in addition to 19 experimental data points due to Kreiner and Robiette [3,4] for GS-GS, 2308 data points (19 for P_0 - P_0 , 893 for P_1 - P_0 and 1396 for P_2 - P_0) from the three sources are fitted by Ouardi et al. [5], using an effective Hamiltonian expanded up to the fourth order for the Pentad. These experimental data were reanalyzed simultaneously, allowing a global analysis of $^{12}\text{CD}_4$ line positions in the region $900\text{--}2400\text{ cm}^{-1}$. This region covers two cold polyads: the Dyad (ν_2, ν_4) or P_1 ($900\text{--}1220\text{ cm}^{-1}$, 2 vibrational levels, 2 sublevels) and the Pentad ($2\nu_4, \nu_2 + \nu_4, \nu_1, 2\nu_2, \nu_3$) or P_2 ($1850\text{--}2400\text{ cm}^{-1}$, 5 vibrational levels, 9 sublevels). Among the 1396 data of P_2 - P_0 , 112 data of ν_3 , were analyzed in polyad scheme.

Infrared spectra of $^{12}\text{CD}_4$ in the Dyad, Pentad and Octad regions have been recently computed from the potential energy and ab initio dipole moment surfaces by Rey et al. [6], who have compared their predictions with the T.D.S. spectroscopic databank containing $^{12}\text{CD}_4$ line lists and energy levels [7].

To ensure assignments for each isolated band $2\nu_4, \nu_2 + \nu_4, \nu_1, 2\nu_2$ and ν_3 , we proposed to study each cold band, considering the upper states as isolated states. And in this concept, the ν_3 band considered in the approximation of the single (0010) upper state model, which summed intensity is high compared to other bands of the pentad will be studied in this work.

In this analysis, 181 data points from the source of data [2] are fitted using an effective Hamiltonian expanded up to the sixth order for the ν_3 fundamental band. For the assignments and analysis, we use the SPVIEW and XTDS software programs that implement the tensorial formalism developed in the Dijon group for tetrahedral molecules. Experimental transitions are assigned up to $J \leq 15$ for the ν_3 cold band. Among the 37 parameters of the effective Hamiltonian for the ν_3 fundamental band (of which 10 are relative to the Ground State (GS or P_0), and 27 are relative to ν_3), 22 relative to ν_3 were fitted. The 32 parameters for ν_3 allow very good simulations to be made.

Perevalov et al. [8,9] have shown that there exist transformations of effective Hamiltonians which lead to ambiguity of

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fitted parameters for isolated F_2 states and interacting E and F_2 states (we shall refer to these transformations as PTZ transformations).

On the basis of our set of 181 fits of experimental data for ν_3 of $^{12}\text{CD}_4$, the ambiguity of effective Hamiltonians for triply degenerate F_2 states of tetrahedral molecules is verified. It is shown that, in agreement with theory, any of q^2f^4 -type parameters cannot be determined from the 181 experimental data in a unique way, and these type of parameters cannot be considered as spectroscopic constants. The behavior of fitted q^2f^4 parameters obey linear equations.

2. Experimental data

Poussigue et al. [2] have recorded and analyzed the rovibrational frequencies of the Pentad lines. (The details of the experimental conditions are given in Ref. [2].) In their analysis, Poussigue et al. [2] fixed the GS and (ν_2, ν_4) parameters and were able to determine the parameters relative to the Pentad $2\nu_4, \nu_2 + \nu_4, \nu_1, 2\nu_2, \nu_3$.

This experimental spectra were recorded at room temperature and at sample pressures and absorption path lengths ranging from 4.8 Torr and 0.055 m to 3.0 Torr and 32.2 m. This allowed a good determination of lines ranging from the very strong ν_3 lines (line strengths of about 1×10^{-19} cm/molecule) to the very weak lines of, e.g., $2\nu_2$ (line strengths of about 5×10^{-24} cm/molecule), forbidden in the infrared spectrum in the zeroth-order approach.

For our purposes, we created an experimental file containing the wave numbers and the intensities of the experimental lines of the Pentad from Ref. [2]. SPVIEW was used to choose the appropriate experimental lines, which were then compared with our calculated lines of ν_3 . From this analysis, we were able to attribute 181 lines relative to the ν_3 cold band of the $^{12}\text{CD}_4$ molecule. The board range of quantum numbers ($J \leq 15$), and the good distribution of the 181 data points by the rotational quantum number J , suggests that very good results may be obtained from this study.

3. Theory: tensorial model for the hamiltonian

As all XY_4 tetrahedral molecules, $^{12}\text{CD}_4$ possesses the stretching modes ν_1 (A_1) and ν_3 (F_2) and the bending modes ν_2 (E) and ν_4 (F_2). The mode ν_1 (A_1) is a non-degenerate oscillator, while the mode ν_2 (E) is doubly degenerate and both ν_3 (F_2) and ν_4 (F_2) modes are triply degenerate. The fundamental frequencies exhibit a simple approximate relation: ν_1 (A_1) \approx ν_3 (F_2) \approx $2 \nu_2$ (E) \approx $2 \nu_4$ (F_2), and

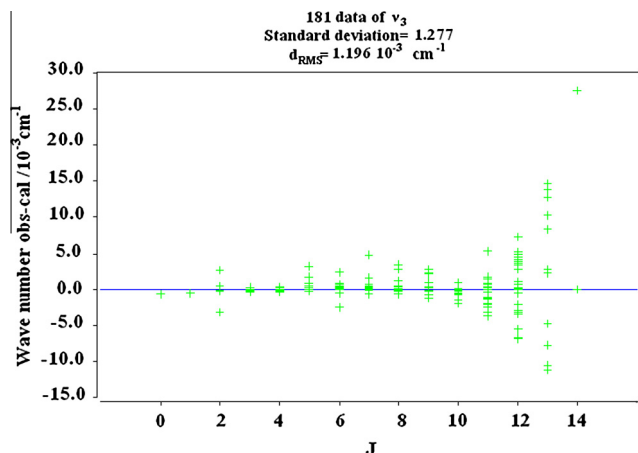


Fig. 1. Observed-calculated line positions and fit statistics for the different transitions of ν_3 .

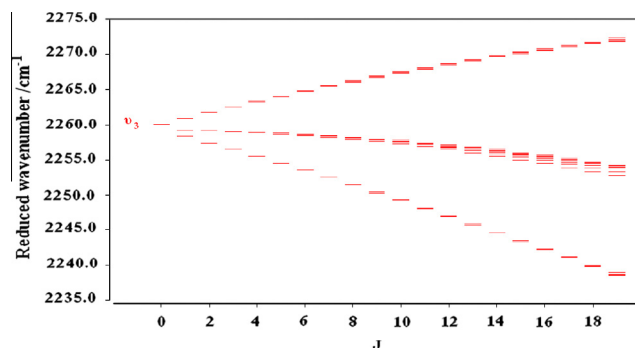


Fig. 2. Calculated reduced upper state energy levels (see text) for the ν_3 cold band.

this relation leads to a well-defined polyad structure, with each polyad P_n defined by the integer n as:

$$n = 2(\nu_1 + \nu_3) + \nu_2 + \nu_4 \quad (1)$$

where the $\nu_i = 0, 1, 2, \dots$ ($i = 1$ to 4) are the vibrational quantum numbers. P_0 is the Ground State (GS) or Monad. Each set of vibrational quantum numbers (i.e., $\nu_1, \nu_2, \nu_3, \nu_4$) defines a vibrational level. Due to the degeneracy of three of the normal vibrations, each vibrational level contains a certain number of vibrational sublevels, whose symmetries can be determined by means of group theoretical methods [10].

The theoretical model used in this paper is based on the tetrahedral tensorial formalism developed in Dijon, France. Details concerning notations and operator constructions are described in Refs. [11–17].

Let us consider an XY_4 molecule for which the vibrational levels are grouped in a series of polyads P_k ($k = 0 \dots, n$) as defined above. In frame of the polyad scheme, the effective Hamiltonian operator can be constructed in the following form:

$$\tilde{H} = \tilde{H}_{\{P_0\}} + \tilde{H}_{\{P_1\}} + \dots + \tilde{H}_{\{P_k\}} \quad (2)$$

In this work, where the ν_3 isolated band will be studied, we use the following effective Hamiltonian:

$$\tilde{H}^{(\nu_3)} = \tilde{H}_{\{\text{GS}\}}^{(\nu_3)} + \tilde{H}_{\{\nu_3\}}^{(\nu_3)} \quad (3)$$

where each term, \tilde{H} , is expanded in the form:

$$\tilde{H} = \sum_{\text{all indexes}} \tilde{t}_{\{s\}\{s'\}}^{\Omega(k,n)\Gamma_v\Gamma_{v'}} \otimes T_{\{s\}\{s'\}}^{\Omega(k,n)\Gamma_v\Gamma_{v'}} \quad (4)$$

In this equation, the $\tilde{t}_{\{s\}\{s'\}}^{\Omega(k,n)\Gamma_v\Gamma_{v'}}$ are the effective Hamiltonian parameters to be determined by fitting to experimental line positions and the $T_{\{s\}\{s'\}}^{\Omega(k,n)\Gamma_v\Gamma_{v'}}$ are the rovibrational operators [18–22].

The order of each individual term in (4) is defined as:

$$O_H = \Omega + \Omega_v - 2 \quad (5)$$

where Ω , is the degree in the a or a^+ operators.

The effective Hamiltonian matrix is diagonalized numerically, and this leads to eigenfunctions obtained from:

$$\tilde{H}^{\text{eff}} |\Psi_\sigma^{J,c\alpha}\rangle = E |\Psi_\sigma^{J,c\alpha}\rangle \quad (6)$$

where $\alpha = 1, 2 \dots$ numbers the functions of the same symmetry C in a given J block.

In order to calculate transition intensities (as in the case, for example, of infrared absorption spectroscopy), the dipole moment operator is expanded in a similar way as for the Hamiltonian [13,15,16,23].

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