

Global Analysis of the Infrared Spectrum of $^{13}\text{CH}_4$: Lines in the Region 0 to 3200 cm^{-1}

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Abstract: We have carried out new measurements of infrared spectra in a wide frequency range for the spherical top molecules $^{12}\text{CH}_4$, $^{13}\text{CH}_4$ and $^{12}\text{CD}_4$ at low (80 K) and at room temperature (298 K). Spectra were recorded at very high resolution (0.0027 cm^{-1} for spectra in the region around 2900 cm^{-1} , which corresponds to the pentad for $^{13}\text{CH}_4$) using the Zürich prototype Bruker 125 spectrometer (ZP 2001) combined with a low temperature cooling cell and a White-type cell. At low temperature, the Doppler full line width at half maximum was reduced by a factor of 1.91 to 0.0045 cm^{-1} in the pentad region for $^{13}\text{CH}_4$. We report the global analysis of $^{13}\text{CH}_4$ -transitions up to 3200 cm^{-1} and compare to previous work. In the present work line positions are reproduced with an rms deviation of 0.0004 cm^{-1} . The complex interacting system is analyzed using the effective Hamiltonian approach elaborated in Dijon.

Keywords: Collisional cooling · $^{13}\text{CH}_4$ · High resolution infrared spectroscopy · Isotopes · Methane

1. Introduction

There has been renewed interest in the spectroscopy of methane and its isotopomers because of new developments in high resolution spectroscopy. We may mention as examples the studies of intramolecular vibrational redistribution^[1,2] or nuclear spin symmetry conservation in supersonic jet expansions.^[3,4] Also pulsed supersonic jet spectrometry using a newly developed high resolution cw-laser cavity ring down spectrometer has been recently applied to

methane overtone spectroscopy.^[4,5] Furthermore, methane, a relatively abundant constituent of planetary atmospheres, has recently been observed in detail on one of the Cassini/Huygens space mission primary targets – Titan.^[6,7] Saturn's largest moon shows several strong CH_4 absorption regions. Even though $^{13}\text{CH}_4$ is much less abundant it is well observed on Titan and other planetary and interstellar objects. The ratio $^{13}\text{C}/^{12}\text{C}$ is important since it sheds light on the formation process of methane and consequently allows conclusions about its origin. Recent work on constructing accurate potential hypersurfaces for polyatomic molecules using the methane molecule as an important prototype^[8–10] gave further motivation for reinvestigating the spectrum of methane. A suitable potential hypersurface should describe spectra and dynamics of all isotopomers of methane. The aims of the present work are related to all of these new developments. As a part of our ongoing project to investigate the low temperature spectra of methane we have recorded new infrared spectra of methane and its isotopomers $^{12}\text{CH}_4$,^[11] $^{12}\text{CH}_3\text{D}$,^[12] $^{12}\text{CH}_2\text{D}_2$,^[13] $^{12}\text{CHD}_3$,^[12] $^{13}\text{CH}_4$,^[14] and $^{12}\text{CD}_4$.^[15] As a long-term goal of such systematic isotopomer studies we should also mention non-Born-Oppenheimer effects in spectra. The present work concentrates on the analysis of the so-called pentad, which corresponds to the CH-stretching fundamental and CH-

bending overtone absorption. Fig. 1 shows a survey of the polyad scheme of $^{13}\text{CH}_4$.

2. Experimental

High purity $^{13}\text{CH}_4$ (99.9%) was purchased from Cambridge Isotope Laboratories and its identity was obvious from the spectra. Room temperature measurements have been carried out using the Zürich prototype Bruker 125 spectrometer (ZP 2001)^[22] combined with a White-type cell.^[23] Cold spectra (80 K) were recorded using the same spectrometer combined with an enclosive flow cooling cell,^[24–26] which provides a very powerful FTIR system. Complex infrared spectra can be simplified by cooling the sample gas. Hot bands appear attenuated and complex polyad patterns may be more easily analyzed. The widths of the rotation–vibration bands decrease approximately proportionally with temperature. In addition, the Doppler width of a single spectral line of the molecules narrows with the square root of the temperature (see Figs 2 and 3). For a detailed description of our experimental setup we refer to [24].

3. Results and Discussion

Like all XY_4 tetrahedral molecules, methane has four normal modes of vibra-

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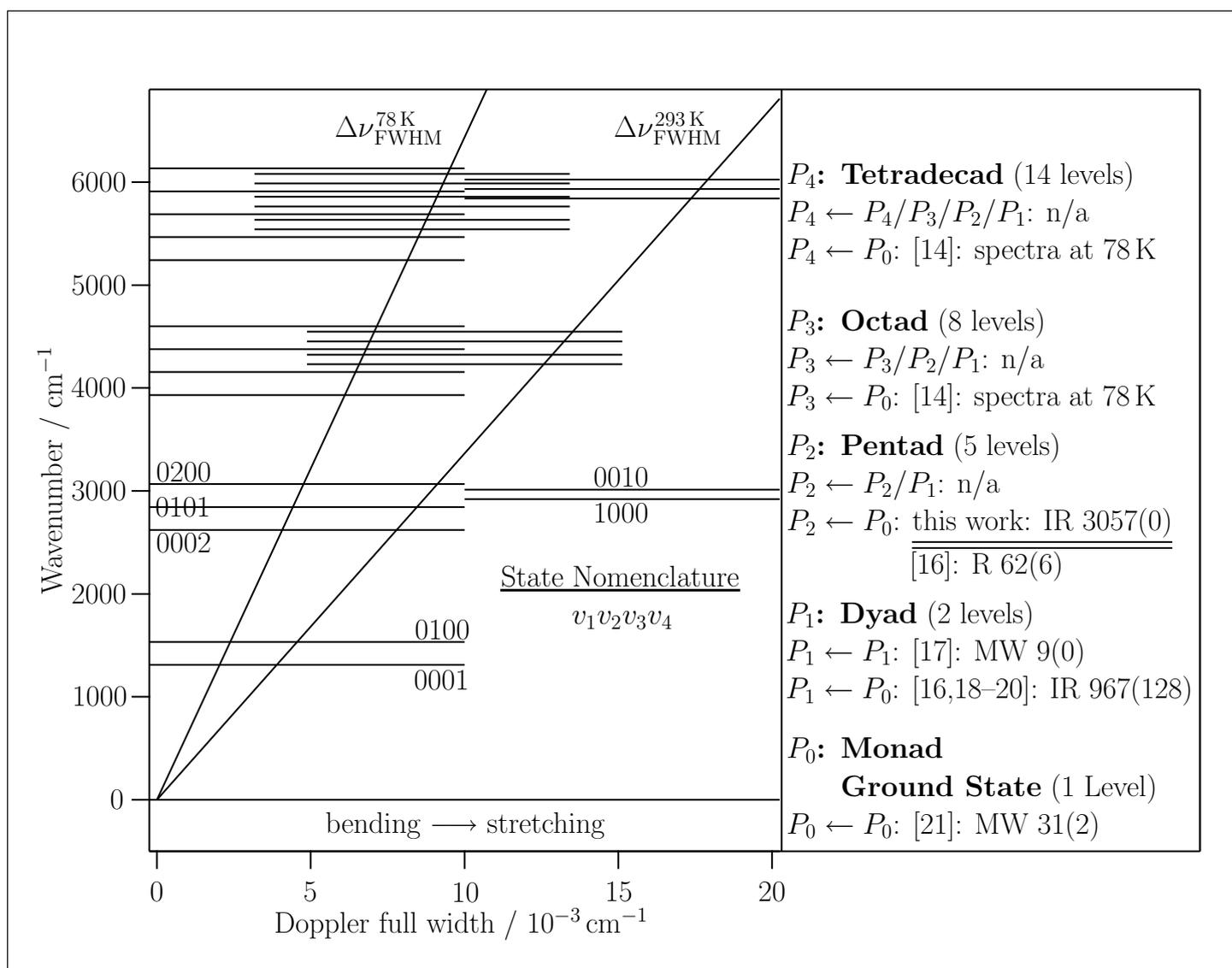


Fig. 1. The polyad scheme of $^{13}\text{CH}_4$. The vibrational levels on the left are positioned according to their stretching and bending character. Wavenumbers of the fundamental levels 1000, 0010, 0001, 0100 are due to this work. We also indicate by straight line diagonals $\Delta\nu_{\text{FWHM}}^T$ the Doppler full widths at half maximum of transitions in the 0–6500 cm^{-1} region at $T = 78\text{ K}$ and 293 K . On the right, references of the data used for this work and the current availability of experimental data are summarized. For each region we also indicate the transition type, i.e. Raman (R), Microwave (MW) and Infrared (IR) and the number of transitions included in the fit. The number of transitions that appear twice in the respective data set is given in parentheses. Experimental data of the hot bands and polyad internal transitions are either not available (n/a) or only so to limited extent.

tion. They can be labeled by the irreducible representations of the T_d point group, according to the symmetry of the associated normal coordinates. The fundamental frequencies exhibit a simple approximate relation, which leads to a well-defined polyad structure: $\nu_1(\text{A}_1) \approx \nu_3(\text{F}_2) \approx 2\nu_2(\text{E}) \approx 2\nu_4(\text{F}_2)$. Polyad P_n gathers all vibrational states (v_1, v_2, v_3, v_4) satisfying $n = 2(v_1 + v_3) + v_2 + v_4$, where $v_i = 0, 1, 2, \dots$ ($i = 1$ to 4) are the vibrational quantum numbers (see Fig. 1). The complex interacting system of the first three polyads has been analyzed using the effective Hamiltonian approach in tensor form reviewed in [27] and implemented in the STDS software package.^[28] A total of 4126 calibrated experimental line positions (2091 newly assigned) were included in the non-linear least-squares fit, minimizing the standard deviation. In this

work the global rms deviation is 0.0004 cm^{-1} , which gives an estimate of the upper limit of the relative experimental accuracy and model limitations (the absolute wavenumber accuracy is estimated to be better than 10^{-5} cm^{-1}). Compared to the preliminary analysis of the pentad of $^{13}\text{CH}_4$ ^[16] we gain about a factor of 2 in accuracy. Further work will include line positions from weaker lines in the intense regions of the dyad and pentad system by using the present results to extract such weak lines from the experimental spectra, and then reinject them into the fit. It should also be possible to investigate hot bands. The results represent a significant improvement compared to previous studies when more highly excited rotational states are considered. As can be seen from Figs 2 and 3 rotationally low lying levels are reproduced fairly

well using parameters according to [16]. However, rotationally highly excited states ($16 \leq J \leq 22$) are only correctly reproduced using the Hamiltonian parameters obtained in the present work, which should be sufficiently reliable to allow an analysis of the next higher polyad, the octad. Moreover, the parameters will certainly be very useful to improve the knowledge of methane's potential energy hypersurfaces. It would also be interesting to check how these new results affect recent investigations of planetary spectra in the pentad region. We plan to analyze in some detail the intensities or integrated absorption cross sections, which will be useful in relation to electric dipole moment hypersurfaces.^[8–10] Intensities are also of obvious importance for astrophysical applications and in particular for the understanding of planetary spectra. The

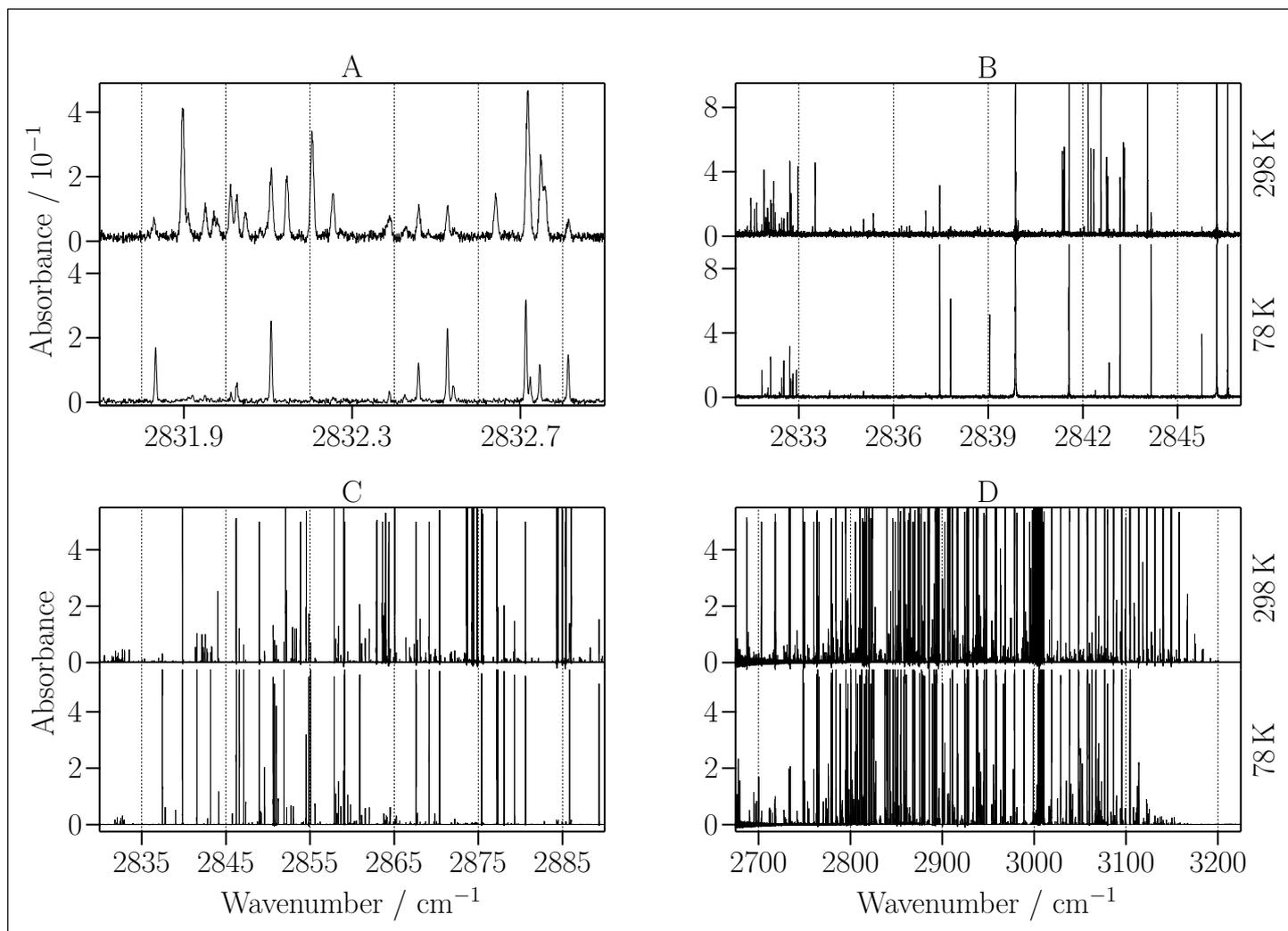


Fig. 2. Figs A–D show small (A,B) and large (C,D) sections of a $^{13}\text{CH}_4$ infrared spectrum recorded at 78 K (lower frame) and a $^{13}\text{CH}_4$ infrared spectrum recorded at room temperature (upper frame). Complex spectra can be simplified by cooling the sample gas. Hot bands appear attenuated and complex polyad patterns can be more easily analyzed.

precision of the effective Hamiltonian parameters obtained from the present analysis is significantly improved as seen for instance from the smaller statistical uncertainties (in parentheses) of the band center deviations: $\nu_4(\text{F}_2) = 1302.7807780(72) \text{ cm}^{-1}$, $\nu_2(\text{E}) = 1533.4927790(99) \text{ cm}^{-1}$, $\nu_1(\text{A}_1) = 2888.15(12) \text{ cm}^{-1}$, $\nu_3(\text{F}_2) = 2989.13(332) \text{ cm}^{-1}$. The newly fitted very high resolution data of the present investigation allowed us to expand the Hamiltonian to higher order than in previous studies.

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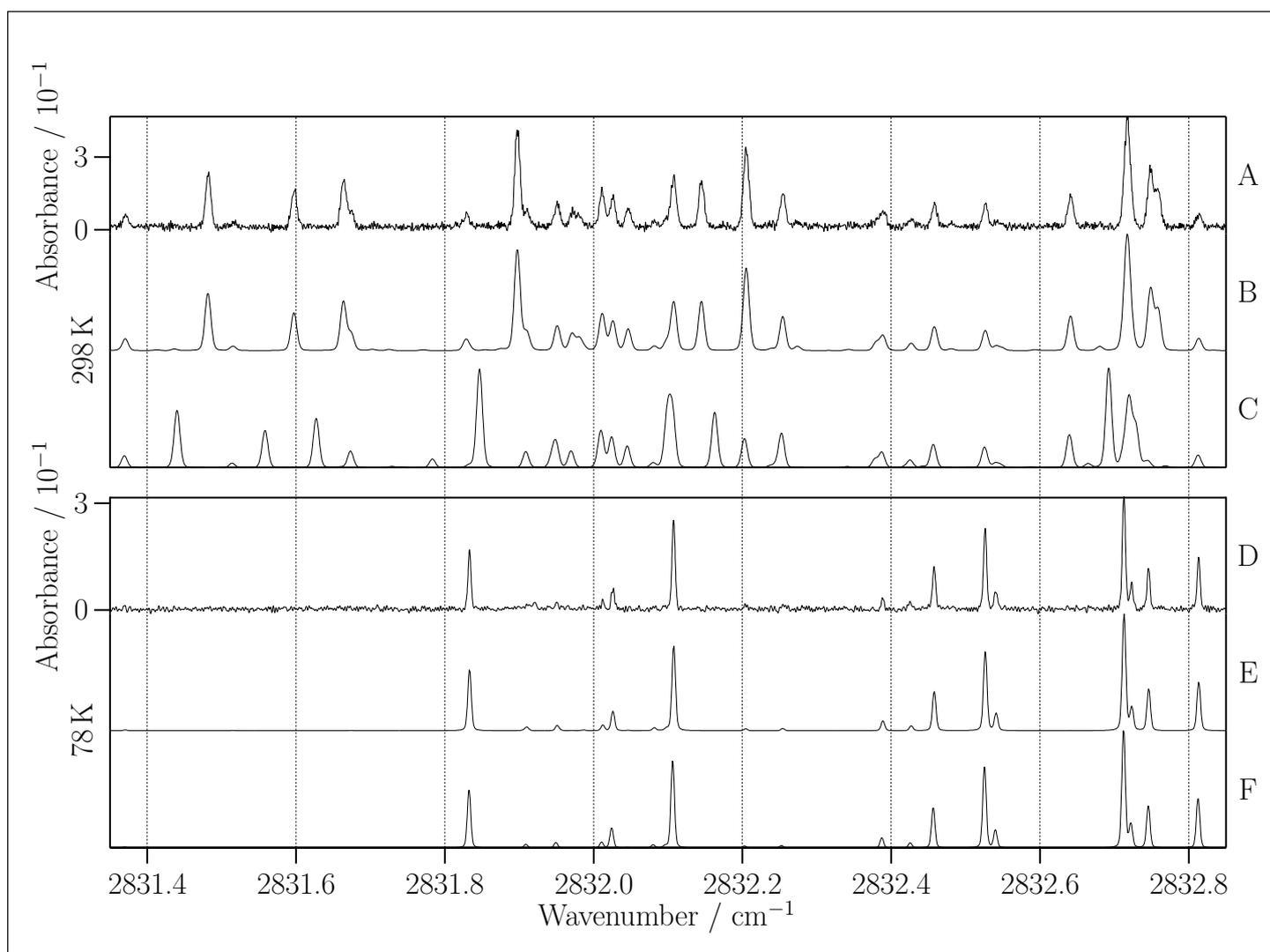


Fig. 3. Details of two exemplary experimental $^{13}\text{CH}_4$ infrared spectra recorded at room temperature (frame A) and at 78 K (frame D). Due to simplification (population shifted towards a few low energy states) and higher resolution (reduced Doppler width), transitions could be distinguished and assigned with very high confidence. For example, transitions around 2832.7 cm^{-1} could be distinguished and unambiguously assigned. The simulations using parameters according to [16] (frames C and F) reproduce rotationally low lying levels about as well as the simulations from the present work (frames B and E). However, rotationally highly excited states are only correctly reproduced in the new simulation (frame B).

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