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Global analysis of the high resolution infrared spectrum of methane $^{12}CH_4$ in the region from 0 to 4800 cm^{-1}

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This paper is dedicated to Prof. W. Kutzelnigg in honor of his 75th birthday.

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ABSTRACT

We report the global analysis of methane ($^{12}CH_4$) lines from high resolution rovibrational spectra including accurate line positions and intensities in the region 0–4800 cm^{-1}. This covers four polyads: The Ground State Monad (rotational levels), the Dyad (940–1850 cm^{-1}, 2 vibrational levels, 2 sublevels), the Pentad (2150–3350 cm^{-1}, 5 vibrational levels, 9 sublevels) and the Octad (3550–4800 cm^{-1}, 8 vibrational levels, 24 sublevels) and some of the associated hot bands (Pentad–Dyad and Octad–Dyad). New Fourier transform infrared (FTIR) spectra of the Pentad and Octad regions have been recorded with a very high resolution (better than *0.001* cm^{-1} instrumental bandwidth, unapodized) at 78 K using the Bruker IFS 125 HR Zürich prototype (ZP2001) spectrometer in combination with a long optical path collisional cooling system [S. Albert, S. Bauerecker, M. Quack, A. Steinlin, Mol. Phys. 105 (2007) 541]. Existing spectra previously recorded with the FTIR spectrometer at the National Solar Observatory on Kitt Peak in Arizona were remeasured selectively to provide new intensities and positions of weaker lines above 4400 cm^{-1}. These were combined with previously reported absorption data from FTIR and laser absorption, as well as high-resolution stimulated Raman and microwave spectra. The effective hamiltonian was expanded up to order 6 for the Ground State, order 6 for the Dyad, order 5 for the Pentad and order 5 for the Octad. A total of 16,738 line positions were used in the least squares adjustment characterized by the following global root mean square deviations d_{RMS} for line positions: 1.3×10^{-4} cm^{-1} for the Dyad, 6.0×10^{-4} cm^{-1} for the Pentad, and 3.5×10^{-3} cm^{-1} for the Octad. Absolute intensities were also analyzed for all the cold bands and some of the hot bands in the region under consideration and we obtained d_{RMS} = 9.6% including 3262 experimental line intensities for the Octad. This analysis represents a large improvement over the previous one [J.-C. Hilico, O. Robert, M. Loëte, S. Toumi, A.S. Pine, L.R. Brown, J. Mol. Spectrosc. 208 (2001) 1] with d_{RMS} = 0.041 cm^{-1} for positions and *15.6%* for intensities in the Octad for a smaller data set. The new results are discussed as benchmarks in relation to accurate potential energy hypersurfaces and for atmospheric and planetary spectra.

1. Introduction

Methane (CH_4) is the prototypical hydrocarbon, which is important in numerous fields of science. One may name here its fundamental role in the history of our understanding of three dimensional molecular structures and chemical bonding [1–3], leading today to the formulation of accurate potential energy hypersurfaces for molecular quantum dynamics [4–9]. The methane molecule has been an important example for studies of time dependent intramolecular quantum wavepacket dynamics [10,11] as well as an example for fully 9-dimensional calculations of time independent vibrational quantum eigenstates [12]. Methane has also been repeatedly used as testing ground for accurate *ab initio* electronic structure calculations [13–15]. CH_4 has been a classic case for the study of nuclear spin symmetry conservation [16]. The subtle balance of electric dipole moments leading to the small electric dipole moment of methane isotopomers CH_3D, CH_2D_2 and CHD_3 has been a long standing problem [17–23] resolved only recently [4,5,17]. At the most fundamental level, the possible role of the parity violating electroweak interaction in relation to methane stereomutation has been discussed as well [24–26].

Towards more applied sciences, methane plays a crucial role in fields such as geosciences, reaction kinetics and combustion

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science, chemical technology of hydrogen generation, biotechnology, astrophysics, atmospheric and environmental science to name but a few. On Earth, CH_4 is the main constituent of natural gas and excepting H_2O it is the second most important greenhouse gas (after carbon dioxide) responsible for the present global warming, as established in Annex B of the Kyoto protocol and demonstrated by many studies [27]. CH_4 is also an important constituent of various planetary atmospheres, like those of the Giant Planets (Jupiter [28,29], Saturn [30], Uranus [31] and Neptune [32]), of Titan (Saturn's main satellite) [33–37], Triton (Neptune's main satellite) and Pluto [38]. It is even suspected to be present in Mars' atmosphere [39]. It is also likely to be abundant in some of the newly-discovered extrasolar planets (the so-called "hot jupiters") and brown dwarfs. As a matter of fact, the discovery of methane in the atmosphere of exoplanet HD 189733b has been reported very recently [40].

Since infrared spectroscopy is generally the best diagnostic tool to study CH_4 in these environments, it appears essential to be able to model its absorption very precisely. This is true for the study of methane itself (*i.e.* its distribution, sources and sinks) but also for the determination of physical conditions, chemistry, optical properties and minor constituents of planetary atmospheres. A striking example is Titan which is presently studied by the Cassini–Huygens mission [33–37]. CH_4 is present in significant amounts (a few %) on Titan at temperatures reaching around 80 K and thus the strong absorption bands make its atmosphere almost opaque, the ground being visible from space only through the methane transparency windows [36,37]. A correct interpretation of Titan's images, as well as the study of the many minor compounds responsible for its complex hydrocarbon chemistry, require first a global modeling of infrared absorption of CH_4.

The vibrational spectroscopy of methane has been studied for a long time [41–43]. Due to the high-symmetry of the molecule and the related polyad structure of close lying levels [44] it is quite complex. Indeed, the four normal mode frequencies ν_i of CH_4 exhibit an approximate relation of stretching and bending frequencies with $\nu_1 \approx \nu_3 \approx 2\nu_2 \approx 2\nu_4$ resulting in vibrational levels being grouped into polyads with levels of similar energy. The number of interacting vibrational levels within each polyad increases rapidly with the polyad number, making the line-by-line assignment analysis more and more difficult when progressing toward the near infrared regions and above.

Fig. 1 shows a survey of the polyad energy level scheme for $^{12}CH_4$ including a definition of the nomenclature. In the convention used here, the polyads P_n are simply numbered with increasing energy starting with $n = 0$ for the Monad, $n = 1$ for the Dyad *etc.* In this nomenclature the polyad number n gives roughly the number of CH-bending quanta with pure bending excitation and $n/2$ roughly the number of CH-stretching quanta with pure stretching excitation. In an alternative nomenclature in the literature one uses the polyad quantum number $N = n/2$, where one has then also polyads with half odd integer index [45]. Fig. 1 shows also the number of levels and sublevels within each polyad labeled with Greek prefix for the number of levels (Monad for 1, Dyad for 2 *etc.*). The number of levels is obtained from counting simply harmonic oscillator excitations with possible combinations of quanta in the modes. However, starting with the Pentad, these levels split into a larger number of vibrational sublevels of well defined symmetry species in the point group T_d (A_1, A_2, E, F_1, F_2), 9 sublevels for the Pentad and 24 for the Octad, see Section 3.1 below). Finally one might also count the number of non-degenerate vibrational states by giving each sublevel a degeneracy corresponding to its species (1 for A, 2 for E and 3 for F). This would be relevant for the approximate average total vibrational density of states which is roughly the number of states in the polyad divided by the polyad width, by definition less than a bending quantum if the polyads are separated. This is relevant in statistical mechanics and kinetics. In many applications, however, the density of vibrational states of a given symmetry species including total parity are relevant [46–48].

The Ground State Monad of $^{12}CH_4$ has been known for a long time from its centrifugal distortion spectrum in the microwave (Q branch) and THz (R branch) regions [49–53]. Intensities in the THz region have been recently reinvestigated [54]. The Dyad 1100–1800 cm^{-1} region is now also very well understood [55,56], including line positions and intensities and also many studies concerning lineshapes, e.g. [57,30]. The Pentad from 2300 to 3300 cm^{-1} region has been modeled with high accuracy by Hilico et al. [58]. The Octad from 3500 to 4700 cm^{-1} has been stud-

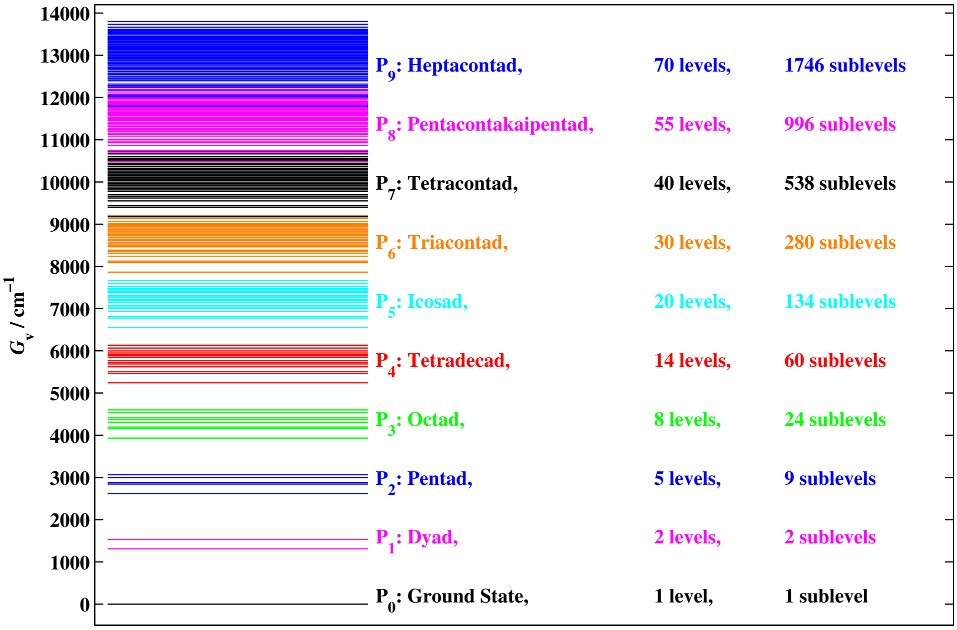

Fig. 1. The vibrational polyads of methane. The ordinate gives the vibrational term value G_v measured from the Ground State zero point level (color online). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)