



# Accurate line intensities of methane from first-principles calculations



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## ABSTRACT

In this work, we report first-principle theoretical predictions of methane spectral line intensities that are competitive with (and complementary to) the best laboratory measurements. A detailed comparison with the most accurate data shows that discrepancies in integrated polyad intensities are in the range of 0.4%–2.3%. This corresponds to estimations of the best available accuracy in laboratory Fourier Transform spectra measurements for this quantity. For relatively isolated strong lines the individual intensity deviations are in the same range. A comparison with the most precise laser measurements of the multiplet intensities in the  $2\nu_3$  band gives an agreement within the experimental error margins (about 1%). This is achieved for the first time for five-atomic molecules. In the Supplementary Material we provide the lists of theoretical intensities at 269 K for over 5000 strongest transitions in the range below  $6166\text{ cm}^{-1}$ . The advantage of the described method is that this offers a possibility to generate fully assigned exhaustive line lists at various temperature conditions. Extensive calculations up to  $12,000\text{ cm}^{-1}$  including high-T predictions will be made freely available through the TheoReTS information system (<http://theorets.univ-reims.fr>, <http://theorets.tsu.ru>) that contains *ab initio* born line lists and provides a user-friendly graphical interface for a fast simulation of the absorption cross-sections and radiance.

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## 1. Introduction

Methane is a high symmetry hydrocarbon molecule ( $\text{CH}_4$ ) of primary importance for many fields of sciences, technologies and environmental applications [1–5]. In the Earth's atmosphere, methane contributes to climate changes acting as a greenhouse gas [6] and is also relevant to the ozone formation and depletion [7]. It contributes to the growing global background concentration of tropospheric ozone, an air pollutant associated with premature mortality [8]. As the most abundant hydrocarbon, methane also modulates the concentration of the free radical OH [9,10] in the troposphere.

In the solar system, methane is a significant constituent of various planetary atmospheres, like those of the Giant Planets [11] (Jupiter, Saturn, Uranus and Neptune) and is the major absorber of the infrared radiation in the atmosphere of Titan [12] (Saturn's main satellite) where it plays a similar role as the water molecule in the Earth but at much lower temperatures.

The methane spectral signatures are considered bio-markers in exosolar planets observations [13]. Together with other elementary hydrocarbon molecules,  $\text{CH}_4$  is among “standard building blocks” for carbon-rich atmospheres of many exoplanets [14–16]. It plays a significant role in the photochemistry of outer atmospheres in many brown dwarfs and some asymptotic-giant-branch (AGB) stars [17]. Strong methane absorption bands dominate their opacity in the infrared spectral range.

As the remote detection *via* high-resolution spectroscopy is generally the best diagnostic tool to study  $\text{CH}_4$  in these environments [11], precise knowledge of the spectral line parameters in the infrared is mandatory for numerous applications. Intensities of spectral transitions and related Einstein coefficients are of particular importance in this context because they permit a retrieval of the temperatures and the molecular abundance.

Up to now the information for methane line intensities was provided by laboratory spectra analyses. Various spectroscopic databases [18,19] report several hundreds of thousands methane vibration-rotation transitions, only a small fraction of line intensities being truly measured because of well-known difficulties of experimental intensity determinations in crowded spectra with overlapping lines. A large part of information on methane transitions available in databases rely on calculations and extrapolations using empirical models. Infrared methane spectra are known to be quite

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complex. This is linked to the high tetrahedral ( $T_d$ ) symmetry of  $CH_4$  giving rise to degeneracies and quasi-degeneracies of vibrational modes and to vast and complicated resonance interactions due to inter-mode couplings. Accuracy of line intensity determination (and of its temperature dependence) from congested spectra is usually quite difficult to evaluate. For example, absorption cross-sections simulations using available databases were recently found not fully consistent with atmospheric observations [20] in some spectral intervals. Related issues are outlined in Section 2.

Very recently a breakthrough in the accuracy of first principle (*ab initio*) calculations of line parameters of medium-size molecules has permitted an access to independent source of line intensity data. The state-of-the-art in *ab initio* spectra predictions for the methane molecule is described in Section 3. The major challenge is constructing accurate dipole moment surfaces and developing an efficient implementation of a variational method for the quantum nuclear motion in the twelve-dimensional configuration space with a full account of the molecular symmetry properties. The issue related to “instable lines”, which are very sensitive to the intensity transfer effects due to accidental resonances is discussed in Section 4.1. For the first time we report here line-by-line comparison of *ab initio* and experimental methane intensities for reliable samples of strong and medium transitions (Section 4.2) with the accuracy approaching the experimental one.

In the Supplementary Material we provide the lists of recommended theoretical values for methane line intensities independent of the existing empirical determinations as a complementary source of information.

## 2. Empirical determinations of line intensities from spectra analyses

Line intensities in absorption/emission are the most important characteristics for various remote detection applications, but contrary to line positions they are not directly observable parameters. Intensities are obtained by a fit to observed transmittance using line profile models. Methane spectra in the infrared are congested and have complex patterns due to the overlapping of numerous sub-bands that belong to so-called polyads: Dyad, Pentad, Octad, Tetradecad, and so on [21]. The line fitting procedure is known to be quite laborious and complicated for such dense spectra involving large number of multiplets and weak lines, many of them being blended.

Because of the importance of methane radiative properties for various applications a lot of studies of high-resolution  $CH_4$  spectra have been conducted during several decades using FTS and laser techniques (see for example Refs. [21–25], the reference list being not exhaustive), but much less number of line intensities than line positions have been measured. The analyses of recorded high-resolution spectra were usually carried out using empirical spectroscopic models [22,26], which are based on effective Hamiltonians (EH) for sets of nearby vibrational states called “vibrational polyads” [27]. These models accounted for strong rovibrational resonance interactions within the corresponding polyads, and the line intensities were extrapolated from empirically fitted effective transition moments (ETM) for observed bands [26]. This step is important for practical applications at least for two reasons. For surely assigned transitions this permits determining the lower state energy and deducing transition probability (or Einstein coefficients) that allows one to extend the intensity data for other temperature conditions. Another reason is that linelists computed via EH/ETM fits help to determine other transitions sitting inside the observed features and to revise measurements iteratively, whereas big outliers serve as markers of wrong or blended lines, possibly due to isotopic species, impurities or technical issues. Typical RMS intensity deviations [21] for the ETM empirical fits were about 9% for

rotational transitions ( $0\text{--}200\text{ cm}^{-1}$ ), 3.4%–5.2% in the Dyad range ( $1000\text{--}1800\text{ cm}^{-1}$ ), 3% in the Pentad range ( $2200\text{--}33,000\text{ cm}^{-1}$ ), 10.4% in the Octad range ( $3700\text{--}4800\text{ cm}^{-1}$ ) and 13.9% in the Tetradecad range ( $4800\text{--}6300\text{ cm}^{-1}$ ). Methane linelists generated in this way were included in several databases as HITRAN [18], GEISA [19], TDS [28], STDS [29], McCaSDa [30] with supplementary empirical corrections in some cases.

The data review by Brown et al. [21] reported that even in lower wavenumber range up to the Octad ( $0\text{--}4800\text{ cm}^{-1}$ ) only 14% of positions and only 6% of intensities among over 130,000  $^{12}CH_4$  lines included in the last HITRAN-2012 edition have been truly measured. These restricted samples of fitted transitions served for the EH/ETM spectra modeling and for the generation of the empirically based linelist (information extracted from Table 2 of [21] and the HITRAN-2012 linelist [www.hitran.org](http://www.hitran.org)). Since then more experimental and theoretical works have been reported [25,31–34] including two-temperatures measurements [24], however experimental spectra analyses in higher wavenumber ranges [21,24,35,36] and for high-T [37–40] remain sparse.

A drawback of the empirical EH/ETM methods is a big number of adjustable parameters. Many of them are statistically poorly determined, in particular those responsible for the resonance coupling and the “intensity borrowing” effects among strong and weaker bands. This is linked to a fundamental ambiguity of the polyad EH models [41,42]. Consequently the intensity extrapolations via empirical EH/ETM approach are not always reliable and practically impossible for those bands which are not included in the model. Despite a significant progress [21] many experimental methane spectra are not fully analyzed and a reliable evaluation of intensity errors in existing databases is a challenging issue that is not yet solved.

## 3. Electronic structure *ab initio* calculations: towards the “spectroscopic accuracy” of potential energy and dipole moment surfaces

Independent and complementary information on line intensities can be provided by *ab initio* calculations. A significant progress in rotationally resolved spectra predictions of small molecules was made possible due to accurate electronic structure calculations of the potential energy surfaces (PES) and dipole moment surfaces (DMS) and to the development of efficient methods for variational nuclear motion calculations ([43–49] and references therein). For triatomics and four-atomics this helps resolving many issues related to the analyses of the spectra. For example, in case of the water molecule [43,50,51] this had led to a breakthrough in the extension of spectra analyses towards higher energy ranges and in interpretation of spectral signatures in solar spots [50]. For the ozone molecule, *ab initio* predictions [52,53] were mandatory for the understanding the shape of the transition state range [54] toward the dissociation threshold that could be relevant for the understanding of the anomalies [55,56] of the ozone formations. A computational effort for *ab initio* predictions of high-resolution spectra increases very rapidly with the number of atoms. One more atom introduces three supplementary degrees of freedom in the nuclear motion. If one considers high overtone bands, for each new degree of freedom at least ten elements are required, this being a minimum both for the grids of geometries in the nuclear configuration space and for vibrational basis sets. In a brute-force approach (without symmetry considerations) there would be thus a factor  $\sim 10^6$  of dimensionality between global spectra calculations of three-atomic and five atomic molecules.

For this reason, a construction of full-dimensional PESs and DMSs of methane is a challenging issue that has been subject of many studies in the past decades [44,48,57–64]. We have reviewed previous studies and a progress in this domain in our recent

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