Convergence of normal mode variational calculations of methane spectra: Theoretical linelist in the icosad range computed from potential energy and dipole moment surfaces

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ABSTRACT

Accurate basis set convergence of first-principles predictions of rotationally resolved spectra at high energy range is a common challenging issue for variational methods. In this paper, a detailed convergence study for the methane spectra is presented both for vibrational and rotational degrees of freedom as well as for intensities. For this purpose, we use our previously reported nine-dimensional potential energy and dipole moment surfaces of the methane molecule [Nikitin et al. Chem Phys Lett 2011;501:179–86; 2013;565:5–11]. Vibration–rotation calculations were carried out using variational normal mode approach with a full account of the T_d symmetry. The aim was to obtain accurate theoretical methane line lists for the wavenumber range beyond currently available spectra analyses. The focus of this paper is the complicated icosad range (6280–7900 cm^{-1}) containing 20 bands and 134 sub-bands where over 90% of experimental lines still remain unassigned. We provide variational line lists converged to a "spectroscopic precision" for icosad transitions for $T=80$ K and $T=296$ K. The first one contains 70 300 lines and the second one 286 170 lines with the intensity cut-off 10^{-29} cm^{-1}/(molecule cm^{-2}) with $J_{max}=18$. An average error in line positions of theoretical predictions up to $J=15$ is estimated as 0.2–0.5 cm^{-1} from the comparisons with currently analyzed bands. Ab initio line strength calculations give the integrated intensity 4.37×10^{-20} cm^{-1}/(molecule cm^{-2}) at $T=80$ K for the sum of all icosad bands. This is to be compared to the integrated intensity 4.36×10^{-20} cm^{-1}/(molecule cm^{-2}) of the experimental icosad line list recorded in Grenoble University [Campargue et al., J Mol Spectrosc 2013;291:16–22] using very sensitive laser techniques. The shapes of absorption bands are also in a good qualitative agreement with experimental spectra.

1. Introduction

Methane (^{12}CH$_4$) is the most abundant hydrocarbon in the Earth's atmosphere acting as a greenhouse gas [1]. It also affects the ozone layer depletion [2]. The knowledge of methane spectroscopy in a wide frequency range is of major importance for environmental sciences and for the modeling of various planetary atmospheres, being the major absorber at Titan [3,4], as well as for other astrophysical applications [5].

Infrared methane spectra are known to be quite complex. This is linked to the high tetrahedral symmetry of CH$_4$ giving rise to degeneracies and quasi-degeneracies of the vibrational modes and to vast and complicated resonance interactions

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due to inter-mode couplings. The four normal mode frequencies of methane exhibit an approximate relation between stretching and bending frequencies with $\omega_1 \approx \omega_3 \approx 2\omega_2 \approx 2\omega_4 \approx 3000 \text{ cm}^{-1}$ resulting in vibrational levels of nearby energies grouped into the so-called *polyads*. Each polyad P_n is characterized by the integer polyad number $n = 2(\nu_1 + \nu_3) + \nu_2 + \nu_4$, where $(\nu_1, \nu_2, \nu_3, \nu_4)$ are the principal vibrational normal mode quantum numbers taking values 0, 1, 2, etc. As the ν_2 mode is doubly degenerate and ν_3 and ν_4 are triply degenerate, the overtone and combination vibrational levels contain vibrational sublevels whose number rapidly increases with the vibration excitation. Overlapping among rovibrational patterns of various vibrational sublevels result in dense polyad structures that are very difficult to analyze. Their complexity increases drastically with the rotational quantum number J.

Experimental spectra analyses commonly employ effective Hamiltonian models [6,7] using parameters empirically fitted to observed data. During more than 30 years, line-by-line analyses have provided quite complete modeling of the rotational $(P_0 - P_0)$ band [8], dyad $(P_1 - P_0)$ [9] and pentad $(P_2 - P_0)$ [10] up to the octad $(P_3 - P_0)$ range [11,12] ($< 4900 \text{ cm}^{-1}$) and to a lesser extent for the tetradecad $(P_4 - P_0)$ range [13,14] ($< 6100 \text{ cm}^{-1}$). In the icosad range $(P_5 - P_0)$ only two band systems ($5\nu_4$ and $\nu_2 + 4\nu_4$) at the lower polyad edge have been analyzed both for line positions and intensities by Nikitin et al. [15] and one sub-band ($\nu_2 + 2\nu_3(F_2)$) for rovibrational line positions by Manca-Tanner et al. [16].

Though a significant progress has been achieved in spectra assignments and data reduction [7] at lower frequency ranges, the extrapolation capabilities of the empirical approach are very limited for highly excited polyads beyond the octad and tetradecad ranges. This is due to numerous resonances and a large number of unknown parameters to be adjusted. Many of these parameters are generally poorly defined, particularly for states coupled by resonance interactions: the determination of coupling parameters from experimental levels is known to be a mathematically ill-defined problem [17,18]. A detailed analysis of high methane polyads thus remains a challenging problem to be solved.

On the other hand, accurate *ab initio* calculations of the potential energy surfaces (PES) and dipole moment surfaces (DMS) for small molecules helps resolving many issues related to the analyses of the spectra and much progress has been achieved in last years in this respect (see for example [19–30] and references therein, the list being not exhaustive). In case of triatomics, accurate theoretical predictions led to a breakthrough in the extension of spectra analyses toward higher energy ranges. This was for example the case of water spectroscopy where global theoretical line lists [19,31,32] have been extremely useful for various applications [33–37]. In case of ozone, *ab initio* predictions [38] were mandatory for assigning complicated spectra [39,40] and for the understanding of the PES properties in the transition state range toward the dissociation threshold [41], while variational calculations for CO_2 helped improving information on hot bands and isotopic spectra [27,42,43]. Theoretical line lists for ammonia [26,44,21] and phosphine [45,28,29] are successful examples of such a trend for four-atomics.

A common problem for global variational spectra predictions is the basis set convergence as the dimensions of full matrices are in principle infinite at every vibrational degree of freedom. Various implementations of variational methods exist in the literature [46–56], however this issue remains particularly challenging when increasing the number of atoms [57–59]. In case of five-atomics, global rotationally resolved spectral calculations at high energy ranges are known to be extremely demanding [60,61].

The aim of this work is twofold. The first one is a careful study of the basis set convergence both for vibrational and rotational degrees of freedom as well as for intensities in order to achieve a "spectroscopic accuracy" of line predictions. By this one usually means the accuracy which could be useful for assignments of high-resolution rotationally resolved experimental spectra. To this end, we use our previously reported PES [62] and DMS [63] for methane as well as the variational normal mode approach employing the symmetry adapted irreducible tensor formulation [64,65] together with the corresponding reduction–compression technique [66,67] for the full Hamiltonian and for the basis set. The second target is to provide a fully converged theoretical methane line list for the wavenumber range beyond currently available spectra analyses. The focus of this paper is the complicated icosad range (6280–7900 cm^{-1}) containing 20 bands and 134 sub-bands where $\approx$ over 90% of the experimental lines still remain unassigned.

2. Theoretical background: computational issues and the role of the symmetry

In order to obtain accurate variationally computed infrared spectra for polyatomic molecules, one essentially needs three things. The first two things are well-behaved representations for the molecular PES and DMS are required for a sufficiently large range of nuclear configurations. These surfaces are usually fitted to electronic *ab initio* energies on a grid of internuclear displacements and expressed in terms of curvilinear or rectilinear coordinates. The third thing is an optimization of parameters involved in the $(3N - 3)$-dimensional rovibrational wavefunctions for large values of the total angular momentum J. An efficient choice of the latter ones is essential as they are further used to build transition matrices for computing line intensities. This last step is probably the most challenging task because it mainly depends on the intrinsic quality of the variational procedure for converging rovibrational states. In case of direct calculations, the PES and DMS parameters appear as external ones for the variational procedure. Strictly speaking even a very accurate PES will be of little use for spectroscopy applications if low-lying states are not properly converged and described. In practice, with the same quality of the primitive functions, the larger is the basis set the better convergence accuracy is expected. This issue will be discussed later in the text. Many studies have been devoted to the determination of methane PES [68–70,62,47] and DMS [71,63,72]. In this work we employ the potential and dipole moment surfaces reported by Nikitin et al. [62,63], hereafter referred to as NRT PES and DMS. These surfaces provided quite accurate rotationally resolved variational spectral calculations for $^{12}CH_4$ and $^{12}CD_4$ (Ref. [65]), $^{13}CH_4$ (Ref. [73]), $^{12}CH_3D$ (Ref. [67]) and both for line positions and intensities, which have