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Methane high-temperature partition function from contact transformations and variational calculations

A.V. Nikitin ^{a,*}, B.M. Krishna ^c, M. Rey ^b, S.A. Tashkun ^{a,c}, V.I.G. Tyuterev ^b^a Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, SB RAS, 1, Academician Zuev square, 634021 Tomsk, Russia^b Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, Université de Reims, U.F.R. Sciences, B.P. 1039, 51687 Reims Cedex 2, France^c Laboratory of Quantum Mechanics of Molecules and Radiative Processes, Tomsk State University, 36 Lenin Avenue, 634050 Tomsk, Russia

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ABSTRACT

The temperature dependence of the methane ¹²CH₄ partition function was investigated up to $T=3000$ K. The ro-vibrational energy levels were calculated using high-order contact transformation (CT) method that permitted building accurate effective Hamiltonian models for highly excited vibration–rotation states from the molecular potential energy surface. Comparisons with variational calculations using large basis sets as well as convergence and extrapolation issues are discussed. The accuracy of the present calculations for the methane partition function was estimated as 1–2% at 2000 K. This estimated error is considerably smaller than the difference with other calculations available in the literature.

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1. Introduction

Methane plays an important role in atmospheric and astrophysical chemistry. Its rotation–vibration spectrum is of key importance for the modeling of the atmospheres of bodies ranging from Titan to brown dwarfs and exoplanets. Precise knowledge of methane absorption/emission is crucial for the study of planetary atmospheres and is essential for the determination of their physical properties [1–3]. Line-by-line analyses of experimental spectra are known to be extremely challenging in the ranges corresponding to highly excited ro-vibrational states. A significant progress in analyses has been recently achieved [4–7] for ¹²CH₄ and for minor isotopologues [8–11] but experimental information on energy levels beyond 7000 cm⁻¹ remains very limited [12,13]. Though high-temperature methane measurements [14,15] and methane spectra at

higher wavenumber ranges [16–19] have been reported in the literature, most of the corresponding rovibrational patterns remain yet unassigned that prevents from an experimental determination of a sufficiently complete energy level set as was outlined in Ref. [13]. Consequently the analyses of high-temperature astrophysical observations can only rely on theoretical predictions [20–23] of absorption/emission properties.

Temperature-dependent modeling of gaseous atmosphere requires knowledge of molecular partition function (PF) usually denoted as $Q(T)$. The importance of an accurate PF for the modeling of reactions involving methane was pointed by Bowman et al. [24] and in references cited therein. This function is necessary for a calculation of spectroscopic and thermodynamic characteristics. Several studies have been devoted to the PF calculations of various types of molecules [25–27] using the product approximation $Q(T)=Q_{vib} \times Q_{rot}$ that results from neglecting the vibration–rotation interactions. In most of the early studies the harmonic oscillator approximation [28] was used for the vibrational partition function Q_{vib} whereas the rotational

* Corresponding author. Tel.: +38 22 491111 1208.
E-mail address: avn@iao.ru (A.V. Nikitin).

partition function was modeled by analytical semi-rigid rotor approximation in works of Fox [29], McDowell [30] or in other similar formulations depending on the molecular symmetry [31,32]. A comparison of this approach with direct sum PF calculations has been discussed by Gamache et al. [25,26,33]. The values of PF for various atmospheric molecules in a large temperature range calculated with Total Internal Partition Sums (TIPS) computational code [34] were included in HITRAN spectroscopic database [35].

The validity of the above mentioned approximations depends on the temperature and on the density of corresponding rovibrational states that could be collisionally excited in these conditions. It was recently argued [36,37] that the anharmonicity and vibration–rotation coupling effects could play a significant role for high-temperature methane PF calculations. Chakraborty et al. [36] have performed calculations of methane PF in the temperature range 100–1000 K using the MULTIMODE program suite [38]. The energy levels up to $J=50$ included in these calculations [36] have been computed by vibrational–rotational configuration interaction method using the Watson Hamiltonian and Jordan–Gilbert (JG) [39] potential energy surface (PES). Recently, Mielke and Truhlar [40] have extended zero-point inclusive PF values to the 300–3000 K range using alternative Feynman path integral method and employing the same PES [39]. Mielke and Truhlar [40] noted that the JG PES [39] is not the most accurate available methane potential energy surface. To our knowledge the accuracy of this PES has not been yet validated with respect to available spectroscopic data. Wenger et al. [37,41] have studied the methane PF based on a “multi-resolution approach” via a direct summation over rovibrational levels up to the dissociation limit. They have included a combination of empirical levels and extrapolation using effective Hamiltonians complemented by a statistical approximation at high energy range.

Direct variational calculations of methane PF from potential energy surfaces for astrophysical applications have been recently reported by Rey et al. [23] and Yurchenko et al. [22]. In Ref. [23] variational normal mode calculations have been extended up to $T=2000$ K. In Ref. [22] the PF $^{12}\text{CH}_4$ values have been tabulated in the 3–3000 K interval. The corresponding table is available on the EXOMOL website (www.exomol.com). Up to 2000 K the PF values from these two latter calculations [23,42] agree quite well but they are significantly different from the values provided by the “multi-resolution approach” [37] recently adopted in HITRAN-2012 [43], the discrepancy rapidly increasing for $T > 2000$ K. This could be explained by the unavoidable constraints in global variational calculations (the cut-off on E_{max} and on quantum numbers) due to the basis set limitations. On the other hand the validity of the statistical approximation in the “multi-resolution approach” [37] is obviously questionable.

In this work we report the results of the comparative study of the methane PF using two complementary direct sum approaches. The first one employs the polyad-by-polyad spectroscopic model obtained from the molecular PES via high-order Contact Transformation (CT) method [44] (Section 3). The advantage is that the dimensionality of the problem can be dramatically reduced while both the

anharmonicity and vibration–rotation interactions are taken into account. These transformations result in a decoupling of the successive polyad blocks that permitted extending predictions to higher J values and to higher vibrational energies. Approximations and extrapolation schemes are discussed.

Another approach is based on a global variational method [21,45] using an efficient diagonalization technique of the full Hamiltonian in a very large basis set (Section 5). Both approaches use the same methane PES [46] that has provided the best currently available accuracy in the previous spectra predictions [47,48]. Convergence and extrapolation issues are also discussed (Section 5).

2. Approximations and limitations of the PF direct summation method

The total internal partition function of a molecule can be expressed as a direct sum of Boltzmann factors at a given temperature T as follows:

$$Q(T) = \sum_{n = \text{all states}} \exp\left(\frac{-E_n}{kT}\right) = \sum_{i = \text{all levels}} g_i \exp\left(\frac{-E_i}{kT}\right) \quad (1)$$

Here g_i denotes the total degeneracy of the E_i levels, E_n represent energies of all possible states including electronic, vibrational and rotational degrees of freedom and $k=0.69503476 \text{ cm}^{-1}/\text{K}$ is the Boltzmann constant (NIST recommended value). For stable molecules having well separated electronic states, a major contribution results from the stationary electronic ground state levels. For polyatomic molecules the direct summation method becomes extremely challenging with the increasing temperature as this requires a complete set of all populated vibration–rotation levels at high energies. As was already mentioned in Section 1, in case of methane experimental levels are not sufficiently well known in this range. Direct summation method should thus rely on some theoretical models. Because J and symmetry type C are good quantum numbers the total PF can be represented as a sum of the corresponding partial contributions $Q(T) = \sum_{J,C} Q_{J,C}(T)$. In this section we briefly outline the approximations which have been used in available direct sum calculations. The corresponding limitations could be the origin for a lack of accuracy that gradually decreases with T .

A quite sophisticated “multi-resolution approach” combining various types of heterogeneous data has been suggested by Wenger et al. [37]. They divided the energy spectrum in the three parts.

As a first step, the lower part of the energy spectrum has been empirically described via the fit of the second-order effective Hamiltonian (EH) to available experimental data below 6000 cm^{-1} . This EH uses the vibrational–extrapolation approach developed by Dijon team [4,37,49] and involves true individual rovibrational levels for lower five polyads: Ground state, Dyad, Pentad, Octad, and Tetradecad. This is the most reliable part of data. The fitted parameters have been then used to predict purely vibrational $J=0$ levels of the subsequent polyads $P=6, 7, 8, 9$ up to $E_{vib}=13,800 \text{ cm}^{-1}$. The second part involved rotationally

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