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# An improved third order dipole moment surface for methane

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## Abstract

In a previous article a dipole moment surface (DMS) of full-electron, multi-reference configuration interaction (MRCI) quality was obtained and used to calculate the rotational spectrum of methane vibrational ground state, by means of a combination of the mean field configuration interaction method (VMFCI) with a generalized perturbation theory. The theoretical line intensities were matching the experimental ones obtained at the SOLEIL synchrotron well within experimental uncertainties. However, not all third order terms were included in this DMS. In the present work, additional DMS points have been calculated and fitted using a complete third order expansion. The new results give R-branch intensities systematically smaller by about 1 percent compared to those previously obtained by using the same ab initio method, so still within experimental errors. The relevance of this DMS to calculate intensities for excited vibrational states, in particular for the dyad, is addressed.

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Keywords:

Dipole moment surface; methane; generalized mean field configuration interaction.

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## 1 Introduction

Methane and its main isotopologues are molecular species of great significance in Earth atmosphere [1], and other Solar System objects such as Jupiter [2], Saturn [3], Titan [4,5], Uranus [6], or Neptune [7], to quote a few. It has also been detected in Brown Dwarfs [8,9] and exoplanets [10]. A precise modelling of the ro-vibrational spectra of methane is of paramount significance for the understanding of the atmosphere of these astrophysical bodies: the better the knowledge of the spectra, the more accurate the derivation of molecular compositions, temperature and pressure profiles, radiative transfer balance, ... will be. In particular, the rotational forbidden spectrum of methane vibrational ground state can be used to derive methane abundances in Titan, Saturn or Neptune atmosphere [11]. However, recent experimental studies have obtained intensity values differing by about 20% [12,13]. More generally, the experimental input to spectroscopic databases, used in astrophysical studies, is crucial. However, the need for theoretical predictions of methane spectrum has been recognized for years [9,14].

The *ab initio* calculation of a molecular ro-vibrational spectrum requires typically three ingredients: i) A potential energy surface (PES); ii) An effective method to solve the ro-vibrational Schrödinger equation and obtain energy levels and their associated eigenfunctions; iii) A dipole moment surface (DMS) to compute electric dipole transitions and intensities.

Proposed PES for methane include those of Gray and Robiette [15], Lee, Martin and Taylor [16], Schwenke and Partridge [17,18], Marquardt and Quack [19,20], Oyanagi et al. [21], and more recently those of Nikitin, Rey and Tyuterev (NRT) [22] and Yurchenko et al. [25]. Other PES that have not been exploited for computational spectroscopy studies, as far as we are aware, are found in Refs. [26,27]. Note that some of these PES have been partly refined using experimental data. In the present study, we have used the NRT PES transformed to mass-weighted Cartesian normal coordinates up to order 10, already employed in our previous studies [28,29].

Methane has served as a benchmark molecule for *ab initio* vibrational calculations and a detailed review of all the methods to solve its nuclear or vibrational Schrödinger equation is out of the scope of the present study. Eigenstates converged to within the  $\text{cm}^{-1}$  accuracy (or better), up to, say, the tetradecad for a given PES have been obtained

by means of various forms of configuration interactions (CI) [30–34] (earlier references can be found therein). We have used the vibrational mean field configuration interaction (VMFCI) method [35–39] to solve methane vibrational, stationary Schrödinger equation. It is implemented in the code CONVIV [40], which can deal with molecules of arbitrary sizes and a wide range of Hamiltonian operators and basis functions: general HO basis “HO( $\omega,\lambda$ )” corresponding to a HO potential of wave number  $\omega$  with minimum shifted by  $\lambda$ , Kratzer potential basis “KRA( $r_0,D_e$ )” eigenfunctions of a Kratzer potential [41] parametrized by equilibrium distance  $r_0$ , and dissociation energy  $D_e$ ; Morse potential basis “MOR( $a,D_e$ )” eigenfunctions of a Morse potential [42] parametrized by exponent  $a$ , and dissociation energy  $D_e$ ; trigonometric Pösch-Teller potential basis “TPT( $\alpha,\mu$ )” eigenfunctions [43] (the parameter  $\nu$  being set to zero); Chebychev polynomials “CHE” and so on. The VMFCI method has been combined with a generalized perturbation theory [28,35,44], to obtain effective rotational observable, from which accurate rotational spectra can be calculated [29,45].

The first DMS for methane to appear was the quartic DMS derived from an analysis of experimental data by Loete [46]. In the same vein, a simultaneous determination of force constants and dipole moment first and (some) second derivatives of methane was performed by Mourbat et al. [47]. First order derivatives were calculated *ab initio* by Hollenstein et al. at the second order Moller-Plesset, double zeta plus polarization, MP2/DZP, level [48]. The same group combined *ab initio* and experimental band strength from CHD<sub>3</sub> to derive a nine dimensional DMS for methane [49]. A modified Marquardt-Sheppard interpolated, fourth order, MP2/cc-pVTZ (“correlation-consistent polarized valence triple-zeta” basis of Dunning [50]), DMS was constructed and used in Ref. [21]. The averaged coupled pair functional method, (ACPF) [51], with a cc-pVTZ basis was chosen in [52] to build another *ab initio* DMS. More recently, we have computed two third order DMS of Frozen-Core-MRCI/VQZ and All-Electron-MRCI/ACV5Z qualities [29], and two independent sixth order DMS have appeared: i) that of Nikitin et al. at the coupled-cluster single and double with triple estimate, CCSD(T), plus first order, one-electron, Douglas-Kroll correction, level of theory using a correlation-consistent polarized valence quadruple-zeta basis, cc-pCVQZ, [53,23,24], and ii) that of Yurchenko et al. at the explicitly correlated F12-coupled-cluster method with single and double excitations including a perturbational estimate of connected triple excitations, in conjunction with the corresponding F12-optimized augmented correlation-consistent polarized va-

lence triple-zeta basis, CCSD(T)-F12c/aug-cc-pVTZ-F12, [25].

In our previous work, we preferred the multi-reference configuration interaction (MRCI) method over the coupled-cluster approach, because (i) the latter is not always reliable at intermediate distances, between equilibrium and dissociation [54], where several Slater determinants have significant weights in the wave function, (ii) only one MRCI calculation is sufficient to obtain the energy and the dipole moment at a given nuclear configuration, and (iii) MRCI dipole moment are obtained analytically and not numerically through the Hellmann-Feynman theorem. In the present case, it is mainly the last two reasons which are determinant, since static correlation was not important at the geometries considered. As for the determination of the equilibrium distance [29], dipole moment derivatives have been found quite sensitive to core-core and core-valence excitations. So, we conducted full electron calculations. A well balanced basis to carry such calculations is the augmented correlation consistent, polarized, core, valence quintuple zeta (aug-cc-pCV5Z or ACV5Z in short) basis set. We adopted this basis set, which is larger than those used for the other *ab initio* DMS. However, our previous DMS, was only designed to compute methane forbidden spectrum [55–60] of the vibrational ground state. So, it was only an incomplete third order expansion in normal coordinates. The purpose of the present paper, is to study the influence of the missing third order terms and to evaluate the reliability of our complete third order DMS to compute transition moments for ro-vibrational excited states.

The article is organized as follows: First, the *ab initio* ro-vibrational calculation scheme is outlined. Then, we analyse the new DMS and give updated results for methane vibrational ground state rotational spectrum. We conclude on the reliability of our DMS for excited states.

## 2 *Ab initio* calculation of methane rotation-vibration eigenstates

The ro-vibrational Hamiltonian used to describe the rotation-vibration degrees-of-freedom (DOF) of methane in the present study, as in [29], is the Eckart-Watson Hamiltonian for non-linear molecules [61,62]. This Hamiltonian may not be suitable to describe molecular states with significant amplitude along some floppy DOF. However, this is not the case of the low-lying vibrational states of methane, we are interested in. The potential energy

surface (PES) in the Hamiltonian is the 10<sup>th</sup> order, normal coordinate PES used in our previous calculation [29]. It has been derived from the Nikitin-Rey-Tuyterev (NRT) PES [22]. For details on the PES and on Watson  $\mu$ -matrix expansion order, we refer the reader to Ref. [29].

The ro-vibrational Hamiltonian has been diagonalized by means of a combination of the VMFCI method with a generalized perturbation theory [28,35,44]. In fact, this approach can be seen as a particular case of a unified method, called the generalized mean field configuration interaction (GMFCI).

### 2.1 The GMFCI method

A detailed account of the GMFCI method will be given in a forthcoming paper, only a brief description follows: The GMFCI method, as the VMFCI method, consists in considering a hierarchy of partitions of DOF. Each partition corresponds to a MFCI step. At each step, for each subset of DOF in the partition, usually called “a contraction”, an effective Hamiltonian, the so-called “mean-field (MF) Hamiltonian”, is constructed and diagonalized in a finite Hilbert space spanned by a possibly truncated set of product basis functions. Such an approximate solution of the stationary Schrödinger equation is also known as a “configuration interaction” (CI) calculation. More precisely, a basis set for a given contraction at step  $n$ , termed “active” and denoted by  $J_\alpha$ , is formed by taking the products of functions belonging to basis sets for its components, that were contractions,  $I_\gamma$ , of step  $(n - 1)$ ,

$$\Phi_{J_\alpha}^{M_\alpha} = \bigotimes_{I_\gamma \subseteq J_\alpha} \phi_{I_\gamma}^{m_\gamma}, \quad (1)$$

with possible truncations on the sum of their quantum numbers or their associated energy eigenvalues,

$$\sum_{I_\gamma \subseteq J_\alpha} E_{I_\gamma}^{m_\gamma} < E_{J_\alpha}^{max}, \quad (2)$$

$m_\gamma$ , is a basis function index for the basis set of  $I_\gamma$ ,  $M_\alpha$  is the multiplet of  $m_\gamma$ 's and serves as an index for the basis functions of the basis set of  $J_\alpha$ , and  $E_{J_\alpha}^{max}$  is a threshold chosen to eliminate high energy states, considered as not useful for the description of the states of interest.

The difference between VMFCI and GMFCI is that, in the VMFCI case, the MF Hamiltonian is constructed according to order 1 of the generalized perturbation theory, whereas in the GMFCI case, the order of perturbation is a flexible parameter, which can range from 0 to any positive integer. So, in VMFCI, the MF Hamiltonian corresponds to the total Hamiltonian averaged over a reference state, usually the product of ground states of the non-active i.e. “spectator” contractions,

$$H_{\alpha}^{eff} = \langle \bigotimes_{I_{\gamma} \notin J_{\alpha}} \phi_{I_{\gamma}}^0 | H | \bigotimes_{I_{\gamma} \notin J_{\alpha}} \phi_{I_{\gamma}}^0 \rangle. \quad (3)$$

In GMFCI with perturbation order strictly more than 1, the “generalized mean-field (GMF) Hamiltonian” will contain corrective terms involving all spectator states, for example, at order 2,

$$H_{\alpha}^{eff} = \langle \bigotimes_{I_{\gamma} \notin J_{\alpha}} \phi_{I_{\gamma}}^0 | H | \bigotimes_{I_{\gamma} \notin J_{\alpha}} \phi_{I_{\gamma}}^0 \rangle + \sum_{(m_{\gamma_1}, m_{\gamma_2}, \dots) \neq (0, 0, \dots)} \frac{\langle \bigotimes_{I_{\gamma} \notin J_{\alpha}} \phi_{I_{\gamma}}^0 | H | \bigotimes_{I_{\gamma} \notin J_{\alpha}} \phi_{I_{\gamma}}^{m_{\gamma}} \rangle \langle \bigotimes_{I_{\gamma} \notin J_{\alpha}} \phi_{I_{\gamma}}^{m_{\gamma}} | H | \bigotimes_{I_{\gamma} \notin J_{\alpha}} \phi_{I_{\gamma}}^0 \rangle}{\sum_{\gamma / I_{\gamma} \notin J_{\alpha}} E_{I_{\gamma}}^0 - E_{I_{\gamma}}^{m_{\gamma}}}, \quad (4)$$

where the summation  $\sum_{(m_{\gamma_1}, m_{\gamma_2}, \dots) \neq (0, 0, \dots)}$  extends over all spectator product functions different from the product of GS functions.

Now, let us consider after the last GMFCI step that contraction 1 is active, with a spectator reference state, more general than the product of GS, equal to the product function

$\bigotimes_{\alpha \in \{2, \dots, n_Q\}} \phi_{J_{\alpha}}^{m_{\alpha}^0}$ . For any observable,  $O$ , the matrix element of its effective counterpart  $O^{eff}$

between two total states  $\phi_{J_1}^{m_1}$  and  $\phi_{J_1}^{m_1'}$  is, up to order 1 in the perturbative expansion,

$$\begin{aligned} \langle \phi_{J_1}^{m_1} | O^{eff} | \phi_{J_1}^{m_1'} \rangle &= \langle \phi_{J_1}^{m_1} \otimes \phi_{J_2}^{m_2^0} \otimes \dots \otimes \phi_{J_{n_Q}}^{m_{n_Q}^0} | O | \phi_{J_1}^{m_1'} \otimes \phi_{J_2}^{m_2^0} \otimes \dots \otimes \phi_{J_{n_Q}}^{m_{n_Q}^0} \rangle \\ &+ \sum_{(m_2, \dots, m_{n_Q}) \neq (m_2^0, \dots, m_{n_Q}^0)} \left( \langle \phi_{J_1}^{m_1} \otimes \phi_{J_2}^{m_2^0} \otimes \dots \otimes \phi_{J_{n_Q}}^{m_{n_Q}^0} | O | \frac{\langle \bigotimes_{\alpha=2}^{n_Q} \phi_{J_{\alpha}}^{m_{\alpha}} | H | \bigotimes_{\alpha=2}^{n_Q} \phi_{J_{\alpha}}^{m_{\alpha}^0} \rangle \phi_{J_1}^{m_1'}}{\sum_{\alpha=2}^{n_Q} E_{J_{\alpha}}^{m_{\alpha}^0} - E_{J_{\alpha}}^{m_{\alpha}}} \otimes \phi_{J_2}^{m_2^0} \otimes \dots \otimes \phi_{J_{n_Q}}^{m_{n_Q}^0} \rangle \right. \\ &\left. + \langle \frac{\phi_{J_1}^{m_1'} \langle \bigotimes_{\alpha=2}^{n_Q} \phi_{J_{\alpha}}^{m_{\alpha}} | H | \bigotimes_{\alpha=2}^{n_Q} \phi_{J_{\alpha}}^{m_{\alpha}^0} \rangle^{\dagger}}{\sum_{\alpha=2}^{n_Q} E_{J_{\alpha}}^{m_{\alpha}^0} - E_{J_{\alpha}}^{m_{\alpha}}} \otimes \phi_{J_2}^{m_2^0} \otimes \dots \otimes \phi_{J_{n_Q}}^{m_{n_Q}^0} | O | \phi_{J_1}^{m_1'} \otimes \phi_{J_2}^{m_2^0} \otimes \dots \otimes \phi_{J_{n_Q}}^{m_{n_Q}^0} \rangle \right) \quad (5) \end{aligned}$$

where the effective operator  $\langle \Psi | H | \Psi' \rangle^{\dagger}$ , is the Hermitian conjugate of,  $\langle \Psi | H | \Psi' \rangle$  acting on the left on  $J_1$ -wave functions. Just like for the Hamiltonian, the summation on components 2 to  $n_Q$  basis functions can be truncated according to an energy criterium, Eq. (2).

## 2.2 GMFCI calculation for methane

Let us number the twelve ro-vibrational DOF of methane. Number 1 is the symmetric stretching DOF of mode  $\nu_1$  carrying an  $A_1$  irreducible representation (irrep.) of the group  $T_d$ , 2 and 3 the bending DOF of mode  $\nu_2$  carrying an  $E$  irrep., 4, 5 and 6 the stretching DOF of mode  $\nu_3$  carrying a  $F_2$  irrep., 7, 8 and 9 the bending DOF carrying also a  $F_2$  irrep., 10, 11 and 12 the three Euler angles [63]. The GMFCI calculation we have performed is the actually combination of VMFCI and perturbation theory used in [29]. It can be denoted compactly as,

$$\begin{aligned}
 & (HO, HO, HO, HO, SYM - TOP) / \\
 & (\{1\}_{[14]}^{(1,1,1,0)}, \{2, 3\}_{[16]}^{(1,1,1,0)}, \{4, 5, 6\}_{[14]}^{(1,1,1,0)}, \{7, 8, 9\}_{[16]}^{(1,1,1,0)}, \{10, 11, 12\})^2 / \\
 & (\{1\}^{(1,1,1,0)}, \{2, 3\}^{(1,1,1,0)}, \{4, 5, 6\}_{[598]}^{(1,1,1,0)}, \{7, 8, 9\}_{[691]}^{(1,1,1,0)}, \{10, 11, 12\})^6 / \\
 & (\{1, 4, 5, 6\}_{(48000)}^{(1,1,0)}, \{2, 3\}^{(1,1,1,0)}, \{7, 8, 9\}^{(1,1,1,0)}, \{10, 11, 12\}) / \\
 & (\{1, 4, 5, 6\}_{(22000)}^{(1,1,0)}, \{2, 3\}_{(20000)}^{(1,1,0)}, \{7, 8, 9\}^{(1,1,0)}, \{10, 11, 12\}) / \\
 & (\{1, 2, 3, 4, 5, 6, 7, 8, 9\}_{(19318)}^{(0)}, \{10, 11, 12\}) / \\
 & (\{1, 2, 3, 4, 5, 6, 7, 8, 9\}, \{10, 11, 12\})_{[J=30]}^{(4)(8281, 8281, 4160)}. \tag{6}
 \end{aligned}$$

The notation means the following:

- The first line specifies the basis sets used for the different DOF. Here, we have used standard harmonic oscillator ‘‘HO’’ basis functions, whose frequencies were derived from the quartic force constant of the PES, for the 9 internal DOF. For the Euler angles, we have used the basis made of eigenfunctions of a symmetric rigid rotator Hamiltonian [64], namely, a ‘‘SYM-TOP’’ basis.

- Each of the other lines describes a GMFCI step as performed in CONVIV, or, when an exponent, ‘‘n’’, follows the last closing parenthesis, as on lines 2 and 3 of expression (6), a GMFCI step iterated  $n$ -times with identical partition, truncations and GMF perturbation orders. Iterating a GMFCI step permits to achieve MF self-consistency as in the vibrational self-consistent field method. The partition of the step is given in parentheses, the subsets of DOF making the partition being given in curly brackets. For example, lines 2 and 3 correspond to contracting degenerate components of internal modes together,



and Euler angles together. In lines 4 and 5, all the stretching modes are contracted together. Finally, in lines 6 and 7, all internal modes are contracted together: it is an instance of the vibrational configuration interaction (VCI) method.

- The superscripts of a curly bracket correspond to the orders of the GMF due to DOF in spectator contractions, when the DOF inside the curly brackets are active. Since the GMF is given by the spectator ground states of the previous step, there are as many order indices as there are spectator contractions at the previous step. For example, on the third line, the contraction  $\{2, 3\}^{(1,1,1,0)}$  indicates that the GMFCI calculation, when the  $E$ -mode is active, is performed with order 1 GMF, (that is the usual MF), from spectator contractions  $\{1\}$ ,  $\{4, 5, 6\}$ ,  $\{7, 8, 9\}$  and order 0, (that is no mean field), from contraction  $\{10, 11, 12\}$ . So, there are four orders specified, whereas there are only three spectator contractions, DOF  $\{1\}$  and  $\{4, 5, 6\}$  being contracted at this step.

- When a proper GMF is used, that is when the GMF order,  $m$ , is more than 1, such as in line 7, the order index may have  $(m - 1)$  numbers as subscript. These numbers describe the truncations on spectator states for the sums appearing in perturbative corrective terms. For example, if the order  $m = 2$ , the sum of Eq. (4), that is in principle infinite, will be truncated in practice, according to one number specified as subscript. By convention, when the numbers of the subscript are in square brackets, the truncation is done according to function indices, (that is to say, according to restrictions on general quantum numbers), when it is in parentheses, the truncation is done according to wave numbers, (that is to say, according to thresholds on eigenvalues). For example, on line 7,  $\{10, 11, 12\}^{(4)(8281, 8281, 4160)}$  means that the sums in second and third order, effective Hamiltonian, corrective terms are limited to the 8281 first spectator (that is to say, vibrational, here,) functions above the ground state, while at order four, only 4160 basis functions are used.

- The same convention is used for the curly bracket subscripts. However, in this case, the numbers specify truncations on the product basis functions of the active contraction, instead of spectator contractions. On line 2, the integers in square brackets correspond to the maximum number,  $M_{J_\alpha}^{max}$ , of degenerate HO quanta that appear in the product basis set of Eq.(1),  $\sum_{I_\gamma \subseteq J_\alpha} m_\gamma < M_{J_\alpha}^{max}$ , (in this particular case, this criteria is more convenient than the energy criterium of Eq.(2)). On line 3, the subscripts means that 599 product basis functions were retained for the stretching mode  $\nu_3$ , and 692 for the bending mode  $\nu_4$ ,

(recall that the ground states are always associated to quantum number 0). On line 4, 5 and 6, the subscripts refer to a truncation on the sum of eigenvalues, Eq. (2). However, we use in fact wave number thresholds in  $\text{cm}^{-1}$ , for the eigenvalue differences with respect to the ground state eigenvalues. For example, at line 4, the subscript of the stretching contraction means that we only retain in the product basis sets the functions whose sum of component wave numbers are less than  $48000 \text{ cm}^{-1}$  above the ZPE. Finally, on line 7, the subscript means that SYM-TOP basis functions up to rotational quantum number [ $J = 30$ ] have been used.

- For the calculation of the effective dipole moment transition elements, a second order expansion has been used. The summations in both first (see Eq. (5)) and second order terms were truncated at the  $8282^{\text{th}}$  vibrational Hamiltonian eigenfunction.

All these details were required to fully specify our GMFCI calculation. All the adjustable parameters have clear physical meanings. Their large number is related to the great flexibility of GMFCI calculations.

### 3 New DMS and resulting forbidden spectra

In the present work, we have only considered the DMS calculated at the highest level of electronic theory of Ref. [29], that is, the full electron MRCI [65,66]/ACV5Z [67,68]. A multi-reference calculation is compulsory to properly describe the electronic GS wave functions where several Slater determinant codominates, which usually occurs away from the equilibrium geometry, at nuclear configurations located on chemical reaction channels. The ACV5Z basis set is perfectly suited to describe core and core-valence correlations, which should not be neglected in high accuracy calculation of geometry sensitive observables, such as the electric dipole moment.

Our basis set is larger than those used in recent similar studies, hence the limited number of grid points. Each point corresponds to a nuclear configuration directly expressed in terms of mass-weighted Cartesian normal coordinates. The grid has been designed according to the spatial extension of the harmonic vibrational GS wave function. The equilibrium geometry and normal coordinates are those of our previous study. However, an augmented grid of 119 points has been used. It is provided as supplementary material

[70]. These points have been fitted with a complete set of polynomial generators allowed by symmetry up to third order. It includes ten third order terms that were omitted in our previous fit of the body-fixed z-component of the dipole moment. The results are given in Appendix A.

Tab. 1, displays the difference between the fitted dipole moment constants up to second order. The introduction of new grid points and new third order terms hardly affect the first and second order constants. This shows the stability of the least square fit, the variations due to the new points being essentially absorbed by the new and some old third order terms. The comparison of the dipole moment z-component expansion given in Appendix with that of Ref. [29], shows that the third order constants involving  $Q_1$  are unchanged. The new terms involving the E-mode coordinates have limited influence on the old ones. This is in contrast with what occurs for the  $F_2$  modes, where the introduction of two new terms coupling  $Q_{3z}$  and  $Q_{4z}$  results in the change of sign of two old third order constants.

The whole 9 dimensional DMS is hard to apprehend. Limiting ourselves to the infra-red (IR) active modes, Figs. (1) and (2), display cuts of the z-component DMS along coordinates which dominates the contribution to the intensity calculations. The upper panel of Fig. (1) shows that the DMS curves along the  $Q_{3z}$  and  $Q_{4z}$  are close to straight lines over the range of nuclear configurations, where the GS wave function is expected to have a significant weight (the reduced masses are  $\sim 69.4$  au and  $\sim 163.2$  au for respectively  $Q_{3z}$  and  $Q_{4z}$ ). So, it is not surprising that a third order fit is able to reproduce their shape quite faithfully. This appears more clearly in the lower panel: there are oscillations in the fit errors but their amplitudes are less than about  $2.10^{-5}$  au, i.e.  $\sim 5.10^{-5}$  Debye. The 2-dimensional section of Fig. (2) confirms the flatness of the DMS in the  $(Q_{3z}, Q_{4z})$  plane. The lower panel shows that, the largest discrepancies in the fit lie along the  $Q_{4z}$ -axis, and corresponds to the extreme points of Fig. (1), panel (b).

Let us look now at the bending modes involved in the lowest excited polyad, namely the Dyad. One can see by inspecting the polynomial expression given in Appendix A, that, the two most important bending coordinates in the z-component DMS expansion are  $Q_{2a}$  and  $Q_{4z}$ . Figure (3) present a 2D-cut of the z-component DMS along these coordinates. The lower panel shows that the fit errors are in the same range as in Figs. (1) and (2). At fixed  $Q_{4z}$ , the curves are quadratic with curvature proportional to  $Q_{4z}$ . The Dyad

wave functions have a strong harmonic character, as seen from the dominant weight in wave function expansions in successive GMFCI steps. Although the amplitude of first excited harmonic wave function is a factor  $\sqrt{3}$  wider than that of the harmonic GS, it is anticipated that our DMS should still be acceptable to calculate transition moments between GS and Dyad states. For example, integrating the absolute value of the fit error on  $Q_{4z}$  would give an upper bound of  $\sim 5.10^{-3}$  Debye. However, the oscillatory behaviour of the error curve on both sides of the origin, that is to say, where first excited harmonic basis functions have constant sign, suggests a much lower upper bound, probably below the milliDebye.

Regarding vibrational GS, rotational transitions, Tab. 2 presents the intensities obtained from the new DMS along those from the old one. The formulas used to derive them from the GMFCI dipole moment transition matrix element have been explained in details in [29]. The new intensities are systematically lower by about 1 percent with respect to the formerly published values. The average relative error with respect to the (reliable) observed intensities changes from 5.85% to 5.93%, which is insignificant given the targeted level of accuracy. In particular, this is well within the experimental average relative uncertainty of 10.62%. So, this supports *a posteriori* the reliability of our DMS for the calculation of the vibrational ground state intensities, despite the fact that it is limited to third order. Updated Q- and R-branch line lists are given as supplementary material [70].

## 4 Conclusion

The present work updates the ACV5Z results of Ref. [29] by including some third order terms that were omitted in the DMS. It permits to assess the influence of the latter terms and the robustness of our intensity predictions.

Recent variational calculations of methane rovibrational line positions and/or intensities [23,24,34] can be seen as particular cases of the MFCI approach, since they correspond to order 1 of our quasi-degenerate perturbation theory [35]. For example, the calculations referred to as “P=n” in [34] amount to performing order 1 perturbation calculations with all vibrational states with polyad number less or equal to n, considered as quasi-degenerate. Similarly, the variational procedure with vibrational subspace compression

of Rey et al. referred to as  $F(n)$  in [23,24] is, in fact, an order 1 perturbation calculation with all vibrational states with  $F = \sum_{i=1}^4 \nu_i$  less than  $n$ , considered as quasi-degenerate. The equivalence has been verified numerically in [71]. The intensities predicted are in very good agreement with existing spectroscopic data up to the  $9300\text{cm}^{-1}$  [24]. However, their rms with respect to the SOLEIL experiment data [13] is in average of 13% [23], compared to the 6% obtained in the present work. In contrast, their rms with respect to older data in HITRAN 2008 [72] is only of 2.5%.

The major factor determining the quality of the DMS is the electronic calculation, provided a sensible choice of grid points and fitting function is made. The All-Electron-MRCI/ACV5Z level of theory represents a good compromise between accuracy and computational cost on an HP cluster platform 4000. It is arguably the highest level of electronic theory employed so far to calculate a DMS for methane.

Although we used a limited number of *ab initio* points and only a third order polynomial expansion for constructing our DMS, it appears sufficient for our purpose, since over the relevant range of nuclear configurations, the DMS is a rather tamed function, with only gentle variations. In fact, the present work shows that, even the third order terms that were omitted in our previous DMS have little influence on the forbidden spectrum intensities of methane. We anticipate that the present DMS will still be useful to deal with the GS-Dyad and Dyad-Dyad spectra.

However, the GMFCI method has allowed us to calculate accurate ro-vibrational energy levels for higher polyads of methane [71]. In view of calculating transition intensities between these levels, we are considering extending the present DMS, with the help of computational invariant theory techniques [73] to derive symmetry-adapted polynomial basis of arbitrary orders in the most economical way. A tabulation of covariant polynomial basis sets for all irreducible representation of methane symmetry group is underway [74].

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## APPENDIX A: BODY-FIXED DIPOLE MOMENT

We give below the result of a least square fit of the dipole moment z-component grid provided as supplementary material [70]. The dipole moment z-component expansion in Cartesian mass-weighted normal coordinates is in atomic units. Note that the arbitrary phase factors in the definition of the normal coordinates are those corresponding to Gray and Robiette's conventions (Tab. 1 of Ref. [15]). The x- and y-components can be deduced by symmetry.

$$\begin{aligned}
D_z(ACV5Z) = & \\
& -3.54425 \cdot 10^{-3} Q_{3z} + 2.32658 \cdot 10^{-3} Q_{4z} - 5.09773 \cdot 10^{-5} Q_1 Q_{3z} - 5.44507 \cdot 10^{-5} Q_1 Q_{4z} \\
& \quad -3.05546 \cdot 10^{-5} Q_{2a} Q_{3z} + 1.75830 \cdot 10^{-5} Q_{2a} Q_{4z} \\
& \quad -9.14627 \cdot 10^{-5} Q_{3x} Q_{3y} - 5.76126 \cdot 10^{-5} (Q_{3x} Q_{4y} + Q_{3y} Q_{4x}) + 6.15606 \cdot 10^{-5} Q_{4x} Q_{4y} \\
& \quad \quad + 9.81662 \cdot 10^{-8} Q_1^2 Q_{3z} + 2.94314 \cdot 10^{-7} Q_1^2 Q_{4z} \\
& \quad \quad -1.08833 \cdot 10^{-7} Q_1 Q_{2a} Q_{3z} + 8.69156 \cdot 10^{-6} Q_1 Q_{2a} Q_{4z} \\
& -1.12720 \cdot 10^{-7} Q_1 Q_{3x} Q_{3y} - 1.72212 \cdot 10^{-7} Q_1 (Q_{3x} Q_{4y} + Q_{3y} Q_{4x}) - 5.27870 \cdot 10^{-7} Q_1 Q_{4x} Q_{4y} \\
& \quad + 7.53758 \cdot 10^{-8} Q_{3z} (Q_{2a}^2 + Q_{2b}^2) + 5.65204 \cdot 10^{-7} Q_{4z} (Q_{2a}^2 + Q_{2b}^2) \\
& \quad + 1.19100 \cdot 10^{-8} Q_{3z} (Q_{2a}^2 - Q_{2b}^2) + 4.17843 \cdot 10^{-7} Q_{4z} (Q_{2a}^2 - Q_{2b}^2) \\
& -1.50088 \cdot 10^{-6} Q_{2a} Q_{3x} Q_{3y} - 5.95730 \cdot 10^{-8} Q_{2a} (Q_{3x} Q_{4y} + Q_{3y} Q_{4x}) - 1.30784 \cdot 10^{-8} Q_{2a} Q_{4x} Q_{4y} \\
& \quad -2.83012 \cdot 10^{-7} Q_{2b} (Q_{3x} Q_{4y} - Q_{3y} Q_{4x}) + 2.53769 \cdot 10^{-8} Q_{3z}^3 - 2.80844 \cdot 10^{-7} Q_{4z}^3 \\
& \quad + 2.21245 \cdot 10^{-7} Q_{3z} (Q_{3x}^2 + Q_{3y}^2 + Q_{3z}^2) - 5.93272 \cdot 10^{-7} Q_{4z} (Q_{3x}^2 + Q_{3y}^2 + Q_{3z}^2) \\
& \quad \quad -2.90606 \cdot 10^{-8} Q_{3z} (Q_{3x} Q_{4x} + Q_{3y} Q_{4y} + Q_{3z} Q_{4z}) + 1.35001 \cdot 10^{-7} Q_{3z}^2 Q_{4z} \\
& \quad \quad + 4.07208 \cdot 10^{-7} Q_{4z} (Q_{3x} Q_{4x} + Q_{3y} Q_{4y} + Q_{3z} Q_{4z}) - 1.14485 \cdot 10^{-6} Q_{3z} Q_{4z}^2 \\
& \quad + 4.90883 \cdot 10^{-7} Q_{3z} (Q_{4x}^2 + Q_{4y}^2 + Q_{4z}^2) + 4.11389 \cdot 10^{-7} Q_{4z} (Q_{4x}^2 + Q_{4y}^2 + Q_{4z}^2)
\end{aligned}$$

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## TABLES

|  | This work  | [29]      | [46]        | [47]        |
|--|------------|-----------|-------------|-------------|
| $\frac{\partial D_z}{\partial q_{3z}}$                   | -0.075013  | -0.075010 | -0.07561(4) | -0.0754(17) |
| $\frac{\partial D_z}{\partial q_{4z}}$                   | +0.0755477 | +0.075561 | +0.07950(8) | +0.0808(16) |
| $\frac{\partial^2 D_z}{\partial q_1 \partial q_{3z}}$    | -0.009173  | -0.009173 | N/A         | -0.0009(01) |
| $\frac{\partial^2 D_z}{\partial q_1 \partial q_{4z}}$    | -0.015024  | -0.015024 | -0.01657    | -0.0145(12) |
| $\frac{\partial^2 D_z}{\partial q_{2a} \partial q_{3z}}$ | -0.007646  | -0.007646 | -0.00800    | -0.0080(03) |
| $\frac{\partial^2 D_z}{\partial q_{2a} \partial q_{4z}}$ | +0.006798  | +0.006798 | +0.01286    | +0.0060(09) |
| $\frac{\partial^2 D_z}{\partial q_{3x} \partial q_{3y}}$ | -0.016135  | -0.016121 | N/A         | -0.0310(15) |
| $\frac{\partial^2 D_z}{\partial q_{3x} \partial q_{4y}}$ | -0.015585  | -0.015587 | -0.01611    | -0.0163(06) |
| $\frac{\partial^2 D_z}{\partial q_{4x} \partial q_{4y}}$ | +0.025537  | +0.025528 | +0.02736    | +0.0337(09) |

Table 1

Electric dipole moment  $z$ -component first and second derivatives of  $^{12}\text{CH}_4$  (in Debye) for adimensional normal coordinates. Values obtained from our new fit are compared to those of [29]. Note, that some of the latter were slightly wrong due to a “copy-paste” error and are corrected here. Similarly, the first derivatives given in  $\text{D}\cdot\text{\AA}^{-1}$  in our previous study should have been  $\frac{\partial D_z}{\partial Q_{3z}} = -0.7264$ ;  $\frac{\partial D_z}{\partial Q_{4z}} = +0.4772$  instead of the published values, so slightly closer to the values of [48]. The sign convention for the normal coordinates is that of Gray and Robiette [15], so the signs of the derivatives including  $q_{2a}$  and  $q_{2b}$  of Loete [46] have been changed accordingly, (see also Tab. 4 of Mourbat et al. [47]).

| Obs <sup>1</sup> | $\nu_{\eta\eta'}$ |             | $S_{\eta\eta'}$ |        |           |                         |           |                         | $J, \text{ irrep.}$ |         |    |    |
|------------------|-------------------|-------------|-----------------|--------|-----------|-------------------------|-----------|-------------------------|---------------------|---------|----|----|
|                  | Cal.              | $Obs - Cal$ | Obs [13]        | Unc. % | [29]      | $\frac{Obs-Cal}{Cal}$ % | This work | $\frac{Obs-Cal}{Cal}$ % | $\eta$              | $\eta'$ |    |    |
| 83.56549         | 83.56381          | 1.68E-03    | 7.909E-26       | 18.0   | 7.965E-26 | -0.7                    | 7.881E-26 | 0.4                     | 7                   | E       | 8  | E  |
| 83.56913         | 83.56746          | 1.67E-03    | 1.366E-25       | 34.0   | 1.364E-25 | 0.2                     | 1.349E-25 | 1.3                     | 7                   | F2      | 8  | F1 |
| 83.57622         | 83.57456          | 1.66E-03    | 2.940E-25       | 3.3    | 2.992E-25 | -1.7                    | 2.960E-25 | -0.7                    | 7                   | A2      | 8  | A1 |
| 93.91555         | 93.91360          | 1.95E-03    | 1.851E-25       | 6.9    | 1.713E-25 | 8.0                     | 1.695E-25 | 9.2                     | 8                   | F1      | 9  | F2 |
| 93.93107         | 93.92913          | 1.94E-03    | 2.259E-25       | 16.0   | 2.164E-25 | 4.4                     | 2.141E-25 | 5.5                     | 8                   | F2      | 9  | F1 |
| 104.22470        | 104.22244         | 2.26E-03    | 3.375E-25       | 13.0   | 3.358E-25 | 0.5                     | 3.322E-25 | 1.6                     | 9                   | A1      | 10 | A2 |
| 104.24737        | 104.24513         | 2.24E-03    | 2.187E-25       | 3.9    | 2.249E-25 | -2.8                    | 2.226E-25 | -1.8                    | 9                   | F1      | 10 | F2 |
| 104.25229        | 104.25006         | 2.23E-03    | 1.326E-25       | 33.0   | 1.703E-25 | -22.1                   | 1.685E-25 | -21.3                   | 9                   | E       | 10 | E  |
| 104.31507        | 104.31292         | 2.15E-03    | 2.432E-25       | 5.8    | 2.869E-25 | -15.2                   | 2.838E-25 | -14.3                   | 9                   | F1      | 10 | F2 |
| 104.31924        | 104.31709         | 2.15E-03    | 2.579E-25       | 11.0   | 2.645E-25 | -2.5                    | 2.617E-25 | -1.5                    | 9                   | F2      | 10 | F1 |
| 104.35000        | 104.34789         | 2.11E-03    | 5.639E-25       | 16.0   | 5.745E-25 | -1.8                    | 5.684E-25 | -0.8                    | 9                   | A2      | 10 | A1 |
| 104.36479        | 104.36270         | 2.09E-03    | 5.884E-26       | 23.0   | 5.561E-26 | 5.8                     | 5.503E-26 | 6.9                     | 9                   | F1      | 10 | F2 |
| 104.39473        | 104.39266         | 2.07E-03    | 5.951E-26       | 10.0   | 6.498E-26 | -8.4                    | 6.429E-26 | -7.4                    | 9                   | F2      | 10 | F1 |
| 114.52344        | 114.52087         | 2.57E-03    | 2.267E-25       | 20.0   | 2.297E-25 | -1.3                    | 2.273E-25 | -0.3                    | 10                  | F1      | 11 | F2 |
| 114.53532        | 114.53276         | 2.56E-03    | 2.576E-25       | 18.0   | 2.670E-25 | -3.5                    | 2.642E-25 | -2.5                    | 10                  | F2      | 11 | F1 |
| 114.61438        | 114.61192         | 2.46E-03    | 1.686E-25       | 7.1    | 1.873E-25 | -10.0                   | 1.853E-25 | -9.0                    | 10                  | E       | 11 | E  |
| 114.61714        | 114.61467         | 2.47E-03    | 2.930E-25       | 6.1    | 2.893E-25 | 1.3                     | 2.862E-25 | 2.4                     | 10                  | F1      | 11 | F2 |
| 114.63941        | 114.63697         | 2.44E-03    | 7.343E-25       | 28.0   | 7.155E-25 | 2.6                     | 7.079E-25 | 3.7                     | 10                  | A1      | 11 | A2 |
| 114.67144        | 114.66904         | 2.40E-03    | 3.632E-25       | 7.9    | 3.652E-25 | -0.6                    | 3.614E-25 | 0.5                     | 10                  | F2      | 11 | F1 |
| 114.69262        | 114.69025         | 2.37E-03    | 6.598E-26       | 24.0   | 5.628E-26 | 17.2                    | 5.569E-26 | 18.5                    | 10                  | F1      | 11 | F2 |
| 114.87932        | 114.87718         | 2.14E-03    | 3.423E-26       | 16.0   | 4.862E-26 | -29.6                   | 4.811E-26 | -28.9                   | 10                  | F2      | 11 | F1 |
| 124.76275        | 124.75985         | 2.90E-03    | 1.632E-25       | 7.8    | 1.575E-25 | 3.6                     | 1.559E-25 | 4.7                     | 11                  | E       | 12 | E  |
| 124.77117        | 124.76827         | 2.90E-03    | 2.414E-25       | 7.6    | 2.434E-25 | -0.8                    | 2.409E-25 | 0.2                     | 11                  | F2      | 12 | F1 |
| 124.78389        | 124.78101         | 2.88E-03    | 4.350E-25       | 3.6    | 4.384E-25 | -0.8                    | 4.338E-25 | 0.3                     | 11                  | A2      | 12 | A1 |
| 124.86687        | 124.86407         | 2.80E-03    | 2.760E-25       | 8.7    | 2.710E-25 | 1.9                     | 2.681E-25 | 2.9                     | 11                  | F2      | 12 | F1 |
| 124.90983        | 124.90707         | 2.76E-03    | 3.801E-25       | 5.4    | 3.856E-25 | -1.4                    | 3.815E-25 | -0.4                    | 11                  | F1      | 12 | F2 |
| 124.95360        | 124.95089         | 2.71E-03    | 2.366E-25       | 5.2    | 2.315E-25 | 2.2                     | 2.290E-25 | 3.3                     | 11                  | E       | 12 | E  |
| 124.95887        | 124.95616         | 2.71E-03    | 3.365E-25       | 2.9    | 3.253E-25 | 3.4                     | 3.219E-25 | 4.5                     | 11                  | F1      | 12 | F2 |
| 125.28147        | 125.27915         | 2.32E-03    | 1.230E-25       | 16.0   | 1.097E-25 | 12.2                    | 1.085E-25 | 13.4                    | 11                  | A2      | 12 | A1 |
| 134.95865        | 134.95539         | 3.26E-03    | 2.026E-25       | 5.1    | 2.118E-25 | -4.3                    | 2.096E-25 | -3.3                    | 12                  | F1      | 13 | F2 |
| 134.97498        | 134.97175         | 3.23E-03    | 2.127E-25       | 1.7    | 2.196E-25 | -3.2                    | 2.173E-25 | -2.1                    | 12                  | F2      | 13 | F1 |
| 135.06476        | 135.06157         | 3.19E-03    | 3.871E-25       | 2.1    | 3.934E-25 | -1.6                    | 3.893E-25 | -0.6                    | 12                  | A2      | 13 | A1 |
| 135.12831        | 135.12520         | 3.11E-03    | 2.870E-25       | 1.8    | 2.811E-25 | 2.1                     | 2.781E-25 | 3.2                     | 12                  | F2      | 13 | F1 |
| 135.13616        | 135.13306         | 3.10E-03    | 2.268E-25       | 4.5    | 2.255E-25 | 0.6                     | 2.231E-25 | 1.7                     | 12                  | E       | 13 | E  |
| 135.18891        | 135.18584         | 3.07E-03    | 2.471E-25       | 6.8    | 2.579E-25 | -4.2                    | 2.552E-25 | -3.2                    | 12                  | F2      | 13 | F1 |

|           |           |          |           |      |           |       |           |       |    |    |    |    |
|-----------|-----------|----------|-----------|------|-----------|-------|-----------|-------|----|----|----|----|
| 135.24148 | 135.23846 | 3.02E-03 | 5.208E-25 | 4.6  | 5.334E-25 | -2.4  | 5.278E-25 | -1.3  | 12 | A1 | 13 | A2 |
| 135.29673 | 135.29379 | 2.94E-03 | 8.246E-26 | 12.0 | 7.948E-26 | 3.8   | 7.864E-26 | 4.9   | 12 | F2 | 13 | F1 |
| 135.65576 | 135.65325 | 2.51E-03 | 3.389E-26 | 4.9  | 4.019E-26 | -15.7 | 3.977E-26 | -14.8 | 12 | F2 | 13 | F1 |
| 135.73905 | 135.73659 | 2.45E-03 | 3.190E-26 | 2.4  | 3.023E-26 | 5.5   | 2.991E-26 | 6.7   | 12 | A1 | 13 | A2 |
| 145.09922 | 145.09559 | 3.63E-03 | 2.920E-25 | 1.1  | 2.833E-25 | 3.1   | 2.803E-25 | 4.2   | 13 | A1 | 14 | A2 |
| 145.11543 | 145.11182 | 3.61E-03 | 1.761E-25 | 9.1  | 1.729E-25 | 1.8   | 1.711E-25 | 2.9   | 13 | F1 | 14 | F2 |
| 145.12193 | 145.11832 | 3.60E-03 | 1.244E-25 | 16.0 | 1.173E-25 | 6.1   | 1.161E-25 | 7.1   | 13 | E  | 14 | E  |
| 145.29512 | 145.29162 | 3.50E-03 | 2.128E-25 | 5.0  | 2.125E-25 | 0.1   | 2.103E-25 | 1.2   | 13 | F2 | 14 | F1 |
| 145.31437 | 145.31088 | 3.49E-03 | 2.656E-25 | 6.7  | 2.653E-25 | 0.1   | 2.625E-25 | 1.2   | 13 | F1 | 14 | F2 |
| 145.38186 | 145.37839 | 3.47E-03 | 1.930E-25 | 4.4  | 1.956E-25 | -1.3  | 1.936E-25 | -0.3  | 13 | F2 | 14 | F1 |
| 145.38969 | 145.38624 | 3.45E-03 | 1.388E-25 | 11.0 | 1.445E-25 | -3.9  | 1.430E-25 | -2.9  | 13 | E  | 14 | E  |
| 145.44356 | 145.44016 | 3.40E-03 | 5.557E-25 | 2.8  | 5.658E-25 | -1.8  | 5.599E-25 | -0.8  | 13 | A2 | 14 | A1 |
| 145.45911 | 145.45571 | 3.40E-03 | 2.502E-25 | 9.6  | 2.519E-25 | -0.7  | 2.492E-25 | 0.4   | 13 | F1 | 14 | F2 |
| 145.53228 | 145.52900 | 3.28E-03 | 7.812E-26 | 11.0 | 7.300E-26 | 7.0   | 7.223E-26 | 8.2   | 13 | F2 | 14 | F1 |
| 155.20508 | 155.20108 | 4.00E-03 | 1.174E-25 | 13.0 | 1.271E-25 | -7.6  | 1.258E-25 | -6.7  | 14 | F1 | 15 | F2 |
| 155.21702 | 155.21303 | 3.99E-03 | 1.238E-25 | 3.7  | 1.295E-25 | -4.4  | 1.281E-25 | -3.4  | 14 | F2 | 15 | F1 |
| 155.43277 | 155.42886 | 3.91E-03 | 1.694E-25 | 14.0 | 1.844E-25 | -8.1  | 1.825E-25 | -7.2  | 14 | F1 | 15 | F2 |
| 155.46268 | 155.45880 | 3.88E-03 | 3.485E-25 | 4.5  | 3.499E-25 | -0.4  | 3.462E-25 | 0.7   | 14 | A1 | 15 | A2 |
| 155.51376 | 155.50982 | 3.94E-03 | 1.512E-25 | 6.9  | 1.522E-25 | -0.6  | 1.506E-25 | 0.4   | 14 | F1 | 15 | F2 |
| 155.60915 | 155.60533 | 3.82E-03 | 2.216E-25 | 19.0 | 2.419E-25 | -8.4  | 2.394E-25 | -7.4  | 14 | F2 | 15 | F1 |
| 155.62286 | 155.61899 | 3.87E-03 | 1.143E-25 | 22.0 | 1.175E-25 | -2.8  | 1.163E-25 | -1.7  | 14 | E  | 15 | E  |
| 155.63624 | 155.63239 | 3.85E-03 | 1.896E-25 | 11.0 | 1.790E-25 | 5.9   | 1.771E-25 | 7.1   | 14 | F2 | 15 | F1 |
| 156.23286 | 156.22982 | 3.04E-03 | 5.215E-26 | 6.2  | 6.036E-26 | -13.6 | 5.972E-26 | -12.7 | 14 | A1 | 15 | A2 |
| 165.24669 | 165.24230 | 4.39E-03 | 6.758E-26 | 11.0 | 5.817E-26 | 16.2  | 5.756E-26 | 17.4  | 15 | E  | 16 | E  |
| 165.25216 | 165.24778 | 4.38E-03 | 9.349E-26 | 9.3  | 8.761E-26 | 6.7   | 8.669E-26 | 7.8   | 15 | F2 | 16 | F1 |
| 165.26211 | 165.25775 | 4.36E-03 | 1.488E-25 | 6.1  | 1.477E-25 | 0.8   | 1.461E-25 | 1.8   | 15 | A2 | 16 | A1 |
| 165.48246 | 165.47805 | 4.41E-03 | 1.189E-25 | 16.0 | 1.251E-25 | -4.9  | 1.237E-25 | -3.9  | 15 | F2 | 16 | F1 |
| 165.52922 | 165.52488 | 4.34E-03 | 1.403E-25 | 16.0 | 1.350E-25 | 3.9   | 1.336E-25 | 5.0   | 15 | F1 | 16 | F2 |
| 165.57721 | 165.57272 | 4.49E-03 | 1.793E-25 | 9.1  | 1.745E-25 | 2.7   | 1.727E-25 | 3.8   | 15 | A1 | 16 | A2 |
| 165.71246 | 165.70816 | 4.30E-03 | 1.466E-25 | 19.0 | 1.381E-25 | 6.2   | 1.366E-25 | 7.3   | 15 | F1 | 16 | F2 |
| 165.71962 | 165.71531 | 4.31E-03 | 1.055E-25 | 9.8  | 1.107E-25 | -4.7  | 1.095E-25 | -3.7  | 15 | E  | 16 | E  |
| 165.72524 | 165.72079 | 4.45E-03 | 1.011E-25 | 14.0 | 1.038E-25 | -2.6  | 1.027E-25 | -1.6  | 15 | F1 | 16 | F2 |
| 165.76086 | 165.75646 | 4.40E-03 | 1.348E-25 | 8.8  | 1.198E-25 | 12.5  | 1.186E-25 | 13.7  | 15 | F2 | 16 | F1 |
| 165.80353 | 165.79916 | 4.37E-03 | 2.266E-25 | 10.0 | 2.155E-25 | 5.2   | 2.132E-25 | 6.3   | 15 | A2 | 16 | A1 |
| 175.23026 | 175.22546 | 4.80E-03 | 6.572E-26 | 13.0 | 5.536E-26 | 18.7  | 5.478E-26 | 20.0  | 16 | F1 | 17 | F2 |
| 175.23920 | 175.23442 | 4.78E-03 | 5.148E-26 | 9.2  | 5.565E-26 | -7.5  | 5.507E-26 | -6.5  | 16 | F2 | 17 | F1 |
| 175.47690 | 175.47191 | 4.99E-03 | 1.414E-25 | 11.0 | 1.336E-25 | 5.8   | 1.322E-25 | 7.0   | 16 | A2 | 17 | A1 |
| 175.52873 | 175.52387 | 4.86E-03 | 8.728E-26 | 32.0 | 8.248E-26 | 5.8   | 8.161E-26 | 6.9   | 16 | F2 | 17 | F1 |

|  |                  |                 |                  |                  |                  |             |                  |             |           |          |           |          |
|--|------------------|-----------------|------------------|------------------|------------------|-------------|------------------|-------------|-----------|----------|-----------|----------|
| 175.54531  | 175.54047        | 4.84E-03        | 6.748E-26        | 42.0             | 5.762E-26        | 17.1        | 5.702E-26        | 18.3        | 16        | E        | 17        | E        |
| 175.75462  | 175.74976        | 4.86E-03        | 8.168E-26        | 20.0             | 8.286E-26        | -1.4        | 8.199E-26        | -0.4        | 16        | F1       | 17        | F2       |
| 175.77014  | 175.76523        | 4.91E-03        | 1.052E-25        | 3.7              | 1.003E-25        | 4.8         | 9.929E-26        | 6.0         | 16        | F2       | 17        | F1       |
| 175.77944  | 175.77428        | 5.16E-03        | 5.211E-26        | 14.0             | 6.232E-26        | -16.4       | 6.166E-26        | -15.5       | 16        | F1       | 17        | F2       |
| 175.80961  | 175.80452        | 5.09E-03        | 4.971E-26        | 21.0             | 4.844E-26        | 2.6         | 4.793E-26        | 3.7         | 16        | E        | 17        | E        |
| 175.88877  | 175.88369        | 5.08E-03        | 8.307E-26        | 10.0             | 7.934E-26        | 4.7         | 7.850E-26        | 5.8         | 16        | F2       | 17        | F1       |
| 175.91944  | 175.91453        | 4.91E-03        | 1.914E-25        | 7.6              | 1.996E-25        | -4.1        | 1.975E-25        | -3.1        | 16        | A1       | 17        | A2       |
| 185.14892  | 185.14369        | 5.23E-03        | 5.447E-26        | 2.2              | 5.432E-26        | 0.3         | 5.375E-26        | 1.3         | 17        | A1       | 18        | A2       |
| 185.15627  | 185.15108        | 5.19E-03        | 2.560E-26        | 4.7              | 3.269E-26        | -21.7       | 3.235E-26        | -20.9       | 17        | F1       | 18        | F2       |
| <i>185.15978</i>                                       | <i>185.15459</i> | <i>5.19E-03</i> | <i>3.178E-26</i> | <i>6.0</i>       | <i>2.183E-26</i> | <i>45.6</i> | <i>2.161E-26</i> | <i>47.1</i> | <i>17</i> | <i>E</i> | <i>18</i> | <i>E</i> |
| 185.72296  | 185.71736        | 5.60E-03        | 3.828E-26        | 3.0              | 3.538E-26        | 8.2         | 3.501E-26        | 9.3         | 17        | E        | 18        | E        |
| 185.75272  | 185.74712        | 5.60E-03        | 5.439E-26        | 3.8              | 5.619E-26        | -3.2        | 5.560E-26        | -2.2        | 17        | F2       | 18        | F1       |
| 185.77760  | 185.77164        | 5.96E-03        | 4.182E-26        | 5.6              | 4.018E-26        | 4.1         | 3.976E-26        | 5.2         | 17        | F2       | 18        | F1       |
| 185.81261  | 185.80712        | 5.49E-03        | 1.109E-25        | 5.7              | 1.125E-25        | -1.4        | 1.114E-25        | -0.4        | 17        | A2       | 18        | A1       |
| 185.95843  | 185.95276        | 5.67E-03        | 6.835E-26        | 16.0             | 6.932E-26        | -1.4        | 6.859E-26        | -0.3        | 17        | F1       | 18        | F2       |
| 195.36349  | 195.35732        | 6.17E-03        | 1.843E-26        | 5.1              | 1.842E-26        | 0.1         | 1.823E-26        | 1.1         | 18        | E        | 19        | E        |
| 195.38122  | 195.37512        | 6.10E-03        | 2.301E-26        | 4.3              | 2.789E-26        | -17.5       | 2.760E-26        | -16.6       | 18        | F1       | 19        | F2       |
| 195.41070  | 195.40470        | 6.00E-03        | 4.622E-26        | 10.0             | 4.793E-26        | -3.6        | 4.743E-26        | -2.6        | 18        | A1       | 19        | A2       |
| 195.69065  | 195.68368        | 6.97E-03        | 4.795E-26        | 3.3              | 3.738E-26        | 28.3        | 3.699E-26        | 29.6        | 18        | A2       | 19        | A1       |
| 195.74041  | 195.73417        | 6.24E-03        | 3.295E-26        | 1.8 <sup>2</sup> | 3.493E-26        | -5.7        | 3.457E-26        | -4.7        | 18        | F2       | 19        | F1       |
| Average of absolute values                             |                  | 3.70E-03        |                  | 10.57            |                  | 6.28        |                  | 6.37        |           |          |           |          |
| Average of absolute values minus italicized transition |                  |                 |                  | 10.62            |                  | 5.85        |                  | 5.93        |           |          |           |          |

Table 2

Comparison with experiment [13] of calculated transition wave numbers and intensities for the R-branch of methane vibrational ground state. Theoretical transition wave numbers,  $\nu_{\eta\eta'}$  in  $\text{cm}^{-1}$  units, were calculated at fourth order of perturbation (second column). Order 2 of perturbation theory has been used to compute effective dipole moments, which in turn, were used to obtain theoretical intensities at 296 K,  $S_{\eta\eta'}$  in  $\text{cm}^{-1}/(\text{molecule}\cdot\text{cm}^{-2})$ . The underlined transition in italics is singled out because it was withdrawn from the fit of the observed spectra, its relative error of 42% being too large.

<sup>1</sup> The line position are taken from Tab.A1 of [13] but actually they were obtained with the STDS code from an effective Hamiltonian fitted on experiments

<sup>2</sup> Jean Vander Auwera, private communication



## FIGURE CAPTIONS

Fig. 1. 1D-sections of the dipole moment z-component along the z-component of the IR active normal coordinates. Gray and Robiette conventions are used to define normal coordinates [15].

Fig. 2. 2D-section of the dipole moment z-component along the z-component of the IR active normal coordinates.

Fig. 3. 2D-section of the dipole moment z-component along two bending coordinates relevant for dyad transitions. Gray and Robiette conventions are used to define normal coordinates [15].