Vibrational transition moments of CH$_4$ from first principles

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New nine-dimensional (9D), ab initio electric dipole moment surfaces (DMSs) of methane in its ground electronic state are presented. The DMSs are computed using an explicitly correlated coupled cluster CCSD(T)-F12 method in conjunction with an F12-optimized correlation consistent basis set of the TZ-family. A symmetrized molecular bond representation is used to parameterize these 9D DMSs in terms of sixth-order polynomials. Vibrational transition moments as well as band intensities for a large number of IR-active vibrational bands of $^{12}$CH$_4$ are computed by vibrationally averaging the ab initio dipole moment components. The vibrational wavefunctions required for these averages are computed variationally using the program TROVE and a new ‘spectroscopic’ $^{12}$CH$_4$ potential energy surface. The new DMSs will be used to produce a hot line list for $^{13}$CH$_4$.

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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 models of the atmospheres of bodies ranging from Titan to brown dwarfs. However, the lack of precise data on methane spectra, particularly at higher temperatures, has severely limited models for atmospheres as diverse as Jupiter[1], exoplanets[2,3] and brown dwarfs[4]. Any temperature-dependent model of the methane spectrum requires a reliable treatment of the associated transition intensities. The construction of a reliable electric dipole moment surface (DMS) which can be used to generate such intensities concerns us in this paper.

Theoretically, a number of methane potential energy surfaces (PES) have been computed ab initio using different levels of theory[5–10]. The surface of Schwenke and Partridge[7] has been used in many benchmark studies as well as for accurate predictions of vibrational and ro-vibrational energies of CH$_4$. However, to our knowledge no accurate and comprehensive ab initio DMSs of CH$_4$ have been published until recently. In some cases ab initio DMSs were used, but not actually provided, for example by Oyanagi et al.[9] (at the CCSD(T)/cc-pVTZ and MP2/cc-pVTZ level of theory) and Warmbier et al.[11] (RCCSD(T)/aug-cc-pVTZ). In 2012 Cassam-Chenai and Lievin[12] presented two reduced-dimension ab initio DMSs of CH$_4$ computed at the MRCC/VQZ and MRCI/ACV5Z levels of theory, respectively on a small grid of 100 geometries and represented them as 3-dimensional Taylor polynomial expansions in terms of normal coordinates. Most recently Nikitin et al.[13] computed ab initio DMSs of methane based on the CCSD(T)/cc-pCVQZ level of theory. The so-called molecular (MB) representation[8,14,15] was used to describe these DMSs analytically and to calculate integrated intensities for seven lower methane polyads, which were found to be in very good agreement with the experimental data. Rey et al.[16] employed these DMSs to simulate the room temperature absorption spectrum of $^{13}$CH$_4$ in the infrared (IR) region. Comparison with experiment demonstrated both the accuracy of the predicted intensities as well as the quality of the underlying ab initio DMSs.

On the experimental side, electric transition dipole moments for CH$_4$ have been the subject of a large number of publications[17–27], where effective dipole moment parameters were derived either through fits to intensity measurements or using perturbation theory. The most recent and comprehensive collection of the effective dipole moment parameters describing excitations in the region up to 4800 cm$^{-1}$ was reported recently by Albert et al.[27]. Many of these studies also provide band intensities. Where possible we use these data to validate our vibrational transition moments as well as our DMSs.

The goal of this paper is to compute, from first principles, the vibrational transition moments and vibrational band intensities of $^{12}$CH$_4$ for a large number of IR-active transitions in the range between 0 and 10 000 cm$^{-1}$. To this end we employed an explicitly correlated (F12) coupled cluster method in conjunction with an F12-optimized basis set to generate nine-dimensional (9D) DMSs of CH$_4$. These surfaces are then vibrationally averaged over vibrational functions of $^{12}$CH$_4$ computed through variationally solving the nuclear motion Schrödinger equation with the TROVE program[28]. This program has been used successfully for accurate and extensive ro-vibrational calculations on different tetrameric
molecules [29–38]. The present work is the first application of TROVE to a larger system. Other variational approaches capable of treating this pentatomic molecule include the Lanczos-method developed by Carrington and Wang [39–42], MULTIMODE [43–46], and GENIUS [47], as well as the methods of Halonen [48], Xie and Tennyson [49,50], Schwenke [51], and Nikitin [52]. The rigorous quantum dynamics algorithm employed by Yu [53,54] should be also mentioned as an alternative accurate approach employed for calculating vibrational energies of CH₄.

The paper is structured as follows. In Section 2 the ab initio method used for generating DMSs of CH₄ is described and an analytical representation for these DMSs is introduced. The PES is detailed in Section 3. The variational approach is described in Section 4 and theoretical vibrational transition moments and band intensities are reported in Section 5. Finally, Section 6 offers some discussion and future prospects.

2. Ab initio calculations

We used the recently proposed explicitly correlated F12 coupled cluster method with single and double excitations including a perturbational estimate of connected triple excitations, CCSD(T)-F12c [55] in conjunction with the corresponding F12-optimized correlation-consistent basis sets, namely aug-cc-pVTZ-F12 [56] (augmented correlation-consistent polarized valence triple-zeta basis) as implemented in Molpro 2010 [57].

Methane has nine vibrational degrees of freedom and thus requires a very extensive grid of geometries in the ab initio calculations. We have computed three ab initio DMSs (one for each Cartesian component) on a fine grid of 114 000 geometries covering the energy range up to 50 000 cm⁻¹ with C–H distances ranging from 0.75 to 2.0 Å, and interbond angles ranging from 50° to 140°. The central finite difference scheme with an added external dipole field of 0.005 a.u. was used to compute the dipole moment components as first derivatives with respect to the external electric field in the dipole approximation.

In order to represent the ab initio dipole moment vector \( \mathbf{\mu} \) of CH₄ analytically we use the so-called symmetrized molecular bond (SMB) representation [8], where \( \mathbf{\mu} \) is projected onto three symmetrized combinations of vectors associated with the four molecular bonds C–H (i = 1, 2, 3, 4). An analogous approach was used to represent the ab initio dipole moment of NH₃ [58] (see also Refs. [8,13] for non-symmetrized MB representations of methane DMSs). The three components of the dipole moment of CH₄ span three components of the \( F_2 \) irreducible representation (\( \Gamma = F_{2x}, F_{2y}, \) or \( F_{2z} \)) of the \( T_d(M) \) molecular symmetry group [59]. We define the following three symmetrically independent reference vectors \( \mathbf{n}_r \) spanning the same representation \( F_2 \):

\[
\mathbf{n}_{2x} = \frac{1}{2} \begin{pmatrix} r_1 + r_2 + r_3 + r_4 \\ r_1 - r_2 + r_3 - r_4 \\ r_1 - r_2 - r_3 + r_4 \end{pmatrix},
\]

\[
\mathbf{n}_{2y} = \frac{1}{2} \begin{pmatrix} r_1 + r_2 - r_3 - r_4 \\ r_1 - r_2 + r_3 - r_4 \\ r_1 + r_2 - r_3 + r_4 \end{pmatrix},
\]

\[
\mathbf{n}_{2z} = \frac{1}{2} \begin{pmatrix} r_1 + r_2 + r_3 + r_4 \\ r_1 - r_2 - r_3 - r_4 \\ r_1 + r_2 - r_3 - r_4 \end{pmatrix},
\]

where \( \mathbf{r}_i \) is a molecular bond vector pointing from C to Hₐ (i = 1, 2, 3, 4). The dipole moment vector \( \mathbf{\mu} \) can now be represented as

\[
\mathbf{\mu} = \mathbf{n}_{2x}\mu_{2x} + \mathbf{n}_{2y}\mu_{2y} + \mathbf{n}_{2z}\mu_{2z},
\]

where the projections \( \mu_{2x}, \mu_{2y}, \mu_{2z} \) are the dipole moment functions also spanning the \( F_2 \) representation. Each component \( \mu_{2x} \) is then expanded as

\[
\mu_{2x} = \sum_{i,j,k,l} \mu_{2x}^{i,j,k,l} \mathbf{n}_i \mathbf{n}_j \mathbf{n}_k \mathbf{n}_l,
\]

in terms of the following set of nine independent internal coordinates:

\[
\varsigma_1 = (r_1 - r_2)e^{r_1 - r_2}, \quad i = 1, 2, 3, 4,
\]

\[
\varsigma_5 = \sqrt{12}(2x_{12} - x_{13} - x_{14} - x_{23} + 2x_{34}),
\]

\[
\varsigma_6 = \frac{1}{2}(x_{13} - x_{14} - x_{23} + x_{24}),
\]

\[
\varsigma_7 = \sqrt{2}(x_{24} - x_{13}),
\]

\[
\varsigma_8 = \frac{1}{2}(x_{23} - x_{14}),
\]

\[
\varsigma_9 = \sqrt{2}(x_{34} - x_{12}),
\]

where \( r_i \) are the bond lengths and \( \varphi_a \) are the interbond angles. The coordinate transformation from the six bending coordinates \( \varphi_a \) to the five independent coordinates \( \varsigma_5, \varsigma_6, \varsigma_7, \varsigma_8, \) and \( \varsigma_9 \) defined by Eqs. (7)–(11) has to be complemented by the redundancy condition [48]:

\[
\begin{bmatrix}
1 & \cos \varphi_{12} & \cos \varphi_{13} & \cos \varphi_{14} \\
\cos \varphi_{12} & 1 & \cos \varphi_{23} & \cos \varphi_{24} \\
\cos \varphi_{13} & \cos \varphi_{23} & 1 & \cos \varphi_{34} \\
\cos \varphi_{14} & \cos \varphi_{24} & \cos \varphi_{34} & 1
\end{bmatrix} = 0.
\]

It should be noted that Taylor-type expansions like Eq. (5) can lead to non-physical behaviour at large angle displacements. Following Hollenstein et al. [60], we have introduced the factor \( \exp(-\beta (r_1 - r_2)^2) \) in order to keep the expansion in Eq. (5) from diverging at large \( r_i \). Here \( r_i \) is a reference expansion center which is conveniently taken at a value close to the molecular equilibrium. Eq. (5) cannot guarantee correct behaviour at large displacements of the inter-bond angle, for example at \( \varphi_a = 180° \). Such geometries correspond to very high energies with negligibly small probability density and thus are never accessed in our approach. However this could be a problem for variational methods based on quadratures that often require explicit values of the DMSs or PES at very large ranges of geometries.

The properties of the components \( \mu_{2x} \) associated with \( F_2 \) impose symmetry relations between the expansion coefficients \( \mu_{2x}^{i,j,k,l} \). These relations can be reconstructed by applying the standard symmetry transformation rules [59,61] between the \( F_{2x}, F_{2y}, F_{2z} \) components of \( F_2 \). We employed the Maple program function ‘solve’ to find a set of independent coefficients \( \mu_{2x}^{i,j,k,l} \) by solving an over-determined system of linear equations (see Ref. [15] for details on the computational procedure). For example, to first order the dipole moment functions \( \mu_{2x} \) are given by the expansions

\[
\mu_{2x} = \mu_7 \varsigma_5 + \mu_1 (\varsigma_1 - \varsigma_2 + \varsigma_3 - \varsigma_4) + O(\varsigma_5^2),
\]

\[
\mu_{2y} = \mu_8 \varsigma_6 + \mu_1 (\varsigma_1 - \varsigma_2 + \varsigma_3 - \varsigma_4) + O(\varsigma_5^2),
\]

\[
\mu_{2z} = \mu_9 \varsigma_7 + \mu_1 (\varsigma_1 - \varsigma_2 + \varsigma_3 - \varsigma_4) + O(\varsigma_5^2),
\]

where the shorthand notations \( \mu_7 = \mu_{0,0,0,1,0,0} \) and \( \mu_1 = \mu_{1,0,0,0,0,0} \) are used. The complete expansion set is given in the Supplementary Material to this paper. A full sixth-order symmetrized expansion requires 680 symmetrically independent dipole moment parameters in total. Taking into account the symmetry relations, the expansion Eq. (5) can be written as:

\[
\mu_{2x} = \sum_{i,j,k,l} \mu_{2x}^{i,j,k,l} \mathbf{n}_i \mathbf{n}_j \mathbf{n}_k \mathbf{n}_l,
\]
where \( \{ \zeta_1^{\text{ref}}, \zeta_2^{\text{ref}}, \ldots, \zeta_n^{\text{ref}} \} \) is a symmetrized combination of different permutations of the internal coordinates consistent with \( T_d(M) \) group operations and spanning the \( F_{2v} \) symmetry.

The actual values of expansion parameters \( \mu_{\text{ref}}^{i_1 i_2 i_3 i_4} \) corresponding to our \textit{ab initio} DMSs were determined through a joint least-squares fit to all \( 3 \times 114400 \) \textit{ab initio} dipole moment values simultaneously. Some parameters with large standard errors that exhibit strong correlation were constrained to zero. The \textit{ab initio} data in these fits were weighted using the following expression proposed by Partridge and Schwenke [62]:

\[
w_i = N \times \frac{\tanh \left[ -0.0004 \text{ cm}^{-1} \times (V_i - 18000 \text{ cm}^{-1}) \right] + 1.00000002}{2.00000002},
\]

where \( N \) is a normalization factor defined by \( \sum w_i = 1 \) and \( V_i \) is the corresponding \textit{ab initio} energy at the \( i \)th geometry (in \text{cm}^{-1}), measured relative to the equilibrium energy and computed using the same level of theory. The \textit{ab initio} energy \( V_i \) is weighted by the factor \( w_i \) in the PES fitting; these weight factors favor the energies below 18000 \text{ cm}^{-1}. In the end 296 parameters were needed to obtain a weighted \( (w_i) \) root-mean-squares (rms) error of 0.00016 D. The expansion parameters are given in the Supplementary Material of the paper along with a Fortran 95 routine incorporating the corresponding analytical form.

3. Potential energy surface

In this work we use a new ‘spectroscopic’ PES generated as follows. First, an \textit{ab initio} PES was generated on the same grid of 114400 geometries employing the same CCSD(T)-F12c approach [55] used for the DMSs, but with the larger aug-cc-pVQZ-F12 basis set [56]. The frozen core approximation was applied in the coupled cluster calculations. We did not include core-valence corrections and higher-order coupled cluster corrections because they cancel to a large extent (see the work by Yachmenev et al. [33]), and also because this would be computationally very costly. Relativistic corrections were computed using the second-order Douglas-Kroll method as implemented in Molpro 2010. With this method we obtained the equilibrium bond length \( r_e = 1.08734 \text{ Å} \), which is close to the value \( r_e = 1.08595 \text{ Å} \) derived in a combined experimental/\textit{ab initio} analysis [63]. The \textit{ab initio} potential energies have been represented using a symmetrized analytical expansion in terms of the four stretching coordinates \( 1 - \exp(-a(r_i - r_0)) \) \( (i = 1, 2, 3, 4) \) and five bending coordinates \( \zeta_j (j = 5, 6, 7, 8, 9) \) from Eqs. (6)-(10). The symmetry relations between potential parameters in the \( T_d(M) \) group were derived employing Maple with the procedure described above. In total 287 symmetrically independent parameters are needed for a full sixth-order expansion. These expansion parameters were obtained from a fitting procedure using the weighting scheme given in Eq. (17). Some parameters showing large standard errors were constrained to zero, which resulted in 288 potential parameters needed to get a weighted rms error of 0.3 \text{ cm}^{-1}.

To improve the quality of the \textit{ab initio} PES, we slightly refined it by fitting to the ‘experimental’ energies of \( ^{12}\text{CH}_4 \) extracted from the HITRAN 2008 [64] database for \( J = 0, 1, 2, 3, 4 \). In the refinement the fitted PES was constrained to follow closely the shape of the initial \textit{ab initio} PES of \( \text{CH}_4 \) in order to guarantee that the PES retains a physically correct shape. This was achieved by simultaneously fitting the refined force constants to the \textit{ab initio} points and to the experimental energy levels [65]. This procedure also allows all potential parameters to be varied irrespective of any shortage of experimental data. By optimizing all 288 potential parameters defining the PES, we improved the observed-minus-calculated energies for \( J \leq 4 \) to have a root-mean-square (rms) error of only 0.1 cm\(^{-1}\). This compares with an rms error of about 4 cm\(^{-1}\) obtained with the initial \textit{ab initio} PES for the same set of experimental data. The fitting approach is described in detail by Yurchenko et al. [66] and implemented in the variational program TROVE [28]. This new ‘spectroscopic’ PES for \( ^{12}\text{CH}_4 \) will be the subject of further improvements and a future publication. Both the initial \textit{ab initio} and refined potential parameters are given as Supplementary Material along with a Fortran 95 program containing the corresponding potential energy function.

4. Variational calculations

The vibrational wavefunctions and energies of \( ^{12}\text{CH}_4 \) were calculated using the variational program TROVE [28]. In this approach the Hamiltonian operator is represented as an expansion around a reference geometry taken presently at the molecular equilibrium. The kinetic energy operator is expanded in terms of the nine linearized coordinates \( \zeta_i \), which are linearized versions of the internal coordinates \( \zeta_i (i = 1, \ldots, 9) \) defined above; for the potential energy function we use \( 1 - \exp(-a_i r_i) \) \( (i = 1, 2, 3, 4) \) for the four stretching and \( \zeta_j (j = 5, 6, 7, 8, 9) \) for the five bending linearized coordinates. The latter expansions were applied to the refined PES introduced above. The kinetic and potential energy parts were truncated after the sixth and eighth order, respectively.

To construct the basis set, TROVE employs a multi-step contraction scheme based on the following polyad truncation. The polyad number in case of \( \text{CH}_4 \) is given by

\[
P = 2(v_1 + v_2 + v_3 + v_4) + v_5 + v_6 + v_7 + v_8 + v_9,
\]

where \( n \) is a vibrational quantum number associated with a one-dimensional primitive basis function \( \phi_n(\zeta'_i) \) \( (i = 1, 2, \ldots, 9) \). At Step 1, nine sets of \( \phi_n(\zeta'_i) \) are generated using the Numerov-Cooley [67,68] method by solving the 1D Schrödinger equations for each of the nine modes separately. The corresponding 1D Hamiltonian operators are obtained from the 9D Hamiltonian operator \( \mathbf{H} \) by freezing all but one vibrational coordinates at their equilibrium values. At Step 2 the 9D coordinate space is divided into the three reduced sub-spaces, (i) \( \{ \zeta'_1, \zeta'_2, \zeta'_3, \zeta'_4 \} \), (ii) \( \{ \zeta'_5, \zeta'_6, \zeta'_7 \} \) and (iii) \( \{ \zeta'_8, \zeta'_9 \} \). The goal of this second step is twofold: (a) to improve the basis set by making it more compact and (b) to prepare the basis functions in a symmetrized representation. The division into the sub-spaces is then dictated by the \( T_d(M) \) symmetry: each of the sub-spaces is symmetrically independent and thus can be processed separately. For each of these sub-spaces, the Schrödinger equations are solved for the corresponding reduced Hamiltonian operators employing as basis the products of the corresponding primitive functions \( \phi_n(\zeta'_i) \) generated at Step 1. The sub-space bases are truncated using the condition \( P \leq P_{\text{max}} \), where \( P \) is given by Eq. (18). In this work we use \( P_{\text{max}} = 12 \), i.e. our reduced sub-space basis sets are defined by

\[
v_1 + v_2 + v_3 + v_4 \leq 6,
\]

\[
v_5 + v_6 \leq 12,
\]

\[
v_7 + v_8 + v_9 \leq 12,
\]

The three sets of eigenfunctions \( \Psi_{\text{ref}}^{(1)}(\zeta'_1, \zeta'_2, \zeta'_3, \zeta'_4) \), \( \Psi_{\text{ref}}^{(2)}(\zeta'_5, \zeta'_6, \zeta'_7, \zeta'_8, \zeta'_9) \), and \( \Psi_{\text{ref}}^{(3)}(\zeta'_5, \zeta'_6, \zeta'_7, \zeta'_8, \zeta'_9) \) resulting from these solutions are symmetrically and assigned local mode quantum numbers \( (i) v_1, v_2, v_3, v_4, (ii) v_5, v_6, (iii) v_7, v_8, v_9 \) and vibrational symmetry \( \Gamma_{\text{vib}} \). The final vibrational basis set is formed from products \( \Psi_{\text{ref}}^{(1)} \times \Psi_{\text{ref}}^{(2)} \times \Psi_{\text{ref}}^{(3)} \), which are contracted with \( P = 12 \) and symmetrized again using the standard technique for transformations to irreducible representations (see, for example, Ref. [59]). Thus our contracted vibrational basis set consists of ten symmetrically independent groups, one for each irreducible representation of the \( T_d(M) \) group \( A_1, A_2, E_s, E_g, F_{2h}, F_{1y}, F_{1z}, F_{2s}, F_{2y}, F_{2z} \). Only the first
component is processed from the degenerate symmetries \( E, F_1, \) and \( F_2. \) Therefore only five vibrational Hamiltonian matrices (one for each symmetry) are constructed and diagonalized. In the diagonalizations we use the eigensolver DSYEV from LAPACK as implemented in the MKL libraries. The dimensions of the matrices to be diagonalized are 2190, 1725, 3901, 5481, and 5940 for \( A_1, A_2, E, F_1, \) and \( F_2, \) respectively. The results are collected in Tables 1–3, where the calculated energies are also compared with the available experimental values from [27, 69–71]. It should be noted that our \( \mu_{\text{calc}} \) (‘final’) can be defined as the vibrational average of a dipole moment component \( \mu_{x, y, z} \):

\[
\mu_{x, y, z}^{(i)} = \langle \Psi_{i} | \mu_x | \Psi_{i} \rangle,
\]

and the vibrational transition moment \( \mu^0 \) is defined as the length of the vector

\[
\mu_{i}^{(i)} = \sum_{a \neq b} \mu_{a}^{(i)} | \Psi_{a} \rangle | \Psi_{b} \rangle.
\]

A number of calculated values of the vibrational transition moments \( \mu^0 \) as well as matrix elements \( \mu_{a}^{(i)} | \Psi_{a} \rangle | \Psi_{b} \rangle \) of \( ^{12}\text{CH}_4 \)

\[
\mu_{x, y, z}^{(i)} = \mu_{x, y, z}^{(i)} + \mu_{x, y, z}^{(i)} + \mu_{x, y, z}^{(i)} + \mu_{x, y, z}^{(i)} + \mu_{x, y, z}^{(i)}.
\]

where \( \mu_{x, y, z} \) are the Cartesian components of the dipole moment in the molecule-fixed frame (defined by the Eckart conditions [72]); \( \mu_{x, y, z}^{(i)} \) and \( \mu_{x, y, z}^{(i)} \) are vibrational eigenfunctions obtained variationally, and \( \Gamma_i \) represents a component of one of the ten irreducible representations \( A_1, A_2, E, F_1, F_2, F_3, F_2, F_2, F_2 \) of \( T_d(M). \) It should be noted that the transition moments defined by Eq. (22) depend on the choice of the molecular-fixed coordinate system [73] as well as on the particular choice of the transformational properties of the irreducible representations \( E, F_1, \) and \( F_2 \) (we use irrep-matrices from Hougen’s monograph [74]). The following quantity, averaged over the Cartesian components \( x, y, z, \) and any degenerate components of the wavefunctions, is independent of these choices:

\[
\bar{\mu}^0 = \sqrt{\left( \mu_{x}^{(i)} | \Psi_{i} \rangle | \Psi_{i} \rangle \right)^2 + \left( \mu_{y}^{(i)} | \Psi_{i} \rangle | \Psi_{i} \rangle \right)^2 + \left( \mu_{z}^{(i)} | \Psi_{i} \rangle | \Psi_{i} \rangle \right)^2},
\]

(23)

and the vibrational transition moment \( \bar{\mu}^0 \) is defined as the length of the vector

\[
\bar{\mu}_{i}^{(i)} = \sum_{a \neq b} \bar{\mu}_{a}^{(i)} | \Psi_{a} \rangle | \Psi_{b} \rangle.
\]

5. Transition moments

The transition moment connecting two states \( i \) (‘initial’) and \( f \) (‘final’) can be defined as the vibrational average of a dipole moment component \( \mu_{x, y, z} \) :
Table 2
Vibrational transition moments, $\mu^i_{\ell f}$ in D, individual matrix elements $\hat{\mu}_m^{(i, f, F_{i/f})}$ ($x-x, y, z$ or $a, b$ and $\beta-x, y, z$) in D, and band intensities, $S_p$ in cm$^{-1}$ atm$^{-1}$, for $^{13}$CH$_4$ for the transitions from the $v_4$ state. The calculated and experimentally derived term values $\Gamma_{\ell}$ of the upper states are given in cm$^{-1}$.

<table>
<thead>
<tr>
<th>$\Gamma_{\ell}$</th>
<th>State $f$</th>
<th>$\vec{\mu}^{(a,b)}_{\ell f}$</th>
<th>$\vec{\mu}^{(c,a)}_{\ell f}$</th>
<th>$\mu^{(i, f, F_{i/f})}_{m}$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\vec{S}^{(a,c)}_{\ell f}$</th>
<th>$\vec{S}^{(c,a)}_{\ell f}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>0 1 0</td>
<td>1533.33</td>
<td>1533.39</td>
<td>-0.00406</td>
<td>a</td>
<td>z</td>
<td>0.00704</td>
<td>0.00013</td>
</tr>
<tr>
<td>$F_2$</td>
<td>0 0 2</td>
<td>2587.04</td>
<td>2586.98</td>
<td>0.05046</td>
<td>z</td>
<td>x</td>
<td>0.08741</td>
<td>0.17802</td>
</tr>
<tr>
<td>$F_2$</td>
<td>0 0 2</td>
<td>2614.26</td>
<td>2614.32</td>
<td>0.05778</td>
<td>y</td>
<td>x</td>
<td>0.14006</td>
<td>0.46701</td>
</tr>
<tr>
<td>$E$</td>
<td>0 0 2</td>
<td>2624.62</td>
<td>2624.61</td>
<td>0.06530</td>
<td>a</td>
<td>z</td>
<td>0.11310</td>
<td>0.30697</td>
</tr>
<tr>
<td>$F_1$</td>
<td>0 1 1</td>
<td>2830.32</td>
<td>2830.28</td>
<td>0.00661</td>
<td>y</td>
<td>x</td>
<td>0.01568</td>
<td>0.00872</td>
</tr>
<tr>
<td>$F_1$</td>
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<td>2846.07</td>
<td>2846.06</td>
<td>0.00007</td>
<td>z</td>
<td>x</td>
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<td>0.000001</td>
</tr>
<tr>
<td>$A_1$</td>
<td>1 0 0</td>
<td>2916.48</td>
<td>2916.54</td>
<td>0.00236</td>
<td>y</td>
<td>x</td>
<td>0.00408</td>
<td>0.000069</td>
</tr>
<tr>
<td>$A_1$</td>
<td>1 0 0</td>
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<td>3019.49</td>
<td>-0.01675</td>
<td>a</td>
<td>z</td>
<td>0.04104</td>
<td>0.05265</td>
</tr>
<tr>
<td>$A_1$</td>
<td>2 0 0</td>
<td>3063.65</td>
<td>3063.61</td>
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<td>z</td>
<td>x</td>
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For higher vibrational order parameters the correspondence between our transition moments and effective dipole moment parameters is less straightforward owing to the complexity of the effective dipole moment operators which are usually given in a tensorial representation.

From the transition moments computed we also generated vibrational band intensities as given by Brown et al. [18], Hilico et al. [19]:

$$S_{\text{vib}} = \frac{8\pi^3}{3\hbar C_v} N T_0 \sum \frac{\Delta \nu}{\nu_0} \sqrt{1 - e^{-\hbar \nu_0/kT}} \nu^2 / \hbar C_v.$$  

(26)

where $\nu_0$ and $E_0$ are the vibrational transition frequency and the lower state energy, respectively, Loschmidt’s number

$L = 2.686754 \times 10^{19} \text{cm}^{-1} \cdot \text{atm}^{-2}$, $T_0 = 273.15 \text{K}$, $k$ is the Boltzmann constant, and $Q_v = 1.002$ is the vibrational partition function at $T = 278.15 \text{K}$. Some of the computed values of $S_{\text{vib}}$ are also illustrated in Tables 1–3, where they are compared to the experimental band intensities from Refs. [19,22,25–27], where available. The agreement is generally very good. In some cases, particularly for combinational bands, there is some ambiguity over how to distribute the individual lines between transitions with the same normal-mode vibrational quantum numbers (see also footnotes to Tables 1–3). This introduces an extra uncertainty into these comparisons.

As an illustration of a possible application of our transition moments, Fig. 1 shows the vibrational band intensities calculated at $T = 298.15 \text{K}$ (filled blue squares) and $T = 1500 \text{K}$ (empty red circles) using Eq. (26) ($Q_v = 3.038$ at $T = 1500 \text{K}$).

6. Conclusion

In this work we present new $ab$ $initio$ DMSs for CH$_4$ which are used to generate the vibrational transition moments and band intensities of $^{12}$CH$_4$ for a large number of vibrationally allowed transitions. These values should be helpful for predicting intensities for individual bands. The dipole matrix elements can also be used for predicting or evaluating effective dipole moment parameters. The analytical representations for the electric dipole moment and potential energy functions of CH$_4$ developed in this work have correct symmetry properties of the $T_d$ group and should be useful for representing similar objects obtained using different methods or levels of theory.

As mentioned above, the vibrational transition moments are less sensitive to the shape of the potential or to the size of the basis set than the (ro-)vibrational energies. For example, using the basis set defined by $P_{\text{max}} = 10$ and the original $ab$ $initio$ PES, we obtain vibrational transition moments that differ by about 0.0002 D on average for transitions involving states below 6000 cm$^{-1}$. Compar-
isons of calculated and experimental (or experimentally derived) band intensities demonstrate the good quality of our new DMSs of CH₄. We are planning to use these DMSs in calculations of a high temperature line list for methane within the framework of the ExoMol project [78] (see www.exomol.com), which has identified methane as a key target species. Such a line list will be important for modelling molecular opacity in atmospheres of (exo-)planets and brown dwarfs.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data for this article are available on ScienceDirect (http://www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/jmsa_hp.htm). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jms.2013.05.014.

References
