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Extending the functional form of the methane PES in redundant coordinates for high excited vibrational energy levels calculation

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Abstract

Potential energy functions (PES) of AB₄-type molecules which are constructed using ten symmetrised combinations of natural four A-B_i valence and six (A-B_i) \leftrightarrow (A-B_j) interbond angled are referred to as (10S) PESs. This set of coordinates is redundant with respect to the conventional set of 3N-6=9 vibrational degrees of freedom. At high energy ranges, it was found that (10S) PESs permitted improving by factor of five the fit quality of *ab initio* electronic energies of methane versus standard nine symmetric coordinates (9S) PES representations both in internal, orthogonal or normal-mode coordinates. We extend predictions of vibrational band origins to spectral range above 10000 cm⁻¹ to help future analyses of experimental spectra. Accuracy at high energies is increased without notable deterioration at low-E levels (*rms* of 0.26 cm⁻¹). Based on a comparison between various variants of (10S) PESs we expect that new theoretical band origins should have accuracy not worse than 1-3 cm⁻¹ up to 13400 cm⁻¹.

1. Introduction

The importance of methane spectral data is recognized in various domains of science and technology [1], [2], [3], [4]. In the solar system, methane is a significant constituent of various planetary atmospheres, like those of the Giant Planets [5] (Jupiter, Saturn, Uranus and Neptune) and is the major absorber of the infrared radiation in the atmosphere of Titan [6] [7] (Saturn's main satellite) where it plays a similar role as the water molecule in the Earth but at much lower temperatures. Knowledge of high energy states is mandatory for interpretation of hot methane spectra in the temperature conditions of many astronomical bodies [5], [8], [9] as exosolar planets [10], [11], [12], [13] and brown dwarfs [14]; [15]; [16], [17]. The analysis of highly excited vibration-rotation energy levels and transitions of the methane molecule is a difficult problem due to complex structures of vibrational polyads, numerous resonance couplings and high dimensionality of the calculation models.

A better knowledge of the molecular potential energy surface (PES) would help resolving many of related issues. Predictions of "dark" vibrational states not yet detected via spectroscopic experiments and of corresponding perturbations of observed bands are of particular interest for spectra analyses. Much progress has been achieved in this domain. Marquardt and Quack [18] have computed a global PES for methane and have determined its analytical representation by adjustments to an *ab initio* data set under special consideration of additional experimental constraints. Schwenke and Partridge [19] have reported sophisticated *ab initio* calculations enabling excellent predictions of the lowest lying vibrational levels of CH₄. Wang and Carrington [20] have empirically optimized the *ab initio* PES of Schwenke [19] using contracted

basis Lanczos method [20] [21]. Majumder *et al.* [22] used *ab initio* MRCI method for methane PES calculation. Yurchenko *et al.* [23] [24] [25] used combined method based on *ab initio* calculations and adjustment PES parameters using empirical rovibrational levels. The corresponding vibration-rotation line lists generated from the PESs of refs. [23] [24] are the part of ExoMol database [26] [26] which have been employed for interpretations of astronomical exoplanetary observations [27] (and reference therein). The methane PES reported in ref. [28] together with *ab initio* dipole moment [29] has been used to compute methane spectra in large range of temperatures [30] [31] in frame of TheoReTS project [32], which in turn served to generate HITEMP methane linelist [33]. Experimental validations of these *ab initio* predictions were reported in high-temperature observations [34] [35] [36], in double resonance experiments [37] and in spectral recording under non-LTE conditions [38]. However, very few assignments of experimental methane spectra above 10000 cm⁻¹ are yet available. A challenge for the *ab initio* theory is to find sufficiently flexible and compact analytical PES representation which would permit reliably model electronic energies at large sets of nuclear displacements and produce accurate vibrational predictions towards higher wavenumber ranges. Note that there are alternative methods for constructing PES based on neural network approaches [39] [40] [41] (see also references therein).

The polyad structure of the methane molecule is essentially governed by the quasi coincidence of the stretching fundamental frequencies with the first overtones of the bending frequencies $\nu_1(A_1) \approx \nu_3(F_2) \approx 2\nu_2(E) \approx 2\nu_4(F_2)$. The polyads P_n are defined by an integer n expressed in terms of the principal vibrational quantum numbers as $n=2(\nu_1+\nu_3)+\nu_2+\nu_4$. The polyad P_0 corresponds to the vibration ground state, P_1 to the dyade, P_2 to the pentade, P_3 to the octad, P_4 to the tetradecad, P_5 to the icosad, P_6 to the triacontad and so on.

Most of all above mentioned PESs were represented as power series in 9 symmetrized coordinated (9S PES forms) with the bending functions of six angles (q_{ij}) between four CH bonds represented by a two-dimensional function of E symmetry type and a three-dimensional function of F_2 symmetry type. The two latter ones are usually associated with doubly degenerate ν_2 and triply degenerate ν_4 angular vibrational modes in AB₄ type molecules. The 9S PESs have permitted accurate modeling of methane spectra in quite large spectral range. In ref [28], the elementary angular functions for the 9S PES development were used in the quadratic cosine form $\phi(q) = \cos(q) - \cos(q_e) + 0.3\alpha(\cos(q) - \cos(q_e))^2$ for better fit *ab initio* electronic energies. At the second step of calculations reported in [28], four harmonic terms were empirically optimized. Considering of an extent of the geometrical grid of the *ab initio* points, the PES of ref. [28] was designed to model vibrational energies up to 7000 cm⁻¹ even though the later

calculations [42] have shown that the corresponding vibrational predictions were physically meaningful up to 10300 cm⁻¹ [42] (see also a modelling of high-temperature methane spectra in [34]). However, an extension towards higher energies faced the problem of a flexibility of the analytical PES representation to appropriately fit *ab initio* electronic energies.

While 9S PES forms have been widely used in methane *ab initio* and empirical calculations, one can notice a lacking symmetry type in the angular variables involved. An exact symmetrization of angular functions $f(q_{ij})$ on the tetrahedral T_d point group should contain also a totally symmetric (A_1) angular combination, which will be denoted as the Q -coordinate given by Eq.(1) below. In our previous work [43], we have included additional ten Q -dependent terms in the analytical representation of the potential function resulting thus in a 10S PES form, which depends on the symmetrized combinations of four CH bonds and of six inter-bond angles. This has permitted improving both the fit of the *ab initio* points and the quality of vibrational predictions without an empirical optimisation of the PES.

It is well known that for a pentatomic non-linear molecule, six angles are redundant (Ref. 59 and references therein) since the total number ($3N-6$) of independent vibrational degrees of freedom should be nine. The techniques of variational calculations of nuclear motion in redundant coordinates with the exact kinetic energy operator for the tetrahedral molecules is described in ref [44] where the reader can find a review of the related works. Some mathematical issues related to redundant coordinates for nuclear motion in molecules have been discussed in [45] [46] (and references therein). Calculations of vibrational CH₄ energies using redundant coordinates with purely *ab initio* 10S PES [43] provided for the first time the best RMS (obs.-calc.) deviation of 0.167 cm⁻¹ up to the Tetradecad range (< 6125 cm⁻¹) and an RMS (obs.-calc.) deviation of 0.37 cm⁻¹ up to the Icosad range (< 7852 cm⁻¹).

A quantitatively accurate prediction of highly excited vibration-rotation states of methane above 10000 cm⁻¹ still remains a problem to be solved. Two issues have to be addressed in the context of current spectroscopic applications: 1) full PES suitable for wide spectral range calculations 2) well converged calculations of vibrational or rovibrational energy levels

In this work, we extend the redundant coordinates approach based on the 10S PES involving the Q -coordinate towards this high energy range. Compared to the previous work [43], we have applied more rigorous *ab initio* calculations of electronic energies at a large grid of 19982 nuclear geometries that permitted to study PES models including all electronic energies on the same footing.

It was found that the inclusion of the Q -dependent terms makes the 10S PES much more flexible during the fit at large values of *ab initio* energies resulting to an improvement of the RMS deviation by factor of 5 or even more with a similar number of parameters. The

convergence of *ab initio* vibration levels can be evaluated using programs based on various algorithms of variational methods [43] [47] [48] [49] [44], and by studying the influence of the dimension of the basis sets [50].

The aim of this Letter is two-fold. First, we show the advantages of using analytical PES representation using redundant coordinates for the modeling of *ab initio* electronic energies (Sections 2, 3). Second, we make a comparative study of different PES forms for vibrational levels and report new optimal sets of theoretical $^{12}\text{CH}_4$ bands origins up to 14000 cm^{-1} (Section 4 and Supplementary materials).

2. Ab initio calculations

In the previous work [43], we were able to apply CCSD(T) method with a large ACV5Z atomic basis set at a restricted grid $G^{(S1)}$ for only 3100 geometries of nuclear displacements. An extension to a full $G^{(R)}$ grid of 19982 geometries at that time was done approximately using an additive correction scheme by extrapolation of the energy difference $\text{diff}_2(S_i)=\text{ACV5Z}-\text{V5Z}$ from much smaller V5Z basis set. This approximation did not allow us including higher electronic energies with the same weight as for lower energies in the PES fit. Consequently, in the PES fits of refs. [28] [43], we used the weighting function $w(E) = \tanh(-(E - E_0)/12000)$ which de-emphasised the high-energy contributions.

Due to increasing computational resources, we calculated in this work electronic *ab initio* energies at the entire $G^{(R)}$ grid of 19982 geometries with more rigorous CCSD(T)/ACV5Z method without use of approximate basis set extrapolations. This allowed us to fit the PES at all *ab initio* energies on an equal footing without weighting function.

The calculation of the Diagonal Born-Oppenheimer corrections (DBOC) and high-order (HO) dynamic electron correlations were carried out in the same way as in ref. [43]. Relativistic corrections were calculated both using MVD (“mass velocity” + Darwin) method [51] at ACV5Z basis and using Douglas-Kroll-Hess [52] at the VTZ basis. Since both methods give very similar results, we include here the same relativistic correction values as in ref. [43].

In addition, we have computed supplementary *ab initio* points at 317 randomly distributed geometries by CCSD(T)/ACV5Z method in the energy range $16000\text{-}22000\text{ cm}^{-1}$. These latter values were not included in the fit and have served only for the tests of extrapolation accuracy of the fitted PESs .

3. Analytical form of the 10S PES and nuclear motion variational calculations

The bending vibrations of AB₄ type molecules are often described in terms of five non-redundant ‘‘polar’’ angular coordinates involving three bending coordinates $\{q_{12}, q_{13}, q_{14}\}$ and two torsion angles $\{t_{23}, t_{24}\}$. Unfortunately, in these internal coordinates, it is difficult to construct the symmetry adapted angular basis functions. Instead of internal coordinates, it is possible to use the symmetrized coordinates that are linear combinations of internal coordinates, which correspond to irreducible representations of the molecule point symmetry group. For example, for AB₄ type molecules (T_d point group), 5 symmetrized angular coordinates are

written in the form [53]: $S_{2a}^E = (2\phi(q_{12}) - \phi(q_{13}) - \phi(q_{14}) - \phi(q_{23}) - \phi(q_{24}) + 2\phi(q_{34})) / \sqrt{12}$,

$$S_{2b}^E = (\phi(q_{13}) - \phi(q_{14}) - \phi(q_{23}) + \phi(q_{24})) / 2, \quad S_{4x}^{F_2} = (\phi(q_{24}) - \phi(q_{13})) / \sqrt{2},$$

$$S_{4y}^{F_2} = (\phi(q_{23}) - \phi(q_{14})) / \sqrt{2}, \quad S_{4z}^{F_2} = (\phi(q_{34}) - \phi(q_{12})) / \sqrt{2}. \text{ Four stretching coordinates could be}$$

written $S^A = (\phi(r_1) + \phi(r_2) + \phi(r_3) + \phi(r_4)) / 2$, $S_x^{F_2} = (\phi(r_1) - \phi(r_2) + \phi(r_3) - \phi(r_4)) / 2$,

$$S_y^{F_2} = (\phi(r_1) - \phi(r_2) - \phi(r_3) + \phi(r_4)) / 2, \quad S_z^{F_2} = (\phi(r_1) + \phi(r_2) - \phi(r_3) - \phi(r_4)) / 2.$$

The additional 10-th coordinate is a full symmetry (A₁) combination of six interbond angles

$$Q = (\phi(q_{12}) + \phi(q_{13}) + \phi(q_{14}) + \phi(q_{23}) + \phi(q_{24}) + \phi(q_{34})) / \sqrt{6} \quad (1)$$

Potential energy functions (PES) of AB₄-type molecules which are constructed using ten symmetrized combinations of natural four A-B_i valence and six (A-B_i) \leftrightarrow (A-B_j) interbond angles are referred to as (10S) PESs. This set of coordinates is redundant with respect to the conventional set of 3N-6=9 vibrational degrees of freedom.

A relevance of the introducing ten redundant symmetrized coordinates to describe high energy ab initio points can be argued as following. Let in general consider six independent angular coordinates of 3q and 3t types (all ranging from 0 to π). One can transform them to another six variables $\cos(q_{12}), \cos(q_{13}), \cos(q_{14})$ of the 3q type with $\cos(q_{23}) = \cos(q_{12})\cos(q_{13}) + \sin(q_{12})\sin(q_{13})\cos(t_{23})$, and similar for $\cos(q_{24})$, and $\cos(q_{34})$ of the 3t type. At the next step one can proceed by uniquely defined linear transformation to five usual $\{S_{2a}^E, S_{2b}^E, S_{4x}^{F_2}, S_{4y}^{F_2}, S_{4z}^{F_2}\}$ 5S-type coordinates and our totally symmetric Q coordinate defined by Eq.(1).

Consider now a 6D function $f(3q, 3t)$ or $\phi(5S, Q)$ of these six coordinates and expand it in a power series around one point in the 6D space. This (equilibrium) point $\{\arccos(-1/3), \arccos(-1/3), \arccos(-1/3), 2\pi/3, 2\pi/3, 2\pi/3\}$ in (3q,3t) is mapped uniquely to a point $\{0,0,0,0,0,0\}$ in (5S,Q)

space. Now, let us define a condition (a section of 6D) such that a combination of 3t coordinated is constant: $t_{23}+t_{24}+t_{34}=2\pi$ and our Taylor series expansion point satisfied to this condition. This section will define a 5D subspace. The question is whether the values of our redundant coordinate Q remain constant within this 5D subspace? By computing Q from natural coordinates on the set of our high energy *ab initio* points we clearly see that Q takes different values. That is why we add the Q -dependence in our (10S) PES.

In this work we will use the (10S) PES in the form:

$$P(S_i, Q) = P_0(S_i) + P_1(S_i)Q + P_2(S_i)Q^2 + P_3(S_i)Q^3, \quad (2)$$

where $S_i \in \{S_1^A; S_{2a}^E, S_{2b}^E; S_{3x}^{F_2}, S_{3y}^{F_2}, S_{3z}^{F_2}; S_{4x}^{F_2}, S_{4y}^{F_2}, S_{4z}^{F_2}\}$ are nine commonly used symmetrized vibrational coordinates of elementary functions depending on CH bond distances r_i and interbond angles q_{ij}

$$\phi(r_i) = 1 - \exp[-1.9(r_i - r_e)], \quad \phi(q_{ij}) = \cos(q_{ij}) - \cos(q_e) \quad (3)$$

defined in [54] [55] [56] [57]. $P_0(S_i)$, $P_1(S_i)$, $P_2(S_i)$, $P_3(S_i)$ are symmetrized polynomial of S_i constructed as full symmetry (A_1) irreducible tensor operators in T_d group as described in [38]. The symmetrisation could be done using internal or orthogonal coordinate sets as reviewed in [44]. The first term $P_0(S_i)$ represents a usual 9S form of the methane PES.

Eq.(1) does not include higher powers Q^n with $n > 3$ because they can be exactly expressed in the form (1). The maximum power of the symmetrized S_i and Q coordinates involved in (1) is called the order of the PES expansion. The sum of powers $S_{2a} + S_{2b} + S_{4x} + S_{4y} + S_{4z} + Q$ coordinates involved in (2) is called angular order. A simpler version of the 10S PES was used in refs. [43] [42]. Since we use Morse function (3) as elementary one in the PES expansion, it has a correct asymptotic behavior at large distances.

According to [58] [56][] the 6 angles between 4 bonds are dependent and linked by the following condition :

$$\begin{vmatrix} 1 & \cos(q_{12}) & \cos(q_{13}) & \cos(q_{14}) \\ \cos(q_{12}) & 1 & \cos(q_{23}) & \cos(q_{24}) \\ \cos(q_{13}) & \cos(q_{23}) & 1 & \cos(q_{34}) \\ \cos(q_{14}) & \cos(q_{24}) & \cos(q_{34}) & 1 \end{vmatrix} = 0. \quad (4)$$

The determinant (4) represents a 2nd-order equation with respect to $\cos(q_{34})$ therefore, for fixed cosines of five angles, there are two variants of the cosine of the sixth angle, for example, $\cos(q_{34})$ satisfying equation (4). In the configuration $q_{12}=q_{13}=q_{14}=q_{23}=q_{24}=\arccos(-1/3)$ the equation has two real solutions $\cos(q_{34}) = -1/3$ and $\cos(q_{34}) = 1$. The first solution

corresponds to the equilibrium angular values of the AB₄ molecule, whereas the second one corresponds to a limiting case when the angle between A-B₃ and A-B₄ bonds vanishes since $q_{34} = 0$, meaning that these two bonds would be aligned exactly in one direction. Such limiting geometrical configurations are physically rarely accessible during molecular vibrations because they correspond to very high values of the potential energy function. However, among 19982 geometries of calculated *ab initio* points with $E > 7000 \text{ cm}^{-1}$ there appear significant amount of point, for which q_{34} takes small but non-zero values. For such points equation (4) possess two close real solutions for $\cos(q_{34})$ being the function of five other angles. By replacing the six angles $\cos(q_{ij})$ in equation (4) with 5S, Q, we can obtain a 4th-order equation for Q. This equation will have two real and two imaginary roots.

Another alternative form of a PES in redundant coordinates was suggested in Ref. [46]. The idea of this work was to introduce elementary angular functions of the form

$$\phi'(q_i) = \phi(q_i) / \sum \phi(q_j) \quad (5)$$

where all six corners are summed up in the denominator. In this case, the Q coordinate is constant. In Ref. [46] it is proposed to use the elementary haversine function.

The PES in the coordinates proposed in [46] converges quite quickly, but the form (5), in addition to its complexity, has another significant drawback. Normally, the power series expansion implies that the function $\phi'(q_i)$ must take zero value at the equilibrium configuration, but this is not possible in the form (5). As a result, the coefficients of power series expansion grow rapidly with increasing degree.

The number N^a of purely angular terms involved in $P_m(S_i)$ of the 10S PES at a given order of expansion is summarised in Table 1. In general, including few Q -dependent terms in the PES (1) permitted better quality of the fit of *ab initio* points than including larger number of parameters in the 9S PES $P_0(S_i)$. The RMS of the fit appears to be the most sensitive to the inclusion of $P_0(S_i)Q$ which is linear in the totally symmetric angular Q coordinate.

Table 1 Number of pure angular terms of symmetry types A₁, A₂, E, F₁, F₂ in $P_m(S_i)$ of Eq.(2).

Order	$N^a(P_0)$	$N^a(P_1)$	$N^a(P_2)$	$N^a(P_3)$	All
0	1,0,0,0,0	0,0,0,0,0	0,0,0,0,0	0,0,0,0,0	1,0,0,0,0
1	0,0,1,0,1	1,0,0,0,0	0,0,0,0,0	0,0,0,0,0	1,0,1,0,1
2	2,0,2,1,2	0,0,1,0,1	1,0,0,0,0	0,0,0,0,0	3,0,3,1,3
3	3,2,3,3,5	2,0,2,1,2	0,0,1,0,1	1,0,0,0,0	6,2,6,4,8
4	5,1,8,7,9	3,2,3,3,5	2,0,2,1,2	0,0,1,0,1	10,3,14,11,17
5	7,5,12,13,17	5,1,8,7,9	3,2,3,3,5	2,0,2,1,2	17,8,25,24,33
6	14,8,19,23,27	□ ...	□ ...	□ ...	29,16,42,46,58
7	16,12,31,37,43	□ ...	□ ...	□ ...	42,26,70,80,96

8	27,18,45,57,63	□ ...	□ ...	□ ...	64,43,107,130,150
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Note: Number of angular terms $N^a(P_i)$ can be obtained from $N^a(P_0)$ using a downward shift by i positions. For example number of terms: third order $N^a(P_3)$ = second order $N^a(P_2)$ =zero order $N^a(P_0)$.

If the number of parameters which are poorly defined in the PES fit is too big, this could result in an appearance of spurious non-physical minima. An optimum choice of the PES expansion is a compromise between the RMS deviation of the fit and the increasing number of terms which could provoke spurious minima at too large orders.

Below the sixth order, the PES fit is not sufficiently accurate to describe vibrational levels up to Icosad spectral range ($< 7500 \text{ cm}^{-1}$). The 9S PES $P_0(S_i)$ of 6-th order (287 terms) with additional angular terms of 8-th order (330 terms altogether) provide sufficiently accurate calculations of vibrational levels up to Icosad. In the present study, we use by defaults the orthogonal coordinate sets [44], and the fits of *ab initio* electronic energies are carried out without weighting function $w(E)$. The RMS deviations of the fits in internal coordinates are systematically larger than in orthogonal coordinates.

The results of *ab initio* fits with various variants (parameter sets) of the PESs are summarized in Table 2. Here and below we use the following notations. The set “6+” means that the PES expansion of the 6-th order was complemented with additional purely angular terms of 7-th and 8-th orders. The set “6++” means that supplementary mixed radial-angular terms with radial powers not larger than two were added to the set “6+”. The set $(1^w)^a$ corresponds to the fit using the weighting function $w(E) = \tanh(-(E - E_0)/12000)$, in which the RMS($w(E)$) deviations are by definition smaller than unweighted fit deviations RMS($w=1$), because the contributions of high energies was de-emphasized.

It is clearly seen that by adding only five or ten Q -dependent parameters of the third order in the 10S PES (sets 2 and 3 in Table 2) one can obtain much smaller RMS deviation than by adding 896 supplementary parameters of 7-th and 8-th order in the standard 9S PES expansion (set 8). By adding supplementary angular parameters of orders 9 and 10 in 9S PESs (1311 parameters altogether) one could slightly improve the RMS deviations, which however are significantly larger than in the sets 2,3 with much smaller number of adjusted parameters. Comparison of the set 1 (9S PES) and the set 3 (10S PES) shows that an inclusion of only ten Q -dependent terms permitted reducing the RMS deviation by factor of five. Of these ten additional parameters (set 3) there are five purely angular parameters (set 2), which provide about 80% of the RMS improvement. Additional 18 parameters of forth orders in $P_1(S_i)$, $P_2(S_i)$, $P_3(S_i)$ slightly improve the fit but have fewer impact on the RMS deviation. The error distribution of

the fits depicted in Fig.1 shows that 10S PESs permit more accurate description of *ab initio* points than 9S PESs with comparable number of parameters.

Second order and third order angular parameters for different PES sets are summarized in Table 3. It is seen that the angular harmonic parameter for the doubly degenerate *E* mode remains nearly the same, whereas this parameter for the triply degenerate *F*₂ mode strongly correlate with the parameters of the *Q*-dependent terms. Therefore, the calculated vibrational levels of *v*₄ and of the *v*₄ overtones should be particularly sensitive to the shape of the PESs.

At the next step of this study, we have computed *ab initio* vibrational levels using the variational method in redundant coordinates for all PES variants of Table 2. In case of the 10S PESs we use the computational formalism described in ref. [44], in which the basis set of primitive wavefunctions is non-orthogonal and requires solving a generalised eigenvalue problem. A smaller basis than [42] was used for calculations: 21646A1+21449A2 +39233E +55782F1 +59716F2. The standard deviation of two calculations (987 energy levels): Calc2 of [42] and set6 of this work is 0.26cm⁻¹. This indicates a fairly good convergence.

Fig 2 show derivatives of vibrational energy levels of dyad, pentad, octad with respect to three parameters associated with *Q*, *Q*², and *Q**S_{RA} terms in Eq.(1). It is seen that the vibrational levels are the most sensitive to the variation of the linear *Q* term.

Table 2. The RMS deviations for the fits of various PES expansions to *ab initio* electronic ¹²CH₄ energies on the grid of 19982 nuclear geometries.

Set	Order	#Terms with <i>Q</i>	Number S coordinates used in PES definition	#Terms in <i>P</i> ₀ (<i>S</i> _{<i>i</i>})	# All Terms	RMS/cm-1	Coordinate sets
1	6+	0	9S	330	330	4.9/13.	Orthogonal/Internal
1 ^w	6+	0	9S	330	330	0.53/1.04 ^a	Orthogonal/Internal
2	6+	5	10S	330	335	1.02/1.25	Orthogonal/Internal
3	6+	10	10S	330	340	0.83/1.05	Orthogonal/Internal
4	6+	28	10S	330	358	0.70/0.9	Orthogonal/Internal
5	6++	0	9S	430	430	4.7/12.	Orthogonal/Internal
6	6++	10	10S	430	440	0.43/0.62	Orthogonal/Internal
7	6++	28	10S	430	458	0.38/0.52	Orthogonal/Internal
8	8	0	9S	1226	1226	4.3/12.	Orthogonal/Internal
9	6+	0	9S	329*	329*	7.3	Normal

10	8	0	9S	1226*	1226*	0.73	Normal
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^a Upper case symbol “w” for the set I^w indicates the fit with the weighting function $w(E) = \tanh(-(E - E_0)/12000)$, for which the RMS(w) deviation does not have the same meaning as in all other columns, in which the fits are unweighted

* linear term is absent by definition of normal coordinates

Table 3. Some low order parameters of the methane PESs

Set	Q	S_E^2	$S_{F_2}^2$	Q^2	Q^3	$Q \times S_{A_1}$
1, 1^w	0.	0.074	0.141	0.	0.	0.
3	0.101	0.074	0.089	-0.049	0.035	0.049
6	0.101	0.074	0.089	-0.049	0.037	0.064
4	0.338	0.074	-0.037	-0.290	0.111	0.079
7	0.430	0.074	-0.086	-0.372	0.133	0.085

Table 4 summarises the RMS (obs.-calc.) deviations for *ab initio* calculations of vibrational $^{12}\text{CH}_4$ levels with various variants of PESs. The RMS deviations for the sets 1, 5 and 8 corresponding to 9S PESs are much larger and are not included in Table 4. All columns except for the set $(1^w)^a$ correspond to unweighted fits ($w=1$) of 10S PESs with all *ab initio* values included on the same footing.

We have also added the set 3^b , in which two harmonic radial parameters of the 10S PES were empirically optimised. For this reason, the RMS values of this set 3^b in the Pentad and Octad ranged are the smallest ones. Otherwise, all 10S PES versions give comparable RMS deviations up to Triacontad. At the last but one column of Table 4, we quote the results corresponding to the best calculation (calc 2) of the previous work [42], whereas two other calculations of ref. [42] based on normal modes give larger RMS deviations for Triacontad.

Recent work [23] reported combined vibrational levels derived both from observed transitions and from the empirical 9S PES fits to experimental data. The RMS deviations of empirical vibrational levels versus the levels reported in [23] are given in the last column of Table 4 except for the Triacontad case. We were not able to fill the case of Triacontad RMS data because of the uncertainties of their identification: the Triacontad levels of [23] are by 10-20 cm^{-1} away from our calculations and from experimental levels of the same symmetry reported in [59].

Table 4. RMS empiric values [59] -calc. deviations for *ab initio* calculations of vibrational $^{12}\text{CH}_4$ levels with various variants of PESs

Set	Max E vib. / cm^{-1}	$(1^w)^a$	2	3	3^b	4	6	7	Ref Calc2 [42]	E vib of ref. ^d [23]
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Dyad	1533	0.013	0.035	0.019	0.021	0.021	0.072	0.065	0.048	0.035
Pentad	3065	0.096	0.123	0.117	0.046	0.108	0.130	0.127	0.099	0.069
Octad	4595	0.115	0.128	0.133	0.077	0.137	0.188	0.185	0.130	0.125
Tetradecad	6124	0.136	0.157	0.164	0.144	0.180	0.232	0.228	0.150	0.126
Icosad	7652	0.226	0.249	0.237	0.260	0.267	0.272	0.272	0.256	0.425
Triacontad ^c	7919	0.348	0.161	0.367	0.348	0.385	0.386	0.390	0.534	-

- ^a this corresponds to the weighted fit, in which the $\text{RMS}(w(E))$ deviation does not have the same meaning as in all other columns where the fits are unweighted
- ^b 2 radial harmonic parameters were fitted
- ^c only 39 experimental vibrational band origins (ref [59]) were considered for Triacontad
- ^d RMS deviations of calculations [23] with a fitted PES [23]

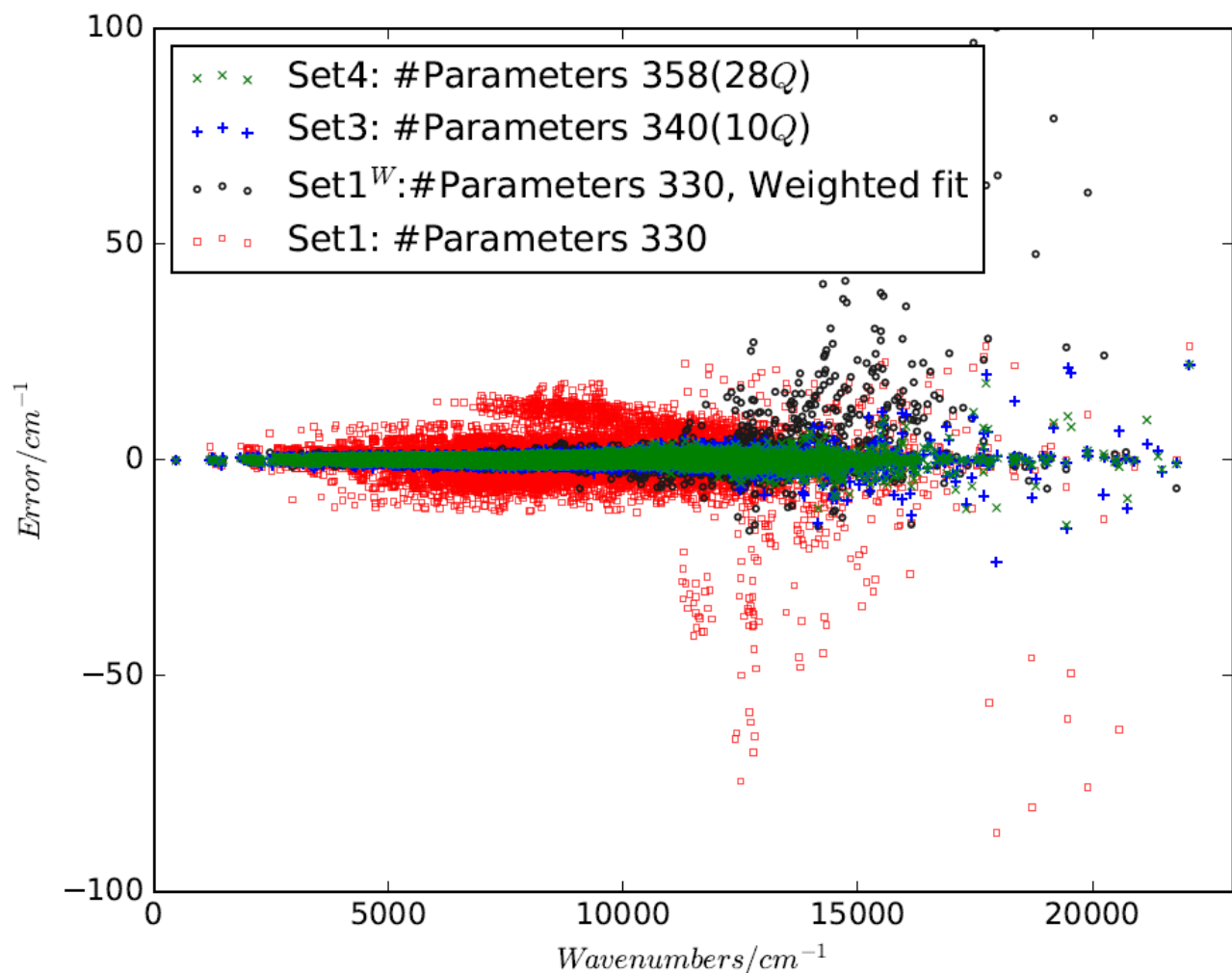


Fig 1. Error distribution of the PES fits to *ab initio* electronic energies. “*w*” mean the fit with the weighting function $w(E) = \tanh(-(E - E_0)/12000)$, otherwise corresponds to an unweighted fit.

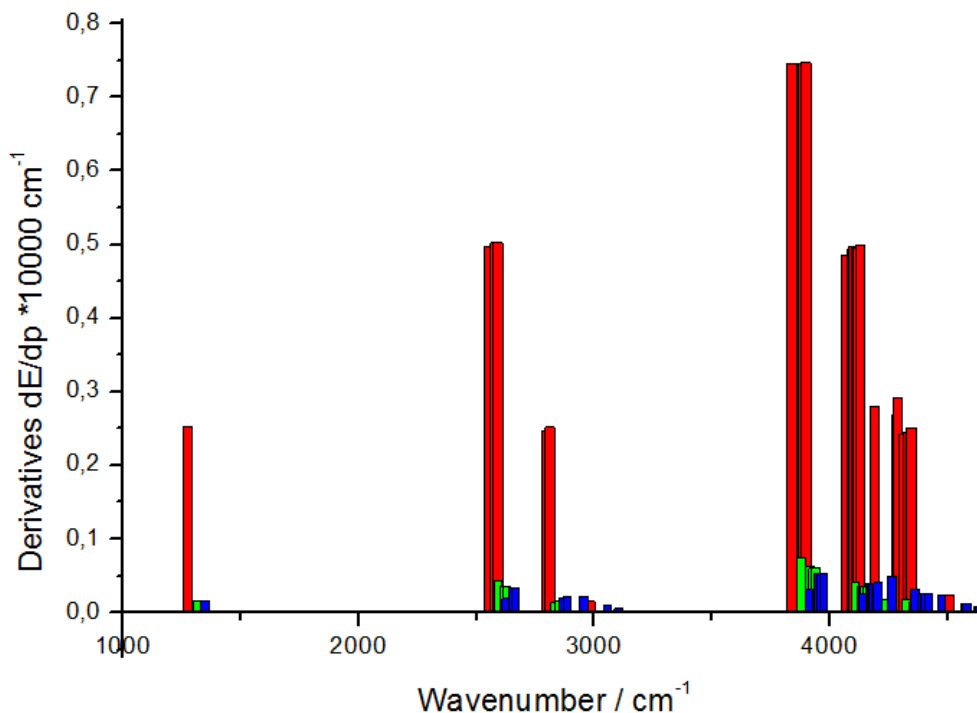


Fig 2. Derivatives of vibrational energy levels of dyad, pentad, octad with respect to three parameters associated with Q (red color), Q^2 (green color), $Q \cdot S_{RA}$ (blue color) term in the 10S PES (1).

4. Methane band origins

The values of $^{12}\text{CH}_4$ vibrational levels computed in the present work are quite close to those of ref. [42] up to 10300 cm^{-1} . Above 11000 cm^{-1} the levels of [42] are systematically underestimated compared to our new calculations provided in the Supplementary materials. Comparison of three calculations corresponding to the PESs of the set 1^w, set 2 and set 4 (Table 2) with empirical vibrational levels is shown in Fig.3. It is seen that the levels calculated from the 10S PES (set 4) agree with the experiments noticeably better than levels of 9S PES (set 1^w) in spectral ranges $6300\text{-}7000 \text{ cm}^{-1}$ and $7200\text{-}8000 \text{ cm}^{-1}$. Obs.-calc. deviations for the set 2 are in average closer to zero, however the scatter is larger than for the set 4 in spectral regions corresponding to high excitations of the ν_4 mode (bands $5\nu_4$, $4\nu_4+\nu_2$, $6\nu_4$, $5\nu_4+\nu_2$ etc.). Figure 3 shows that significant deviations between 9S PES and 10S PESs concern the range of high overtones of ν_4 .

The obs.-calc. deviations in the range near 7100 cm^{-1} for both calculations can be explained by the fact that the current *ab initio* ansatz does not provide sufficiently accurate description of the stretching ν_1 , ν_3 bands and of their overtones. The deviations of both calculations near 7300 cm^{-1} correspond to the spectral range of the $5\nu_2$ band, but the upper empirical states of these sublevels have quite significant uncertainties.

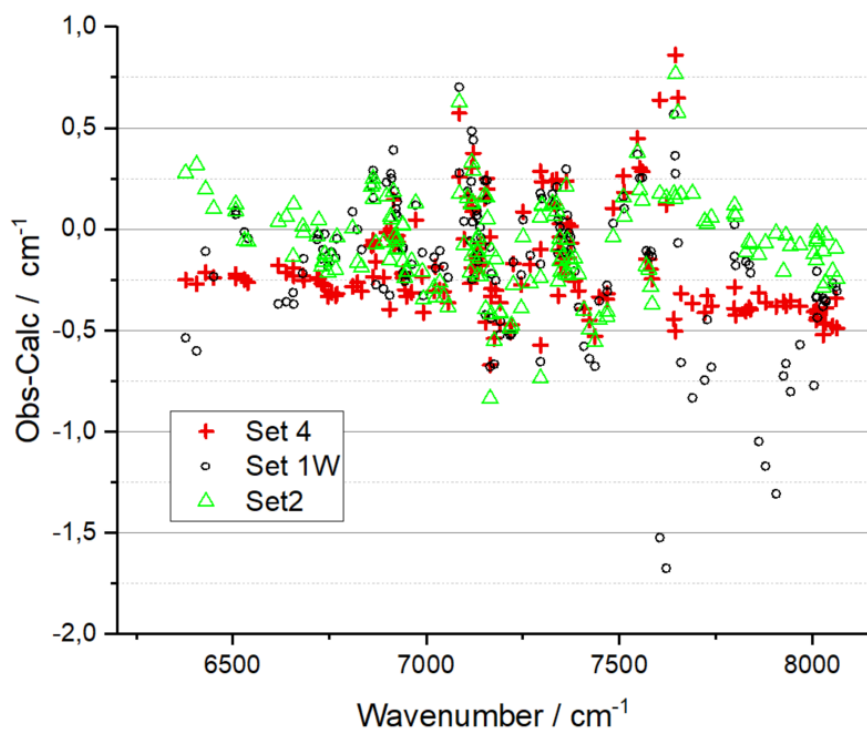


Fig 3. Comparison of empirical and calculated vibrational levels corresponding to 9S PES (set 1^w) and 10S PESs (set 2 and set4).

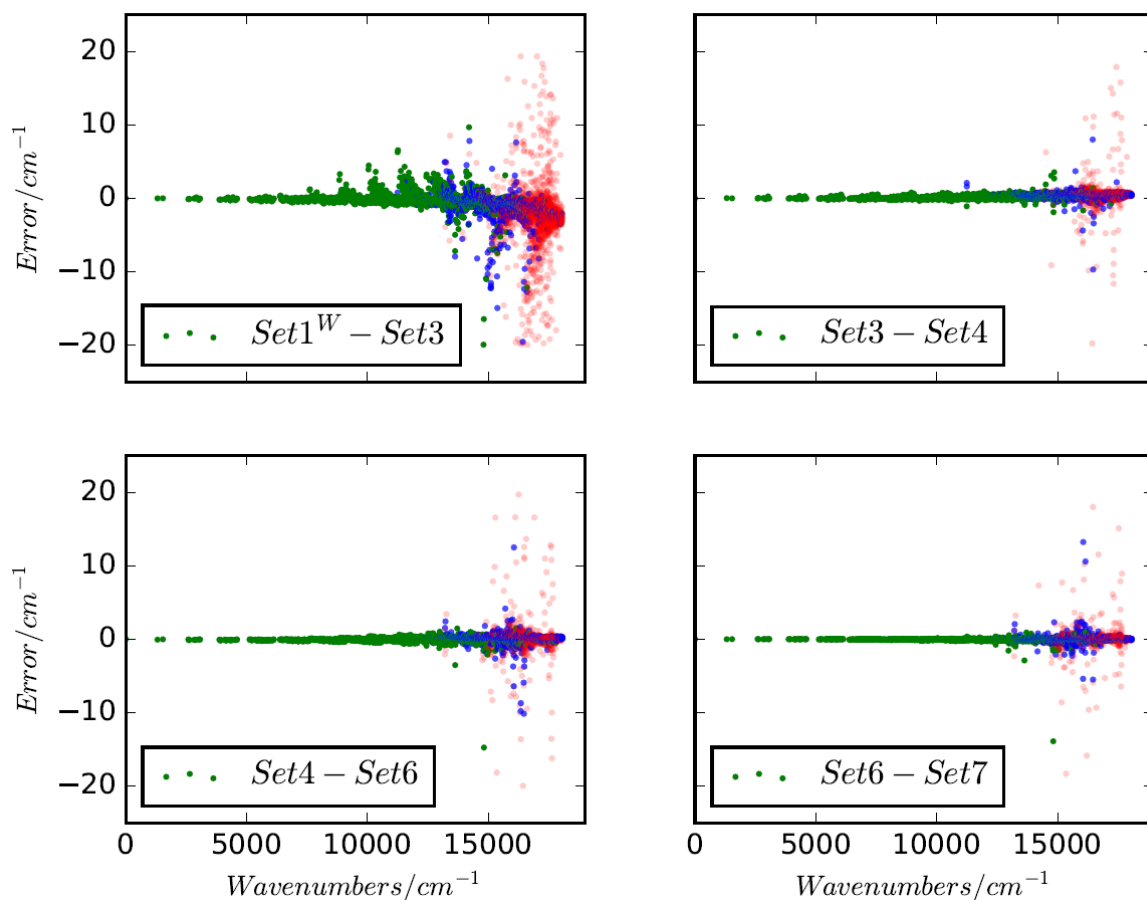


Fig 4. Upper left: difference in calculated vibrational levels using 9S PES (set 1^w) and more accurate 10S PES (set 3). Note a systematic negative trend ($E_{vib}(\text{set } 1^w) - E_{vib}(\text{set } 3)$) in the range 10000-15000 cm^{-1} . Upper right: difference in calculated vibrational levels using Set3 and Set4 PESs. Lower left: difference in calculated vibrational levels using Set4 and Set6 PESs. Lower right: difference in calculated vibrational levels using Set6 and Set7 PESs. Green points

correspond to levels, for which the same vibrational assignment is unambiguous in both calculations. Blue points correspond to a low probability of misassignments between two calculations. Red points correspond to the levels with strongly mixed basis set functions where the one-to-one correspondence cannot be assured.

Figure 4 (upper left) shows that vibrational levels calculated using 9S PES (set 1^w) and 10S PES (set 3) coincide quite well below 10000 cm⁻¹ but exhibit systematic differences for higher energies.

The vibrational assignment for an identification of the pairs of compared levels was determined by a main contribution of the basis set functions. For levels above 13000 cm⁻¹ the vibrational basis set functions are heavily mixed due to increasing intrapolyad anharmonic coupling and due to an overlapping of different polyads. At this range, a main basis set contribution can drop to 0.1 or 0.2 making the vibrational assignment ambiguous. Examples of assignments are provided in the Supplementary files. For this reason, a one-to-one matching of levels in two calculations could be also ambiguous. Different cases are specified by different colours in Figure as explained in the legend of Fig 4: red points correspond to high probability of ambiguously defined pairs of levels, blue points to high probability of unambiguously defined pairs of levels, and green points to unambiguous assignments.

Comparison of predicted vibrational levels between two variants of 10S PESs (set 6 and set 4) is shown in Fig 4 Lower left. It is seen that an overall agreement is much better than in the previous Figures, though the parametrisation and thus the shape of two potentials is not the same. Energy levels up to 14000 cm⁻¹ calculated with these two versions of the 10S PESs are provided in Supplementary materials. Comparison of vibrational levels between two other variants of 10S PESs (set 6 and set 7, see fig4 lower right) exhibits similar trend. All other vibrational calculations among 10S PESs (from sets 2 to set 7) also give consistent results.

5. Conclusion

In this study, we have shown that ten-dimensional PESs (1) in redundant coordinates S_i , Q permit significantly better fit of *ab initio* electronic ground state energies of methane molecule compared to standard nine-dimensional PES representations both in internal, orthogonal or normal-mode coordinates. The corresponding *ab initio* calculations were carried out on a sample of 19982 *ab initio* nuclear geometries extended up to 20000 cm⁻¹ from the equilibrium at the CCSD(T)/ACV5Z level of the theory including relativistic, diagonal Born-Oppenheimer corrections and high-order correlations.

For similar number of parameters, the 10S PESs assure about 5 times better RMS deviation of the *ab initio* fit than 9S PESs. To achieve the overall RMS deviation of 0.7 cm⁻¹ on the entire grid, the 10S PES in our tests required 358 parameters, whereas PES in normal coordinates required 1226 parameters, that is larger by a factor of 3.4. Too many adjustable parameters can lead to non-physical features as spurious minima in a PES that could false vibrational predictions. On the contrary, a few number of additional *Q*-dependent parameters in Eq.(1) resulted in a significant improvement of the RMS deviation versus 9S forms.

Analytical 10S representations for the methane PES built in this work possess the following properties:

- 1) They enable a fit to *ab initio* electronic energies with the accuracy of 1 cm⁻¹ or even better for a larger set of nuclear displacements with the ratio of number of geometries to number of parameters of the order of 55-60.
- 2) Vibrational energy levels computed from these PESs agree well with available empirical levels derived from analyses of high-resolution spectra.
- 3) Different variants of 10S PESs (sets 2-7 of Table 2), which exhibit slightly different shapes, are consistent in the sense that they give well converged variational predictions that are close to each other.

Based on a comparison between various variants of 10S PESs we expect that the vibrational band origins predicted in this work should have accuracy not worse than 1-3 cm⁻¹ up to 13400 cm⁻¹. In future works we plan calculations of vibration-rotation patterns and line intensities that could help assignments and modelling of experimental methane spectra in high wavenumber ranges.

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