Lower Rydberg series of methane: A combined coupled cluster linear response and molecular quantum defect orbital calculation

A. M. Velasco
Departamento de Química Fisica y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain

J. Pitarch-Ruiz, Alfredo M. J. Sánchez de Merás, and J. Sánchez-Marín[a)]
Universitat de València, Institut de Ciència Molecular, Edificio de Institutos, Apartado de Correos 22085, E-46071, Valencia, Spain

I. Martin
Departamento de Química Fisica y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain

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Vertical excitation energies as well as related absolute photoabsorption oscillator strength data are very scarce in the literature for methane. In this study, we have characterized the three existing series of low-lying Rydberg states of CH_4 by computing coupled cluster linear response (CCLR) vertical excitation energies together with oscillator strengths in the molecular-adapted quantum defect orbital formalism from a distorted C_s geometry selected on the basis of outer valence green function calculations. The present work provides a wide range of data of excitation energies and absolute oscillator strengths which correspond to the Rydberg series converging to the three lower ionization potential values of the distorted methane molecule, in energy regions for which experimentally measured data appear to be unavailable. © *2006 American Institute of Physics*.
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I. INTRODUCTION

The structure and physicochemical behavior of CH_4 has attracted the attention of scientists for several good reasons. Methane is the most abundant of the minor constituents in the upper atmospheres of the outer planets, and is the dominant continuous photoabsorber in the above atmospheres in the energy region comprised between 8 and 14 eV.[1–3] The observational data confirm that CH_4 is present in auroral emissions.[4–6] Nevertheless, for a better understanding of the spectroscopic and collisional properties of this molecule at various temperatures and under the influence of different perturbers, new experimental and theoretical investigations are clearly needed.

Methane is a natural gas emitted from areas such as rice cultures, forests, and farms, and also from industrial areas and gas pipelines. Despite its natural origin, a growing number of sources for this compound are man made nowadays. Thus, such hydrocarbon is increasingly present in the atmosphere, but it usually reacts away very rapidly with OH radicals. As a consequence, its influence on the Earth's climate is much less severe than that of fluorinated hydrocarbons. On the other hand, electron collisions with hydrocarbon molecules are important in many other fields of science and technology, ranging from astrophysics[7] to semiconductor processing.[8] For instance, in almost all currently operating fusion processes, plasma-wall interactions are an abundant source of hydrocarbon molecules that contaminate the hydrogenic plasma. The composition of hydrocarbon fluxes entering the plasma covers a wide spectrum of molecules, from CH_4 to C_3H_8.[9]

Due to its small size and simple electronic structure, CH_4 has been the subject of extensive theoretical and experimental studies. The accurate determination of its ionization and fragmentation energies is an important basis for the understanding of many electron-impact phenomena. In particular, most of the high-energy chemical processes are initiated by the interaction of medium-energy electrons (5–50 eV) with matter.

Methane is a representative example of a highly symmetrical molecule affected by the Jahn-Teller effect. If one of the six $1t_2$ electrons of CH_4 is vertically excited into a Rydberg state, the resultant CH_4^+ ion core suffers a strong Jahn-Teller distortion and can be considered to remain in a high vibrational state: the tetrahedral structure of neutral methane becomes distorted in the lowest state of methanium cation.

The photoionization peak of the six electrons in the $1t_2$ valence orbital is spread out between 12.5 and 16 eV.[10] The center of gravity of this broad peak lies approximately at 14.25 eV, almost 2 eV beyond the adiabatic ionization potential (IP) of CH_4. The first band in the photoelectron spectrum of CH_4, as recently determined by Kimura *et al.*[11] with photoelectron spectroscopy, is the terminating member of a Rydberg series, and displays three maxima, at 13.6, 14.4, and 15.0 eV, respectively. The vibrational envelope of this band is described as resulting from the Jahn-Teller splitting of the degenerate state of the ion.[12–16]

Other several studies[10,12,17] indicate that a distortion of

[a)]Author to whom all correspondence should be addressed. Electronic mail: jose.sanchez@uv.es

TABLE I. Exponents and coefficients for the ANO Rydberg functions of CH_4.

Exponents	Coefficients					
			s functions			
0.024 624	0.643 460 61	−0.484 662 19	0.398 719 24	−2.647 136 64	2.525 649 54	−3.465 605 36
0.011 253	0.404 349 98	−0.712 090 19	0.772 597 87	4.176 787 24	−7.584 206 82	14.914 072 09
0.005 858	−0.010 542 90	0.865 643 09	−1.542 392 22	0.228 487 77	8.391 958 96	−33.046 699 03
0.003 346	−0.013 849 78	0.709 028 79	−1.664 636 45	−3.312 898 40	0.330 971 11	42.958 714 38
0.002 048	−0.018 619 79	0.125 740 29	1.823 273 38	−0.541 457 75	−6.720 791 84	−30.256 212 75
0.001 324	0.018 594 31	−0.106 369 66	0.691 098 47	2.409 889 42	0.716 886 50	9.335 159 66
0.000 893	−0.008 356 44	0.052 799 37	0.072 064 96	−0.577 743 20	2.966 537 48	−2.517 196 34
0.000 624	0.002 060 17	−0.013 895 29	−0.006 172 52	0.202 403 10	−0.187 192 14	2.174 173 74
			p functions			
0.042 335	0.260 989 76	−0.298 984 13	0.406 373 81	−0.953 532 56	1.168 589 95	−2.456 452 22
0.019 254	0.573 272 90	−0.526 027 65	0.363 939 25	0.240 233 70	−1.350 118 20	7.383 015 97
0.009 988	0.173 828 54	0.183 843 95	−0.647 425 47	1.784 307 66	−1.642 588 13	−11.721 091 95
0.005 689	0.124 604 77	0.577 778 35	−0.829 451 80	−0.639 056 71	4.450 297 11	11.318 832 81
0.003 476	−0.107 929 32	0.446 111 57	0.103 692 69	−1.845 988 61	−1.342 613 08	−8.376 823 52
0.002 242	0.088 962 36	−0.017 309 35	0.857 494 45	0.340 835 52	−2.402 010 36	9.579 264 08
0.001 511	−0.050 559 29	0.044 524 17	0.331 726 39	0.545 437 57	−0.592 669 40	−11.000 030 88
0.001 055	0.013 686 73	−0.013 842 82	0.080 912 09	0.607 431 36	2.226 695 51	5.232 893 81
			d functions			
0.060 540	0.076 346 20	−0.075 628 58	0.116 857 13	−0.566 346 60	1.095 559 18	−1.587 747 39
0.027 446	0.268 016 70	−0.250 643 94	0.288 435 55	−0.600 150 00	−0.849 091 89	3.571 929 64
0.014 204	0.399 193 53	−0.328 994 50	0.135 178 16	0.673 102 42	−1.045 042 25	−3.713 946 49
0.008 077	0.299 443 15	−0.053 669 72	−0.022 612 53	1.026 542 02	1.473 938 79	1.044 364 50
0.004 927	0.091 062 97	0.427 342 95	−1.057 026 76	−0.801 794 31	0.401 226 59	0.397 577 60
0.003 175	0.014 485 92	0.472 793 16	0.449 547 94	−0.241 505 91	0.618 884 30	3.566 477 61
0.002 137	−0.001 558 80	0.184 140 58	−0.712 288 86	−1.168 065 16	−4.083 173 52	−7.144 409 67
0.001 491	0.000 446 97	0.030 547 13	1.510 554 22	1.439 373 21	2.886 124 95	3.792 400 33

CH_4^+ from the tetrahedral configuration to a D_{2d} geometry is energetically favored. The 13.6 eV maximum may be interpreted as due to a $^2B_2$ state in the D_{2d} structure.[10] Then, the molecule would be deformed in a C_{2v} fashion so as to incipiently produce CH_2^+ and H_2, and in a C_{3v} fashion to lead to $CH_3^+ + H$.[18] These predissociation processes into $CH_3^+ + H$ and $CH_2^+ + H_2$ occur at 14.4 and 15.0 eV, respectively.[19,20]

Three Koopmans' IPs can be obtained from a single calculation on neutral methane if an appropriately distorted geometry is selected. Therefore, we have found more useful ways to determine a suitable geometry that facilitates to assign the series of Rydberg states out of the calculated vertical excitation energies (VEEs) and the corresponding ionization potentials than performing a detailed study of the vibronic couplings associated to the excitation to low-lying Rydberg states. To determine the VEEs, we have adopted a response function approach with a coupled cluster reference function. This wave function guarantees a size-extensive treatment of the dynamic correlation and ensures an accurate description of those systems characterized by a single-reference description. Together with a subsequent linear response calculations, this method provides good theoretical estimations of second-order properties and has satisfactorily been applied to the calculation of VEEs and IPs.[21,22]

Once the required Rydberg series and ionization energies were identified, one-photon transition intensities were calculated with the molecular-adapted quantum defect orbital (MQDO) approach.[23] This theoretical procedure has been also previously used successfully to compute oscillator strengths for transitions involving molecular Rydberg states of different compounds of relevance in the Earth's atmosphere and in astrophysical regions.[24,25]

TABLE II. Displacement vector applied to the experimental T_d geometry of CH_4 and the cartesian coordinates. All values are given in angstroms for the distorted geometry (C_s symmetry group). See text for details.

	Displacement vector [$Q_{3b}(t_2)$ mode]			Coordinates		
Atoms	*X*	*Y*	*Z*	*X*	*Y*	*Z*
C1	0.06	−0.07	0	0	0	0
H2	0.01	−0.01	0	−0.627 879	0.888 520	−0.000 015
H3	0.02	−0.01	−0.01	−0.627 879	−0.888 520	−0.000 015
H4	−0.40	−0.40	0.41	0.576 691	0	−0.771 545
H5	−0.40	0.40	−0.42	0.675 812	0	1.005 769

TABLE III. Valence vertical ionization potentials (in eV) of CH_4.

Ionization process	Koopmans' process[a]	OVGF[b]	EOM-CCSD[c]	Expt.[d]
$CH_4 \rightarrow CH_4^+ + e^-$	$(4a')^{-1}$	13.62	13.813	13.6
$CH_4 \rightarrow CH_3^+ + H + e^-$	$(1a'')^{-1}$	14.21	14.421	14.4
$CH_4 \rightarrow CH_2^+ + H_2 + e^-$	$(3a')^{-1}$	14.80	15.008	15.0

[a]As described in the distorted C_s geometry. See text for details.
[b]This work. C_s distorted geometry. Basis set 6-31G(2*d*,1*p*).
[c]This work. C_s distorted geometry. Basis set [5*s*4*p*3*d*1*f*/4*s*3*p*1*d*+6*s*6*p*6*d*].
[d]Kimura *et al.* (Ref. 11).

TABLE IV. Vertical excitation energies (eV) for the IP=14.421 eV of CH_4.

	T_d		C_s	
State	CCSD	CCSD(3)	CCSD	CCSDR(3)
3*s*	10.63	10.59	10.61	10.57
4*s*	12.81	12.78	12.82	12.79
3*p*	11.84	11.80	11.88	11.84
4*p*	13.18	13.15	13.17	13.13
3*d*II[a]	12.71	12.67	12.81	12.77
4*d*II[a]	13.46	13.43	13.51	13.48
3*d*I[b]	12.64	12.60	12.70	12.67
4*d*I[b]	13.43	13.40	13.47	13.44

[a]II=x^2-y^2.
[b]I=xz,yz.

II. COMPUTATIONAL DETAILS

Green function based methods can provide fairly improved IPs that include the Dyson self-energy effective potential evaluated perturbatively up to third order plus renormalization terms starting from the Koopmans' IPs as zero-order approach. In particular, the outer valence green function (OVGF) method supplies correlated values of the outer valence IPs at a moderate computational cost. Therefore, the outer valence IPs were calculated within the OVGF approach in a systematic exploration of a set of deformed geometries constructed using the SCF/6-31G(2d,p) normal coordinates.

Vertical excitation energies were computed inside a coupled cluster linear response formalism using a linked triples corrected CCSD wave function as reference function,[26–28] with the effect of connected triples estimated by means of the CCSDR(3) method.[29] For systems that can be properly described by simple reference methods, triples corrected coupled cluster methods give excitation energies that are correct to third order in the fluctuation potential.[29] As coupled cluster of singles and doubles linear response (CCSDLR) provides exactly the same excitation energies than the equation of motion coupled cluster of singles and doubles (EOM-CCSD) method, this last approximation was used to compute the IPs at the CCSD level. The 1*s* core orbitals were kept frozen in all the coupled cluster calculations.

We have used an atomic natural orbitals (ANO) basis set[30] with contractions [5*s*4*p*2*d*1*f*] and [4*s*3*p*1*d*] for carbon and hydrogen, respectively. It has been shown in a previous work[31] that this basis delivers essentially the same results than Dunning's correlation consistent aug-cc-pVTZ basis. In addition, the ANO set has been augmented with a series of 6*s*6*p*6*d* Rydberg functions allocated on the carbon atom and built by following the technique proposed by Roos *et al.* to generate a universal Gaussian basis set.[32] Table I shows the coefficients and exponents obtained for the Rydberg function basis set.

The EOM calculations were carried out with the ACESII (Ref. 33) code, and the other coupled cluster calculations with the use of the DALTON program,[34] in which the above-mentioned algorithms are implemented. GAUSSIAN 03 (Ref. 35) was used for the OVGF calculations as well as for the SCF geometry optimization.

TABLE V. Energy levels in eV and quantum defects (δ) for the Rydberg series of CH_4 corresponding to the D_{2d} symmetry (IP=13.813 eV).

	E/eV					δ
State	Expt.[a]	Expt.[b]	Expt.[c]	Theor.[a]	CCSDR(3)[d]	CCSDR(3)[d]
$3sa_1$	9.70	9.698	9.70	9.70	10.02	1.11
$4sa_1$	11.80	11.54	11.61	11.95	12.20	1.10
$5sa_1$					12.91	1.12
$6sa_1$					13.23	1.17
$3p_{x,y}e$					11.25	0.70
$4p_{x,y}e$					12.56	0.70
$5p_{x,y}e$					13.07	0.72
$6p_{x,y}e$					13.31	0.80
$3p_zb_2$					11.31	0.67
$4p_zb_2$					12.61	0.64
$5p_zb_2$					13.08	0.69
$6p_zb_2$					13.33	0.69
$3d_{z2}a_1$	12.1			12.09	12.09	0.19
$4d_{z2}a_1$					12.82	0.30
$5d_{z2}a_1$					13.16	0.44
$3d_{x^2-y^2}b_1$					12.02	0.25
$4d_{x^2-y^2}b_1$					12.83	0.28
$5d_{x^2-y^2}b_1$					13.18	0.36
$3d_{xy}b_2$					11.99	0.27
$4d_{xy}b_2$					12.81	0.32
$5d_{xy}b_2$					13.16	0.44
$3d_{xz,yz}e$					12.19	0.10
$4d_{xz,yz}e$					12.89	0.16
$5d_{xz,yz}e$					13.22	0.21

[a]Au *et al.* (Ref. 42).
[b]Lee and Chiang (Ref. 43).
[c]Robin (Ref. 44).
[d]This work.

The MQDO method was formulated for calculating intensities of transitions involving Rydberg states.[23] In the MQDO formalism a model, one-electron Hamiltonian with a parametric potential is employed. The radial quantum defect orbitals are analytical solutions of the corresponding Schrödinger equation. The angular counterparts are linear combinations of spherical harmonics chosen so that the complete MQDOs form basis functions for the different irreducible representations of the pertinent molecular symmetry group.

III. RESULTS AND DISCUSSION

A. Selection of the geometry

The threefold degeneracy of the t_2 valence molecular orbital (MO) makes it difficult a simple assignment of each state in the vertical manifold of excitations to a particular Rydberg series converging to one of the three outer valence IPs of CH_4. However, by removing such degeneracy, one can obtain three estimated valence IPs that can be unambiguously assigned to each of the three highest occupied MO on the basis of Koopmans' theorem.[36] Then, a given state can be simply assigned by inspection of the hole MO in the excita-

TABLE VI. Energy levels in eV and quantum defects (δ) for the Rydberg series of CH_4 corresponding to the C_{3v} symmetry (IP=14.421 eV).

	E/eV						δ
State	Expt.[a]	Expt.[b]	Expt.[c]	Theor.[a]	Theor.[d]	CCSDR(3)[e]	CCSDR(3)[e]
$3sa_1$	10.50	10.41	10.37	10.50	10.59	10.57	1.12
$4sa_1$	12.8			12.75	12.64	12.79	1.11
$5sa_1$					13.34	13.50	1.16
$6sa_1$						13.82	1.24
$3p_{x,y}e$				12.04	11.66	11.84	0.70
$4p_{x,y}e$					12.98	13.13	0.75
$5p_{x,y}e$						13.66	0.77
$6p_{x,y}e$						13.92	0.79
$3p_za_1$				12.04	11.66	11.89	0.68
$4p_za_1$					12.98	13.21	0.65
$5p_za_1$						13.66	0.77
$6p_za_1$						13.91	0.84
$3d_{z^2}a_1$					12.62	12.68	0.20
$4d_{z^2}a_1$					13.32	13.31	0.50
$5d_{z^2}a_1$						13.72	0.59
$3d_{x^2-y^2,xy}e$I				12.75	12.62–12.63	12.67	0.21
$4d_{x^2-y^2,xy}e$I				13.49	13.32–13.33	13.44	0.28
$5d_{x^2-y^2,xy}e$I						13.80	0.32
$3d_{xz,yz}e$II	12.9			12.89	12.66	12.77	0.13
$4d_{xz,yz}e$II	13.5			13.55	13.33	13.48	0.20
$5d_{xz,yz}e$II						13.81	0.28

[a]Au *et al.* (Ref. 42).
[b]Lee and Chiang (Ref. 43).
[c]Robin (Ref. 44).
[d]Cacelli *et al.* (Ref. 41).
[e]This work.

tions representing it. The main drawback of this approach is that a direct correlation to a particular structure of the CH_4^+ cation with specific symmetry resulting from the Jahn-Teller effect[37] coupled to the ionization process is not possible.

Clearly the easiest way to accomplish the removal of degeneracy is distorting the geometry of the highly symmetrical T_d structure of methane. With this aim, we have deformed the experimental geometry (R_{CH}=1.087 Å) along those normal coordinates that break completely the threefold degeneracy. Therefore the modes $\nu_{4a}(t_2)$, $\nu_{3c}(t_2)$, and $\nu_{2a}(e)$ were discarded. From the other modes, a set of distorted geometries R were built according to $R=R_0+k\ Q_i$, where R_0 stands for the vector of experimental nuclear coordinates at equilibrium, k is a scaling factor, and Q_i denotes the vector of mass-weighted Cartesian displacement corresponding to the i normal coordinate. At each geometry R, valence IPs were calculated with the OVGF approach,[38,39] to minimize the mean absolute error of calculated IPs with respect to experiment.

The best mean absolute error in the OVGF IP values was obtained with the $\nu_{3b}(t_2)$ normal coordinate, using a value of k=0.20. The components of the selected Q_i vector, as well as the final geometry, of C_s symmetry, adopted in the present calculations, are given in Table II.

B. Ionization potentials and transition energies

The calculated ionization potentials, together with the more recent experimental values, reported by Kimura *et al.*[11] are displayed in Table III. We have also included the dissociative ionization processes associated with each IP. The EOM-CCSD results reported in Table III have been used along with the CCLR values in the calculation of the quantum defects.

In order to have a general view of the effect of the geometry distortions on the excitations we present, in Table IV, some of the calculated energies (i.e., those for the Rydberg series that converges to 14.421 eV). As can be observed, there are no important differences between the energy values obtained, independently if we consider T_d or C_s symmetry. Note, however, that the three series would be degenerate in the T_d case. It seems also apparent in Table IV that inclusion of linked triples in the CCSDR(3) calculations, diminishes the magnitude of all excitation energies in approximately 0.02–0.03 eV. Therefore, given the small difference between the two sets of excitation energies and the systematic nature of the triples correction, we have only considered the CCSDR(3) results in the remaining of this section.

The presently calculated VEEs, together with some of the few existing comparative values, are displayed in Tables V–VII. Accordingly to the pioneering work of Mulliken,[40]

TABLE VII. Energy levels in eV and quantum defects (δ) for the Rydberg series of CH_4 corresponding to the C_{2v} symmetry (IP=15.008 eV).

	E/eV		δ
State	Expt.[a]	CCSDR(3)[b]	CCSDR(3)[b]
$3sa_1$	11.11[c]	11.14	1.12
$4sa_1$		12.96	1.42
$5sa_1$		14.09	2.15
$6sa_1$		14.41	2.23
$3p_xb_1$		12.41	0.71
$4p_xb_1$		13.71	0.76
$5p_xb_1$		14.25	0.76
$6p_xb_1$		14.49	0.87
$3p_yb_2$		12.44	0.7
$4p_yb_2$		13.75	0.71
$5p_yb_2$		14.25	0.76
$6p_yb_2$		14.50	0.82
$3p_za_1$		12.47	0.68
$4p_za_1$		13.75	0.71
$5p_za_1$		14.25	0.76
$6p_za_1$		14.49	0.87
$3d_{z^2-x^2-y^2}a_1$		13.28	0.19
$4d_{z^2-x^2-y^2}a_1$		14.04	0.25
$5d_{z^2-x^2-y^2}a_1$		14.38	0.35
$3d_{xy}a_2$		13.18	0.27
$4d_{xy}a_2$		13.96	0.40
$5d_{xy}a_2$		14.33	0.52
$3d_{xz}b_1$		13.35	0.14
$4d_{xz}b_1$	14.1	14.07	0.19
$5d_{xz}b_1$		14.4	0.27
$3d_{yz}b_2$		13.36	0.13
$4d_{yz}b_2$	14.1	14.07	0.19
$5d_{yz}b_2$		14.4	0.27

[a]Au *et al.* (Ref. 42).
[b]This work.
[c]Extrapolated using a quantum defect of 1.13.

we have written the *nl* atomic orbital notation corresponding to atomic neon (the united-atom limit of CH_4), with which the ending MO in a given molecular electron excitation may be correlated. The *nl* nature associated with the Rydberg MOs was determined by inspecting the nodal structure and the magnitude of the quantum defect of each of the atomic orbitals found in the dominant configuration of the molecular excited states. The quantum defects have also been included in the tables, together with the irreducible representation symbol, Γ_i, to which the states belong. This notation is commonly used because the motion of the outermost electron in a Rydberg state is almost independent of the state of the inner ion. The polarization effects on the inner ion due to the outermost electron are rather small and may not affect the geometrical structure of the molecule. That is, the potential surfaces of the Rydberg series can be considered to follow that of the corresponding ionized state.

To the best of our knowledge, the most extensive *ab initio* calculation reported on this problem is the one by Cacelli *et al.*,[41] who carried out a selected singles and doubles configurations interaction using a rather limited basis set. Cacelli *et al.*[41] used the one-center expansion (OCE) approximation, with which they performed all their calculations in the fixed experimental ground-state geometry, within the static exchange frozen orbital approximation. A vertical IP closer to the C_{3v} ionization band was adopted.

Our results conform well with the theoretical values reported by Cacelli *et al.*,[41] and also with the experimental data available in the literature.[42–44] Au *et al.*[42] performed electron energy loss measurements using dipole (e,e) spectroscopy, and also predicted transition energies using the Rydberg formula. They calculated the *ns*, *np*, and *nd* excitation energies using a quantum defect for the *ns* Rydberg series equal to 1.13, and assuming average values for δ_p and δ_d equal to 0.6 and 0.0, respectively. In a similar way, in Table VII we have included a new energy value for the 3*s* Rydberg state, that has been obtained by employing the same quantum defect as Au *et al.*,[42] equal to 1.13. The so-obtained energy value for the 3*s* Rydberg state is in good agreement with our calculations.

However, there exist significant deviations between two of our computed excitation energies with respect to experiment. In particular, the 3*s* and 4*s* states, which converge to the lowest IP, (see Table V) exhibit errors of the order of 0.3–0.4 eV, unlike the expected error of around 0.1 eV. These large deviations reflect the fact that the selected distorted geometry may not be the optimal one for these states, but, in a sense, this is a price to pay to get an overall good description of the whole set of quantum defects.

Inspection of any of the Tables V–VII reveals that in analogous Rydberg series, as are the ones under study, important similarities in the magnitude of the quantum defects occur, in particular, for the first members of each Rydberg series. This feature may be explained on the grounds of assuming that the term values, $t=E-\mathrm{IP}$, are transferable from one IP limit to another in transitions occurring within different Rydberg series, in this context. This is most likely due to the highly nonbonding and diffuse nature of the Rydberg orbitals, on to which the molecular core acts nearly as a point charge.

C. MQDO oscillator strengths

The oscillator strengths for all the allowed transitions of the present distorted form of CH_4, originating in the ground state (GS) and ending in a Rydberg state have been collected in Table VIII. In the table, the transitions have been grouped according to the IP to which the higher-lying Rydberg states converge.

The electron configuration of the $^1A_1$ ground state of CH_4 in its T_d tetrahedral form is $(1a_1)^2(2a_1)^2(1t_2)^6$, where the $1t_2$ MO may be correlated to the $2p$ AO of the united atom limit, Ne atom.[45] Given the $2p$ character of the least-bound electron in the GS,[45] only transitions to states with *ns* or *nd* character are listed. It is a well-known fact that those molecular Rydberg transitions that obey Laporte's selection rule are much stronger than otherwise.

The notation used in Table VIII for the GS (i.e., the

TABLE VIII. Oscillator strengths for different Rydberg electronic transitions from the ground state of CH_4.

D_{2d}		C_{3v}		C_{2v}	
Transition	MQDO	Transition	MQDO	Transition	MQDO
$1b_2 \rightarrow 3sa_1$	0.0943	$3a_1 \rightarrow 3sa_1$	0.0893	$3a_1 \rightarrow 3sa_1$	0.0808
$1b_2 \rightarrow 4sa_1$	0.0173	$3a_1 \rightarrow 4sa_1$	0.0166	$3a_1 \rightarrow 4sa_1$	0.0248
$1b_2 \rightarrow 5sa_1$	0.0068	$3a_1 \rightarrow 5sa_1$	0.0070	$3a_1 \rightarrow 5sa_1$	0.0079
$1b_2 \rightarrow 6sa_1$	0.0036	$3a_1 \rightarrow 6sa_1$	0.0038	$3a_1 \rightarrow 6sa_1$	0.0032
$1b_2 \rightarrow 3da_1$	0.0387	$3a_1 \rightarrow 3da_1$	0.0357	$3a_1 \rightarrow 3da_1$	0.0310
$1b_2 \rightarrow 4da_1$	0.0211	$3a_1 \rightarrow 4da_1$	0.0273	$3a_1 \rightarrow 4da_1$	0.0157
$1b_2 \rightarrow 5da_1$	0.0126	$3a_1 \rightarrow 5da_1$	0.0208	$3a_1 \rightarrow 5da_1$	0.0093
$1b_2 \rightarrow 3de$	0.0456	$3a_1 \rightarrow 3de$II	0.0430	$3a_1 \rightarrow 3db_1, b_2$	0.0387
$1b_2 \rightarrow 4de$	0.0240	$3a_1 \rightarrow 4de$II	0.0198	$3a_1 \rightarrow 4db_1, b_2$	0.0208
$1b_2 \rightarrow 5de$	0.0135	$3a_1 \rightarrow 5de$II	0.0138	$3a_1 \rightarrow 5db_1, b_2$	0.0122

initial state in the transitions) is that of the outermost MO in the D_{2d}, C_{3v}, or C_{2v} symmetry group, that is, $1b_2$, $3a_1$, or $3a_1$, respectively, as done before. An inspection of the table reveals the same order of magnitude for those oscillator strengths that belong to analogous Rydberg series among those sets that converge to different IPs. This feature is easily explained on the grounds of the close similarities in the quantum defects that characterize the above different Rydberg series. Following the argument given in the last paragraph of the precedent section, the term values, $t=E-\mathrm{IP}$, are transferable from one IP to another of the Rydberg transitions' limits, with the consequence that the intensity of the analogous transitions belonging to different Rydberg series are very much alike. It may be worth mentioning that transition probabilities from the GS to the degenerate pair of ndb_1 and ndb_2 Rydberg states in the C_{2v} structure, i.e., the one converging to the third of the IPs considered in this work, have been added up and collected in the pertinent location of Table VIII.

Table IX displays the absolute MQDO oscillator strengths obtained after integration in different energy ranges comprised between 8.55 to about 11 eV, given the experimental fact that, as a careful analysis reveals, in these energy ranges more than one transition takes place. More specifically, those intervals comprise the transitions from the ground state to the three Jahn-Teller components of the $3s$ Rydberg state, as indicated in Table IX. Addition of the three individual MQDO oscillator strength values is required for a comparison with the experimental data. A few comments on the experimental techniques that have helped supply the comparative f values are in order.

TABLE IX. Integrated oscillator strengths of CH_4.

Transitions	MQDO[a]	Expt.
$1b_2 \rightarrow 3sa_1$ $3a_1 \rightarrow 3sa_1$ $3a_1 \rightarrow 3sa_1$	0.2644	0.277 ± 0.0355[b] 0.36 ± 0.04[c] 0.29 ± 0.03[d] 0.26[e] 0.39 ± 0.04[f] 0.27 ± 0.03[g] 0.29[h] 0.425[i]

[a]This work.
[b]Harshberger and Lassettre (Ref. 46).
[c]Edwards and Raymonda (Ref. 51).
[d]Sun and Weissler (Ref. 47).
[e]Watanable *et al.* (Ref. 49).
[f]Moe and Duncan (Ref. 50).
[g]Ditchburn (Ref. 48).
[h]Robin (Ref. 44).
[i]Lee and Chiang (Ref. 43).

Harshbarger and Lassettre[46] found, in an electron impact experiment, the integrated oscillator strength within the 8.55–10.95 eV energy region. The f values reported by these authors have also been attributed to an integration of the absorption coefficients obtained in earlier optical absorption studies by Sun and Weissler,[47] by Ditchburn,[48] and by Watanable *et al.*,[49] through an analogous integration procedure to the one used in their electron impact spectra. The data quoted from Moe and Duncan[50] and from Edwards and Raymonda[51] in Table IX are the oscillator strengths determined, according to their own authors, by deconvoluting the overlapping bands of the first and second transitions. Moe and Duncan,[50] from measurements over the 8.55–11.27 eV entire region, warned the likely presence of a large error in the experimental results due to unresolved rotational fine structure. The reported absolute intensities by Edwards and Raymonda,[51] from vacuum ultraviolet spectra, achieved absolute intensities that should be reliable, according to the own authors, to 25%. An integrated oscillator strength of 0.425 was measured by Lee and Chiang[43] with synchrotron radiation covering the 8.73–11.697 eV energy region. Finally, Robin[44] integrated the energy loss in methane from 8.55 to 10.95 eV, which yielded an oscillator strength of 0.29.

An overall inspection of Table IX makes apparent the general similarities of the presently calculated oscillator strengths with the scarce experimental values that are, to our knowledge, available. We associate this fact to the good quality of the VEEs and IPs achieved in a previous step of this work with accurate *ab initio* calculations, as well as to the undoubtedly correct assignment of the resulting manifold of Rydberg states in the C_s distorted geometry of CH_4 to the three Rydberg series that converge, respectively, on each of the three different IPs presently calculated.

IV. CONCLUSIONS

Complete series of Rydberg states and transitions converging to each of the three different valence IP values exhibited by a selected distorted geometry of the neutral methane molecule have been calculated. Through coupled cluster approaches, a wide manifold of transitions, that presented a seriously difficult individual assignment to the very few existing experimental data, was obtained. The scarcity of experimental data may be possibly due to the large Jahn-Teller coupling experienced by the t_2^{-1} ground state of the CH_4^+ cation. Our assignments conform satisfactorily well to the scarce data that can be found in the literature. The technique followed in the present work has relied on a careful examination of the quantum defects associated with each of the initial manifold of states, calculated in C_s symmetry. Then, by discerning, one by one, the Rydberg states of higher symmetries (D_{2d}, C_{3v}, and C_{2v}), a set of practically constant quantum defects that match all the terms in each *nl* different Rydberg series was sought. This procedure was applied within the spirit of the MQDO method, which was also further used to calculate absorption oscillator strengths.

In summary, the LR-CCSD and LR-CCSDR(3) VEEs used along the EOM-CCSD calculated values for the IPs, were analyzed on the grounds of the expected limit symmetry of the cation. In addition, the use of the MQDO approach allowed us to perform the assignment of quantum defects to each Rydberg state on the basis of the above *ab initio* data. As an additional test, we ensured that each of the newly found series of Rydberg states did converge to one of the three calculated IPs.

We may summarize our analysis by remarking that both energy and transition probability indicators in the present calculations show consistency with the values reported from experimental measurements. We take this fact as an assessment of the accuracy of the LR-CCSDR(3) approach and, also, of the adequacy of the MQDO methodology in performing a clear-cut classification of Rydberg states of unknown symmetry. The MQDO methodology has also proved, in a number of molecular studies, to yield good-quality transition intensities.

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[1] G. H. Mount and H. W. Moos, Astrophys. J. **224**, L35 (1978).
[2] B. Carli and M. Carlotti, in *Spectroscopy of the Earth's Atmosphere and Interstellar Medium*, edited by R. K. Narahari and A. Weber (Academic, New York, 1992).
[3] E. Karkoschka, Icarus **111**, 174 (1994).
[4] J. Ajello, D. Shemonsky, W. Prior *et al.*, J. Geophys. Res. **103**, 20125 (1998).
[5] W. R. Pryor, K. Ajello, K. Tobiska *et al.*, J. Geophys. Res. **103**, 20149 (1998).
[6] S. T. Durrance, P. D. Feldman, and H. W. Moss, Geophys. Res. Lett. **9**, 652 (1982).
[7] A. Dalgarno, *Dissociative Recombination: Theory, Experiment and Applications IV* (World Scientific, Singapore, 2000).
[8] V. Tarnovsky and K. Becker, Plasma Sources Sci. Technol. **4**, 307 (1995).
[9] R. K. Janev, Comments At. Mol. Phys. **36**, 83 (1991).
[10] A. W. Potts and W. C. Price, Proc. R. Soc. London, Ser. A **326**, 165 (1972).
[11] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, *Handbook of He l Photoelectron Spectra of Fundamental Organic Molecules* (Japan Scientific Society, Tokyo, 1981).
[12] N. Dixon, Mol. Phys. **20**, 113 (1971).
[13] C. R. Brundle, M. B. Robin, and H. Bosh, J. Chem. Phys. **53**, 2196 (1970).
[14] B. P. Pullen, T. A. Carlson, W. Moddeman, G. K. Shweitzer, W. E. Bull, and F. A. Grimm, J. Chem. Phys. **53**, 768 (1970).
[15] H. J. Lempka, D. G. Strects, A. W. Potts, and W. C. Price, Philos. Trans. R. Soc. London, Ser. A **268**, 59 (1970).
[16] J. W. Rabalais, T. Bergmark, L. O. Werme, L. Karlsson, and K. Siegbahn, Phys. Scr. **3**, 14 (1971).
[17] F. A. Grimm and J. Godoy, Chem. Phys. Lett. **6**, 336 (1970).
[18] S. Karplus and R. Bersohn, J. Chem. Phys. **51**, 2040 (1969).
[19] W. A. Chupka, J. Chem. Phys. **48**, 2337 (1968).
[20] V. H. Dibeler, M. Krauss, R. M. Rees, and F. N. Harlee, J. Chem. Phys. **42**, 379 (1965).
[21] O. Christiansen, H. Koch, P. Jørgensen, and J. Olsen, Chem. Phys. Lett. **256**, 185 (1996).
[22] J. F. Stanton and J. Gauss, J. Chem. Phys. **101**, 8938 (1994).
[23] I. Martín, C. Lavín, A. M. Velasco, M. O. Martín, J. Karwowski, and G. H. F. Diercksen, Chem. Phys. Lett. **202**, 307 (1996).
[24] A. M. Velasco, I. Martín, J. Pitarch-Ruiz, and J. Sanchez-Marín, J. Phys. Chem. A **108**, 6724 (2004).
[25] J. V. Ortiz, I. Martín, A. M. Velasco, and C. Lavín, J. Chem. Phys. **120**, 7949 (2004).
[26] H. Koch and P. Jørgersen, J. Chem. Phys. **93**, 3333 (1990).
[27] O. Christiansen, H. Koch, A. Halkier, P. Jørgersen, T. Helgaker, and A. Sánchez de Merás, J. Chem. Phys. **105**, 6921 (1996).
[28] H. Koch, A. Sánchez de Merás, T. Helgaker, and O. Christiansen, J. Chem. Phys. **104**, 4157 (1986).
[29] O. Christiansen, J. Kock, and P. Jørgersen, J. Chem. Phys. **103**, 7429 (1995).
[30] P. O. Widmark, P. A. Malmqvist, and B. O. Roos, Theor. Chim. Acta **77**, 291 (1990).
[31] A. M. Sánchez de Merás, I. García Cuesta, and H. Koch, Chem. Phys. Lett. **348**, 469 (2001).
[32] B. O. Roos, M. Fülscher, P. A. Malmqvist, M. Merchán, and L. Serrano-Andrés, *Theoretical Studies of the Electronic Spectra of Organic Molecules* (Kluwer Academic, Dordrecht, 1995).
[33] Computer code ACESII, Advanced Concepts in Electronic Structure II, Quantum Theory Project, Version 0.3 (University of Florida, Gainsville, 1999).
[34] T. Helgaker, H. L. Aa. Jensen, P. Jørgersen *et al.*, computer code DALTON, a molecular electronic structure program. Release 1.2 (2001), see http://www.kjemi.uio.no/software/dalton/dalton.html.
[35] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, computer code GAUSSIAN 03 (Gaussian, Pittsburgh, 2003).
[36] A. Koopmans, Physica (The Hague) **1**, 104 (1933).
[37] G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, New York, 1966), Vol. II.
[38] J. V. Ortiz, J. Chem. Phys. **89**, 6348 (1988).
[39] J. V. Ortiz, Int. J. Quantum Chem., Quantum Chem. Symp. **23**, 321 (1989).
[40] R. S. Mulliken, J. Chem. Phys. **3**, 517 (1935).
[41] I. Cacelli, V. Carravetta, and R. Moccia, J. Phys. B **18**, 1375 (1985).
[42] J. W. Au, G. Cooper, G. R. Burton, T. N. Olney, and C. R. Brion, Chem. Phys. **173**, 209 (1993).
[43] L. C. Lee and C. C. Chiang, J. Chem. Phys. **78**, 688 (1983).
[44] M. B. Robin, *Higher Excited States of Polyatomic Molecules* (Academic, New York, 1985), Vol. III.
[45] G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, New York, 1966), Vol. III.

[46] W. R. Harshbarger and E. N. Lassettre, J. Chem. Phys. **58**, 1505 (1973).
[47] H. Sun and G. L. Weissler, J. Chem. Phys. **23**, 1160 (1955).
[48] R. W. Ditchburn, Proc. R. Soc. London, Ser. A **229**, 44 (1955).
[49] K. Watanable, M. Zelikoff, and E. L. Y. Inn, "Absorption coefficients of several atmosferic gases," Air Force Cambridge Research Center. Technical Report 53-23 (Boston, MA, 1953).
[50] G. Moe and A. B. F. Duncan, J. Am. Chem. Soc. **74**, 3140 (1952).
[51] L. Edwards and J. W. Raymonda, J. Am. Chem. Soc. **91**, 5937 (1969).