A theoretical determination of the electronic spectrum of formaldehyde

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Summary. The electronically excited states of formaldehyde are examined by means of multiconfigurational second-order perturbation (CASPT2) theory with extended ANO-type basis sets. The calculations comprised five valence excited states plus all singlet $3s$, $3p$, and $3d$ members of the Rydberg series converging on the first ionization. The computed vertical excitation energies were found to be within 0.2 eV of the available experimental energies. Full geometry optimization has been performed for five valence excited states. Assuming a planar geometry, the "0–0" transition for the valence $^1A_1(\pi \to \pi^*)$ state is calculated to appear near 7.9 eV, close to the $(n_y \to 3p)$ region. This state is, however, not planar and the true adiabatic energy is 7.4 eV, which is 2.3 eV below the corresponding vertical transition.

1 Introduction

A detailed understanding of the electronic structure and spectra of small carbonyl compounds can contribute to the understanding of the important role they play in many areas of chemistry. Formaldehyde is the prototype molecule for this type of important chromophore. Its electronically excited states have therefore been extensively investigated both experimentally [1–12] and theoretically [13–28]. The early experimental work on the excited states of formaldehyde has been reviewed by Moule and Walsh in 1975 [5], and in 1983 Clouthier and Ramsay [8] compiled the most important spectroscopic data. The importance of including both valence and Rydberg transitions in the *ab initio* calculations for the proper determination of the electronic spectrum of formaldehyde was clearly shown as early as 1969 by Whitten and Hackmeyer [13]. Later Peyerimhoff et al. [15] extended the study to more states, yielding results of similar accuracy. In spite of the limited basis sets employed, the results obtained in these earlier *ab initio* investigations were in agreement with the available experimental data. The 1982 review of Davidson and McMurchie [20] gives a recount of the *ab initio* studies performed to that date.

Formaldehyde has continued to evoke interest up till today. Because of its apparent simplicity and the numerous studies available of its various electronic excited states, formaldehyde is frequently used for testing new theoretical methods developed to treat excited states. It is small enough to be amenable for high level theoretical treatments to which approximate methods can be compared. Not surprisingly, results obtained with many different approaches can be found in the literature. The reader is referred to the recent papers for a more complete list of references. Here we shall only comment on the earlier studies, which are of direct interest for the present investigation. The recent MRCI results for the vertical transition energies of formaldehyde reported by Hachey et al. [28] are in agreement with the present findings.

It is the presence of the π system together with the oxygen lone-pair orbital (hereafter named n_y) that creates the interesting features of the electronic spectrum. As a result, both $n_y \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are known for carbonyl compounds, and they are responsible for the important photochemical transformations. The scientific development of the interpretation of the electronic spectrum of formaldehyde has not been free of problems (see Ref. [22] for a selective discussion). At present there is consensus in the basic assignments of the vertical transitions of the lower energy part, which this investigation also supports. However, the location and nature of the singlet excited states of valence character, except for the lowest $^1A_2(n_y \rightarrow \pi^*)$ state, is one of the as yet unresolved key problems. In particular, theoretical calculations used to place the vertical transition energy for the $^1A_1(\pi \rightarrow \pi^*)$ intravalence transition near or above the first ionization potential at 10.89 eV [29], where it is embedded in a multitude of $^1A_1$ states. Due to its high energy, the valence excited state can possibly also mix with nearby Rydberg states, similar to what has been found for the V state of ethylene [30]. The degree of mixing and their relative location with respect to the ground state will vary with the geometry of the molecule. As pointed out by Fitzgerald and Schaefer [21], the adiabatic $^1A_1(\pi \rightarrow \pi^*)$ state might lie well below the ionization continuum even if this is not so for the vertical transition. Allen and Schaefer [22] have reported an adiabatic transition energy, T_0, of 8.50 eV. A similar result was obtained in a CIS-MP2 perturbation calculation [25]. Recent, more accurate, work by Hachey et al. [27] give a value close to 8 eV. All these values have been obtained with the assumption of a planar molecule. The study of Hachey et al. [27] shows, however, that the potential surface of the valence excited state has a minimum at a pyramidal (C_s) geometry. They computed the excitation energy for the corresponding $2^1A'$ state to be 7.5 eV. Keeping the molecule planar and varying the CO bond length they found an equilibrium geometry for the $^1B_1(\sigma \rightarrow \pi^*)$ state at about 8 eV, while the $^1B_2(n_y \rightarrow \sigma^*)$ state was found repulsive. As will be discussed later, full geometry optimization (which was not performed by Hachey et al. [27]) is important for an accurate prediction of the adiabatic transition energies. In particular, the $^1B_1(\sigma \rightarrow \pi^*)$ state is found below the $^1A_1(\pi \rightarrow \pi^*)$ state in the present study.

The present theoretical study uses the complete active space (CAS) SCF approximation [31] in combination with a recently developed multiconfigurational second-order perturbation approach, the CASPT2 method [32–34]. Its validity in calculating the differential correlation effects on excitation energies has been demonstrated in a number of earlier applications [35]. As indicated above, this communication serves two purposes. First, we analyze the vertical spectrum of formaldehyde. We also attempt to determine the theoretical requirements for a quantitative evaluation of the adiabatic transition energies and equilibrium geometries of the valence excited states. The results obtained give information

that is useful in studies of more complex molecules containing the same chromophore. We are presently studying acetone, a molecule of current experimental interest [36].

2 Methods and computational details

2.1 Basis sets and geometry

Generally contracted basis functions based on atomic natural orbitals (ANOs) were used to construct the molecular orbitals [37]. The contraction scheme used in most of the calculations was C, O[$4s3p1d$]/H[$2s1p$], which has been shown in previous studies [35] to be flexible enough for a proper description of the valence excited states. Larger contracted sets were used in some cases to test the validity of this assumption. The inclusion of diffuse functions is required in order to treat in an adequate way the $3s$, $3p$, and $3d$ Rydberg states obtained by excitations out of the HOMO. Using a recently developed procedure to obtain optimal Rydberg functions for a given system [38], a final set of s-, p-, and d-type diffuse functions was built for formaldehyde. The original basis set was supplemented with a $1s1p1d$ set of Rydberg functions (contracted from a set of $8s8p8d$ primitives), which was placed in the charge centroid of the $^2B_2$ state of the formaldehyde cation. The universal exponents [38], generated as described by Kaufmann et al. [39], together with the corresponding contraction coefficients obtained for formaldehyde are given in Table 1.

The vertical spectrum was computed at the experimental ground state equilibrium geometry [40]. Calculations of the vertical spectrum were carried out within C_{2v} symmetry, with the molecule in the yz plane and the z axis bisecting the HCH angle. With the constraint of C_{2v} symmetry (three independent parameters) the geometry was optimized for the ground state and the valence $^1A_2$, $^1B_1$, and $^1A_1$ excited states. The lowest $^1A'$ and $^1A''$ states of C_s symmetry, generated from planarity by keeping only the xz symmetry plane, were also optimized (four independent parameters). A pointwise procedure was used, which is described in detail elsewhere [41]. All geometry optimizations were performed at the CASPT2 level with the C, O[$4s3p1d$]/H[$2s1p$] basis set. The adiabatic excitation energies were computed as energy differences between the energy minimum for the ground and excited state, respectively.

Table 1. Exponents (coefficients) of the Rydberg orbitals used for formaldehyde

s-type	p-type		d-type
0.024624 (−0.494131)	0.042335	(0.381686)	0.060540 (−0.185220)
0.011253 (−0.503026)	0.019254	(0.433400)	0.027446 (−0.172151)
0.005858 (0.218493)	0.009988	(0.326474)	0.014204 (−0.583213)
0.003346 (−0.635865)	0.005689 (−0.166567)		0.008077 (0.020633)
0.002048 (0.743649)	0.003476	(0.227736)	0.004927 (−0.437712)
0.001324 (−0.646137)	0.002242 (−0.204158)		0.003175 (0.332223)
0.000893 (0.350224)	0.001511	(0.116549)	0.002137 (−0.208134)
0.000624 (−0.087326)	0.001055 (−0.031035)		0.001491 (0.060140)

2.2 CASSCF and CASSI calculations

Multiconfigurational wave functions were initially determined at the CASSCF level of approximation [31]. Unless otherwise stated, the carbon and oxygen $1s$ electrons were kept frozen in the form determined by the ground state SCF wave function. At the experimental geometry employed [40], the total SCF energy for the ground state ($^1A_1$) of formaldehyde was calculated to be -113.910785 a.u. The choice of an active space is determined by the type of excited states to be studied. In this case they are the vertical valence excited states and excitations from the HOMO to the $3s$, $3p$, and $3d$ Rydberg orbitals. In order to limit its size, different active spaces are used for different types of excited states. The π valence active space plus the HOMO is denoted (0210), where the label gives the number of active orbitals in each of the four irreducible representations of the molecular point group, C_{2v}: (a_1, b_1, b_2, a_2). The number of active electrons is 4. This active space has been used in the computation of the low-lying $^3A_2$ and $^3A_1$ states. For the study of the vertical singlet excited states the active space was extended to include the corresponding Rydberg orbitals of symmetry a_1 ($3s$, $3p_z$, $3d_{z^2}$, $3d_{x^2-y^2}$), b_1($3p_x$, $3d_{xz}$), b_2($3p_y$, $3d_{yz}$), and a_2($3d_{xy}$) as appropriate. For the $^1A_1$ states extra orbitals of b_1 and b_2 symmetry were included in the active space to minimize the effect of intruder states in the CASPT2 calculations. The active spaces used and the type of states computed are summarized in Table 2.

Table 2 also lists the active spaces used for the computation of the adiabatic transitions of the valence excited states. These calculations also involve the $\sigma \rightarrow \pi^*$ excitation, and since the CO bond distance varied extensively for the different excited states the active space had to include both the σ and the σ^* orbitals. The valence active space was thus enlarged and now includes the σ, σ^* and π, π^* MOs,

Table 2. CASSCF wave functions (number of active electrons) employed to compute the valence and Rydberg transitions of formaldehyde

Wave function[a]	States	No. conf.[b]	N_{states}^c
Vertical transitions			
CASSCF (0210) (4)	$^3A_2(n_y \rightarrow \pi^*)$	1	1
CASSCF (0210) (4)	$^3A_1(\pi \rightarrow \pi^*)$	1	1
CASSCF (0340) (4)	$^1A_1(n_y \rightarrow 3p_y, 3d_{yz}, \pi \rightarrow \pi^*)$	104	4
CASSCF (2200) (4)	$^1B_1(\sigma \rightarrow \pi^*)$	8	1
CASSCF (0211) (4)	$^1B_1(n_y \rightarrow 3d_{xy})$	4	1
CASSCF (4210) (4)	$^1B_2(n_y \rightarrow 3s, 3p_z, 3d_{x^2-y^2}, 3d_{z^2})$	36	4
CASSCF (0410) (4)	$^1A_2(n_y \rightarrow \pi^*, 3p_x, 3d_{xz})$	20	3
Adiabatic transitions			
CASSCF (41) (6)	$^1A''(n_y \rightarrow \pi^*)$	20	1
CASSCF (2210) (6)	$^1A_2(n_y \rightarrow \pi^*)$	10	1
CASSCF (40) (4)	$^1A'(\sigma \rightarrow \pi^*, \pi \rightarrow \pi^*)$	20	2
CASSCF (2200) (4)	$^1B_1(\sigma \rightarrow \pi^*)$	8	1
CASSCF (2200) (4)	$^1A_1(\pi \rightarrow \pi^*)$	12	2
CASSCF (2210) (6)	$^1B_2(n_y \rightarrow \sigma^*)$	10	1

[a] Within parentheses the number of active orbitals of symmetry a_1, b_1, b_2, a_2, and a', a'' of the point group C_{2v} and C_s, respectively
[b] Number of configurations in the CASSCF wave function
[c] States included in the average CASSFCF calculation

with 4 active electrons. The same active space was also used for the calculation of the vertical energy of the $^1B_1(\sigma \rightarrow \pi^*)$ state. In the states where the n_y orbital is involved the active space was accordingly enlarged (5 active orbitals/6 active electrons).

The energy of each excited state is referred to a ground state energy computed with the same active space. The molecular orbitals for the excited states were obtained from average CASSCF calculations, where the averaging includes all states of interest of a given symmetry. The number of states included in the state average CASSCF calculations is listed in Table 2 together with the number of configurations in the CASSCF wave function.

The transition dipole moments were computed with the CASSCF state interaction (CASSI) method [42, 43]. As explained in previous applications [35], the CASPT2 energy differences were used in the formula for the oscillator strength.

2.3 The CASPT2 method

The CASPT2 method [32–34] computes the first-order wave function and the second-order energy in the full CI space with a CASSCF wave function constituting the reference function. The full Fock matrix in the definition of the zeroth-order Hamiltonian was used [33], therefore the results will be labeled PT2F. The weight of the CASSCF reference in the first-order wave function was found to be within the range 0.90–0.94 in all cases. This weight is a measure of how a large fraction of the wave function is treated variationally. Normally a balanced calculation with respect to the treatment of electron correlation shows about the same weight for the ground and the excited states.

The calculations were performed on the IBM 9021/500-2VF computer of the University of Valencia using the MOLCAS-2 quantum chemistry software [44].

3 Results and discussion

3.1 Vertical excitation energies

The numerical results of this part of the investigation are collected in Table 3. The first column identifies the different excited states of formaldehyde. The second and third columns give the vertical transition energies obtained by the CASSCF and PT2F calculations, respectively. Column four contains the experimental transition energies. In the remainder of the table, μ is the dipole moment computed at the CASSCF level (in a.u.), and $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$ are the expectation values (in a.u.) of x^2, y^2, and z^2, respectively. The latter can be used to identify the nature of the state. Oscillator strengths are given next. Selected previous results from the most recent *ab initio* studies are given in the last three columns. These include vertical excitation energies computed at the CIS-MP2 [25], CCSD [26], and MRD-CI [28] levels. Comparison with earlier theoretical results can be easily achieved from previous papers (see e.g. Table 3 in Ref. [25]). Vertical excitations energies computed at the CIS(D) level have also been recently published [26].

Comparison of the CASSCF and PT2F results gives a measure of the contribution of dynamic electron correlation to the transition energy. For the excited states considered here the contribution ranges from 0.2 to 0.7 eV. Another general observation is that the $\langle r^2 \rangle$ values of the Rydberg states are, as expected,

Table 3. Calculated and experimental excitation energies (in eV) and other properties of the vertical excited states of formaldehyde

| State | CASSCF | PT2F | Exp. | μ^a | Total[b] | | | Osc. Str. | Other results | | |
					$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$		CIS-MP2[c]	CCSD[d]	MRD-CI[e]
Ground state ($1\,^1A_1$)				−0.955	−8.8	−8.6	−8.8				
Singlet states											
$1\,^1A_2(n_y \to \pi^*)$	4.62	3.91	3.79[f], 4.07[g]	−0.547	−10.5	−7.0	−8.3	Forbidden	4.58	3.95	4.05
$1\,^1B_2(n_y \to 3s)$	6.88	7.30	7.09[h]	+1.288	−23.7	−25.8	−25.0	0.0055	6.85	7.06	7.15
$2\,^1B_2(n_y \to 3p_z)$	7.63	8.09	8.14[i]	−0.301	−21.1	−19.1	−38.8	0.0230	7.66	7.89	8.05
$2\,^1A_1(n_y \to 3p_y)$	7.70	8.12	7.97[i]	+0.240	−19.9	−43.0	−19.5	0.0412	8.47	8.00	8.10
$2\,^1A_2(n_y \to 3p_x)$	8.17	8.32	8.37[j]	−0.412	−46.5	−18.9	−18.6	Forbidden	7.83	8.23	8.32
$1\,^1B_1(\sigma \to \pi^*)$	10.18	9.09		−0.198	−10.0	−8.6	−8.2	0.0120	9.97	9.26	9.35
$3\,^1B_2(n_y \to 3d_{x^2-y^2})$	8.56	9.13	8.88[k]	+0.001	−46.6	−53.8	−31.0	0.0061	8.96		9.05
$2\,^1B_1(n_y \to 3d_{xy})$	8.49	9.23		+0.098	−58.3	−56.4	−23.1	0.0003			9.32
$3\,^1A_1(n_y \to 3d_{yz})$	8.78	9.24		−0.076	−25.3	−58.7	−58.8	0.0026			9.25
$4\,^1B_2(n_y \to 3d_{z^2})$	8.70	9.31		−1.780	−47.0	−23.9	−67.9	0.0011	8.46	9.07	9.25
$3\,^1A_2(n_y \to 3d_{xz})$	9.08	9.31	9.22[j]	+0.659	−60.8	−23.7	−61.0	Forbidden	10.08		9.34
$4\,^1A_1(\pi \to \pi^*)$	10.24	9.77		−0.295	−13.5	−12.0	−14.9	0.2770	9.19	9.27	9.60
Triplet states											
$1\,^3A_2(n_y \to \pi^*)$	3.75	3.48	3.50[f]	−0.445	−10.2	−7.7	−8.9		4.15		
$1\,^3A_1(\pi \to \pi^*)$	5.52	5.99	5.82[f]	−0.349	−9.0	−8.7	−9.6		6.72		

a Dipole moment (CASSCF) in a.u.
b Expectation value (CASSCF) of x^2, y^2, and z^2 (in a.u.)
c CIS-MP2 results from Ref. [25]
d CCSD results from Ref. [26]
e MRD-CI results from Ref. [28]
f Electron-impact data from Ref. [12]
g Ref. [10]
h Absorption data from Refs. [9, 11]
i Absorption data from Refs. [2, 6, 9, 11]
j Electron energy-loss data from Ref. [7]
k Absorption data, Ref. [11]

appreciably larger than those of the ground and valence excited states. The $^1A_1(\pi \to \pi^*)$ excited state has a value somewhat larger than the ground state, indicating a certain small valence–Rydberg mixing. The detailed interpretation of the results presented in Table 3 is discussed below.

3.1.1 Valence excited singlet states ($1\,^1A_2$, $1\,^1B_1$, and $4\,^1A_1$). The lowest singlet state is of $^1A_2$ symmetry. The vertical excitation energy calculated at the PT2F level, 3.91 eV, is in agreement with experimental evidence [5, 10, 12]. For formaldehyde the lowest energy band observed in the electron-impact spectrum reported by Walzl et al. [12] is that due to the $^1A_2(n_y \to \pi^*)$ transition with a maximum at 3.79 eV. This corresponds closely to the observed weak peak in the absorption spectrum [5, 10].

All theoretical models also predict the lowest singlet excited state of formaldehyde to be $^1A_2$. The deviation from experiment is, however, sometimes large. The PT2F excitation energy is 0.71 eV smaller than the CASSCF value, indicating that for this transition a well-balanced treatment of electron correlation effects is important. Similar values (within 0.1 eV) were obtained for this transition at the CCSD and MRD-CI levels. The CIS-MP2 result overestimates it by more than 0.5 eV.

The second valence excited state corresponds to the $1\,^1B_1$ state and is located at 9.09 eV with a computed intensity of 0.01. It corresponds to a $(\sigma \to \pi^*)$ transition involving the highest occupied orbital of a_1 symmetry. The CIS-MP2 result for this transition deviates from the PT2F excitation energy by about 1 eV. The present result is, however, consistent with the CCSD and MRD-CI results. It has not been experimentally observed.

The third valence excited state calculated is the $4\,^1A_1$ state. In the present study this state is found at 9.77 eV, with an intensity of 0.28. This is thus the expected $(\pi \to \pi^*)$ valence transition for which there seems to be no experimental evidence neither in absorption nor in electron scattering spectra [5]. $4\,^1A_1$ state appears as the fourth root of the average CASSCF calculation. At both the CASSCF and PT2F levels the Rydberg $^1A_1(n_y \to 3p_y)$ and $^1A_1(n_y \to 3d_{yz})$ states are placed below. The difference between the CASSCF and PT2F results is 0.47 eV, somewhat lower than expected for a valence transition. That this state has mainly a valence character is clearly shown from the analysis of the multiconfigurational wave function. The weight of the $(\pi \to \pi^*)$ configuration is 83.7%, the next most important configuration accounts for intravalence correlation through a contribution of the closed-shell ground state configuration, 5.8%. The weights of the $n_y \to 3p_y$ and the $n_y \to 3d_{yz}$ configurations are 3.0% and 3.7%, respectively. Thus, we conclude that the amount of Rydberg character in the $^1A_1(\pi \to \pi^*)$ state is small, which supports previous conclusions [19].

The earliest *ab initio* results usually placed this transition in the range 10–11 eV [20]. The CIS-MP2 and CCSD results are however around 9 eV (cf. Table 3). The PT2F result, 9.77 eV, supports the MRD-CI value, 9.60 eV. The current interpretation that the singlet vertical $(\pi \to \pi^*)$ transition lies near the first ionization limit and thus might be part of a series of $^1A_1$ states cannot therefore be discarded.

3.1.2 Rydberg excited singlet states. The first and second ionization potentials of formaldehyde are separated by more than 3 eV from each other [29]. The corresponding members of Rydberg series converging to these two ionization potentials are expected to lie within the same energy range of each other. The first member in the first series appears at 7.3 eV (computed value for $3s$). Thus the Rydberg series

converging to the second ionization limit are expected to start close to the first ionization potential. Here we discuss the PT2F energies and assignments for excitations out of the n_y, HOMO $2b_2$ orbital, to the $3s$, and the different components of the $3p$ and $3d$ Rydberg orbitals and compare them with the experimental assignment and the results of previous calculations.

$n_y \rightarrow 3s$ (1^1B_2). The calculated vertical transition energy from the ground to the $3s$ Rydberg orbital is 7.30 eV. The oscillator strength is around 0.01. This energy corresponds to the interval 7.02–7.48 eV in the optical spectrum. This region is dominated by a narrow and intense band with the absorption maximum at 7.09 eV [9, 11]. The same transition has also been reported from electron-impact spectroscopy, with an observed maximum at 7.10 eV [4]. The vertical PT2F results are therefore consistent with experiment, in both excitation energy and assignment. The CCSD and MRD-CI energies are of similar accuracy, while the transition energy computed at the CIS-MP2 level is somewhat too low.

$n_y \rightarrow 3p$ (2^1B_2, 2^1A_1, and 2^1A_2). The 2^1B_2 state is calculated to lie 8.09 eV and the 2^1A_1 state 8.12 eV above the ground state, the latter with about twice the intensity of the former. Both are more intense than the $1^1B_2(n_y \rightarrow 3s)$ transition. The assignment of the 7.97 and 8.14 eV bands in the VUV spectrum has been discussed for a long time [2, 6, 9, 11]. A concise and clear historical background on whether the $2^1A_1(n_y \rightarrow 3p_y)$ transition occurs experimentally at 8.14 or 7.97 eV, along with an analysis of previous theoretical results, was given by Allen and Schaefer [22]. The calculated separation between the two states, 0.03 eV, is small and well within the expected error bars of the calculation. Thus, the results do not unequivocally assign the 2^1B_2 and 2^1A_1 Rydberg states. But in either case the agreement between theory and experiment is good. The $2^1A_2(n_y \rightarrow 3p_x)$ state is placed at 8.32 eV in agreement with experimental evidence [7].

The same relative energy ordering of the ($n_y \rightarrow 3p$) Rydberg states is given by the CCSD and MRD-CI calculations. The CCSD results are slightly shifted to lower energy values. The CIS-MP2 results, by contrast, have larger deviations.

$n_y \rightarrow 3d$ (3^1B_2, 2^1B_1, 3^1A_1, 4^1B_2, and 3^1A_2). These five members of the $3d$ series have been computed to lie in the energy range 9.13–9.31 eV. The 3^1B_2 and 3^1A_1 states are most intense. They can be related to the Rydberg series observed in absorption spectra with one band peak at 8.88 eV [2, 11]. The quantum defect obtained was, however, somewhat large for an $n_y \rightarrow 3d$ Rydberg transition [3]. Valence–Rydberg mixing was invoked to explain the unusually large quantum defect [2, 5]. The present results characterize all these states by singly excited configurations. The $\pi \rightarrow \pi^*$ configuration, in particular, contributes only little (3.4%) to the wave function for the 3^1A_1 state, in disagreement with previous predictions [2, 5].

The computed transition energy to 3^1A_2, 9.31 eV, gives support to a previous assignment based on data from an electron energy-loss spectrum [7]. Taylor et al. [7] reported a feature around 9.30 eV exhibiting a behavior and quantum defect (≈ 0.12) consistent with the transition to the $3d_{xz}$ $^1A_2$ state. The CIS-MP2 calculations place this transition at higher energies, while the PT2F and MRD-CI results are similar.

3.1.3 Valence excited triplet states (1^3A_2, 1^3A_1). The two low-lying valence triplet states of formaldehyde have also been treated in this study. These states occur at 3.48 eV (1^3A_2) and 5.99 eV (1^3A_1). Walzl et al. [12] reported a spin-forbidden band with a maximum at 3.50 eV, which partially overlaps the $n_y \rightarrow \pi^*$ $^1A_2$ band. The underlying band was assigned to the $n_y \rightarrow \pi^*$ $^3A_2$ transition. It was previously

observed in a comparable electron scattering experiment by Taylor et al. [7]. Transitions to the $^3A_2$ state are forbidden in optical spectra by the spin selection rule although very weak absorption (to low vibrational levels of the state) was observed by Robinson and Digiorgio [1]. In electron-impact spectroscopy a band with a maximum at 5.82 eV was observed, which was assigned to the $\pi \rightarrow \pi^*$ $^3A_1$ transition [7, 12]. Our calculated results are in agreement with the experimental data.

3.2 Adiabatic singlet valence excited states

Knowledge about the vertical transitions does not lead very far towards the understanding of the spectroscopy of formaldehyde. The complicated photochemistry has been described clearly in the recent papers by Hachey et al. [27, 28]. They studied the potential surfaces for the most important excited states as functions of the CO distance. Their calculation, although describing some important features of the excited state potential surfaces, does not arrive at the true adiabatic excitation energies, since not all geometry parameters were varied. As we shall see below, it is important to allow the HCH angle to relax, which for the planar geometry gives a $^1B_1$ state below the 2^1A_1 state, a result not obtained by Hachey et al. Full geometry optimization has been performed here both for the planar (C_{2v}) geometries (three geometry parameters) and for the non-planar structure, where the CH_2 group is tilted (four parameters). These calculations were performed at the CASPT2 level by a pointwise optimization of the geometries.

The equilibrium geometries obtained for the ground and valence excited states are listed in Table 4. For the sake of comparison, literature data of previous theoretical results as well as available experimental derived information are also included.

Because of the nature of the considered transitions, which involves excitation into the antibonding π^* orbital, the C–O bond length is expected to increase with respect to the ground state. To properly describe such a situation, a multiconfigurational wave function with enough flexibility in the CO bond region is required. This is accomplished by including both the σ, σ^* and π, π^* MOs in the active space (four active electrons). For states, where the electron is excited out of the oxygen lone pair, the active space is enlarged to five active orbitals with six active electrons (cf. Table 2). Since the states of interest are of valence nature, in particular in the regions around the equilibrium geometries, the ANO-type C, O[$4s3p1d$]/H[$2s1p$] basis set without the Rydberg functions was used. Diffuse functions can be expected to have a minor effect on the geometry. In this respect, the predictions of the optimum geometry and adiabatic excitation energy of valence excited states are easier than the prediction of the vertical excitation energy. The equilibrium geometries of the Rydberg states converging to the first ionization potential can be expected to be close to the ground state equilibrium geometry of the formaldehyde cation, 1^1B_2 state, which is similar to the ground state geometry for the neutral system. At the equilibrium geometries of the excited valence states, which are significantly different from that of the ground state, the large energy separation between the valence and nearest Rydberg state makes the valence–Rydberg mixing negligible. The influence of enlarging the one-electron basis on the computed transition excitation energies was however checked (vide infra).

With the CASSCF(2200) wave function as the reference function, which comprises 12 configurations, the geometrical parameters obtained at the PT2F level for

Table 4. Equilibrium geometries for the ground state and the singlet valence excited states of formaldehyde (in Å and degrees) and transition energies, T_e (in eV)

	$r_e(CO)$	$r_e(CH)$	$\theta_e(HCH)$	ϕ_e^a	T_e	Method (ref.)
Ground state (1^1A_1)	1.221	1.105	116.2			PT2F (this work)
	1.220	1.103	116.5			TCSCF-CI (3 ref.) [22]
	1.186	1.091	116.3			CIS [24]
	1.208	1.116	116.5			From MW data [40]
	1.203	1.101	116.2			From MW data [45]
$1^1A''(n_y \to \pi^*_x)$	1.352	1.092	120.6	30.8	3.37	PT2E (this work)
	1.248	1.088	117.3	30.7	4.54 (4.33)	CIS (CIS-MP2) [25]
	1.323	1.103	118.1	34.0	3.50[b]	From MW data [46]
$1^1A_2(n_y \to \pi^*)$	1.354	1.090	124.8		3.40	PT2F (this work)
	1.248	1.084	121.0		4.55 (4.35)	CIS (CIS-MP2) [25]
$2^1A'(\sigma \to \pi^*, \pi \to \pi^*)$	1.492	1.094	118.4	46.2	7.43	PT2F (this work)
	1.489	1.079	121.9	46.5	8.14 (8.49)	CIS (CIS-MP2) [25]
	1.528	1.080	111.3	≈44	7.53	MRD-CI [27]
$1^1B_1(\sigma \to \pi^*)$	1.470	1.089	139.1		7.70	PT2F (this work)
	1.480	1.069	142.6		8.35 (8.79)	CIS (CIS-MP2) [25]
	1.418				8.27[c]	MRD-CI [27]
$2^1A_1(\pi \to \pi^*)$	1.552	1.095	121.6		7.84	PT2F (this work)
	1.564	1.090	119.4		8.50[d] (7.99)[e]	TCSF-CI (3 ref.) [22]
	1.454	1.074	124.4		8.65 (8.60)	CIS (CIS-MP2) [25]
	1.588				7.95[c]	MRD-CI [27]

[a] Out-of-plane angle
[b] Optical and electron-loss data, Ref. [8]
[c] All other geometrical parameters were fixed at the ground state values, see Ref. [27]
[d] Including zero-point corrections, otherwise 8.59 eV [22]
[e] Including the Langhoff-Davidson correction, as reported in Ref. [27]

the ground state are similar to previous findings at the TCSCF-CI level, which corresponds to three reference configurations [22]. The results are in reasonable agreement with the microwave (MW) data [40, 45], although the C–O bond length is slightly overestimated probably due to limitations in the AO basis set.

The $n_y \to \pi^*$ state is known to be non-planar (C_s symmetry) [5]. Analysis of the MW data predicted an out-of-plane angle of 34° [46]. The computed parameters agree with the structure derived from the experimental information. The C–O bond length is again somewhat overestimated; it is 0.03 Å longer than the experimental value. By contrast, the C–O bond length computed at the CIS level is significantly shorter than the experimental estimate. The adiabatic (T_e) transition energy, 3.37 eV, is in agreement with experimental evidence [5, 8]. The energy difference between the planar optimized geometry and the pyramidal optimized geometry gives the inversion barrier in the singlet $n_y \to \pi^*$ state. The computed value, 0.03 eV, is close to the experimentally determined inversion barrier of 350 cm^{-1} (0.043 eV) [46]. It may be noted that the pyramidalization does not lead to any appreciable changes in the other geometry parameters.

Most of the present results for the other excited states confirm the previous findings by Hachey et al. [27] which were obtained at the MRD-CI level. The differences can be related to the limited geometry optimization performed by them. In the case of planar states only the CO-stretch potential curves were considered with the remaining parameters fixed at the geometry of the ground state [27], while in the present study a full geometry optimization has been carried out. The major difference is that here the $^1B_1(\sigma \to \pi^*)$ state is pushed down below to 8 eV, to a lower energy than the $^1A_1(\pi \to \pi^*)$ state (cf. Table 4). This is due to a significant enlargement of the HCH angle in the $^1B_1$ state with respect to the ground state. The $^1B_1(\sigma \to \pi^*)$ state is well characterized by a single configuration described by an electron promotion from the bonding $\sigma(CO)$ to the carbonyl π^* orbital. The presence of the partially filled π^* orbital has the effect of lengthening the CO bond, as noted for the other valence excited states. Since the electronic promotion is from the $\sigma(CO)$ orbital, decreasing the electron charge density in the σ space has also the effect of a pronounced opening of the HCH angle. It can be related to the decrease of steric repulsion in the σ space between the CO and CH bonds. Similarly the ground state of methylene ($^3B_1$) shows a larger HCH angle than the low-lying $^1A_1$ excited state [47]. Actually, the orbital picture is similar to that in methylene. The σ orbital has a large weight on carbon $2p$ and the π^* orbital is also located mainly on the carbon atom. The excited state therefore has a character similar to the $^3B_1$ state in methylene, where the bond angle is 132°. For the remainder valence states of formaldehyde (C_{2v} symmetry), the promoted electron comes from the non-bonding MO (n_y) or from the bonding π orbital, which does not directly involve the σ CO and CH bonds. Therefore, the values of the HCH angle are not so much affected.

For formaldehyde there is no currently accepted experimental result for the singlet $\pi \to \pi^*$ state. All the small aldehydes were at one time believed to have an $^1A_1(\pi \to \pi^*)$ state near 7–8 eV and earlier semi-empirical methods were calibrated to reproduce this result [5, 20]. It is now established that the lowest vertically excited $^1A_1$ state corresponds instead to an $n_y \to 3p_y$ Rydberg state. As discussed in the preceding section, the vertical excitation from the ground state to the $^1A_1(\pi \to \pi^*)$ state is high in energy; the valence state is placed above the $n_y \to 3p$, $3d$ Rydberg members, at 9.8 eV. The consensus is that the $(\pi \to \pi^*)$ transition most likely takes the form of a broad, undetected feature, underlying the somewhat congested Rydberg region between 7 and 12 eV, in the same way as the Rydberg

transitions of ethylene are superimposed on the broad singlet ($\pi \to \pi^*$) transition. Indeed, inspection of the electron energy-loss spectra of formaldehyde shows that the spectral peaks above ≈ 8 eV, corresponding to Rydberg series converging on the first ionization limit, are positioned on a non-zero background [7]. The band origin of the ($\pi \to \pi^*$) state could be expected close to 8 eV. The present results indicate a more complex structure in this region, although it may be noted that the computed lowest excitation energy for the planar geometry is 7.84 eV.

The effect of enlarging the one-electron basis set on the computed transition energies was checked in different ways. First, the basis set C, O[$4s3p1d$]/H[$2s1p$] was supplemented with the above-mentioned $1s1p1d$ set of Rydberg functions. The computed values were the same both at the CASSCF level and at the PT2F level. The same results were also obtained by using the C, O[$4s3p2d$]/H[$3s2p$] basis set. A small increase was however found when the basis set was further incremented including up to f-type functions. The C, O[$5s4p3d2f$]/H[$3s2p1d$] basis set resulted in the following PT2F transition energies for the $^1A''$, $^1A_2$, $^1A'$, $^1B_1$, and $^1A_1$ states, respectively: 3.46, 3.48, 7.52, 7.72, and 7.92 eV. The largest deviation from the results given in Table 4 is 0.09 eV.

4 Conclusions

In this paper results have been presented from an *ab initio* study of the main features of the electronic spectrum of formaldehyde up to 10 eV. An appropriate CASSCF wave function was used as reference function in a multiconfigurational second-order perturbation treatment. Computed vertical transition energies are found to be in agreement with available experimental data and recent MRD-CI results to about 0.2 eV.

The vertical excitation energy of the controversial intravalence $^1A_1(\pi \to \pi^*)$ state was computed to be 9.8 eV. However, this state has been found to have a CO distance, which is 0.27 Å longer than that of the ground state, and the CH_2 group is tilted $46°$. A full geometry optimization stabilizes the state with 2.3 eV and places the adiabatic excitation energy at 7.4 eV. The corresponding energy for a molecule, which is restricted to be planar, is 7.8 eV. It is therefore most likely that the underlying valence feature with origin around 8 eV, which has been found in the formaldehyde spectrum, is due to this transition. In a forthcoming publication we shall discuss, in more detail, the corresponding features in the electronic spectrum of acetone [48].

References

1. Robinson GW, Digiorgio VE (1958) Can J Chem Soc, p 31
2. Mentall JE, Gentieu EP, Krauss M, Neumann D (1971) J Chem Phys 55:5471
3. Weiss MJ, Kuyatt CE, Mielczarek S (1971) J Chem Phys 54:4147
4. Chutjian A (1974) J Chem Phys 61:4279
5. Moule DC, Walsh AD (1975) Chem Rev 75:67

6. Lessard CR, Moule DC (1977) J Chem Phys 66:3908
7. Taylor S, Wilden DG, Comer J (1982) Chem Phys 70:291
8. Clouthier DJ, Ramsay DA (1983) Ann Rev Phys Chem 34:31
9. Brint P, Connerade J-P, Mayhew C, Sommer K (1985) J Chem Soc Faraday Trans 2 81:1643
10. Robin MB, (1985) In: Higher excited states of polyatomic molecules, Vol. 3. Academic Press, New York
11. Suto M, Wang X, Lee LC (1986) J Chem Phys 85:4228
12. Walzl KN, Koerting CF, Kuppermann A (1987) J Chem Phys 87:3796
13. Whitten JL, Hackmeyer M (1969) J Chem Phys 51: 5584
14. Buenker RJ, Peyerimhoff SD (1970) J Chem Phys 53:1368
15. Peyerimhoff SD, Buenker RJ, Kammer WE, Hsu H (1971) Chem Phys Lett 8:129
16. Whitten JL (1972) J Chem Phys 56:5458
17. Langhoff SR, Elbert ST, Jackels CF, Davidson ER (1974) Chem Phys Lett 29:247
18. Harding LB, Goddard III WA (1975) J Am Chem Soc 97:6293
19. Harding LB, Goddard III WA (1977) J Am Chem Soc 99:677
20. Davidson ER, McMurchie LE (1982) In Excited states, Vol. 5. Academic Press, New York
21. Fitzgerald G, Schaefer III HF (1985) J Chem Phys 83:1162
22. Allen WD, Schaefer III HF (1987) J Chem Phys 87:7076
23. Galasso V (1990) J Chem Phys 92:2495
24. Foresman JB, Head-Gordon M, Pople JA, Frisch MJ (1992) J Phys Chem 96:135
25. Hadad CM, Foresman JB, Wiberg KB (1993) J Phys Chem 97:4293
26. Head-Gordon M, Rico RJ, Oumi M, Lee TJ (1994) Chem Phys Lett 219:21
27. Hachey M, Bruna PJ, Grein F (1994) J Chem Soc Faraday Trans 90:683
28. Hachey MRJ, Bruna PJ, Grein F (1995) J Phys Chem 99:8050
29. Niu B, Shirley DA, Bai Y (1993) J Chem Phys 98:4377
30. Serrano-Andrés L, Merchán M, Nebot-Gil I, Lindh R, Roos BO (1993) J Chem Phys 98:3151
31. Roos BO (1987) In: Lawley KP (ed) Advances in chemical physics; ab initio methods in quantum chemistry – II, Ch. 69, Wiley, Chichester, p 399
32. Andersson K, Malmqvist P-Å, Roos BO, Sadlej AJ, Wolinski K, (1990) J Phys Chem 94:5483
33. Andersson K, Malmqvist P-Å, Roos BO (1992) J Chem Phys 96:1218
34. Andersson K, Roos BO (1994) In: Yarkony R (ed) Modern electron structure theory, Vol. 1. World Scientific Publishing, New York
35. Roos BO, Fülscher MP, Malmqvist Per-Åke, Merchán M, Serrano-Andrés L (1994) In: Langhoff SR (ed) Quantum mechanical electronic structure calculations with chemical accuracy. Kluwer, Dordrecht
36. McDiarmid R, private communication
37. Widmark P-O, Malmqvist P-Å, Roos BO (1990) Theor Chim Acta 77:291
38. Fülscher MP, Lorentzon J, Malmqvist P-Å, Roos BO (to be published)
39. Kaufmann K, Baumeister W, Jungen M (1989) J Phys B: At Mol Opt Phys 22:2223
40. Takagi K, Oka T (1963) J Phys Soc Jpn 18:1174
41. Andersson K, Roos BO (1993) Int J Quantum Chem 45:591
42. Malmqvist P-Å (1986) Int J Quantum Chem 30:479
43. Malmqvist P-Å, Roos BO (1989) Chem Phys Lett 155:189
44. Andersson K, Blomberg MRA, Fülscher MP, Kellö V, Lindh R, Malmqvist P-Å, Noga J, Olsen J, Roos BO, Sadlej AJ, Siegbahn PEM, Urban M, Widmark P-O (1992) MOLCAS version 2 user's guide. Department of Theor Chem, Chem Center, University of Lund, Lund
45. Duncan JL (1974) Mol Phys 28:1177
46. Jensen P, Bunker PR (1982) J Mol Spectr 94:114
47. Bauschlicher CW, Shavitt I (1978) J Am Chem Soc 100:739
48. Merchán M, Roos BO, McDiarmid R (to be published)