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REGULAR ARTICLE

Oscillator strengths and photoionisation cross sections for Rydberg transitions in acetaldehyde

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Abstract Oscillator strengths for electronic transitions involving Rydberg states of acetaldehyde, as well as cross sections for all the dipole allowed photoionisation channels, all ending in the ground state of the molecular cation, are reported. The molecular quantum defect orbital method, which has proved to be reliable in previous applications to molecular Rydberg states, has been used. Despite its relevance for atmospheric chemistry and astrophysics, only a few data seem to be available in the literature. The continuity of the calculated differential oscillator strength across the ionisation threshold has been adopted as a quality criterion. To our knowledge, predictions of oscillator strengths for transitions to high-lying Rydberg states, as well as of photoionisation profiles on acetaldehyde are made here for the first time and we are not aware of any reported experimental data. We, thus, hope the present results may be useful in the interpretation of the spectrum of acetaldehyde and might be of help in future experimental measurements.

Keywords Acetaldehyde · Rydberg states · Oscillator strengths · Photoionisation cross sections

1 Introduction

Acetaldehyde, CH_3CHO, plays an important role in atmospheric chemistry because its photodissociation generates free radicals [1]. This molecule is also relevant in astrophysics and astrobiology. Since the time acetaldehyde was first detected in the interstellar medium [2], it has also been found in a variety of interstellar environments, such as dark molecular clouds, star-forming regions and comets [3–5]. Several authors [4, 6] have pointed out that organic molecules, which include acetaldehyde, are of special interest to understand the astrochemical evolution of many astronomical objects. They have also been found to be of potential prebiotic importance. Because of aforementioned features, among others, it is apparent that the interpretation of the atmospheric and interstellar observations as well as the modelling of physical and chemical processes occurring in the Earth's atmosphere and interstellar space requires reliable spectroscopic data of the existing molecular species in those regions.

The electronic spectrum of acetaldehyde has been less investigated than those of its carbonyl homologues, formaldehyde and acetone, even though acetaldehyde can provide information as an intermediate case of the two other carbonyl molecules. The first vacuum ultraviolet absorption spectrum of acetaldehyde was photographed by Walsh [7], who found three Rydberg series leading to the first ionisation potential. Since then, a few more experimental investigations [8–13] on the highly excited electronic states of this molecule have been performed. The most relevant works, in what concerns the present study, are the high-resolution spectra obtained by Brint et al. [12] and by Limao-Vieira et al. [13]. From their measurements, Brint et al. [12] resolved the *ns*, *np* and *nd* Rydberg series up to a principal quantum number of $n = 13$, 45 and 10, respectively. More recently, Limao-Vieira et al. [13] measured photoabsorption cross sections of acetaldehyde using a synchrotron radiation source. In their analysis of the so-obtained spectrum, these authors could assign two

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nd-component Rydberg series converging to the ground state of CH_3CHO^+, that is, the nd_{xy} and nd_{z^2} series. From these works, several important features inherent to the absorption spectrum of acetaldehyde in the vacuum ultraviolet region could be inferred. Below the first ionisation limit, the spectrum consists mainly of bands associated with transitions from the outermost electron in the ground state to a number of Rydberg states. Predissociation resulting from valence–Rydberg interaction is not expected to play an essential role here. Little vibrational or rotational structure seems to be observed in the Rydberg series, other than 3*s* and 3*p* band systems.

As to some existing theoretical studies, most of the calculations on acetaldehyde have mainly focused on the determination of excitation energies for the low-lying electronic states. To our knowledge, only three works have reported intensity data for electronic transitions in the bound spectral region of this molecule employing different theoretical techniques. For instance, Galasso [14] applied the random phase approximation (RPA) in his study. A configuration interaction calculation in which all single excitations were included was performed by Hadad et al. [15]. Gwaltney and Barlett [16] used the equation-of-motion coupled cluster (EOM-CC) method in their calculations. In all these works, values of oscillator strengths were supplied for transitions to the lower members ($n = 3$, 4) of the Rydberg series only. Moreover, considerable discrepancies among them have been detected.

As regards the continuum spectrum of acetaldehyde, the only values of ionisation cross section data found in the literature are those of Vacher et al. [17]. These authors determined total cross sections for the formation of the $C_2H_4O^+$ and other ionic fragments from electron impact ionisation studies of acetaldehyde. In spite of the attention attracted by the variation in the photoionisation cross sections with the increasing excitation energy for specific ionic states, no such studies on acetaldehyde, as far as we know, have been reported.

The above discussion shows the scarcity of intensity data for transitions to Rydberg states in acetaldehyde, in spite of its electronic spectrum below the ionisation limit being mostly dominated by such excitations. Moreover, there seems to be a real need of further studies which may discern some of the existing controversies concerning the assignment of some of the electronic states of acetaldehyde. Hence, in order to gain a better insight into the spectral features of this molecule and so derive a much needed knowledge of the role played by the different Rydberg series in the spectrum of acetaldehyde, intensities for electric dipole transitions involving high Rydberg states, including the continuum region of spectrum, have been calculated in the present work.

We have proceeded by calculating the absorption oscillator strengths, or *f* values, for transitions from the ground electronic state of acetaldehyde to the states of the *ns* Rydberg series, and for states which constitute the components of the *nd* Rydberg series up to $n = 9$. We are well aware of some of the characteristics of low-symmetry molecules, to which acetaldehyde belongs. In this kind of molecules, experimental difficulties are encountered while attempting to distinguish Rydberg states with the same orbital angular momentum quantum number, *l*, but different symmetry. This problem is created by the lack of rotational resolution of the spectral bands [18]. However, properties such as the transition intensities can, as claimed by Hachey and Grein [19], be a good supplement to the one provided by the excitation energy, in the assignment of the peaks observed in the spectrum to specific molecular states. We have, then, made immediate use of the just calculated transition intensities to perform a tentative assignment for the two observed *d* Rydberg series. Some discrepancies with the assignment reported by Limao-Vieira and coworkers [13] can be noticed.

Since the acetaldehyde molecular cation has been shown to be stable in its ground state [20, 21], we have calculated photoionisation cross section for the production of the molecular ion in its lowest electronic state. Cross sections for the different Rydberg series that may act as ionisation channels are also supplied. Photoionisation cross sections studies are of great usefulness, in the sense they provide a basis for band assignment and, moreover, these properties can reveal crucial details regarding the electronic structure of the studied molecular system [22].

The present calculations have been carried out with the molecular quantum defect orbital (MQDO) method. This approach has proven to work rather well for supplying accurate spectroscopic data such as oscillator strengths and photoionisation cross sections, in particular when Rydberg states are involved, as in some very recent applications [23, 24]. Particularly relevant for the present work has been our recent study [25] of the electronic spectrum of formaldehyde in both the discrete and continuum regions. The calculated *f* values and photoionisation cross sections showed a good agreement with experimental data. Therefore, on the basis of our experience on formaldehyde, we are confident of the ability of the theoretical approach adopted for this study Rydberg transitions on its homologue molecule, acetaldehyde.

2 Method of calculation

The MQDO method, based on a semiempirical model potential, has proven to be appropriate in dealing with molecular Rydberg states, mainly because they possess an atomic-like character, with the spherical ionic core replaced by a molecular cation which imposes internal crystal field splitting according to its symmetry. Given that the method has been described in detail [26, 27], only a brief survey of it will be given.

The quantum defect orbitals are obtained through the analytical solution of a one-electron Schrödinger equation whose radial part contains a model potential of the following form:

$$V(r)_a = \frac{(c - \delta_a)(2l + c - \delta_a + 1)}{2r^2} - \frac{Z_{\text{net}}}{r}, \qquad (1)$$

where a represents the set of quantum numbers that define a given molecular state, c is an integer chosen to ensure the normalisation of the orbitals and their correct nodal pattern, δ_a is the quantum defect and Z_{net} is the molecular core's effective charge acting on the Rydberg electron. The angular part of the MQDO wave functions is expressed as a symmetry-adapted combination of spherical harmonics, in such a way that the complete MQDO's form bases for the different irreducible representations of the molecular symmetry group.

In this study, the discussion of spectral intensities will be done in terms of oscillator strengths and photoionisation cross sections for the discrete and continuum region, respectively. In the MQDO formalism, the absorption oscillator strength for a transition between two bound states, i and f, may be expressed as

$$f_{if} = \frac{2}{3} N \Delta E Q_{if} \left| R_{if} \right|^2, \qquad (2)$$

where N is the number of equivalent electrons in the molecular orbital from which the electronic transition originates, ΔE is the transition energy, in atomic units, Q_{if} results from the angular integration, and R_{if} is the radial transition moment. An important computational advantage of the MQDO method is that the radial integrals result in closed-form analytical expressions.

For a bound-continuum transition, the photoionisation cross section is defined (in units of megabarns, Mb) as

$$\sigma = 2.6891 N \left[\frac{Z_{\text{net}}}{(n - \delta)^2} + k^2 \right] \frac{1}{2k} Q_{if} \left| R_{if} \right|^2 \qquad (3)$$

with $k = (2E)^{1/2}$.

As a consequence of the one-centre character of the MQDO wave functions, the Laporte selection rule applies to electronic transitions, in addition to restrictions imposed by molecular symmetry. This selection rule is approximately valid in transitions to Rydberg molecular states since they possess mainly one-cente character. Although transitions complying with $\Delta l = \pm 1$ are usually much stronger than the others, Laporte-forbidden transitions may be anomalously strong owing to vibronic interaction with nearby states of the same symmetry, as it has been reported for some $3p$ Rydberg transitions in acetaldehyde. However, this drawback of the model may be compensated by its ability to predict spectral intensities for transitions to high Rydberg states, including the continuum, of this molecule. It should be mentioned that ab initio methods still have difficulties in calculating transition probabilities to Rydberg states, other than the low-lying Rydberg states. Additionally, theoretical approaches for the determination of continuum wave functions are less advanced than those for bound wave functions [22].

3 Results

For the acetaldehyde molecule, we have adopted the geometrical setup of Singleton and Brint [18], i. e. the C_s symmetry with the z axis being perpendicular to the plane of the molecule. The $\mathrm{X}^1\mathrm{A}'$ ground state electronic configuration is given by Tam and Brion [9] as $(1s_{\mathrm{O}})^2$ $(1s_{\mathrm{CO}})^2$ $(1s_{\mathrm{CH3}})^2$ $(1a')^2$ $(2a')^2$ $(3a')^2$ $(4a')^2$ $(5a')^2$ $(1a'')^2$ $(6a')^2$ $(2a'')^2$ $(7a')^2$. The highest occupied molecular orbital (HOMO), $7a'$, has been reported to be an oxygen non-bonding orbital, mostly oxygen $2p_y$ atomic orbital [28]. The electronic transitions presently studied consist in the promotion of the $7a'$ electron from the ground state to states that belong to Rydberg series converging to the ground state of $\mathrm{CH_3CHO^+}$. Given that the Rydberg states have essentially atomic character, it is normal practice to characterise them with the atomic quantum numbers n and l in the discrete region and k, instead of n, in the continuum region.

The calculation of f values with the MQDO procedure requires the knowledge of the quantum defects associated with the states involved in the transition studied. Those are deduced from experimental energy level data, when they are available, through the well-known Rydberg formula. For the ionisation energy of $\mathrm{CH_3CHO}$, we have adopted the value of 82,526.45 ± 0.05 $\mathrm{cm^{-1}}$, which is claimed [12] to be very accurate, as it has been determined by extrapolation from a Rydberg series observed up to $n = 45$. For the ns series and for two components of the nd Rydberg series, experimental energies [13] have been taken. As it has been already mentioned, the assignment of nd Rydberg states in acetaldehyde is controversial. Limao-Vieira et al. [13] identified two Rydberg series starting at 8.434 and 8.707 eV, which they assigned, in C_s symmetry, as the nd_{z^2} and nd_{xy} series, respectively. An inspection of their spectrum reveals that the first of the two d series is the most intense. But, this appears to be inconsistent with a d_{z^2} component since this orbital is expected to have a smaller overlapping with the non-bonding $2p_y$ orbital of the ground state than the nd_{xy} orbital does. On the other hand, Hachey and Grein [19] suggested that the prominent d-series observed by Brint et al. [12] at energies similar to the first of the two Rydberg series mentioned above is consistent with the d_{yz} component of the *nd* manifold, which possesses A″ symmetry. In contrast, very accurate calculations on acetaldehyde made by Head-Gordon et al. [29] with the full EOM-CCSD method, predicted the Rydberg state at 8.39 eV to be of A′ symmetry, rather than A″ symmetry. This is confirmed by more recent high-level calculations [30] on this molecule. Bearing these features in mind, the energies reported by Limao-Vieira et al. [13] for the series whose first members are found at 8.434 and 8.707 eV, respectively, have been adopted for the nd_{xy} and nd_{z^2} series in the present calculations. Although there is clear evidence of the occurrence of other *d*-transitions [9, 12], no experimental energy data for them appear to be available. On the theoretical part, the calculations of Head-Gordon et al. [29] predicted 3*d* Rydberg states of A′, A′ and A″ symmetries to lie at 8.39, 8.51 and 8.57 eV, respectively. Assuming that the lowest energy state is the $3d_{xy}\ ^1A'$, possible assignments for the other two energy levels are the $3d_{x^2-y^2}$ A′ and $3d_{yz}$ A″ states. Hence, quantum defects of 0.19 and 0.13 for the $3d_{x^2-y^2}$ and $3d_{yz}$ states, respectively, obtained from EOM-CCSD vertical excitation energies [29], have been taken in our calculations. Given that for higher members of these series no energy data have been found in the literature, and, on the grounds of the well-known fact that the quantum defects associated with an unperturbed Rydberg series exhibit a very nearly constant value, we have used the quantum defects derived for the lowest members of each of these two *d* series.

The MQDO oscillator strengths calculated for transitions from the HOMO, the $7a'$ nonbonding orbital, to the $ns\ ^1A'$ with $n = 4$–9 and $nd_{xy}\ ^1A'$, $nd_{x^2-y^2}\ ^1A'$, $nd_{yz}\ ^1A''$ and $nd_{z^2}\ ^1A'$ with $n = 3$–9 Rydberg states are displayed in Table 1. The $7a' \rightarrow 3s$ transition has not been dealt with in the present work since it has been shown to exhibit considerable vibrational structure [31]. Other data from different theoretical sources have also been included for comparative purposes. These comprise the results obtained by Galasso [14] by using the RPA, the *f* values computed with the configuration interaction with single excitation (CIS) method by Hadad et al. [15] and the data from the calculations with the EOM-CC method by Gwaltney and Barlett [16]. It should be mentioned that the RPA and CIS approaches do not include (or only partially) electronic correlation, whereas EOM-CC model does it [16].

Table 1 Oscillator strengths for the $7a' \rightarrow ns$ ($n = 4$–9) and $7a' \rightarrow nd$ ($n = 3$–9) Rydberg transitions in CH_3CHO

Transition	MQDO[a]	Comparative
$7a' \rightarrow 4s\,^1A'$	0.01647	0.01731[b]
$7a' \rightarrow 5s\,^1A'$	0.00681	
$7a' \rightarrow 6s\,^1A'$	0.00329	
$7a' \rightarrow 7s\,^1A'$	0.00197	
$7a' \rightarrow 8s\,^1A'$	0.00112	
$7a' \rightarrow 9s\,^1A'$	0.00084	
$7a' \rightarrow 3d_{xy}\,^1A'$	0.07379	0.00196[b], 0.0028[c], 0.014[d]
$7a' \rightarrow 4d_{xy}\,^1A'$	0.02799	0.00200[b]
$7a' \rightarrow 5d_{xy}\,^1A'$	0.01323	
$7a' \rightarrow 6d_{xy}\,^1A'$	0.00747	
$7a' \rightarrow 7d_{xy}\,^1A'$	0.00453	
$7a' \rightarrow 8d_{xy}\,^1A'$	0.00308	
$7a' \rightarrow 9d_{xy}\,^1A'$	0.00214	
$7a' \rightarrow 3d_{x^2-y^2}\,^1A'$	0.06448	0.01454[b], 0.055[d]
$7a' \rightarrow 4d_{x^2-y^2}\,^1A'$	0.02581	0.00136[b]
$7a' \rightarrow 5d_{x^2-y^2}\,^1A'$	0.01264	
$7a' \rightarrow 6d_{x^2-y^2}\,^1A'$	0.00710	
$7a' \rightarrow 7d_{x^2-y^2}\,^1A'$	0.00438	
$7a' \rightarrow 8d_{x^2-y^2}\,^1A'$	0.00289	
$7a' \rightarrow 9d_{x^2-y^2}\,^1A'$	0.00201	
$7a' \rightarrow 3d_{yz}\,^1A''$	0.05622	0.08157[b], 0.0035[c], 0.024[d]
$7a' \rightarrow 4d_{yz}\,^1A''$	0.02353	0.01717[b]
$7a' \rightarrow 5d_{yz}\,^1A''$	0.01175	
$7a' \rightarrow 6d_{yz}\,^1A''$	0.00668	
$7a' \rightarrow 7d_{yz}\,^1A''$	0.00415	
$7a' \rightarrow 8d_{yz}\,^1A''$	0.00275	
$7a' \rightarrow 9d_{yz}\,^1A''$	0.00192	
$7a' \rightarrow 3d_{z^2}\,^1A'$	0.01408	0.00011[b], 0.0124[c], 0.005[d]
$7a' \rightarrow 4d_{z^2}\,^1A'$	0.00643	0.00110[b]
$7a' \rightarrow 5d_{z^2}\,^1A'$	0.00336	
$7a' \rightarrow 6d_{z^2}\,^1A'$	0.00192	
$7a' \rightarrow 7d_{z^2}\,^1A'$	0.00121	
$7a' \rightarrow 8d_{z^2}\,^1A'$	0.00081	
$7a' \rightarrow 9d_{z^2}\,^1A'$	0.00057	

[a] MQDO, this work

[b] RPA [14]

[c] CIS [15]

[d] EOM-CC [16]

The 4*s* band has been reported [12] to be broader than any other bands in the spectrum of acetaldehyde. This feature has been attributed to interact with an underlying molecular valence state of dissociative nature. For this band, a good agreement between the MQDO and RPA *f* values is found. No theoretical comparative data for transitions to higher member of the Rydberg series seem to be available. The accuracy of the present MQDO *f* values for transitions to high *ns* series members was assessed by testing its compliance with the expected systematic trends along the Rydberg series. For an unperturbed atomic Rydberg series the oscillator strength decreases as n^{*-3}, where n^* is the effective principal quantum number. According to Hachey and Grein [19], although there is no fundamental reason by which molecular Rydberg states should exhibit the same behaviour, there is also no reason

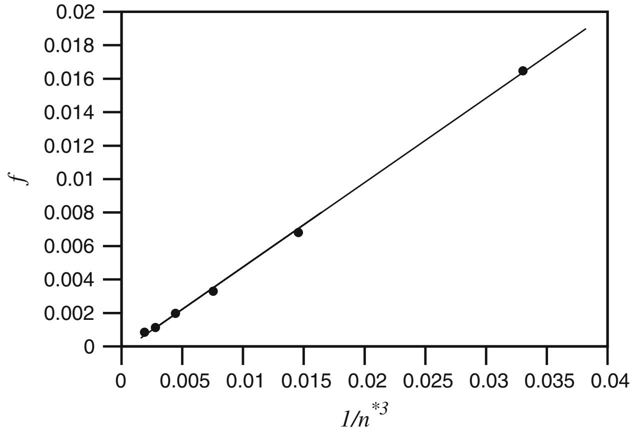

Fig. 1 Systematic trends of the MQDO oscillator strengths along the $7a' \to ns$ spectral Rydberg series in the acetaldehyde molecule

to expect the intensity (f value) variation to be different from that predicted for atomic series. As it can be seen in Fig. 1, in which MQDO f values are plotted versus $1/n^{*3}$, the ns Rydberg series of acetaldehyde exhibits atomic-like intensity behaviour. It is worth mentioning here that a monotonic decay for this series is observed in a high-resolution spectrum [12].

A few words concerning the assignment done in Table 1 of the d states reported by other researchers may be appropriate here. Gwaltney and Barlett [16] assigned their theoretical states for this molecule in terms of their symmetry only. Consequently, in order to make a comparison between the two sets of results, we have correlated their $3d$ states with the $3d$ components that were assigned according to the ordering of energies previously discussed. Galasso [14] classified their states according to C_{2v} symmetry on the basis of orbital composition and $\langle r^2 \rangle$ values. In this way, the d_{yz}, d_{xz} and d_{xy} orbitals were identified, and the other two d-components were labelled as d_σ and $d_{\sigma'}$ (in increasing energy order). We have assumed the state of higher energy, $d_{\sigma'}$, to be the d_{z^2} Rydberg state and, thus, we denote the states of their d_σ Rydberg seies as $d_{x^2-y^2}$ orbitals.

Regarding the theoretical comparative oscillator strengths for transitions to $3d$ Rydberg states, they exhibit a clear disparity between each other. As it has previously been mentioned, Limao-Vieira et al. [13] assigned the most intense band of the $3d$ system, the one at 8.434 eV, to the $7a' \to 3d_{z^2}$ ^{1}A′ transition. However, the present calculations, as well as those determined with the RPA approach [14], predict the $7a' \to 3d_{z^2}$ ($7a' \to 3d_{\sigma'}$ in the notation used by Galasso) transition to be much weaker than any of the other $3d$ Rydberg transitions. Consequently, we tentatively propose that the assignment of the two Rydberg series suggested by Limao-Vieira et al. should be the other way around, that is to say, the series whose first member is found at 8.434 eV would be the nd_{xy} series, and that starting at 8.707 eV would be the nd_{z^2} series. Comparison with intensities for $3d$ transitions in formaldehyde supports our assignments. For this molecule, the stronger $3d$ band corresponds to the transition from the $2p_y$ nonbonding orbital to the $3d_{yz}$ Rydberg state. Notice that in formaldehyde it is the x axis the one chosen to be perpendicular to the molecular plane instead of the z axis.

As it occurs in the ns Rydberg series, a monotonically decay of intensity as the excitation is greater is observed in the nd Rydberg series in high-resolution spectra [12]. It is worth mentioning the small values of the oscillator strengths for the $7a' \to 3d_{xy}$ ^{1}A′ and $7a' \to 3\ d_{z^2}$ ^{1}A′ transitions reported by Galasso [14], which are even lower than those for the $7a' \to 4d_{z^2}$ ^{1}A′ and $7a' \to 4d_{z^2}$ ^{1}A′ transitions, in opposition to the expected decrease in the f values as n increases in a Rydberg series. By contrast, this behaviour is fulfilled by all nd Rydberg series object of the present calculations, as is apparent in Table 1.

As mentioned in Sect. 1, in addition to studying the discrete spectrum, we have calculated spectral intensities in the continuum region, in terms of photoionisation cross sections. We have done so for each of the single ionisation channels through which the excitation of the $7a'$ electron in the ground state of acetaldehyde takes place. Our results for the different Rydberg channels, ks, kd_{xy}, $kd_{x^2-y^2}$, kd_{xy} and kd_{z^2}, in the energy range of 11–50 eV, are given in Table 2. Since no comparative data of either experimental or theoretical character seem to be available in the literature, we have assessed the oscillator strength distribution in the whole spectral region on the basis that the properties of a given spectral series in the discrete region of the spectrum ought to relate closely to the corresponding properties in the continuum. Following the procedure developed by Fano and Cooper [32], in the discrete part of spectrum, the oscillator strengths are represented in the form of a histogram. In the continuum region, the oscillator strength spectral density is obtained from the MQDO photoionisation cross section through the following expression:

$$\sigma(E) = 1.098 \times 10^{-16}\ \mathrm{cm}^2\ \mathrm{eV}\left(\frac{\mathrm{d}f}{\mathrm{d}E}\right). \tag{4}$$

In Fig. 2 we display the MQDO oscillator strength spectral density for both the bound and continuum regions of spectrum corresponding to the $7a' \to ns$ ($n = 4$–9, continuum). An inspection of Fig. 2 makes apparent that the MQDO results show continuity at the ionisation threshold between the spectral density df/dE in the continuum and the df/dE curve obtained for the discrete spectral region. This behaviour has also been complied with by the remaining ionisation channels, as can be observed in Fig. 3. These features exhibited by the current

Table 2 MQDO cross sections (in Mb) for Rydberg photoionisation channels arising from the excitation of the outermost electron in the ground state, X^1A', of CH_3CHO

E/eV	$7a' \rightarrow ks$	$7a' \rightarrow kd_{xy}$	$7a' \rightarrow kd_{x^2-y^2}$	$7a' \rightarrow kd_{yz}$	$7a' \rightarrow kd_{z^2}$
11.00	1.4791	5.0762	5.1361	5.1070	1.6466
12.00	1.2457	4.4898	4.6729	4.7161	1.5695
13.00	1.0630	3.9674	4.2223	4.3111	1.4701
14.00	0.9173	3.5114	3.8064	3.9234	1.3645
15.00	0.7992	3.1170	3.4319	3.5656	1.2605
16.00	0.7022	2.7768	3.0987	3.2415	1.1621
17.00	0.6215	2.4830	2.8039	2.9507	1.0709
18.00	0.5537	2.2289	2.5436	2.6910	0.9872
19.00	0.4962	2.0083	2.3138	2.4595	0.9110
20.00	0.4470	1.8161	2.1105	2.2531	0.8418
21.00	0.4047	1.6481	1.9304	2.0689	0.7791
22.00	0.3679	1.5006	1.7704	1.9042	0.7223
23.00	0.3358	1.3706	1.6279	1.7567	0.6708
24.00	0.3076	1.2555	1.5006	1.6243	0.6240
25.00	0.2827	1.1534	1.3865	1.5052	0.5816
26.00	0.2606	1.0624	1.2841	1.3978	0.5430
27.00	0.2410	0.9810	1.1918	1.3006	0.5077
28.00	0.2234	0.9080	1.1085	1.2125	0.4756
29.00	0.2076	0.8423	1.0330	1.1325	0.4462
30.00	0.1934	0.7830	0.9645	1.0596	0.4192
31.00	0.1805	0.7294	0.9022	0.9931	0.3944
32.00	0.1688	0.6807	0.8453	0.9323	0.3717
33.00	0.1583	0.6365	0.7933	0.8765	0.3507
34.00	0.1486	0.5961	0.7456	0.8253	0.3313
35.00	0.1398	0.5592	0.7019	0.7782	0.3134
36.00	0.1317	0.5255	0.6617	0.7347	0.2968
37.00	0.1242	0.4944	0.6246	0.6946	0.2815
38.00	0.1174	0.4659	0.5903	0.6575	0.2672
39.00	0.1111	0.4397	0.5587	0.6231	0.2539
40.00	0.1052	0.4154	0.5293	0.5911	0.2415
41.00	0.0998	0.3930	0.5021	0.5614	0.2300
42.00	0.0948	0.3722	0.4768	0.5338	0.2192
43.00	0.0901	0.3529	0.4532	0.5081	0.2091
44.00	0.0858	0.3350	0.4313	0.4840	0.1997
45.00	0.0817	0.3183	0.4108	0.4615	0.1908
46.00	0.0779	0.3028	0.3916	0.4405	0.1825
47.00	0.0744	0.2883	0.3737	0.4208	0.1747
48.00	0.0711	0.2747	0.3569	0.4023	0.1673
49.00	0.0680	0.2621	0.3411	0.3849	0.1604
50.00	0.0651	0.2502	0.3263	0.3685	0.1539

MQDO data make us feel confident in their reliability, since the continuity of the oscillator strength spectral density across the threshold is of general validity, even if perturbations happen to occur in the photoionisation continuum [33].

Finally, we have calculated the photoionisation cross sections for the production of the CH_3CHO^+ cation in its ground state, at different photon energies. This corresponds to the ejection of the electron from the $7a'$ orbital in the ground state to all the allowed continuum Rydberg states and is obtained by adding up the MQDO photoionisation cross section contributions from the five compatible ionisation channels. In Fig. 4, the MQDO photoionisation cross sections for the individual channels and the total cross section for the photoionisation from the $7a'$ orbital in the ground state of acetaldehyde have been plotted versus

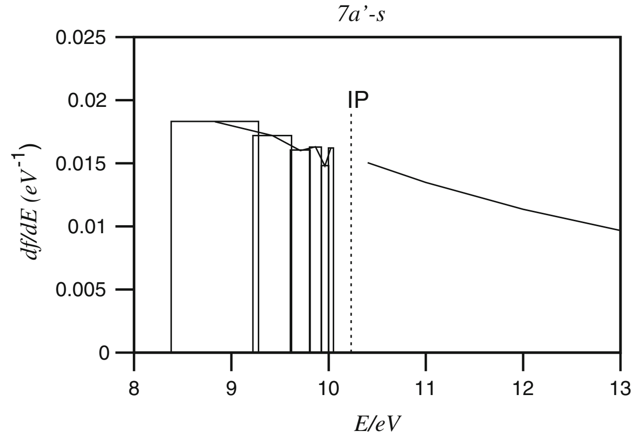

Fig. 2 MQDO oscillator strength spectral density for bound and continuum spectral regions of the $7a' \rightarrow ns$ ($n = 4$–9, continuum) Rydberg series in CH_3CHO

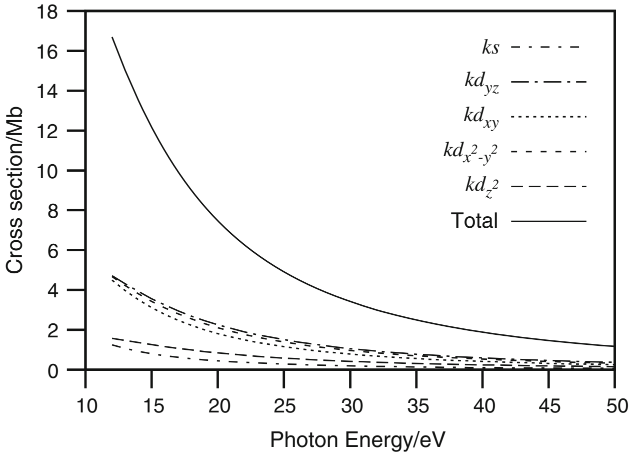

Fig. 4 MQDO total and individual photoionisation profiles for the Rydberg channels that arise from the $7a'$ molecular orbital of CH_3CHO in its ground state

photon energy. A study of Fig. 4 reveals that the cross sections decrease monotonically with increasing photon energy. This behaviour can be explained on the basis of the continuum orbital exhibiting rapid oscillations as the kinetic energy of the photoelectron increases. In consequence, the contributions of opposite sign to the matrix element for photoionisation tend to cancel. It can also be seen from Fig. 4 that the bulk of the photoionisation cross section comes from ionisation into *kd* Rydberg channels, while contributions of *ks* channel are smaller but not negligible. No comparative cross section data dealing with the ionisation from the outermost orbital of acetaldehyde have been found in the literature. However, we would like to

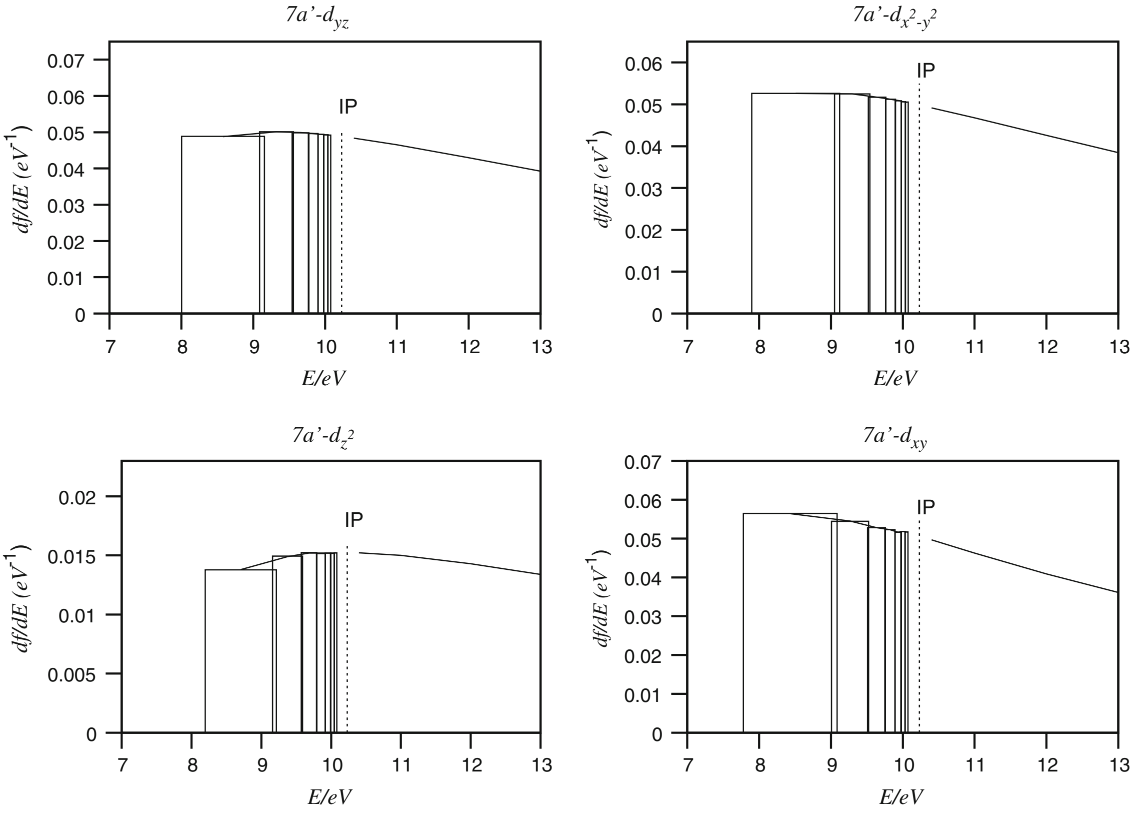

Fig. 3 MQDO oscillator strength spectral density for bound and continuum spectral regions of the $7a' \rightarrow nd$ ($n = 3$–9, continuum) Rydberg series in CH_3CHO

stress that in our very recent application of the MQDO method to the calculation of photoionisation cross sections for the production of the formaldehyde cation, the results obtained were in good agreement with measurements resulting from a dipole (e,e + ion) coincidence spectroscopy technique [34].

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