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Theoretical Study of Spectral Intensities of Formaldehyde in the Discrete and Continuum Regions

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Theoretical absorption oscillator strengths for transitions involving Rydberg states in molecular formaldehyde as well as cross sections for photoionization Rydberg channels associated with the production of the lowest parent ion electronic state are reported. The calculations have been performed with the molecular quantum defect orbital (MQDO) method. A test on the MQDO f values has been its comparison with previous experiments and calculations and its compliance with the expected systematic trends along the Rydberg series. The use of the MQDO method as an alternative to ab initio methods, which find serious difficulties in calculating spectral intensities in formaldehyde, is proposed. We hope that the spectroscopic data, many of them reported here for the first time, may be useful for the interpretation of the vacuum ultraviolet spectrum of this molecule.

I. Introduction

Molecular formaldehyde, H_2CO, has received great attention not only because of its central position in the description of the electronic structure of organic molecules but also because it plays a key role in the photochemistry of the Earth's atmosphere and hydrocarbon combustion processes. Formaldehyde has also aroused much interest from its discovery in the interstellar medium.[1] The $H_{2n}C_nO$ polyatomic species, among which formaldehyde is included, may represent the astrochemical evolution of the interstellar medium and have potential prebiotic importance.[2,3] A detailed knowledge of the spectroscopic properties of H_2CO is, therefore, necessary to understand the important role that it plays in the photochemistry and photophysics of the atmosphere and the interstellar medium. For instance, absorption oscillator strengths and cross sections for this molecule can be used to obtain abundances, as well as quantum yields and rate constants, for processes related to its photoionization and photodissociation.

The vacuum-ultraviolet (VUV) absorption spectrum of H_2CO was first studied by Price in 1935.[4] From its photographic spectrum, obtained using a hydrogen discharge as radiation source, this author identified two Rydberg series. Since then, a number of investigations have been performed using optical,[5−8] electron scattering,[9] and dipole (e,e)[10] techniques and the most accurate theoretical methods.[11−15] The discrete bands observed below the first ionization potential (IP) are mostly attributed to Rydberg states converging to the ground state of H_2CO^+, X $^2B_2$. The most comprehensive study of the excited electronic states of H_2CO has, to our knowledge, been reported by Brint et al.,[7] as a result of their observations with a very high resolution spectrograph and a synchrotron-radiation light source. These authors assigned the *n*s, *n*p, *n*d, and *n*f Rydberg series up to n equal to 5, 12, 12, and 9, respectively.

In the discussion of spectral intensities, a highly useful quantity is the oscillator strength, since it provides a means for reporting and comparing the strengths of radiative transitions.[16] For a continuum extending over a wide energy range, the quantity used is the photoionization cross section. Relatively little information has been found in the literature on oscillator strengths or f-values of formaldehyde, although they are needed for the theoretical simulation of spectra and of the dynamics of photophysical and photochemical processes.[14] Some measurements of oscillator strengths for the transitions to low-lying Rydberg states of formaldehyde were obtained from photoabsorption,[5,8] from electron energy loss,[9] and from dipole (e,e) spectroscopy.[10] On the theoretical part, extensive ab initio calculations in H_2CO have been performed by different authors.[11,12,14] There is, however, considerable discrepancy in the literature regarding theoretical and experimental values of oscillator strengths for transitions to Rydberg states. In addition, most work of both experimentalists and theoreticians has focused on transitions to Rydberg states with $n = 3$. Transitions to high lying electronic states have been less investigated. This situation calls for further studies on the discrete spectrum of this molecule.

The photoelectron−photoion coincidence experiments[17] show that for direct ionization processes the ejection of the electron from the outermost orbital in the ground state of formaldehyde leads exclusively to production of the molecular ion at its ground state, which is stable. Concerning the partial photoionization oscillator strengths (cross sections) for the production of molecular ion, the most recently reported, as far as we know, experimental measurements are those by Cooper et al.[10] In order to rationalize the experimental cross section profiles, theoretical investigations may be helpful since the connection between these profiles and the electronic structure of the concerned system is not direct at all.[18] In this context, calculations of partial-channel photoabsorption cross sections in this molecule have been carried out by Langhoff,[19] using the Stieltjes−Tchebycheff technique and separate-channel static exchange, and by Cacelli et al.[20] in the random phase approximation (RPA) approach.

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Langhoff et al.[19] reported profiles for the total and individual channels associated with the three final-state symmetries from the excitation of the highest orbital in the ground state. However, their calculations do not allow to disentangle the contribution of each electronic state to the photoionization cross section. It is, thus, desirable to have a method that allows calculation of cross sections for the different Rydberg photoionization channels in formaldehyde, with the aim of extracting useful information on the photoionization dynamics.

In earlier papers,[21,22] we reported the oscillator strengths for transitions from the ground state to the *n*s and to two components of the *n*d Rydberg series and differential oscillator strengths for the *k*s photoionization channel in formaldehyde. In order to better understand the spectrum of H_2CO, in this work, we have calculated intensities for electric dipole transitions to Rydberg states in both discrete and continuum. In particular, *f* values for transitions to the $n\text{d}_{xy}$ and $n\text{d}_{z^2}$ Rydberg series and the photoionization cross sections for a number of Rydberg series that serve as ionization channels for this molecule have been determined. Moreover, oscillator strengths for $n\text{d}_{x^2-y^2}$ and $n\text{d}_{yz}$ transitions have been now recalculated using previous results of energies obtained from ab initio methods by some of the authors.[15] We have carried out the present calculations with the molecular quantum defect orbital (MQDO) method. For transitions involving a long series of excited states, calculations with high level ab initio methods are difficult to carry out because of the large number of states and symmetries involved and the large basis set required. Concerning the photoionization cross section of molecules, little theoretical work has been possible so far because it is difficult to obtain accurate continuum electronic wave functions. In this scenario, the MQDO approach, based on a semiempirical model potential, has proved very helpful in treating the molecular electronic high excited states including the continuum region of the spectrum.[23,24] In the present work, we have analyzed the contribution of the different Rydberg channels to the production of molecular ion, H_2CO^+, that, to our best knowledge, has not been previously reported.

II. Method of Calculation

The MQDO method has been described in detail in previous papers.[25,26] In this approach, the radial quantum defect orbitals are the analytical solutions of a one-electron Schrödinger equation that contains a parametric potential. This potential is intended to provide a physically reasonable description of electron screening through a single parameter related to both the orbital angular momentum quantum number and the quantum defect associated with the Rydberg electron. The inclusion of such a parameter in the model potential generates orbitals that are approximately valid in the molecular core region and possesses the proper long-range behavior. The angular part of the MQDO wave functions is expressed as a symmetry-adapted linear combination of spherical harmonics, in such a way that the complete MQDO's form bases for the different irreducible representations of the molecular point group (i.e., C_{2v} in the case of H_2CO). Since the radial MQDO wave functions are expressible in terms of the confluent hypergeometric functions,[27] all radial integrals involved in the computation of transition probabilities are given by closed-form analytical expressions that can be calculated at the desired numerical precision. The calculations of oscillator strengths and photoionization cross sections with wave function expansions founded on large and very diffuse basis sets can face numerical convergence difficulties related to linear dependences in the basis sets and to the large volumes spanned by the states. Consequently, one of the main advantages of the MQDO approach is that these convergence problems are avoided. A drawback of the method is its semiempirical character, in the sense that it requires the quantum defects for the states involved in the transitions as an input. However, for the low-lying Rydberg states of formaldehyde, the excitation energies calculated with size-extensive ab initio methods by some of us[15] are helpful in their estimations. For higher Rydberg states, this may, at least partly, be overcome if use is made of regularities in the quantum defects along each given spectral series in a molecule. As is well-known, the quantum defects mainly depend on the angular momentum quantum number and remain practically constant as the principal quantum number varies in a given spectral series. Another drawback of the model is that transitions between Rydberg states for which the difference between orbital angular momentum quantum number values is other than ±1 are forbidden as a consequence of the one-center character of the MQDO wave functions. Though these transitions are usually weak, this is not the case for formaldehyde. However, the MQDO approach is still useful since the discrepancies between ab initio calculations and experiment occur in the excitation intensities to 3d Rydberg states, rather than to 3p states. Nonetheless, these weaknesses of the method are compensated by its simplicity and its ability to determine spectral intensities for transitions to high excited states with a relatively high accuracy. In this context, the application of the MQDO method to the study of formaldehyde is of particular interest since high Rydberg states have been observed experimentally.[7]

III. Results and Discussion

Following the general consensus of experimental and theoretical studies, the $^1A_1$ ground state of formaldehyde can be described with the leading electronic configuration:

$$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1b_2)^2(5a_1)^2(1b_1)^2(2b_2)^2$$

The highest occupied molecular orbital has been reported to be a nonbonding orbital, almost pure oxygen $2p_y$.[7,28] Rydberg-type transitions have been observed in the electronic excitation of the $2b_2$ nonbonding electron. These transitions result in little geometrical rearrangement, and therefore, they imply little vibrational excitation of the ionic core, as suggested by photoelectron spectroscopy on H_2CO.[29] The molecular and Rydberg states of formaldehyde have both been reported to be planar with a C_{2v} geometry, where H_2CO is in the *yz* plane, with the CO bond lying on the *z* axis. The transitions we are considering are these excitations from the $2b_2$ ground state HOMO to Rydberg orbitals in both the discrete and continuum regions. Configuration interaction calculations have shown that low-lying Rydberg states of formaldehyde are dominated by the corresponding single excitations. In relation with the higher member series, Lessard and Moule[6] suggested that the Rydberg orbitals in formaldehyde become more atomic-like as *n* increases, where *n* in the principal quantum number. This is supported by the very high resolution VUV spectrum reported by Brint et al.,[7] who found a nine-member series of fairly sharp absorption bands of consistent band shape that identified as the d-type series ($n = 4-12$). Therefore, one could hope that assuming that the orbital angular momentum quantum number, *l*, of the Rydberg electron is a good quantum number is essentially correct in the case of Rydberg states involved in the transitions studied in the present work. In this paper, we use a notation for the molecular Rydberg orbitals that is commonly found in the literature, that is, *nl*. The *l* components are differentiated by the Cartesian representation subscripts. For continuous Rydberg orbitals, *k* is used, instead of *n*, to indicate their energy above IP.

In the present calculations, the vertical ionization energy reported by Brint et al.[7] has been adopted. Other input data also needed in the MQDO procedure are the quantum defects of the states involved in the transition studied. These are deduced preferably from experimental energy level data through the well-known Rydberg formula. In formaldehyde, the energies for the different symmetry components of the nd ($d_{x^2-y^2}\ {}^1B_2$, $d_{yz}\ {}^1A_1$, $d_{z}^{2}\ {}^1B_2$, $d_{xy}\ {}^1B_1$, and $d_{xz}\ {}^1A_2$) Rydberg series are difficult to establish experimentally because none of them show any rotational structure.[7] The vertical excitation energies of formaldehyde have been calculated in a previous work[15] by means of size-extensive ab initio methods. The MQDO results reported in the present work have been calculated by using the vertical excitation energies[15] obtained with the size-extensive corrected MR-SDCI method known as size-consistent self-consistent multireference singles and doubles configuration interaction, $(SC)^2$-MR-SDCI.[30,31] These energies lead to quantum defects values of 0.341, 0.012, 0.175, and 0.060 for the $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{z^2}$, and $3d_{yz}$ orbitals, respectively. The quantum defect of 1.10 that is obtained from the 3s state has been adopted for the *k*s Rydberg channel. It must be indicated, however, that transition energies from the linear-reponse on a coupled clusters of singles and doubles including triples method known as LR-CCSDR(3)[32,33] are also available for the same calculation conditions.[15] The MQDO oscillator strengths for transitions to 3d states calculated with quantum defects deduced from $(SC)^2$-MR-SDCI and LR-CCSDR(3) energies differ by less than 0.001 unit, with the single exception of the transition to the $3d_{x^2-y^2}\ {}^1B_2$ state, for which the difference amounts to 0.002 unit. In order to estimate energies of the higher Rydberg states, the quantum defects for the lowest *n* are used in the assumption that quantum defects remain nearly constant along each particular Rydberg series.

Absorption oscillator strengths calculated in this work for transitions from the $2b_2$ orbital in the ground state to the $nd_{x^2-y^2}\ {}^1B_2$, $nd_{xy}\ {}^1B_1$, $nd_{z^2}\ {}^1B_2$, and $nd_{yz}\ {}^1A_1$ Rydberg states with $n = 3-12$ are displayed in Table 1. Other oscillator strengths, from the most accurate ab initio calculations and experiments found in the literature have been included in the table for comparative analysis. The theoretical data are three sets of *f*-values obtained by Muller[14] with the multiconfigurational self-consistent field MCSCF, the multireference configuration interaction with size-extensivity corrections (CI + Q), and the multireference-averaged quadratic coupled-cluster with linear-response theory (LRT) approachs, respectively, and the multiconfigurational second-order perturbation theory (CASPT2) results by Merchán and Roos.[12] The experimental data comprise reported electron energy loss measurement of Weiss et al.,[9] oscillator strengths obtained using optical methods[5,8] and more recent *f* values determined by dipole (e,e) spectroscopy.[10] Inspection of Table 1 reveals that, for transitions to individual components of 3d Rydberg series, MQDO calculations are in better agreement with experimental results than the high level ab initio calculations, which appear to be too low. Concerning transitions to more highly excited states, we have only found in the literature, the oscillator strength reported by Hadad[34] for the $4d_{yz}$ component, calculated with the configuration interaction with single excitations method including a correction via Moller−Plesset perturbation theory through second order (CIS-MP2). It compares well with the MQDO *f* value. A remark concerning the $2b_2 \rightarrow nd_{x^2-y^2}\ {}^1B_2$ transitions may be in order. In a previous study of the spectrum of formaldehyde by some of us,[22] the experimental quantum defect assigned to the $3d_{x^2-y^2}\ {}^1B_2$ state[5,6] was used to obtain oscillator strengths for this spectral series. For the transition to the first member of this series, the present *f* value ($f = 0.01359$) calculated with the theoretical quantum defect is in better accord with the measurements than the earlier MQDO result ($f = 0.006$).

TABLE 1: Oscillator Strengths for the $2b_2 \rightarrow n$d ($n = 3-12$) Rydberg Transitions in H_2CO

transition	MQDO[a]	theory	experiment
$2b_2 \rightarrow 3d_{x^2-y^2}\ {}^1B_2$	0.01359	0.003,[b] 0.008,[c] 0.010,[d] 0.0061[e]	0.010 ± 0.003,[g] 0.015,[h] 0.018,[i] 0.0198[j]
$2b_2 \rightarrow 4d_{x^2-y^2}{}^1B_2$	0.00403		
$2b_2 \rightarrow 5d_{x^2-y^2}\ {}^1B_2$	0.00176		
$2b_2 \rightarrow 6d_{x^2-y^2}\ {}^1B_2$	0.00093		
$2b_2 \rightarrow 7d_{x^2-y^2}\ {}^1B_2$	0.00056		
$2b_2 \rightarrow 8d_{x^2-y^2}\ {}^1B_2$	0.00036		
$2b_2 \rightarrow 9d_{x^2-y^2}\ {}^1B_2$	0.00024		
$2b_2 \rightarrow 10d_{x^2-y^2}\ {}^1B_2$	0.00017		
$2b_2 \rightarrow 11d_{x^2-y^2}\ {}^1B_2$	0.00013		
$2b_2 \rightarrow 12d_{x^2-y^2}\ {}^1B_2$	0.00010		
$2b_2 \rightarrow 3d_{xy}\ {}^1B_1$	0.01325	0.000,[b] 0.001,[c] 0.000,[d] 0.0003[e]	
$2b_2 \rightarrow 4d_{xy}\ {}^1B_1$	0.00484		
$2b_2 \rightarrow 5d_{xy}\ {}^1B_1$	0.00232		
$2b_2 \rightarrow 6d_{xy}\ {}^1B_1$	0.00130		
$2b_2 \rightarrow 7d_{xy}\ {}^1B_1$	0.00080		
$2b_2 \rightarrow 8d_{xy}\ {}^1B_1$	0.00053		
$2b_2 \rightarrow 9d_{xy}\ {}^1B_1$	0.00037		
$2b_2 \rightarrow 10d_{xy}\ {}^1B_1$	0.00027		
$2b_2 \rightarrow 11d_{xy}\ {}^1B_1$	0.00020		
$2b_2 \rightarrow 12d_{xy}\ {}^1B_1$	0.00015		
$2b_2 \rightarrow 3d_{z^2}\ {}^1B_2$	0.00561	0.003,[b] 0.001,[c] 0.000,[d] 0.001[e]	
$2b_2 \rightarrow 4d_{z^2}\ {}^1B_2$	0.00187		
$2b_2 \rightarrow 5d_{z^2}\ {}^1B_2$	0.00086		
$2b_2 \rightarrow 6d_{z^2}\ {}^1B_2$	0.00047		
$2b_2 \rightarrow 7d_{z^2}\ {}^1B_2$	0.00028		
$2b_2 \rightarrow 8d_{z^2}\ {}^1B_2$	0.00019		
$2b_2 \rightarrow 9d_{z^2}\ {}^1B_2$	0.00013		
$2b_2 \rightarrow 10d_{z^2}\ {}^1B_2$	0.00009		
$2b_2 \rightarrow 11d_{z^2}\ {}^1B_2$	0.00007		
$2b_2 \rightarrow 12d_{z^2}\ {}^1B_2$	0.00005		
$2b_2 \rightarrow 3d_{yz}\ {}^1A_1$	0.01482	0.008,[b] 0.009,[c] 0.018,[d] 0.0026[e]	0.012 ± 0.004,[g] 0.017,[h] 0.018,[i] 0.0238[j]
$2b_2 \rightarrow 4d_{yz}\ {}^1A_1$	0.00527	0.0059[f]	
$2b_2 \rightarrow 5d_{yz}\ {}^1A_1$	0.00250		
$2b_2 \rightarrow 6d_{yz}\ {}^1A_1$	0.00139		
$2b_2 \rightarrow 7d_{yz}\ {}^1A_1$	0.00085		
$2b_2 \rightarrow 8d_{yz}\ {}^1A_1$	0.00056		
$2b_2 \rightarrow 9d_{yz}\ {}^1A_1$	0.00039		
$2b_2 \rightarrow 10d_{yz}\ {}^1A_1$	0.00028		
$2b_2 \rightarrow 11d_{yz}\ {}^1A_1$	0.00021		
$2b_2 \rightarrow 12d_{yz}\ {}^1A_1$	0.00016		

[a] This work. [b] MCSCF.[14] [c] CI+Q.[14] [d] LRT.[14] [e] CASSCF.[12] [f] CIS-MP2.[30] [g] Mentall et al.[5] [h] Weiss et al.[9] [i] Suto et al.[8] [j] Cooper et al.[10]

The nature of 3d Rydberg states of H_2CO deserves a few remarks. Hachey et al.[13] have interpreted the high absorption intensity of 3d Rydberg series as resulting from valence−Rydberg interactions, mainly involving the $\pi\pi^*$ valence state. Hachey and Grein[35] suggested that $\pi\pi^*$−Rydberg mixing is essential for getting an overall *f* value greater than 0.053 for the 3d bands. Such interpretation is based on the fact that ab initio *f* values for $2b_2 \rightarrow 3d$ transitions are too weak to account for the observed intensities. Mentall et al.[5] have also suggested valence-Rydberg mixing to explain the unusually large quantum defect for a 3*d* orbital ($\delta \sim 0.4$). However, calculations of Merchán and Roos[12]

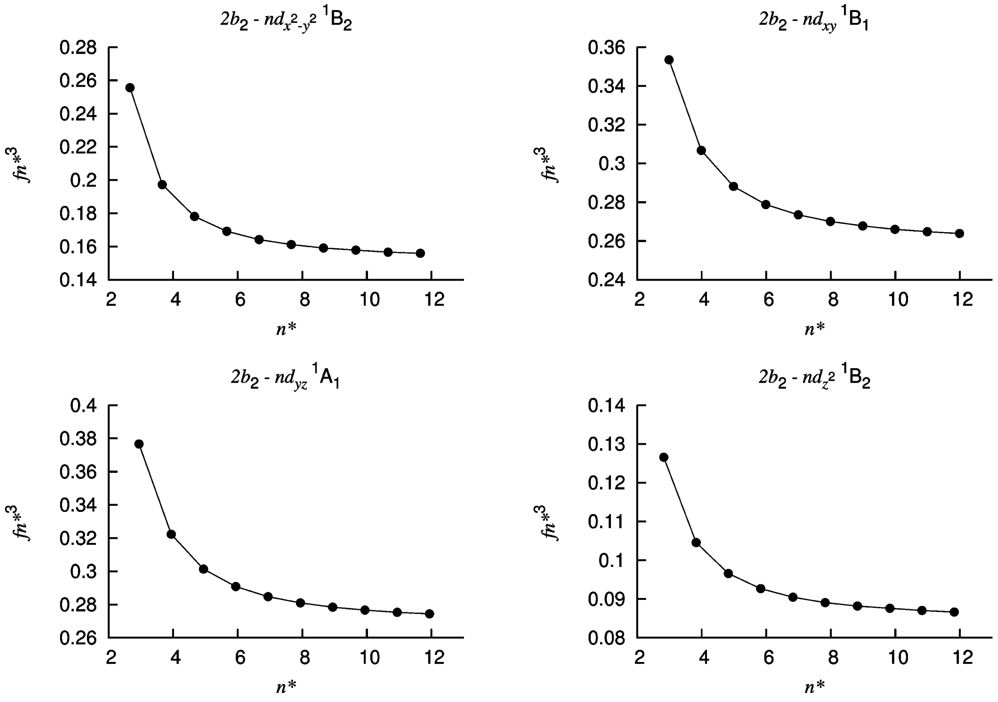

Figure 1. MQDO systematic trends of the oscillator strengths along the individual components of the $2b_2 - n$d spectral Rydberg series.

characterize all 3d states as essentially singly excited in nature, with a very little valence mixing. For instance, they evaluate the weight of the $\pi\pi^*$ configuration to the wave function for the $3d_{yz}$ $^1A_1$ state to be 3.4%. The one-electron MQDO method predicts a f value of 0.047 for the total $2b_2 \rightarrow 3d$ transition. Thus, the valence−Rydberg interaction appears to be negligible in the 3d Rydberg states.

Since nd series seems to be free of perturbations, one may expect to find regularities in the behavior of the f values along this spectral series. It has long been established[36] that for unperturbed spectral series the square of the radial integral, to which the oscillator strength is proportional, diminishes as n^{-3}, i.e., for high n, fn^3 approaches a constant. If the quantum defects are not small, as in the present case, n should be replaced by the effective principal quantum number n^*. These trends are easily observed if the product $f(n^*)^3$ is plotted against n^* along a Rydberg series as is done in Figure 1. The regularities exhibited by the MQDO results for the $2b_2 \rightarrow nd_{x^2-y^2}$ $^1B_2$, $2b_2 \rightarrow nd_{xy}$ $^1B_1$, $2b_2 \rightarrow nd_{z^2}$ $^1B_2$ and $2b_2 \rightarrow nd_{yz}$ $^1A_1$ Rydberg transitions provide additional assessment to the correctness of the MQDO oscillator strengths.

The ks, $kd_{x^2-y^2}$, kd_{z^2}, kd_{yz} and kd_{xy} Rydberg series constitute different possible photoionization channels from the outermost valence electron of formaldehyde. In this work, we have calculated the contribution from the different Rydberg states to the production of the electronic ground state of the H_2CO^+ cation. Ionization from $2b_2$ orbital to kp Rydberg channel has been ignored. Nonetheless, the $2b_2$ orbital has almost pure oxygen p-orbital character, and hence the contribution of a p orbital is expected to be insignificant. In Table 2, we display the MQDO photoionization cross sections for Rydberg channels arising from the excitation of the $2b_2$ orbital of H_2CO in the photon energy range from 12 to 50 eV. The corresponding continuum photoionization profiles are shown in Figure 2. No comparative data are available for cross sections of the individual channels. However, the total photoionization cross sections formed by the combination of the profiles of the Rydberg channels can be compared with the partial photoion-

TABLE 2: MQDO Cross Sections (in Mb) for Rydberg Photoionization Channels from the Excitation of $2b_2$ Valence Orbital of H_2CO

E/eV	$2b_2 \rightarrow k$s	$2b_2 \rightarrow kd_{x^2-y2}$	$2b_2 \rightarrow kd_{z^2}$	$2b_2 \rightarrow kd_{yz}$	$2b_2 \rightarrow kd_{xy}$
12	1.463	4.496	1.516	4.436	4.358
13	1.227	4.015	1.405	4.222	4.196
14	1.043	3.583	1.291	3.964	3.976
15	0.898	3.202	1.183	3.694	3.733
16	0.780	2.869	1.082	3.430	3.487
17	0.684	2.577	0.990	3.178	3.249
18	0.604	2.323	0.907	2.944	3.023
19	0.538	2.100	0.832	2.727	2.812
20	0.481	1.906	0.765	2.529	2.618
21	0.433	1.734	0.704	2.348	2.438
22	0.392	1.583	0.650	2.183	2.274
23	0.356	1.449	0.601	2.032	2.123
24	0.324	1.330	0.557	1.895	1.984
25	0.297	1.225	0.517	1.769	1.857
26	0.273	1.130	0.481	1.655	1.741
27	0.252	1.045	0.448	1.550	1.634
28	0.232	0.969	0.419	1.454	1.536
29	0.215	0.900	0.392	1.367	1.446
30	0.200	0.838	0.367	1.286	1.363
31	0.186	0.782	0.344	1.211	1.286
32	0.174	0.731	0.324	1.143	1.215
33	0.163	0.684	0.305	1.080	1.150
34	0.153	0.641	0.287	1.021	1.089
35	0.143	0.602	0.271	0.967	1.032
36	0.135	0.567	0.256	0.917	0.980
37	0.127	0.534	0.242	0.870	0.931
38	0.120	0.503	0.230	0.827	0.886
39	0.113	0.475	0.218	0.786	0.844
40	0.107	0.450	0.207	0.749	0.804
41	0.101	0.426	0.197	0.713	0.767
42	0.096	0.404	0.187	0.681	0.732
43	0.091	0.383	0.178	0.650	0.700
44	0.087	0.364	0.170	0.621	0.669
45	0.083	0.346	0.162	0.594	0.641
46	0.079	0.329	0.155	0.568	0.614
47	0.075	0.314	0.148	0.544	0.588
48	0.072	0.299	0.142	0.522	0.564
49	0.069	0.286	0.136	0.500	0.542
50	0.066	0.273	0.130	0.480	0.520

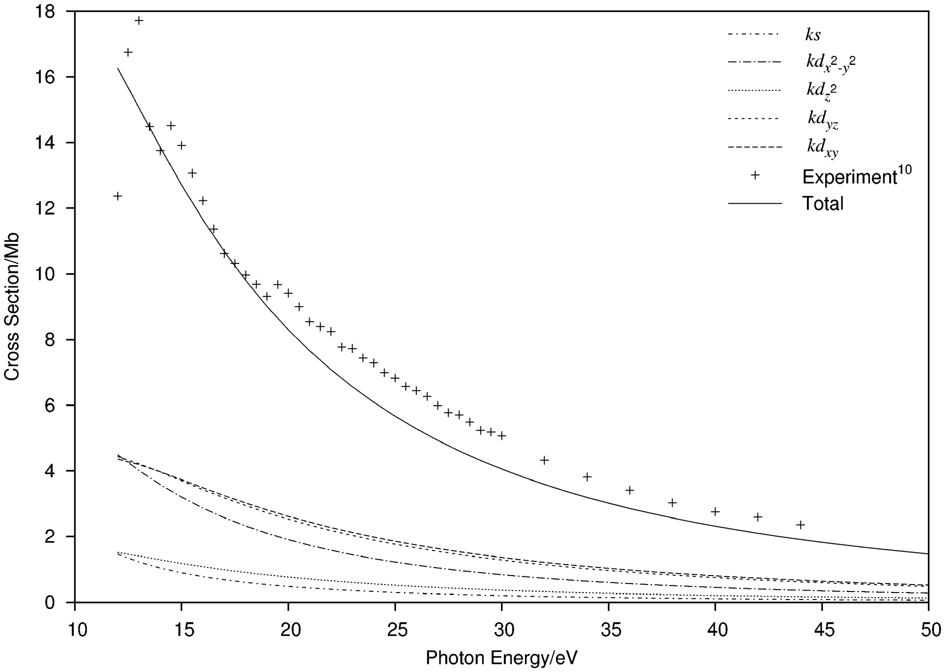

Figure 2. MQDO total and individual photoionization profiles for the Rydberg channels that arise from the $2b_2$ valence orbital of H_2CO in its ground state and experimental photoionization cross sections for the production of the H_2CO^+.

ization cross sections for the production of the molecular ion from formaldehyde obtained by Cooper et al.[10] with dipole (e,e + ion) coincidence spectroscopy. MQDO total and experimental photoionization profiles also represented in Figure 2 show an overall good agreement in both shape and magnitude. In addition, inspection of this figure reveals that for the $2b_2$ orbital the bulk of the photoionization cross section comes from ionization into the kd_{xy}, kd_{yz} and $kd_{x^2-y^2}$ channels while contributions of kd_{z^2} and ks channels are smaller but not negligible.

Cooper et al.[10] have also derived photoionization oscillator strengths for the production of the ground state of the formaldehyde cation in the 14−30 eV region using their dipole (e,e) spectroscopy results in combination with photoelectron−photoion coincidence measurements[17] and experimental[37] and theoretical valence shell photoelectron branching ratios.[19] From 14 to 19 eV the MQDO total cross sections are lower than those obtained by experiment.[10] In this region, the photoabsorption spectrum reported by Cooper et al.[10] shows strong bands, which they attributed to superexcited states. These are states that could be lead to Rydberg series terminating on the second and higher ionization potentials as suggested by Brint et al.[7] Thus, the differences between MQDO calculations and experiment are probably caused by autoionization effects. For photon energies higher than 19 eV, the agreement between theory and experiment is good and indicates the same trend. From this fact, it is possible to conclude that Rydberg states dominate in the ionization from the outermost valence orbital of H_2CO for high photon energies. Theoretical profiles for the ionization of $2b_2$ orbital have been reported by Langhoff et al.[19] using the Stieltjes−Tchebycheff technique and separate-channel static exchange. These authors predicted resonances in the photoionization cross sections of $2b_2$ located at approximately 12 and 14 eV, which they have associated with transitions involving the $6a_1\sigma^*(C{=}O)$ and $\pi^*(CO)$ valence orbitals. These states lie above the ionization threshold. Therefore, the difference between their profile and the presently calculated one should be due to the fact that our results do not reproduce the resonance structures since we are just considering one configuration. Despite of this limitation, the MQDO calculations do allow to distinguish the contribution of each Rydberg-type orbital to the photoionization cross section.

IV. Conclusions

The present work represents, to the best our knowledge, the first theoretical calculation of oscillator strengths for excitations from the ground state to nd_{z^2} $^1B_2$ and nd_{xy} $^1B_1$ states, with n = 4−12. The accuracy of the present results for H_2CO has been assessed by comparison with experimental data as well as by its regular behavior along the spectral Rydberg series. We have also calculated the contributions of different Rydberg electronic states to the photoionization cross section leading to the ground state of H_2CO^+, which had not been performed so far in calculations of photoionization cross section of formaldehyde. The range from 12 to 50 eV of energy has been covered. Such spectroscopic data concerning the cross section can shed some light on the nature of continuum electronic states of formaldehyde. From this work, it is possible to infer that the Rydberg channels provide the main contribution to the ionization from the outermost valence orbital of formaldehyde in the region above 20 eV.

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References and Notes

(1) Snyder, L. E.; Buhl, D.; Zuckerman, B.; Palmer, P. *Phys. Rev. Lett.* **1969**, *22*, 679.
(2) Kuan, Y.-J.; Charnley, S. B.; Huang, H.-C.; Kisiel, Z.; Ehrenfreund, P.; Tseng, W.-L.; Yan, C.-H. *Adv. Space Res.* **2004**, *33*, 31.
(3) Whang, J.; Li, Y.; Zhang, T.; Tian, Z.; Yang, B.; Zhang, K.; Qi, F.; Zhu, A.; Cui, Z.; Ng, C.-Y. *Astrophys. J.* **2008**, *676*, 416.
(4) Price, W. C. *J. Chem. Phys.* **1935**, *3*, 256.
(5) Mentall, J. E.; Gentieu, E. P.; Krauss, M.; Neumann, D. *J. Chem. Phys.* **1971**, *55*, 5471.

(6) Lessard, C. R.; Moule, D. C. *J. Chem. Phys.* **1977**, *66*, 3908.

(7) Brint, P.; Connerade, J. P.; Mayhew, C.; Sommer, K. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1643.

(8) Suto, M.; Wang, X.; Lee, L. C. *J. Chem. Phys.* **1986**, *85*, 4228.

(9) Weiss, M. J.; Kuyatt, C. E.; Mielczarek, S. *J. Chem. Phys.* **1971**, *54*, 4147.

(10) Cooper, G.; Anderson, J. E.; Brion, C. E. *Chem. Phys.* **1996**, *209*, 61.

(11) Harding, L. B.; Goddard, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 677.

(12) Merchán, M.; Roos, B. O. *Theor. Chim. Acta* **1996**, *92*, 227.

(13) Hachey, M. R. J.; Bruna, P. J.; Grein, F. *J. Phys. Chem.* **1995**, *99*, 8050.

(14) Muller, T.; Lischka, H. *Theor. Chem. Acc.* **2001**, *106*, 369.

(15) Pitarch-Ruiz, J.; Sánchez-Marín, J.; Sánchez de Merás, A.; Maynau, D. *Mol. Phys.* **2003**, *101*, 483.

(16) Huestis, D. L. In *Atomic, Molecular and Optical Physics Handbook*; Drake, G. W. F., Ed.; American Institute of Physics: Woodbury, NY, 1996.

(17) Bombach, R.; Dannacher, J.; Stadelmann, J. P.; Vogt, J. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *40*, 275.

(18) Stener, M.; Decleva, P. *J. Electron Spectrosc. Relat. Phenom.* **1998**, *94*, 195.

(19) Langhoff, P. W.; Orel, A. E.; Rescigno, T. N.; McKoy, B. V. *J. Chem. Phys.* **1978**, *69*, 4689.

(20) Cacelli, I.; Moccia, R.; Montuoro, R. *Chem. Phys. Lett.* **2001**, *347*, 261.

(21) Martín, I.; Velasco, A. M.; Lavín, C.; Olalla, E.; Bustos, E. *Int. J. Quantum Chem.* **2001**, *85*, 345.

(22) Olalla, E.; Lavín, C.; Velasco, A. M.; Martín, I. *Chem. Phys. Lett.* **2002**, *366*, 477.

(23) Bustos, E.; Velasco, A. M.; Martín, I.; Lavín, C. *J. Phys. Chem. A* **2002**, *106*, 35.

(24) Lavín, C.; Martín, I.; Velasco, A. M. *Astrophys. J.* **2006**, *644*, 1334.

(25) Martín, I.; Lavín, C.; Velasco, A. M.; Martín, M. O.; Karwowski, J.; Diercksen, G. H. F. *Chem. Phys.* **1996**, *202*, 307.

(26) Martín, I.; Lavín, C.; Karwowski, J. *Chem. Phys. Lett.* **1996**, *255*, 89.

(27) Martín, I.; Simons, G. *J. Chem. Phys.* **1975**, *62*, 4799.

(28) Moule, D. C.; Walsh, A. D. *Chem. Rev.* **1975**, *75*, 67.

(29) Turner, D. W. *Int. J. Mass Spectrom. Ion Phys.* **1968**, *1*, 285.

(30) Daudey, J. P.; Heully, J. L.; Malrieu, J. P. *J. Chem. Phys.* **1993**, *99*, 1240.

(31) Sánchez-Marín, J.; Nebot-Gil, I.; Malrieu, J. P.; Heully, J. L.; Maynau, D. *Theor. Chim. Acta* **1997**, *95*, 215.

(32) Christiansen, O.; Koch, H.; Jorgensen, P. *J. Chem. Phys.* **1995**, *103*, 7429.

(33) Christiansen, O.; Koch, H.; Halkier, A.; Jorgensen, P.; Helgaker, T.; Sánchez de Merás, A. *J. Chem. Phys.* **1996**, *105*, 6921.

(34) Hadad, C. M.; Foresman, J. B.; Wiberg, K. B. *J. Phys. Chem.* **1993**, *97*, 4293.

(35) Hachey, M. R. J.; Grein, F. In *The Role of Rydberg States in Spectroscopy and Photochemistry Low and High Rydberg States*; Sándorfy, C. Eds.; Kluwer Academic Publishers: Dordrecht, 1999.

(36) Martin, W. C.; Wiese, W. L. *Atomic, Molecular and Optical Physics Handbook*; American Institute of Physics: Woodbury, NY, 1996.

(37) Holland, D. M. P. *Chem. Phys.* **1989**, *133*, 453.

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