

Photoionization cross sections and asymmetry parameters for ethanol. A theoretical study

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ABSTRACT

Photoionization cross-sections and asymmetry parameters for the outermost orbital of ethanol has been determined with the Molecular Quantum Defect Orbital (MQDO) method. The individual ionization cross-sections corresponding to the Rydberg series that constitute the ionization channels for the production of the molecular cation in its ground state are reported. Good agreement has been found with the experiment for the photoionization cross-sections. To our knowledge, predictions of the asymmetry parameter for the ethanol are made here for the first time. It is hoped the MQDO data will be useful in combustion chemistry and astrophysics.

Keywords: photoionization cross-sections; asymmetry parameters; Rydberg channels; VUV spectrum; ethanol.

1. Introduction

Over the last decades, considerable attention has been paid to the estimation of reliable values of photoionization cross-sections, largely motivated by their fundamental importance and their applications in atmospheric chemistry and astrophysics [1]. In the last years, there is a renewed interest in the study of these spectroscopic properties due in part to their applications in combustion chemistry. An accurate knowledge of the photoionization cross-sections of a large number of reaction intermediates is necessary for the determination of flame species concentrations [2,3]. However, despite their importance in the development of combustion models, photoionization cross-section data for several flame species, among which ethanol is included, is far from complete.

Ethanol, C_2H_5OH , is an important organic molecule in many areas of chemistry and in astrophysics. It is a common hydrocarbon combustion intermediate and an environmental friendly fuel [4]. In addition, ethanol has been reported to play a relevant role in plasma-assisted chemical deposition processes of diamond-like film [5]. Properties related to the spectrum of this molecule are of considerable interest in the study of the hydrocarbon combustion processes [2] and in the study of the interstellar medium, where this molecule is present [6]. Most of the spectroscopic studies have been mainly focused on the determination of the energies of their electronically excited states. Concerning the spectral intensities, photoabsorption measurements of ethanol have been performed by several experimentalists using emission line sources [7-9], synchrotron radiation sources [5, 10] and high-resolution dipole (e,e) spectroscopy [11] in the vacuum ultraviolet region covering from 5 to 32 eV. By contrast, photoionization cross-section data are scarce. A careful literature search has revealed that only a few experimental data of photoionization cross-sections have been previously reported for this molecule. Cool et al. [2] have measured absolute photoionization cross-sections with Photoionization Mass

Spectrometry (PIMS), using synchrotron radiation for photon energies from 10.22 to 11.72 eV. Person and Nicole [9] measured total photoionization cross-sections and photoionization yields for ethanol, using the dual-beam single ion chamber technique at photon energies between 10.32 and 11.78 eV. On the other hand, Refaey and Chupka [12] determined the photoionization efficiency curves of the parent and major fragment ions of ethanol. Theoretical investigations on direct photoionization cross sections for C_2H_5OH , as far as we know, are completely lacking.

Studies of the variation in the partial photoionization cross section, that is, the cross section for specific ionic states, over wide spectral ranges, are required in fields such as astrophysics and gas phase chemistry. To the best of our knowledge, no experimental work on partial cross sections of ethanol has been reported to data, in spite of its importance in both applied and fundamental research [13]. It is thus, desired to have a method that may be able to determine cross sections for a specific state of the molecular ion. In this context, the Molecular Quantum Defect Orbital (MQDO) method has shown to be very efficient in this kind of studies [14, 15].

Given the scarcity of photoionization cross section data and their importance to combustion modeling, we have recently undertaken a theoretical spectroscopic study of hydrocarbon combustion intermediates. In particular, we have calculated photoionization cross-sections for specific ionic states of methyl radical [16], methanol [17], acetone [18] and formaldehyde [19]. Motivated by the good results we have obtained for these molecules, it is the purpose of the present study to supply partial photoionization cross-section data of ethanol at photon energies where these data are unavailable. Thereby, we have determined photoionization cross-sections for the production of molecular ion, $C_2H_5OH^+$, in the ground state up to a photon energy of 70 eV. In the calculations, we have

used the MQDO method. We compare our results with previously published data, where such data are available, in order to assess their reliability.

Another parameter relevant in photoionization studies and closely related with the photoionization cross sections is the asymmetry parameter. This parameter, which characterizes the photoelectron angular distribution, is not easy to determine from an experimental point of view. Thus, an additional goal of this work was to calculate the asymmetry parameter by means the MQDO method, which has proved, in earlier works [17,20], to be a useful tool for this kind of estimations. Although it contains a wealth of information about molecular electronic structure and dynamics [21,22], neither experimental nor theoretical asymmetry parameter data for ethanol have been reported to date.

2. Method of calculation

The MQDO approach, which has been broadly used to successfully determine one-photon transition intensities involving Rydberg states, has been described in previous papers [14,23], so we shall outline here the major points.

The radial parts of the MQDO wave functions are represented by orbitals that are the exact solutions of a one-electron Schrödinger equation that contains an effective potential as follows:

$$V(r) = \frac{\lambda(\lambda + 1) - l(l + 1)}{2r^2} - \frac{1}{r} \quad (1)$$

where λ is a parameter which determines the electron screening and is related to the quantum defect, δ and the orbital angular moment, l .

The angular parts of the MQDO wave function are symmetry-adapted linear combinations of spherical harmonics, so that the complete molecular orbitals (MO's) form bases for the different irreducible representations of the molecular symmetry group. This allows the factorization of the transition moment into radial and angular contributions, both as closed-form analytic expressions. Thus, the photoionization cross-section for a transition between a bound state and a continuous state adopts the following form:

$$\sigma = 2.6891 \left[\frac{1}{(n - \delta)^2} + k^2 \right] \frac{1}{2k} N Q \{a \rightarrow b\} |R_{ab}|^2 \quad (2)$$

where $Q\{a \rightarrow b\}$ are the angular factors resulting from the angular integration in the transition integral, R_{ab} is the radial transition moment, k^2 is the kinetic energy of the free electron upon ionization in Rydberg units, and N is the number of equivalent electrons in the orbital where the transition originates.

The asymmetry parameter for the photoionization of an electron with an orbital angular momentum quantum number l , following the central potential approximation, is expressed as follows [24]:

$$\beta = \frac{l(l-1)R_{l-1}^2 + (l+1)(l+2)R_{l+1}^2 - 6l(l+1)R_{l-1}R_{l+1} \cos(\xi_{l+1} - \xi_{l-1})}{(2l+1)[lR_{l-1}^2 + (l+1)R_{l+1}^2]} \quad (3)$$

where $R_{l\pm 1}$, the radial dipole matrix elements, are calculated with the MQDO method and $\xi_{l\pm 1}$, the phase shifts of the respective scattered waves, are presently determined as the sum of a Coulomb shift and a non-Coulomb shift.

3. Results and discussion

The ground state valence electronic configuration of ethanol with C_s symmetry, in its equilibrium geometry, is $\dots(7a')^2(1a'')^2(8a')^2(9a')^2(2a'')^2(10a')^2(3a'')^2 X^1A'$. There is generally agreement that the outermost occupied molecular orbital in the ground state, $3a''$, is mainly a $2p$ orbital located on the oxygen atom [25].

In this work, we have calculated the photoionization cross-sections leading to the ground state of $CH_3CH_2OH^+$ up to a photon energy of 70 eV. To this end, we have determined the photoionization cross-sections for each one of the excitations from the highest occupied molecular orbital in the ground state of ethanol, $3a''$, to continuum states that belong to Rydberg series converging to the ground state of $CH_3CH_2OH^+$. Taking into account the electric dipole transition selection rules, the continua accessible Rydberg channels arising from the photoionization of the outermost electrons of the ground state of ethanol are restricted to the $3a'' - ksa'$, $3a'' - kda''$ and $3a'' - kda'$ channels.

The MQDO method requires as input data the vertical ionization energy and quantum defects for the Rydberg series. For the vertical ionization energy of the ethanol $3a''$ orbital we have used the value of 10.64 eV measured by Kimura et al. [26] using high-resolution photoelectron spectroscopy. Quantum defects for the s and d Rydberg series have been calculated from the well-known Rydberg formula using vertical excitation energies reported by Robin and Kuebler [25].

The cross-section for the photoionization from the $3a''$ outermost orbital of the ground state of ethanol, has been obtained adding the contributions of all compatible ionization channels, i.e., $3a'' - ksa'$, $3a'' - kda''$ and $3a'' - kda'$. The MQDO results are plotted versus the incident photon energy up to 70 eV in Figure 1. Numerical values of the cross-sections corresponding to the different allowed ionization channels from 11 to

50 eV photon energies are collected in Table 1. As can be seen from table 1, the main contribution to the partial photoionization cross section of ethanol comes from kd ionization channels.

No studies for the cross section of Rydberg ionization channels appear to be available to test the accuracy of the present calculations. Nonetheless, cross-sections, for the absolute photoionization of ethanol, have been measured at photon energies up to 11.72 eV with PIMS [2]. As the second ionization potential position of ethanol is at 12.18 eV, it might be a good assumption to consider that, in the interval where the experimental data are available, the contribution to the total photoionization is derived from the $3a''$ orbital. Based on this fact, we have employed these experimental values as a reference for comparison with our calculations in the region where they are available. The experimental data together with our calculations have been included in Table 2. Cool et al. [2] assign an uncertainty in their measurements of 20%. Taking into account this error, it can be observed in Table 2 that the MQDO cross sections are in good quantitative agreement with the measurements, except for photon energy values less or equal to 10.87 eV, where our results are higher than the measurements. On the other hand, photoabsorption cross sections for ethanol in the energy range involving present calculations have been found in the literature. Koizumi et al. [10] and Han et al. [5] have measured photoabsorption cross sections using synchrotron radiation. The estimated uncertainties of the previous measurements are about 15 - 20% for the values of Koizumi et al.[10], and about 10 and 15 % for the results of Han et al.[5]. More recently, Feng and Brion [11] have measured absolute photoabsorption oscillator strengths using high- and low-resolution dipole (e,e) spectroscopy with an uncertainty of about 5%. The total photoabsorption cross sections, σ_{abs}^T , can be converted into the total photoionization cross sections, σ_{ion}^T , through the following equation [1]:

$$\sigma_{ion}^T = \Gamma \sigma_{abs}^T, \quad (4)$$

where Γ is the total photoionization efficiency.

Since in the energy range between the first and second ionization potential of ethanol, the ionization is due mainly to the ejection of the $3a''$ valence electrons, the MQDO photoionization cross sections can also be compared with those derived from photoabsorption cross sections by using equation 4. In order to convert photoabsorption cross sections into photoionization cross sections, we have used the photoionization yields measured by Person and Nicole [9]. The photoionization cross section derived from photoabsorption measurements of Koizumi et al. [10], Han et al. [5] and Feng and Brion [11] together with the present calculations are shown in Figure 1. The early photoionization cross section measurements of Person and Nicole [9] have also been included in Figure 1. It should be mentioned that photoionization cross section data of Person and Nicole [9] and Cool et al [2] are very close to each other. Given that the results reported by the latter authors are displayed in Table 2 and in order to avoid congesting in Figure 1, they are not shown in the figure. We have digitized the figures corresponding to the photoabsorption cross sections of ethanol of Refs. 5, 9 and 10, which were presented in graphical form.

As can be seen in figure 1, MQDO predictions and experimental data show a similar behavior near the threshold. That is, both the experimental and the present results exhibit a sudden increasing with the increasing photon energy. It is also observed in Figure 1 that the MQDO photoionization cross-section profile for the production of the molecular cation in its ground state shows a maximum located a few electron-volts above the threshold, followed by a smooth decrease with increasing the photon energy. In order to get a better view of the comparison between the present results and the experimental

ones, in Figure 2 we have plotted our results together with the most recent photoionization cross section data reported by Cool et al. [2] and those derived from photoabsorption measurements [5,10, 11] over the narrow range of photon energies for which the experimental results are available. The MQDO results are in rather good agreement, within the error bars, with the photoionization measurements [2] and with the photoionization cross section derived from measurements reported by Koizumi et al.[10], except for photon energy less than 10.9 eV. Photoionization cross sections derived from measurements performed by Ham et al. [5] are systematically lower than the MQDO and the other experimental results.

Finally, we have also calculated the asymmetry parameters for the outermost orbital $3a''$ of ethanol. The MQDO results are displayed versus the photoelectron energy up to 70 eV in Figure 3. It can be seen in the figure that the photoelectron angular distribution profile shows an increasing with the increasing photoelectron energy and finally reaches an asymptotic value of about 1.5. From the asymmetry parameter, information about the orbital character of the photoelectron ejected in the photoionization process can be derived [21, 22]. As we have mentioned before, the outermost orbital of ethanol has been reported to be a nonbonding 2p orbital of the oxygen atom. The asymmetry parameters for the 2p orbitals of atomic oxygen have been reported by Yeh and Lindau [27] and by Manson [28], which are also included in Figure 3. As can be seen, the asymmetry parameter MQDO profile corresponding to the photoionization of $3a''$ orbital, shows an analogous behavior to that of oxygen 2p subshell. This atomic-like behavior supports the fact that the $3a''$ molecular orbital in ethanol is rather localized in a 2p oxygen atom.

4. Conclusions

The present work represents, to the best of our knowledge, the first calculation of photoionization cross-sections and asymmetry parameter profiles for the direct photoionization of the outermost orbital of ethanol. Contributions of each one of the allowed Rydberg continuous channels to the photoionization cross-section for the production of the molecular cation have been determined for the first time, as far as we know. The MQDO photoionization cross sections are found to be in rather good accord with PIMS measurements. A similar profile for the photoionization asymmetry parameter of 3a'' outermost valence orbital of ethanol and the corresponding to the 2p orbitals of oxygen atom have been found. The photoionization cross-sections presented here, along with those previously published in molecular systems, proved, in our view, the utility of the MQDO methodology for determining photoionization parameters relevant to combustion chemistry and astrophysics.

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Table 1. Photoionization cross-sections, in units of Mb, for the different Rydberg channels of CH₃ CH₂OH leading to the ground state of the cationic core.

Photon Energy/eV	ksa'	kda'	kda''
11.0	2.435	3.361	2.206
11.5	2.891	3.915	2.610
12.0	3.715	4.888	2.960
12.5	3.715	4.888	3.258
13.0	4.329	5.582	3.511
14.0	4.768	6.054	3.895
15.0	5.171	6.452	4.148
16.0	5.253	6.522	4.301
17.0	5.381	6.599	4.379
18.0	5.392	6.590	4.399
19.0	5.360	6.490	4.378
20.0	5.332	6.438	4.326
21.0	5.211	6.244	4.252
22.0	4.994	5.933	4.163
24.0	4.743	5.596	3.955
26.0	4.482	5.256	3.731
28.0	4.223	4.925	3.504
30.0	3.972	4.610	3.283
32.0	3.732	4.315	3.074
34.0	3.507	4.039	2.877
36.0	3.297	3.784	2.693
38.0	3.101	3.548	2.523
40.0	2.919	3.331	2.366
42.0	2.750	3.130	2.220
44.0	2.594	2.945	2.086
46.0	2.449	2.774	1.963
48.0	2.315	2.616	1.849
50.0	2.190	2.470	1.744
60.0	1.394	1.551	1.034
70.0	1.394	1.551	1.034

Table 2. Photoionization cross-sections, in units of Mb, of ethanol.

Photon Energy/eV	MQDO ^a	Expt. ^b
10.72	6.978	4.19
10.77	7.148	4.86
10.82	7.317	5.44
10.87	7.484	6.02
10.92	7.649	6.50
10.97	7.812	6.87
11.02	7.972	7.28
11.07	8.131	7.79
11.12	8.288	8.10
11.17	8.443	8.37
11.22	8.596	8.77
11.27	8.747	8.83
11.32	8.896	8.99
11.37	9.043	9.30
11.42	9.188	9.59
11.47	9.331	9.72
11.52	9.473	10.03
11.57	9.612	10.21
11.62	9.749	10.32
11.67	9.884	10.79
11.72	10.018	11.09

^aThis work

^bCool et al. [2]

Figure 1. Cross-sections for the photoionization of the outermost orbital of C_2H_5OH as a function of photon energy

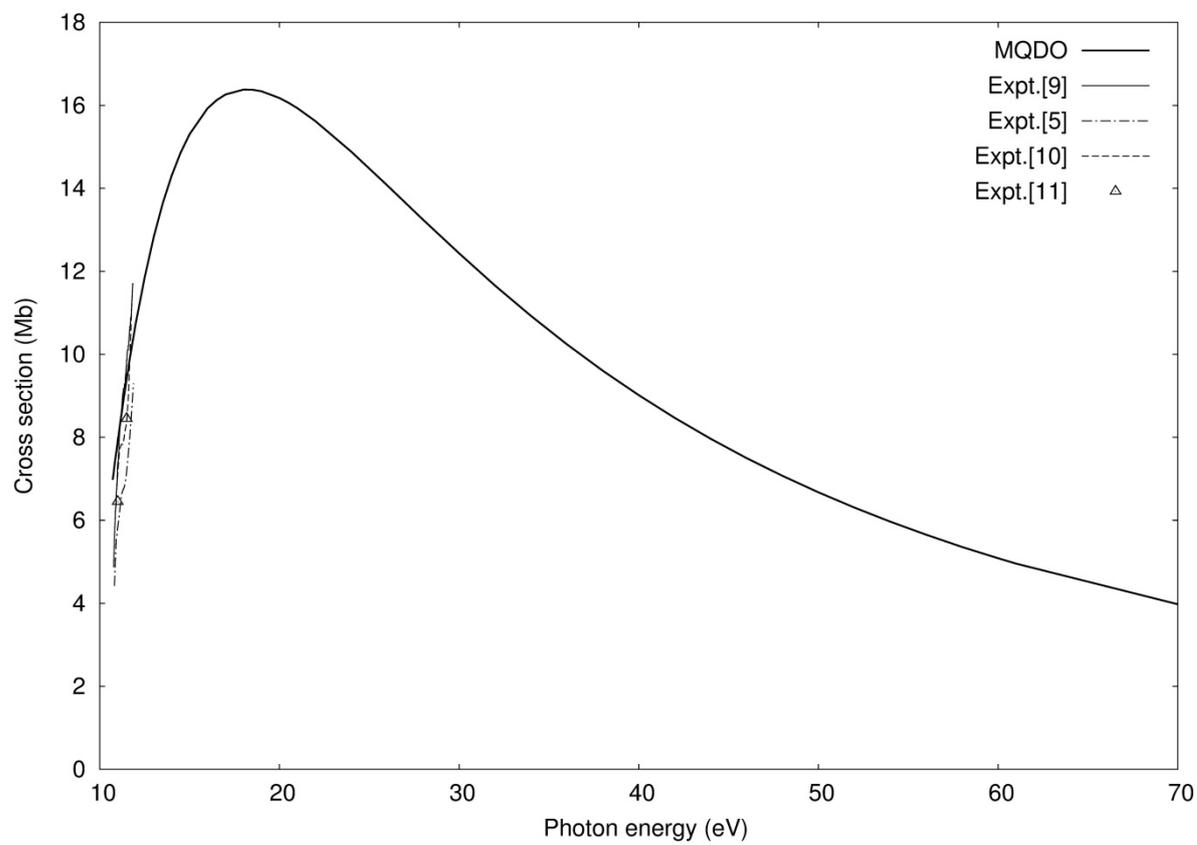


Figure 2. Cross-sections for the photoionization of the outermost orbital of C_2H_5OH as a function of photon energy over a range from 10.7 to 12 eV.

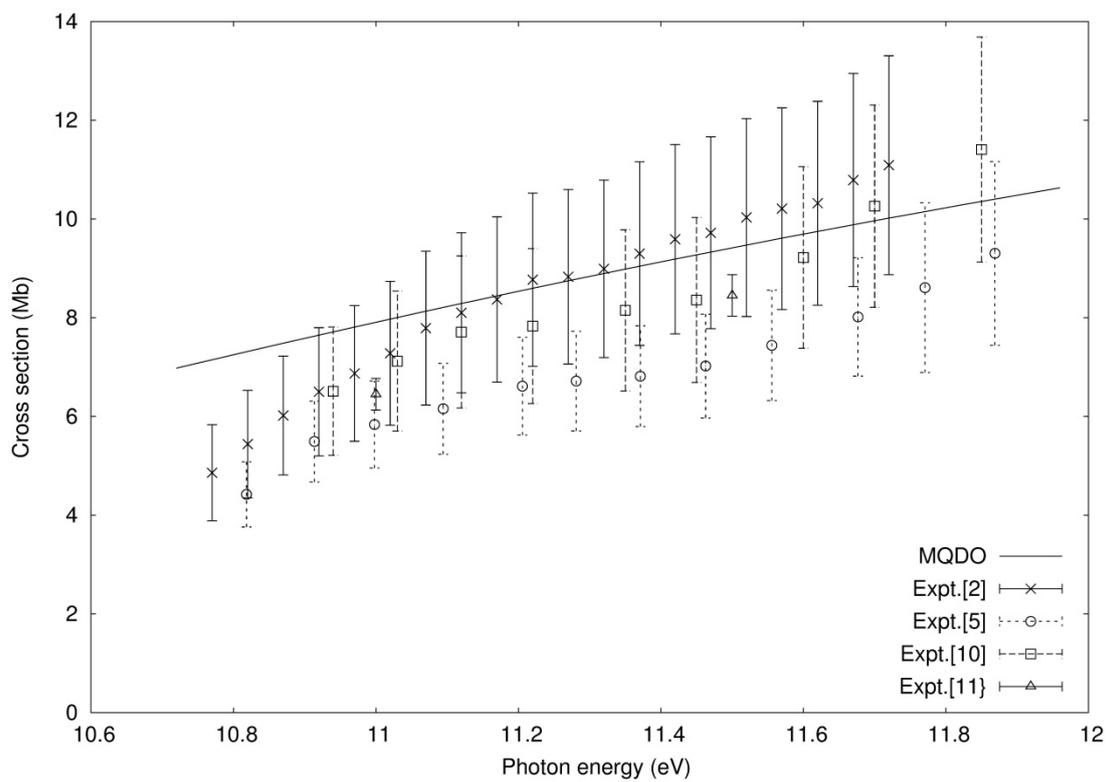


Figure 3. Asymmetry parameter for the photoionization of the outermost orbital of C_2H_5OH as a function of photoelectron energy

