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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 have 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 that the MQDO data will be useful in combustion chemistry and astrophysics.

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 in part due 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

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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 of 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:

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

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:

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

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]:

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

where $R_{l\pm1,}$ the radial dipole matrix elements, are calculated with the MQDO method and $\xi_{l\pm1,}$ 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 $\ldots(7a')^2\,(1a'')^2\,(8a')^2\,(9a')^2\,(2a'')^2\,(10a')^2(3a'')^2\ X^1A'$. 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