Photoelectron spectroscopy of a series of acetate and propionate esters

CrossMark

Małgorzata A. Śmiałek [a,b,*], Julien Guthmuller [c], Michael A. MacDonald [d], Lucia Zuin [d], Jacques Delwiche [e], Marie-Jeanne Hubin-Franskin [e], Tadeusz Lesniewski [f], Nigel J. Mason [b], Paulo Limão-Vieira [g]

[a] Department of Control and Power Engineering, Faculty of Ocean Engineering and Ship Technology, Gdańsk University of Technology, Gabriela Narutowicza 11/12, 80-233 Gdańsk, Poland
[b] School of Physical Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom
[c] Department of Theoretical Physics and Quantum Information, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Gabriela Narutowicza 11/12, 80-233 Gdańsk, Poland
[d] Canadian Light Source Inc., 44 Innovation Boulevard, Saskatoon SK S7N 2V3, Canada
[e] Département de Chimie, Université de Liège, Institut de Chimie-Bât. B6C, B-4000 Liège, Belgium
[f] Institute of Experimental Physics, Faculty of Mathematics, Physics and Informatics, University of Gdańsk, 80-308 Gdańsk, Poland
[g] Laboratório de Colisões Atómicas e Moleculares, CEFITEC, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

ARTICLE INFO

ABSTRACT

The electronic state and photoionization spectroscopy of a series of acetate esters: methyl acetate, isopropyl acetate, butyl acetate and pentyl acetate as well as two propionates: methyl propionate and ethyl propionate, have been determined using vacuum-ultraviolet photoelectron spectroscopy. These experimental investigations are complemented by *ab initio* calculations. The measured first adiabatic and vertical ionization energies were determined as: 10.21 and 10.45 eV for methyl acetate, 9.99 and 10.22 eV for isopropyl acetate, 10.07 and 10.26 eV for butyl acetate, 10.01 and 10.22 eV for pentyl acetate, 10.16 and 10.36 eV for methyl propionate and 9.99 and 10.18 eV for ethyl propionate. For the four smaller esters vibrational transitions were calculated and compared with those identified in the photoelectron spectrum, revealing the most distinctive ones to be a C–O stretch combined with a C=O stretch. The ionization energies of methyl and ethyl esters as well as for a series of formates and acetates were compared showing a clear dependence of the value of the ionization energy on the size of the molecule with very little influence of its conformation.

1. Introduction

Esters are emitted to the atmosphere both through anthropogenic and natural [1] sources. In industry they play an important role, among others, as solvents [2] and in use of fragrances and flavourings, while recently they have also become a significant additive in biodiesel fuels [3]. Esters are also of astrochemical interest, since it has been shown that small esters are present in the interstellar space [4].

In order to assess the role of such compounds in atmospheric and interstellar chemistry, it is necessary to acquire an accurate kinetic chemistry data including their reactions in the gas phase as well as detailed information on their electronic structure and properties, such as their ionization energies (IEs). TThe electronic state and photoionization spectroscopy of those esters that have a high vapour pressure can be obtained by the use of VUV photoelectron energy analysis assisted by the state-of -the-art *ab initio* calculations.

In this paper we provided a detailed photoelectron spectroscopy (PES) analysis of the series of acetate and propionate esters: methyl acetate, isopropyl acetate, butyl acetate, pentyl acetate, methyl propionate and ethyl propionate. Electronic excitation of these compounds have been described with aid of quantum chemistry calculations. Combining our findings with data obtained for those esters that have been studied previously: methyl formate [5], ethyl formate [6], isobutyl formate [7], isobutyl acetate [8], ethyl acetate [9], methyl butyrate and methyl valerate [10] we can draw some conclusions on the influence of the increase in the alkyl and aryl group on the ionization energy of ester molecules.

2. Experimental section

2.1. Ester samples

The liquid samples used both in He(I) and synchrotron PES experiments were purchased from Sigma-Aldrich, all with a purity better than 99 %. The samples were degassed by repeated freeze–pump–thaw cycles with no further purification of the samples.

2.2. Photoelectron spectra measurements

The He(I) (21.22 eV) photoelectron spectra of methyl acetate, pentyl acetate, methyl propionate and ethyl propionate (Figs. 3 and 5) were measured at the Université de Liège, Belgium. The apparatus has also been described in detail previously [11]. Briefly, it consists of a 180° hemispherical electrostatic analyser with a mean radius of 5 cm, the analyser is used in the constant pass energy mode. The incident photons are produced by a d.c. discharge in a two-stage differentially pumped helium lamp. The energy scale is calibrated using the $X^2\Sigma_g^+$, $v' = 0$ and $A^2\Pi_u$, $v' = 0$ peaks of N_2^+, rounded to three decimal places [12,13]. The resolution of the present spectrum is 40 meV and the accuracy of the energy scale is estimated to be $\pm$ 2 meV. The photoelectron spectra presented here are the sum of at least 70 individual spectra. This procedure allows a good signal-to-noise ratio while keeping the pressure in the spectrometer low ($< 5 \times 10^{-6}$ mbar).

The photoelectron spectra of isopropyl acetate and butyl acetate (Fig. 3) were measured at the VLS-PGM beamline [14] at the Canadian Light Source facility in Saskatoon, Canada, using a Double Toroidal Coincidence Spectrometer, described previously [15]. Although designed and primarly used for analysis of Noble gases and small, diatomic molecules it has been successfully applied to measurements of more complicated systems such as pyrimidine and its heavier derivatives [16] or other esters [7]. Briefly, a photoelectron-photoelectron coincidence spectrometer has been developed in which two electrons, of specified energies, are detected over a wide range of emission angles. The spectrometer is based on a toroidal geometry and has properties ideally suited for measuring electron angle distributions since toroidal analysers can be made to energy select the photoelectrons while preserving the initial angle of emission. The spectrometer consists of two toroidal analyzers, each focused on the interaction region. One collects electrons over an azimuthal range of 180°, the other over 120°. The electrostatic analyzers are independent, i.e. they are able to detect dissimilar electron energies albeit with different resolutions. Both analyzers were set at a pass energy of 4 eV. In these experiments we have used the data collected by the 180° toroidal detector. The measured resolution from the nitrogen calibration spectra was 40 meV. The photoexcitation energy of the photoelectron spectrum presented here was 80 eV, recorded with the entrance and exit slits of the VLS-PGM beamline set at 50 μm. The recorded spectra were calibrated against the $X^2\Sigma_g^+$, $v' = 0$ and $A^2\Pi_u$, $v' = 0$ peaks of N_2^+, rounded to three decimal places [12,13].

2.3. Computational methods

The ground state geometry, harmonic vibrational frequencies, and normal coordinates of the neutral singlet state (S_0) and ionic doublet state (D_0) of the different esters were obtained with the Gaussian 09 program [17] by means of second-order Møller-Plesset (MP2) calculations [18] in association with the aug-cc-pVTZ basis set. The ionic state was described by open-shell unrestricted calculations. The first ionization energies (IE) were computed from the energy difference between the neutral and ionic ground states. The vertical IE was calculated at the ground state geometry of the neutral compound and the adiabatic IE was evaluated using the opti-
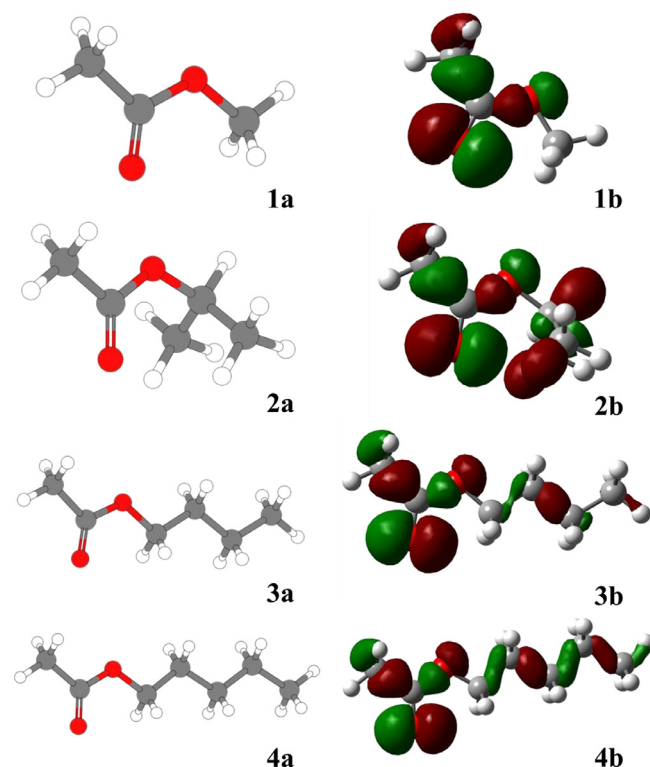

Fig. 1. Structure (a) and HOMO orbitals (b) of 1: methyl acetate, 2: isopropyl acetate, 3: butyl acetate and 4: pentyl acetate.

mized geometries of the neutral and ionic ground states. Additionally, the first IE was calculated with the coupled-cluster singles and doubles (CCSD), and the coupled-cluster singles, doubles and perturbative triples (CCSD(T)) methods [19,20] using the aug-cc-pVTZ basis set and employing the optimized geometries at the MP2/aug-cc-pVTZ level of approximation. Furthermore, the zero point vibrational energy (ZPVE) correction to the adiabatic IEs was determined from the MP2/aug-cc-pVTZ harmonic vibrational frequencies. This correction was also applied to the values calculated with the CCSD and CCSD(T) methods. Higher IEs were obtained with the Partial Third Order (P3) and Outer Valence Greens Function (OVGF) propagator methods [21] using the aug-cc-pVTZ basis set and the MP2/aug-cc-pVTZ geometry. The Franck–Condon (FC) factors, associated with the first photoelectron band, were calculated using recursive relations and include Duschinsky rotation effects [22–25]. These calculations made use of the ground state geometries, harmonic frequencies and normal coordinates calculated with the MP2/aug-cc-pVTZ method for the neutral (S_0 state) and ionic (D_0 state) forms of the esters.

3. Results and discussion

3.1. Structure and properties of acetates and propionates

The molecular structure of acetate esters is presented in Fig. 1 (1–4a). In all cases, in accord with previous studies of formate [5–7] and acetate [8,9] esters, the highest occupied molecular orbital (HOMO) in the neutral ground state is localized largely on the terminal oxygen in-plane lone pair (n_{O1}), as seen in Fig. 1 (1–4b). For methyl acetate the HOMO is $(16a')^2$, for isopropyl acetate – $(20a')^2$, for butyl acetate – $(25a')^2$, and for pentyl acetate – $(28a')^2$.

Analogously, in the propionate esters, methyl and ethyl, Fig. 2 (1a and 2a), the HOMO is also localised in the neutral ground state on the terminal oxygen in-plane lone pair (n_{O1}, Fig. 2 (1b and 2b)).