



Threshold photoelectron spectroscopy of acetaldehyde and acrolein



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ABSTRACT

High-resolution (6 meV and 12 meV) threshold photoelectron (TPE) spectra of acetaldehyde and acrolein (2-propenal) have been recorded over the valence binding energy region 10–20 eV, employing synchrotron radiation and a penetrating-field electron spectrometer. These TPE spectra are presented here for the first time. All of the band structures observed in the TPE spectra replicate those found in their conventional HeI photoelectron (PE) spectra. However, the relative band intensities are found to be dramatically different in the two types of spectra that are attributed to the different dominant operative formation mechanisms. In addition, some band shapes and their vertical ionization potentials are found to differ in the two types of spectra that are associated with the autoionization of Rydberg states in the two molecules.

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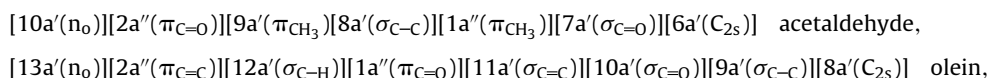
1. Introduction

The carbonyl group ($\text{C}=\text{O}$) is found in many molecules of the type ($\text{RR}'\text{C}=\text{O}$), where R and R' can be organic or inorganic atoms or groups (e.g., H, CH_3 , OH, Cl, and NH_2). In organic molecules, this pervasive functional group determines much of the molecule's physical and chemical properties. In particular, the properties are dominated by the electronic structure of the carbonyl group, and specifically with regard to the nonbonding nature of the ground state of the molecular ion. In general, the formation of the ground-state ion is usually the result of the removal of a nonbonding electron mainly localized on the carbonyl oxygen. We have initiated a research program to investigate the photoionization behavior of some simple organic molecules containing the carbonyl group using threshold photoelectron (TPE) spectroscopy and total photoion yield (TPIY) spectroscopy. We previously reported on the TPE and TPIY spectra of formic and acetic acid in this regard [1]. Here we extend our photoionization studies to the simple aldehydes acetaldehyde and acrolein.

Studies of the photoionization of acetaldehyde are far more abundant than are those of acrolein. The most accurate values of the lowest adiabatic ionization potentials for acetaldehyde and acrolein to date were measured to be $82,505 \pm 5 \text{ cm}^{-1}$ ($10.2293 \pm 0.0007 \text{ eV}$) and $81,500 \pm 50 \text{ cm}^{-1}$ ($10.105 \pm 0.006 \text{ eV}$), respectively, from Rydberg-series analyses of their measured absorption spectra [2,3]. The most accurate photoionization energy values of the lowest adiabatic ionization potentials for acetaldehyde and acrolein have been reported to be $10.2295 \pm 0.0007 \text{ eV}$ [4] and $10.10 \pm 0.01 \text{ eV}$ [5], respectively. The earliest HeI photoelectron spectra of acetaldehyde and acrolein were both reported in 1966 [6] and subsequently reported a number of times [7–18] and [17,19–26], respectively, at varying degrees of resolution, while their HeII photoelectron spectra have also been reported [27,28] and [24,29,30], respectively. Neither molecule has had their TPE nor their TPIY spectra reported previously, to the best of our knowledge, although studies of the photoionization mass spectrometry of acetaldehyde [31–35] and the electron impact mass spectrometry of acetaldehyde [36] and acrolein [37] have been published. In addition, three photoelectron-photoion coincidence studies of acetaldehyde [18,38,39] and one threshold photoelectron-photoion coincidence study of acrolein [40] have been reported. Numerous ab initio theoretical molecular orbital calculations have been performed on the molecules acetaldehyde

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and acrolein [9,11,17,19,23,24,26,28,30] with the consensus for the arrangement of the valence molecular orbitals, in the order of increasing ionization energy, being:



where a' and a'' indicate in-plane and out-of-plane molecular orbitals, respectively, in C_s symmetry.

2. Experimental

All spectra reported here were recorded at the Synchrotron Radiation Source (SRS) of the Daresbury Laboratory (UK) on beamline 3.2. Two types of spectra were recorded simultaneously as a function of synchrotron radiation energy: one was the threshold photoelectron (TPE) spectra and the other was the total photoion yield (TPIY) spectra of the molecules acetaldehyde and acrolein. The apparatus used was a purpose-built vacuum chamber containing electron and ion detection systems that was attached to the exit slit of a 5-m normal incidence grating McPherson monochromator. A detailed description of this apparatus and the experimental arrangement for obtaining simultaneously TPE and TPIY spectra has been given recently [1], so only a brief account will be presented here.

Threshold electrons of near-zero kinetic energy (<20 meV, with ~95% within 3 meV of zero) were detected by a channel electron multiplier (CEM) as a function of photon energy using a penetrating-field energy analyzer [41,42]. The analyzer was tuned to accept primarily threshold electrons using the argon ion doublet lines, $^2P_{3/2}$ and $^2P_{1/2}$. An effusive beam of target gas entered the ionization region of the apparatus through a platinum/iridium needle of 0.8-mm bore mutually perpendicular to the 1-mm diameter photon beam and the entrance axis of the electron analyzer; the needle was positioned ~2 mm above the center of the photon beam. The ion detector was mounted opposite to the entrance of the electron analyzer with an entrance aperture in a grounded shielding plate, behind which was mounted a three-element, single-focusing lens, followed by a CEM. The entrances to the electron and ion detector systems were 12 mm from the gas/photon beam interaction region. The temperature of the main chamber of the apparatus was maintained at ~63 °C to minimize local patch fields due to contact potential variations.

In this study, survey TPE spectra were recorded for both acetaldehyde and acrolein with a step size of 5 meV and with dwell times of 18 s per point for the former and 5 s per point for the latter. These survey spectra were from the onset of ionization (10 eV) to a binding energy of 20 eV at a resolution of ~12 meV (measured at 15.759 eV). In addition, two sets of TPE (electron) and TPIY (ion) spectra were recorded simultaneously for both acetaldehyde and acrolein; a high-resolution set in the onset of ionization region and a set with good counting statistics in the higher binding energy region. In the former, TPE and TPIY spectra were obtained simultaneously for both acetaldehyde and acrolein with a step size of 2 meV and a resolution of ~6 meV over the binding energy regions 10–11 eV and 10–13 eV, respectively, with dwell times of 15 s per point for both. In the latter, TPE and TPIY spectra were recorded simultaneously for both acetaldehyde and acrolein over the binding energy regions 11–18 eV and 13–20 eV, respectively. The step size for these spectra were 5 meV and the resolution was ~12 meV (measured at 15.759 eV) for both and with dwell times of 54 s and 35 s per point, respectively. All TPE and TPIY spectra presented here were energy calibrated and corrected for the variation in the photon flux as a function of energy and decay of the synchrotron current as detailed elsewhere [43].

The acetaldehyde and acrolein sample liquids used in this study were both obtained from Sigma–Aldrich (Steinheim, Germany) and were stated to be >99.5% and >99% pure, respectively, and were

used directly. The partial pressure of these substances in the main chamber of the apparatus was of the order of 6–8 10^{-5} mbar, with no indication of any dimerization detected in either system studied, while the base pressure of the apparatus was about 6×10^{-7} mbar.

3. Results and discussion

3.1. Comparison of the threshold photoelectron spectra with the Hel photoelectron spectra of acetaldehyde and acrolein

The overall survey TPE spectrum of acetaldehyde is shown in the lower two traces in Fig. 1 between 10 and 20 eV binding energy at a resolution of 12 meV (measured at 15.759 eV). The identity of the seven-band systems seen in the TPE spectrum in Fig. 1 are based on the one electron–one hole molecular orbital picture of ionization by the sequential removal of a single electron from a molecular orbital based on the electron configuration given above. In the upper trace in Fig. 1 is shown a published Hel PE spectrum of acetaldehyde [17] over the same binding energy region for comparison. It is clear that all seven-band systems are present in both types of spectra, but their relative band intensities (qualitatively given by their peak heights) are vastly different. However, it must be kept in mind that the peak heights are susceptible to the conditions of resolution that

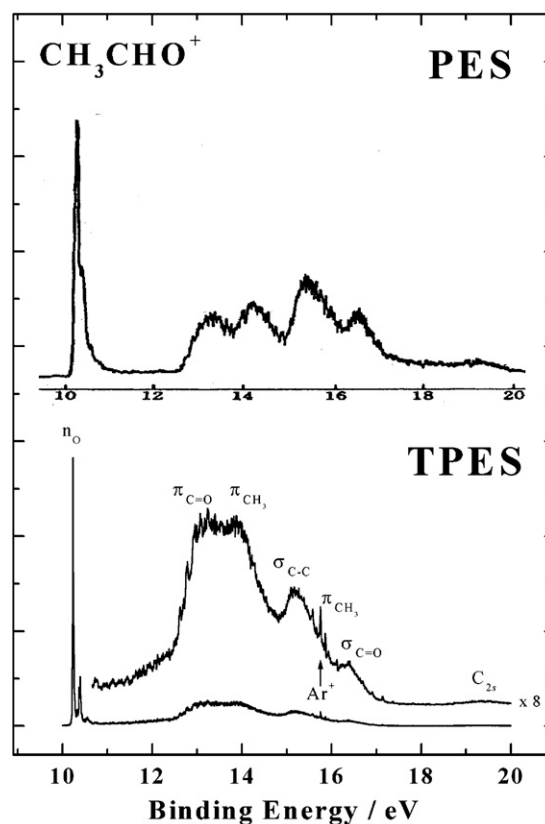


Fig. 1. Survey threshold photoelectron spectrum (TPES) of acetaldehyde over the ionization energy range 10–20 eV at a resolution of 12 meV (measured at 15.759 eV) compared with the Hel photoelectron spectrum (PES) taken from Ref. [17]. The identification of the band structure is given in the TPES.

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