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Valence Shell Ionization Spectra of Propane by (e, 2e) Spectroscopy *

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The measurements of the valence shell ionisation energy spectra (6–32 eV) for propane (C_3H_8) by high resolution ($\Delta E = 0.9\,eV$ and $\Delta p = 0.1$ a.u.) (e, 2e) spectrometer at impact energy of 1200 eV plus binding energy and symmetric noncoplanar kinematics are reported. The spectrum is consistent with a single particle picture of ionization from each of the seven outer-valence orbitals and the three inner-valence orbitals. The ionization energies are in agreement with published photoelectron spectroscopy data.

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In the last two decades many experiments have demonstrated that electron momentum spectroscopy (EMS) is a powerful experimental tool for studying the electronic structure of atoms and molecules, and that it can provide detailed information on electron motion and also the role of electron correlation in atoms and molecules.[1] EMS is based on the (e, 2e) ionizing collision in the knockout region. The (e, 2e) experiment is an electron impact ionization process in which the kinematics of the incident electron and two outgoing electrons is fully determined, except their spins. Thus these experiments are of great value for direct comparison with collision theory. If the independent particle or Hartree-Fock approximation for the molecule is made, the molecule can be considered as having N electrons moving independently in self-consistent characteristic orbitals and having a characteristic orbital binding or separation energy.

The (e, 2e) experiment involves a measurement for an incident electron energy E_0 and momentum p_0, the incident electron scattered with energy E_a and momentum p_a, and the ejected electron with energy E_b and momentum p_b. The experimental coincidence rate is related to the triple differential cross-section (TDCS) which in turn is directly proportional to the square of the momentum space wavefunction of the characteristic orbital from which the electron is ejected under appropriate kinematics conditions satisfying the plane wave impulse approximation (PWIA),[1] i.e.,

$$\sigma_{\mathrm{TDCS}} = (2\pi)^4 \frac{p_a p_b}{p_0} f_{\mathrm{ee}} \sum_{\mathrm{av}} \left| \left\langle \boldsymbol{p}\, \Psi_{\mathrm{f}}^{N-1} \middle| \Psi_{\mathrm{i}}^{N} \right\rangle \right|^2,$$

where f_{ee} is simply the Mott electron–electron scattering factor, $\sum_{\mathrm{av}}$ denotes the usual procedure of summing over the final states and averaging over the initial states, and the structure factor $\langle \boldsymbol{p}\, \Psi_{\mathrm{f}}^{N-1} | \Psi_{\mathrm{i}}^{N} \rangle$ is the momentum representation of the overlap amplitude of the target atom and the residual ion's eigenstates. This amplitude involves the integration over the coordinates of the $N-1$ common electrons of the target atom and final ion's momentum space wavefunctions, and is therefore a function of only the momentum of the ejected electron.

Up to date, only a limited number of saturated hydrocarbons molecules have been studied by (e, 2e) spectroscopy, such as the methane and ethane molecules.[2–4] The large number of electrons in C_3H_8 render the calculation quite difficult, thus the availability of good experimental data is an important aid for developing a satisfactory theoretical method. In particular, the inner-valence region provides a very sensitive test of the many-body calculations which take the initial and final states correlation into account.

In our work, the electron momentum distributions have recently been measured for C_3H_8. We report here the valence shell binding energy spectrum of C_3H_8 measured at two relative azimuth angles using the non-coplanar symmetric (e, 2e) reaction. The incident energy was 1200 eV plus the binding energy. A sufficiently high impact energy (>1200 eV) and momentum transfer were used to ensure the validity of the PWIA.

A high resolution ($\Delta E = 0.9$ eV and $\Delta p = 0.1$ a.u.) (e, 2e) spectrometer at Tsinghua University was used to measure the TDCS as a function of impact energy and relative azimuth angle. Details of the (e, 2e) spectrometer have been reported elsewhere[5,6] and only a brief description is given in this paper. Two hemispherical electron energy analysors, each having a five element cylindrical retarding lens system, are mounted inside a μ-metal shielded vacuum system on two independent horizontal concentric turntables. In the present work, the polar angles of both analysors are

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kept fixed and equal to 45°. One analysor's turntable was kept fixed, and the other one rotated by a computer controlled stepping motor to vary the relative azimuth angle. Each energy analysor has a position sensitive detector consisting of microchannel plates and a resistive anode in their energy disperse exit plane. The energy range of each analysor was set at 600±4 eV with passing energy E_p of 50 eV. Electron impact ionization was carried out under the symmetric noncoplanar geometry with pre-set kinematics parameters for the incident as well as two outgoing electrons. The energy resolution obtained in the coincidence experiment is a convolution of the two analysor functions and the energy distribution of the incident electron beam. It also depends on the deceleration ratio of the lens. This resolution, as well as the separation energy scale, was measured directly by using helium as a calibration gas. The energy resolution of the spectrometer was measured to be 0.86 eV full width at half maximum (FWHM) as shown in Fig. 1. The experimental momentum resolution was estimated to be 0.1 a.u. from a consideration of the argon $3p$ angular correlation. Propane was obtained commercially (99.9% purity) and used without further purification.

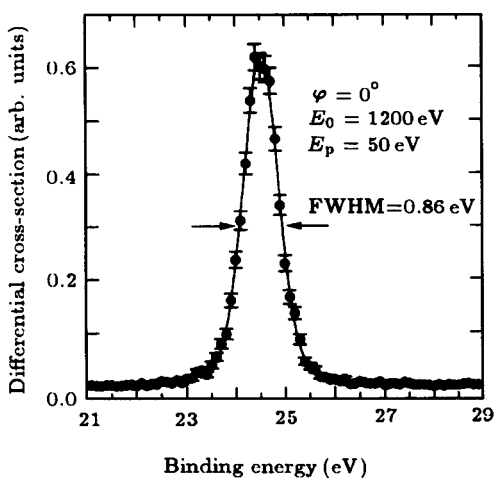

Fig. 1. Binding energy spectrum of He ($1s$).

The point group symmetry of C_3H_8 is C_{2v}. The valence shell electronic configuration of ground state can be written as

$(\text{Core})^6(3a_1)^2(2b_2)^2(4a_1)^2$
Inner-valence orbits,
$(1b_1)^2(5a_1)^2(3b_2)^2(1a_2)^2(4b_2)^2(6a_1)^2(2b_1)^2$
Outer-valence orbits.

The valence electrons in propane are distributed over ten molecular orbitals. All the canonical molecular orbitals are a-type or b-type. There is no degeneracy in these orbitals. In the ground state, the twenty-six electrons are arranged in thirteen doubly-occupied orbitals in the independent particle description. Since C_3H_8 is of lower symmetry C_{2v} than that of CH_4 (T_d) and C_2H_6 (D_{3d}), the spectra cannot be complicated by the Jahn-Teller effect. The assignment of the order of occupation for these valence orbitals, both in photoelectron spectroscopy (PES) experiments and in molecular orbital calculations, has been discussed by Kimura *et al.*[7] and Bieri *et al.*[8] The experimental and theoretical binding energies of C_3H_8 from these literature and those used in the present work are shown in Table. 1.

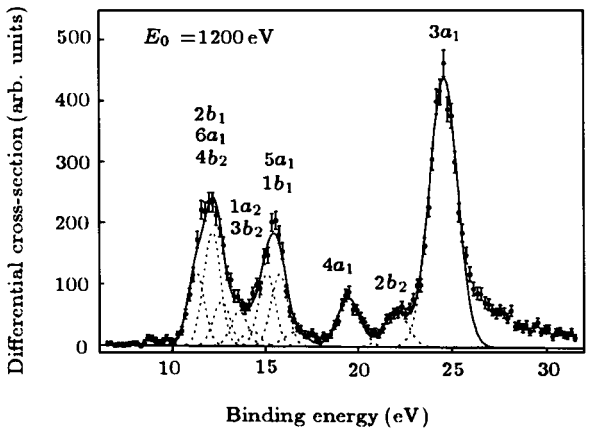

Fig. 2. Binding energy spectra of propane at $\varphi = 0°$.

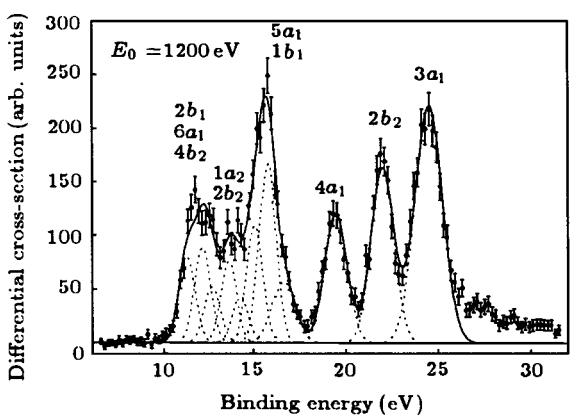

Fig. 3. Binding energy spectra of propane at $\varphi = 6°$.

Figures 2 and 3 show the binding energy spectra of C_3H_8 in the range of 6–32 eV for measurements at two relative azimuth angles of $\varphi = 0°$ and 6°. The spectra in Figs. 2 and 3 are fitted with a set of individual Gaussian peaks whose widths are combinations of the instrumental energy resolution and the corresponding Franck-Condon widths derived from PES data. The relative energy values are given by the relative ionization energies determined by high resolution PES. The absolute binding energy scale was set by assigning the energy of the $(3a_1)^{-1}$ peak to the ionization potential given by PES data.[9] The fitted Gaussians for individual peaks are indicated by dotted lines while their sum, i.e., the overall fitted spectrum is represented by the solid line. Figure 2 shows the binding energy spectrum obtained at the azimuth angle $\varphi = 0°$ corresponding to a momentum $p \approx 0.06$ a.u., and it is

Table 1. Experimental and theoretical binding energies of C_3H_8 (in eV).

Orbital	Experimental					Theoretical			
	PES			XPS	(e,2e)	SCF	HAM/3	FOA(R)	MRD-CI
	Ref.7	Ref.8	Ref.9	Ref.10	This work	Ref.7	Ref.8		
$3a_1$		24.7	24.5	24.60	24.5		24.15	25.31	29.02
$2b_2$		22.1	22.1	22.08	22.0		21.89	22.65	25.28
$4a_1$		19.5	19.15	19.57	19.45		19.60	19.56	21.53
$1b_1$	15.85	16.0			15.76	17.01	15.70	15.82	16.33
$5a_1$	15.33	15.2		15.64	15.24	16.29	14.80	15.19	15.61
$3b_2$	14.2	14.1			14.33	14.91	13.73	13.76	14.30
$1a_2$	13.52	13.5		13.70	13.57	14.43	13.40	13.30	13.67
$4b_2$	12.6	12.6			12.63	12.88	12.02	12.00	11.97
$6a_1$	12.14	12.1		12.04	12.10	12.81	12.43	11.72	11.91
$2b_1$	11.51	11.5			11.25	12.59	12.01	11.51	11.87

therefore dominated by "*s*-type" symmetric orbitals which have a maximum cross-section at $p = 0$. Those orbitals having "*p*-type" characteristics, i.e., antisymmetric in position space and hence having a cross-section minimum at $\varphi = 0°$, are more prominent in Fig. 3 which were taken at the azimuth angle $\varphi = 6°$ ($p \approx 0.49$ a.u.). The relative intensities in $\varphi = 0°$ and 6° spectra reflect the different symmetries of the valence orbitals of C_3H_8. In particular, the innermost orbitals clearly indicate that $3a_1$ orbitals have '*s*-type' symmetry and $2b_2$ and $4a_1$ orbitals have "*p*-type" symmetry.

The PES spectra of the seven orbitals of the outer-valence region were given by Kimura *et al.*[7] using He I radiation source. In the present work, the vertical ionization potentials of the $2b_1$, $6a_1$, $4b_2$, $1a_2$, $3b_2$, $5a_1$, and $1b_1$ orbitals were determined to be 11.25, 12.10, 12.63, 13.57. 14.33, 15.34, and 15.96 eV, respectively. The photoionization studies by Potts *et al.*[9] covered some of the inner-valence region of C_3H_8, they showed that the structures at 19.15, 22.1, and 24.5 eV were assigned to the $4a_1$, $2b_2$, and $3a_1$ orbitals, respectively. The excellent fit to our experimental data in Figs. 2 and 3 indicates that it is in close coincidence between the present (e, 2e) data and PES data of the outer- and inner-valence orbitals. The binding energies of C_3H_8 for all the peaks in Figs. 2 and 3 are determined and given in Table 1. The three peaks corresponding to the removal of an electron from the $3a_1$, $2b_2$, and $4a_1$ inner-valence orbitals at 24.5, 22.0, and 19.45 eV binding energy are clearly separated, in which the differences in FWHM are explained by the vibrational broadening of electron lines. In addition, one additional weak structure is observed at about 16.6 eV and some rather weak structure is also observed above 26 eV in the spectra of Figs. 2 and 3, which are due mainly to correlation effects in the target or in the residual ions' final states. It should also be noted that our present energy resolution (0.9 eV FWHM), which is already among the best of (e, 2e) spectrometer, did not allow us to separate satisfactorily the outer-valence orbitals. This spectrum (Fig. 3) is similar to that obtained by Pireaux *et al.*[10] using x-ray photoelectron spectroscopy (XPS). Compared to the PES, the advantage of (e, 2e) spectrometer is that it can measure the orbital electrons momentum distribution but the former cannot. The momentum measurement will be described in a separate paper.

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