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Electron yield spectra in the range of $280 \leq h\nu \leq 300$ eV which basically resemble the absorption spectra, have been measured for gaseous methane, ethane, ethylene, benzene and acetylene using synchrotron radiation. The spectra being fairly simple compared to the valence shell absorption are characterized by weak maxima for energies below the ionization threshold for C 1s for methane and ethane whereas additional strong resonances are observed in the spectra from molecules containing π -electrons. The nature of these excitations is discussed on the basis of their term values using information from XPS-measurements.

1. Introduction

The ionization potentials (IP's) of simple hydrocarbons have been the subject of numerous experiments and theoretical calculations. Precise and detailed information has been obtained from photoelectron spectroscopy with ultraviolet (UV) radiation about the outermost valence electrons^{1,2} and from x-ray photoelectron spectroscopy about the more tightly bound molecular orbitals (MO's), in particular those formed by the carbon C 1s electrons³⁻⁶. However, in those experiments information is mainly obtained about the occupied MO's, their binding energies, shifts and splittings in various molecular geometries. Insight into the electronic structure of highly excited states is obtained from absorption and electron impact spectroscopy^{7,10}. Despite a continuing interest for inner shell spectra from a theoretical point of view¹¹ the experimental information for simple hydrocarbons in the range of the carbon C 1s edge ($h\nu \approx 290$ eV) is still scarce. The absorption spectrum of methane was obtained by Chun¹² with synchrotron radiation in 1969. Together with the excitation spectrum of CH₄ obtained by Wight and Brion in electron impact experiments¹³ it constitutes the only detailed experimental piece of information currently available for simple hydrocarbons. It has been discussed subsequently in comparison with theoretical calculations^{14,15}.

The reason for the lack of experimental data is twofold: (1) there is no strong, continuous light source available for the spectral region of interest (280 - 300 eV) other than synchrotron radiation and (2) the reflectivity of mirrors and gratings is extremely sensitive to the omnipresent contaminations from hydrocarbons in this spectral range. Spectroscopy at the onset of C 1s excitations therefore suffers from low intensity and a large background of straylight. For our experiments we used synchrotron light and applied an electron yield method which is considerably more sensitive than

an ordinary absorption measurement. This method will be described in detail in section 2.

In view of the need for experimental information on the highly excited states of simple hydrocarbons we present these 'quasi absorption spectra' although some reservations have to be made with respect to the relative intensities of the observed structures.

2. Experimental Details

Synchrotron radiation from the 7.5 GeV electron synchrotron at DESY was monochromatized by a specially designed grazing incidence monochromator which is described elsewhere¹⁶. This instrument has a resolution of about 0.5 eV in the region of interest (250 - 300 eV). The fixed monochromatic beam enters an ionization chamber through a collimated hole structure having a geometric optical transparency of about 50 % and a gas flow conductance of 0.5 l/sec. A first differential pumping stage which is installed between this collimator and the exit slit of the monochromator together with the pumping system of the monochromator allowed for sustaining a pressure difference of five orders of magnitude between the ionization chamber and the monochromator. The ionization chamber was filled up to pressures of 1000 microns (1 Torr). During the course of the measurements (20 days) a loss in intensity due to contamination of the optical components of the monochromator by a factor ~ 5 was observed. Originally all optical components but a sensitive paraboloid were replaced by new ones with a fresh coating of Au.

We measure the ion (respectively electron) current in an ionization chamber while we scan the photon energy. The ion chamber consists of a 1 mm thick wire parallel to the light beam and a collector tube of about 10 cm length

and 3 m diameter surrounding the beam. The wire is biased positive with respect to ground at a potential between 100 V and 500 V while the tube collects the positive ions and is connected to a sensitive Carry 401 "vibrating reed" electrometer. By increasing the negative voltage at the wire we can induce gas amplification in a region of linear response at voltages below that at which a break down discharge would occur. As expected with Ar and other rare gases a large amplification is obtained while this effect is less pronounced with the hydrocarbons. Nevertheless the signals are sufficiently intense to obtain spectra of good quality. It is necessary to maintain a pressure of the gases which is low enough to absorb only a small fraction of the photons entering the ionization chamber for all photon energies. In this case the number of absorbed photons is proportional to the absorption coefficient.

It is well known that a hole in the carbon K shell decays predominantly by an Auger process which produces ions and electrons. Fluorescence is negligible. We therefore identify a peak in the ion current with a peak in the absorption coefficient. While the ion yield (number of charges produced per absorbed photon) is expected to be roughly constant below the C 1s ionization limit it would increase by one above threshold. The onset of this additional process is, however, not observed as a step in our spectra (see below) but rather as a slowly increasing contribution to the yield above the IP. A slow onset of ionization of inner shells has been explained in such cases as a post collisional interaction¹⁷. Depending on the gas pressure the measured ion yield can be larger than the original Auger yield due to gas multiplication of the fast Auger electrons. Thus the electron (or ion) yield measurement should provide a replica of the absorption spectrum with a possible distortion at the ionization threshold. Similar considerations hold for the electron yield spectra of solid samples.¹⁸

We have tested the method by measuring the yield from gaseous Ar and CO₂. In Fig. 1 the Ar 2p absorption as measured directly¹⁹ and by means of the electron yield method is shown. Taking into consideration the lower resolution of our monochromator the agreement of both measurements is good. In the region of the C 1s excitations we cannot rely as much on the relative intensities of peaks and structures since corrections had to be made for the monochromator characteristics. The relative intensity of the monochromator output was measured with Ar gas. Ar has a structureless slowly varying spectrum in the spectral region 280 - 300 eV. The amount of straylight in the Ar spectrum and in the spectra of the hydrocarbons was estimated from measurements with Ag, Al and glassy evaporated C filters.

3. Results and Discussion

The spectra for methane and ethane (Fig. 2) show only weak structures below the IP's which has been determined in XPS measurements to be at 290.7 eV¹. For methane the optical absorption cross section is $\sigma = 0.05 \times 10^{-18} \text{ cm}^2$ below the edge ($\hbar\omega \approx 280 \text{ eV}$) and $1 \times 10^{-18} \text{ cm}^2$ above the edge at $\hbar\omega \approx 292 \text{ eV}$ as determined by Lukirskii et al. by use of characteristic x-ray and bremsstrahlung spectra²⁰. Below the IP the methane spectrum presented in Fig. 2 is in good agreement with the results of the earlier absorption measurement by Chun¹² and the electron energy loss spectrum as obtained by Wight and Brion¹³. We note that above the C 1s IP the measured yield is increasing for methane (as well as for the other molecules studied) whereas the optical cross section actually declines²⁰. This behaviour has been discussed in section 2.

For the spectra of ethylene, benzene and acetylene (Fig. 3) strong resonances are observed below the ionization potentials in addition to weaker bands. For benzene this resonance is remarkably sharp, whereas for ethylene an

additional shoulder is observed and for acetylene a fairly broad resonance occurs. The observed peak positions for the various excitations as well as the IP's³⁻⁶ are compiled in Table 1.

X-ray absorption spectra are in general less complicated than the valence electron absorption spectra. Electrons are excited from one core level (or core levels separated far enough in energy) to unoccupied MO's, whereas for the valence shell, transitions from a number of more or less tightly bound valence MO's overlap. For the molecules investigated all the molecular core orbitals are formed from carbon 1s atomic orbitals and are essentially localized on the carbon nuclei. Our assignment for the observed excitations from these orbitals are given in the last column of Table 1. They are based on a simple one electron picture. For methane and ethane only transitions to Rydberg orbitals are observed whereas for ethylene benzene and acetylene two types of transitions namely Rydberg excitations and transitions to empty valence shell MO's (core \rightarrow V) occur. The situation encountered here is similar to what is known for the valence shell spectra: For the molecules containing π -electrons strong $\pi \rightarrow \pi^*$ transitions have been observed, whereas the spectra of the saturated alkanes show only Rydberg transitions, however slightly disturbed by some admixture of antibonding valence character⁷. The assignment of the Rydberg transitions rests essentially on a consideration of their term values^{7,8,21}, where 4.0 to 2.6 eV are typical for the lowest member of an ns series, 2.6 to 2.2 eV for a np series and about 1.6 eV for nd series.

For methane our assignment given in Table 1 follows the earlier interpretations of the absorption spectrum on the basis of calculations of the Rydberg states of the $1a_1^{-1}$ C (1s) hole state by Bagus et al.¹⁵. According to the one center Hartree-Fock calculations for the allowed $1s \rightarrow 3p$ transition by

Deutsch and Kunz¹⁴ the equilibrium positions for both states are nearly the same, suggesting that the observed transition at 288.0 eV is essentially vertical. We note, however, that Gelius⁵ could resolve vibrational subbands in the XPS spectrum with a vibrational energy of 0.43 eV (symmetric breathing mode). This accounts for the comparatively broad asymmetric band observed in the excitation spectrum. Similarly for ethane the observed peak are also assigned to Rydberg transitions. The forbidden $1s \rightarrow 3s$ transition becomes allowed due to the lower symmetry of the molecule and is more intense here compared to the $3p$ transition.

In ethylene, benzene and acetylene the lowest intense core excitations are assigned to transitions to π^* valence orbitals. The term values and the intensity for these transitions rule out any Rydberg assignment. We note that the term values for these core to π^* transitions, 6 eV for ethylene, 5.1 eV for benzene and 5.6 eV for acetylene are considerably larger than those for the corresponding intense $\pi \rightarrow \pi^*$ valence shell transitions (3.0 eV, 2.3 eV and ~ 4.3 eV respectively). This difference of 2 to 3 eV reflects the change of the exchange interaction of the excited electron with the remaining $N-1$ electrons of the molecule in going from valence to core shell transitions. The sharpness of the strong resonance in the benzene spectrum concurs with the sharp XPS C $1s$ peak of 0.57 eV half width as determined by Gelius⁵ for benzene. It is due to the rigidity of the σ electron C-C skeleton of the benzene ring, whereas for ethylene rotation of CH_2 groups and for acetylene twisting of the linear molecule leads to upper state curves having minima of the potential curves at other places than where the vertical transition would terminate^{22,23}.

The remaining weaker structures in the spectra (Fig. 3) are assigned to core to Rydberg transitions (see Table 1). Since the term values of 3.2 eV for benzene and 2.5 eV for acetylene leave some ambiguity for an assignment as either 3s or 3p we have given the 3s assignment in brackets, preferring the 3p being allowed on the basis of atomic selection rules.

In conclusion we maintain that spectra as discussed here with their assignments provide a first order information and a challenge for ab initio calculations. Further measurements are desirable which suffer less from contamination of the optical components and with higher resolution at least by a factor of two. Finally, when very accurate absorption and electron yield measurements will become available a detailed study of the differences of these spectra which are expected to show up especially at threshold should provide useful information in the ionization mechanism.

Acknowledgement

We would like to thank W.H.E. Schwarz and M.J. van der Wiel for helpful discussions.

Table 1 Excitation energies, ionization potentials and term values for the carbon 1s shell for methane, ethane, ethylene, benzene and acetylene; sh denotes shoulders. All energies are in eV.

	excitation energies	IP C 1s	term values	assignment
methane		290.7		
CH ₄	286.9		3.8	C(1s) → 3s
	288.0		2.7	C(1s) → 3p
	289.4		1.3	C(1s) → 4p
ethane		290.7		
C ₂ H ₆	286.8		3.9	C(1s) → 3s
	288.0		2.7	C(1s) → 3p
	289.6		1.1	C(1s) → 4p
ethylene		290.6		
C ₂ H ₄	284.4		6.2	C(1s) → π*
	284.8 sh		5.8	C(1s) → π*
	286.8		3.8	C(1s) → 3s
	287.4 sh		3.2	C(1s) → 3p
	289.0		1.6	C(1s) → 4p
benzene		290.3		
C ₆ H ₆	285.2		5.1	C(1s) → π*
	287.1		3.2	C(1s) → 3p(3s)
	288.9		1.4	C(1s) → 4p
acetylene		291.2		
C ₂ H ₂	285.6		5.6	C(1s) → π*
	288.7		2.5	C(1s) → 3p(3s)
	290.0		1.2	C(1s) → 4p

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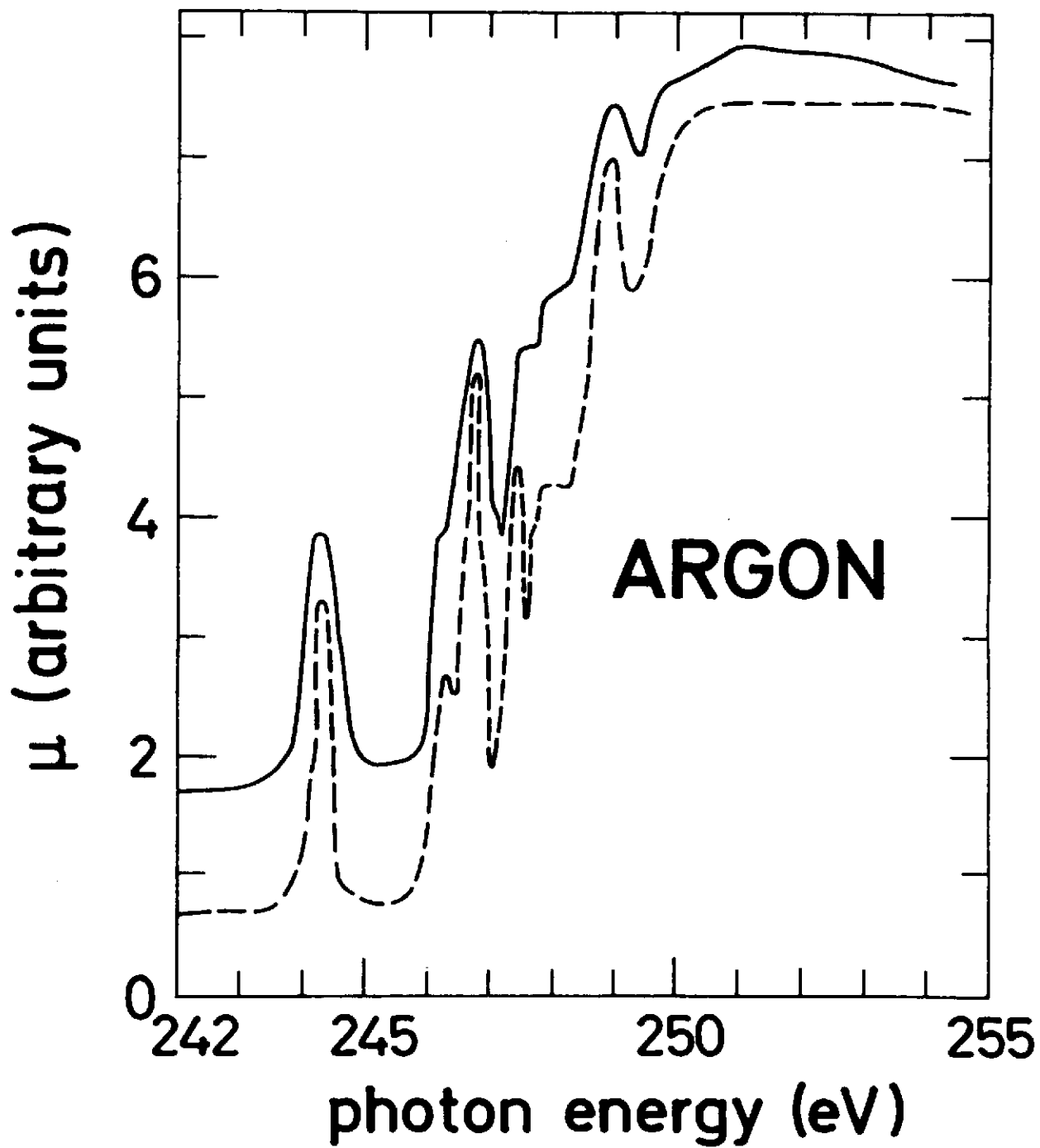
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Figure Captions

Fig. 1 Electron yield spectrum of argon in the range of the $L_{II,III}$ absorption (solid curve) compared to the optical absorption spectrum (Ref. 19, dashed curve).

Fig. 2 Electron yield spectra of gaseous methane and ethane in the range of the C 1s absorption. Energies of the peak positions and the ionization potentials³⁻⁵ are given for each spectrum.

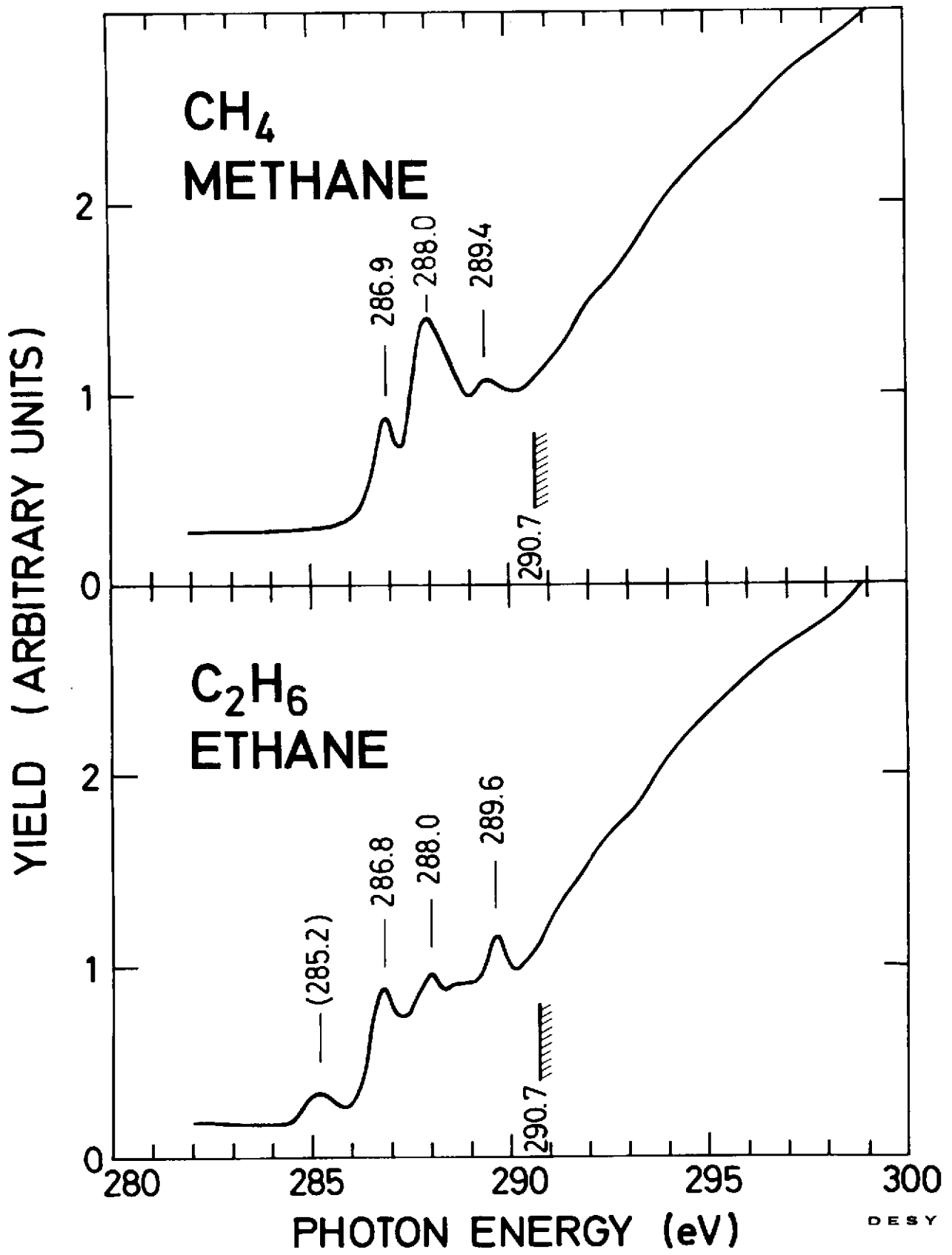
Fig. 3 Electron yield spectra of gaseous ethylene, benzene and acetylene in the range of the C 1s absorption. Energies of the peak positions and the ionization potentials³⁻⁵ are given for each spectrum.



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Fig. 1



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Fig. 2

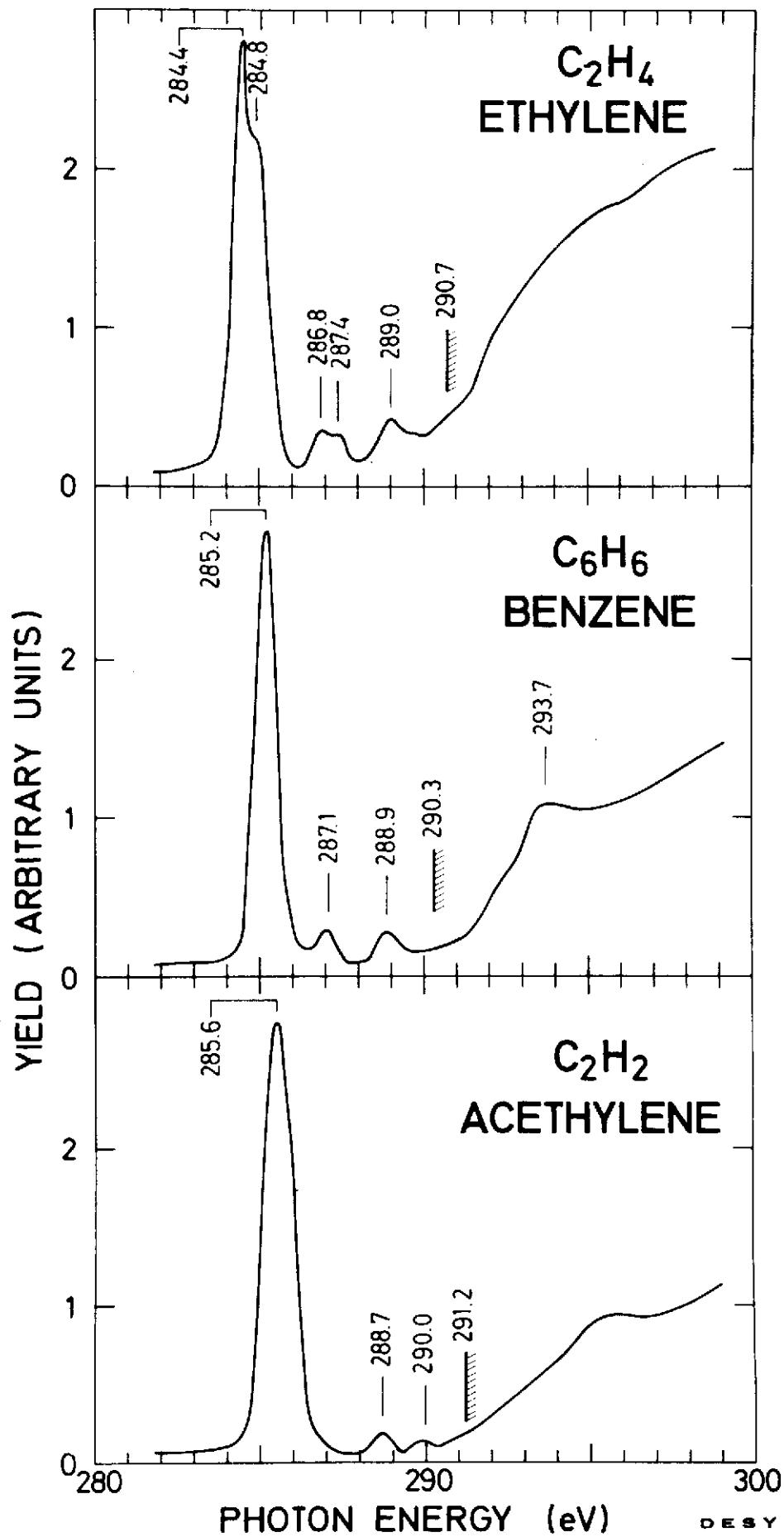


Fig. 3

