Mass Selected ZEKE-Spectra of FeC_2-Anions: A Spectroscopic Access to Intermediates in Catalytic Reactions of Hydrocarbons on Metal Surfaces

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Zero-kinetic-energy (ZEKE) photoelectron spectra of metalcarbide anions are presented, allowing a high resolution spectroscopic access to intermediates in catalytic reactions of hydrocarbons on metal surfaces. As a first compound, FeC_2 (an intermediate of the iron/acetylene system) has been chosen. Important for successful ZEKE spectroscopy was a special anion source and the selection by time-of-flight mass spectrometry. In addition, conventional laser induced photodetachment photoelectron spectroscopy in combination with our anion source and mass analyzer delivered valuable new information.

Metal carbon complexes, as well as their hydrides, play an important role during catalytic processes of hydrocarbons on metal surfaces. In order to understand these processes it is necessary to study those intermediate molecular species. As an example, acetylene reacting on an iron surface gives rise to a multitude of intermediate $Fe_xC_yH_z$-complexes, which are precursors of the final catalytic products, e.g. polymers of the primary molecule. However, it turns out that the study of $Me{-}C_yH_z$-complexes is extremely difficult due to the high reactivity causing short lifetimes and small concentrations. The study of surfaces with adsorbed molecular species is difficult due to the many different sites and geometric arrangements a primary molecule may find on the metal surface. For some very small primary molecules, such as CO, surface spectroscopic techniques (e.g. high resolution electron energy loss spectroscopy (HREELS)) [1] help to characterize the different possible intermediates. As soon as more complex intermediates attach to the surface it becomes impossible to discriminate single ones. For a better insight into catalytic mechanisms it is therefore necessary to isolate possible single intermediate complexes and to study them separately.

We have found a possible approach to this problem, which is twofold: (a) isolation of single intermediate species and (b) finding an appropriate technique to study them. To demonstrate this, we have chosen the iron/acetylene system mentioned above. Our approach to problem (a) is a special anion source which is a combination of laser induced emission of metal atoms and electrons from a metal wire with a supersonic beam of argon with acetylene seeded in it, whose orifice is positioned very near to this wire. This way a large variety of different negatively charged species is obtained, containing all kinds of intermediates composed of iron, carbon and hydrogen.

In a special time-of-flight mass spectrometer these species are mass selected and therefore accessible as isolated species. Starting with anions instead of neutrals not only makes a mass and therefore species selection possible, but also enables a very direct access to their neutral counterparts, namely by photodetachment of the additional electron. Thus our approach to problem (b) is mass selected laser photodetachment photoelectron spectroscopy (PD-PES) or, in particular, mass selected photodetachment zero-kinetic-energy (PD-ZEKE) electron spectroscopy. This is achieved by focussing a second laser beam with fixed (PD-PES) or tunable (PD-ZEKE) wavelength into the spacefocus [2] of the time-of-flight analyzer ion source. A detailed description of our anion source and secondary, mass selected laser excitation has been given in [3, 4]. Mass selected PD-PES of anions has been performed by several authors [5]. The ZEKE-technique has been developed in our institute [6], and has been applied to anions, already [7]. To measure the kinetic energies of the photoelectrons, a field (electric and magnetic) free drift tube is used as time-of-flight analyzer or discriminator. Its axis is aligned vertically to the anion trajectories and intersects the latter at the point of laser photodetachment. By selecting photoelectrons with zero-kinetic-energy (ZEKE) by means of a waiting time and pulsed extraction, ZEKE spectroscopy has been performed. Finally, by synchronizing laser pulse and arrival time of the anion of interest, species selective spectroscopy is possible. For further details see [3, 4].

In Fig. 1, PD-ZEKE spectra of the FeC_2-anion are represented, delivering spectroscopic information about the neutral FeC_2. In addition, Fig. 1 shows a well resolved photodetachment photoelectron spectrum of this species; 10^6 electron counts have been accumulated for this spectrum. Due to the necessity of

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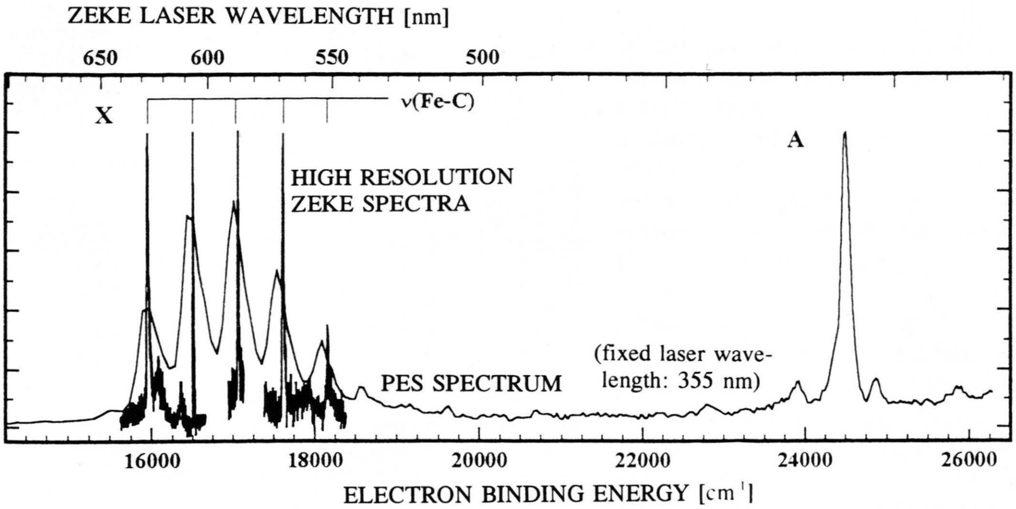

Fig. 1. Mass selected photodetachment photoelectron spectrum and highly resolved photodetachment ZEKE-spectra of FeC_2. The PES-spectrum has been induced by a fixed laser wavelength of 355 nm, for ZEKE spectra the photoelectron detaching laser wavelength had to be tuned between 650 and 540 nm. The absolute position of the electron binding energy has been calibrated by the ZEKE laser wavelength.

changing laser dyes for different wavelength ranges and of keeping the anion source constant for considerably longer times, the single ZEKE spectra are much shorter than a single PD-PES spectrum. The PD-PES spectrum has been taken at a laser wavelength of 355 nm; for the ZEKE spectra the laser wavelength has been tuned between 650 and 540 nm (see upper scale in Figure 1). The electron binding energies (lower scale in Fig. 1) are determined from the flight times (representing the kinetic energies) of the detached electrons (PD-PES) or the detaching laser wavelength (PD-ZEKE). The latter gives much more accurate values, being independent of disturbing fields (e.g. of charged surfaces, space charges etc.). Therefore, a first invaluable advantage of ZEKE spectroscopy is the possibility to calibrate photoelectron data precisely. Of course, the main advantage of high resolution ZEKE is to reveal or discriminate substructures (e.g. spin orbit components) which may either shift the centroids of PES-peaks resulting in wrong molecular constants or congest the PES-spectra totally (e.g. for larger members of the iron/acetylene system). For some ZEKE-peaks we even could observe fine structure which probably is due to single rotational transitions; however, the reproducibility of their intensities is not yet satisfying due to fluctuations of the anion source. An improved anion source is under construction. Nevertheless, these results encourage to even resolve rotational sublevels, thus gaining valuable information about the molecular structure of isolated FeC_2.

The first spectroscopic results deduceable from our ZEKE-spectra are (i) the electron affinity EA = 15 950 cm^{-1} (origin of the anionic to neutral groundstate ZEKE transition), (ii) the iron carbon stretching vibration frequency of 558 cm^{-1} in the neutral X ground state, (iii) a small anharmonicity constant of less than 3 cm^{-1} (deduced from four quanta of this vibration) and (iv) some peaks which are tentatively assigned to spin orbit components. As for the intensities of these peaks, one should pay attention to the fact that selection rules governing the peak intensities may be different for PES and ZEKE-spectroscopy; e.g. with PD-ZEKE mainly emitted electrons represented by so-called s-waves (angular momentum $l = 0$) are detected. In addition to our first ZEKE-spectra, also our well resolved PD-PES spectrum delivers new information; e.g. it reveals an electronic excited state of the neutral FeC_2-molecule at 8542 ($\pm$ 100) cm^{-1} above the neutral ground state. Furthermore, while the Franck-Condon structure of the X-state indicates a geometric change (Fe–C-bond length) between anionic and neutral ground state, this seems not to be the case for the neutral A-state. The small peak on the high energy side of the vibrationless A-band indicates a frequency of the Fe–C-stretching mode in the A-state of 374 cm^{-1}; this value corresponds well to the energy distance of about 425 cm^{-1} between the X-origin and the small peak on its low energy side. This small peak at 15 525 cm^{-1} may be assigned to a hot band thus representing the Fe–C-stretching mode in the anionic ground state. This correspondence supports the structural conclusions deduced from the Franck-Condon envelopes. However, a final confirmation and more accurate values may only become available by further ZEKE-spectra. In Table 1, bandpositions and assignments, deduced from our spectra in Fig. 1, are summarized. In addition vibrational frequencies of the iron carbon stretching mode are given; in the case of the X-band progression the frequencies of the additional vibrational quanta is given. From the hotband at 15 525 cm^{-1} and from the A-band system the iron carbon stretching frequencies of the anion and the first excited neutral state are deduced.

Table 1. Bandpositions and assignments of photoelectron- and ZEKE spectra of the $FeC_2 \leftarrow FeC_2^-$ photodetachment transition (see Figure 1).

Bandposition (cm^{-1})	Assignment	Vibrational frequency (ν (Fe$\leftrightarrow$C) cm^{-1})	PES/ZEKE
X band (neutral ground state)			
15 525 cm^{-1}	0–1	425	PES
15 950	0–0	origin	ZEKE
16 508	1–0	558	ZEKE
17 062	2–0	554	ZEKE
17 616	3–0	554	ZEKE
18 165	4–0	549	ZEKE
23 955	?		PES
A band (first neutral excited state)			
24 492	0–0	origin	PES
24 866	1–0	374	PES

In conclusion, with the successful measurement of mass selected ZEKE-spectra of FeC$_2$-anions we could demonstrate for the first time that a high resolution spectroscopic access to metal carbides and therefore to important intermediate species of catalytic reactions between hydrocarbons and metal surfaces is possible. This opens experimental possibilities to determine molecular parameters such as rotational constants, vibrational frequencies, electronic energies and thus the molecular structures of this class of compounds. This may finally help to understand the reactivity and reaction paths of catalytic processes on metal surfaces.

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