

# Photodetachment-photoelectron spectroscopy of jet-cooled chrysene

Martin Tschurl, Ulrich Boesl\*

*Department Chemie, Technische Universität München, Lichtenbergstrasse 4, 85748 Garching, Germany*

Received 26 October 2005; received in revised form 30 November 2005; accepted 30 November 2005

Available online 9 January 2006

## Abstract

Jet-cooled chrysene anions have been produced by attachment of slow laser-induced photoelectrons. The molecules have been studied by photodetachment-photoelectron spectroscopy using various wavelengths of the detachment laser. The adiabatic electron affinity of chrysene was directly determined to be  $0.32 \pm 0.01$  eV. In the  $S_0$  state of neutral chrysene two different vibrational modes are visible. Both are assigned to breathing modes of the aromatic ring system. In addition, the first excited triplet state is observed and a singlet triplet energy gap of  $2.64 \pm 0.01$  eV has been determined. In this state it was also possible to resolve a vibrational mode. At 355 nm an anion resonance was found that ended up in vibrationally highly excited neutral chrysene. As an explanation a special relaxation pathway is suggested.

© 2005 Published by Elsevier B.V.

**Keywords:** Chrysene; Electron affinity; Photodetachment; Photoelectron spectroscopy

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are major components of coal tars and crude oils. They are formed by nearly all combustion processes of fossil resources [1,2] and are also a by-product of petroleum manufacture [3,4]. Obviously they play an important role as pollutants and therefore their biological activity for some of them is well documented [5].

Because of their ubiquity, spectroscopic and thermodynamic properties have been studied for many years [3,4]. During the last decades PAHs, especially linear polyacene, have been in the focus of several scientists, because of being a prototypical model for organic molecular crystals [6,7]. However, while ionisation potentials are well known [8–10], the electron affinity (EA) of many PAHs are not well characterised, although it is one of the most important properties to understand their charge-transfer behaviour.

Beside their terrestrial importance, it was observed in the last years that PAHs are abundant in most interstellar objects associated with gas and dust [11–13]. Snow and Witt [14] estimate the amount of cosmic carbon tied up in PAHs at between 10%

and 30%. They strongly absorb UV radiation and emit in the IR region. Depending on the local condition in the interstellar medium, PAHs can exist in their neutral, cationic or anionic form.

Another hot topic concerning PAHs, is their carcinogenicity. Since, their health effect differs from harmless to highly carcinogenic [15,16], the understanding of metabolising a PAH is of main importance. Different approaches used in theoretical description of the chemical carcinogenesis suggest that compounds classified as carcinogens do not necessarily possess similar chemical structure [17,18]. In general, carcinogenic substances are or will become metabolites in electrophilic substances and should tend to participate in the reaction with DNA as electron acceptor. In this case, the electron affinity of the substance is of major importance.

The photodetachment-photoelectron spectroscopy (PD-PES) is one of the most powerful methods for determining EAs. First of all it yields a direct value of the electron affinity and secondly the combination of mass spectrometry and spectroscopy eliminates the influence of impurities of the sample and interactions with the matrix. Additionally, with this technique it is also possible to investigate states of the neutral species starting from the anion geometry. Due to a change of spin-selection rule, for anion–neutral transitions, low-lying triplet states of the neutral species can be examined.

\* Corresponding author. Tel.: +49 89 289 13397; fax: +49 89 289 14430.  
E-mail addresses: [tschurl@ch.tum.de](mailto:tschurl@ch.tum.de) (M. Tschurl), [ulrich.boesl@ch.tum.de](mailto:ulrich.boesl@ch.tum.de) (U. Boesl).

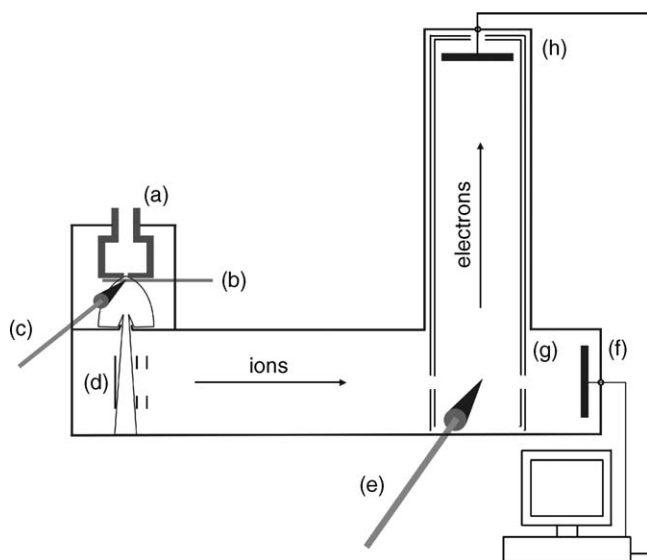


Fig. 1. Experimental set-up. Molecules are introduced into the MS by a solenoid valve (a). Anions are formed by attachment of photoelectrons, created by a laser beam (c) focused onto a hafnium-wire (b); anions are accelerated in the ion optics (d) and recorded by a detector (f). Photoelectrons are produced by a second laser beam (e) and recorded by another detector (h). Their drift region is magnetically shielded by a double-walled  $\mu$ -metal (g).

In this work, we will present PD-PES spectra of chrysene at different wavelengths. While anthracene [19], coronene [20] and recently pyrene [21] are well-investigated by using PD-PES, there is few experimental data available for chrysene.

## 2. Experiment

A detailed description of our apparatus has been published in [22,23]. Therefore, only a brief overview is given in this chapter, which is supported by Fig. 1. Since, chrysene has a reasonable vapour pressure at 443 K, the substance was directly introduced into a heated nozzle, which is in fact a fast working solenoid valve. Nitrogen gas at 3 bar seeded with chrysene molecules has been expanded into the vacuum chamber. Due to the big pressure difference, the short opening times and the small orifice size (200  $\mu$ m) of the valve, a supersonic jet was formed in which the molecular degrees of freedom were cooled down.

With a laser beam of 266 nm (the 4th harmonic of a Nd:YAG laser) focused on a hafnium wire, slow photoelectrons (kinetic energy: 0.8 eV) were produced for electron attachment to neutral molecules. The so-formed cold anion beam was skimmed and entered the ion optics of the mass spectrometer. The “vibrational temperature” of the anions should be significantly below 300 K as concluded from the appearance of weakly bound molecular clusters in the mass-spectrum and the missing of hot bands in the PD-PES-spectrum (see Section 3). The rotational “temperature” is some 10 K which is typical for medium-sized molecules seeded in supersonic beams at the experimental conditions mentioned above.

Within the ion optics the anions were accelerated perpendicularly to the inlet beam by a pulsed voltage of 1.2 kV. The ions were detected using a Wiley McLaren-type TOF MS. The

mass selected anions were photodetached by a second laser beam shortly before arriving at the mass detector. The so-formed photoelectrons passed a magnetically shielded field-free drift region of about 0.4 m length. A detector mounted at the end of the electron drift region recorded the flight time of the electrons. Each photodetachment-spectrum consists of an accumulation of at least 40,000 laser shots. The spectra at 355, 532 or 800 nm were calibrated by recording an  $O_2$  reference-spectrum. Spectra at 266 nm were calibrated by measuring a chlorine reference-spectrum.

## 3. Results and discussion

The appearance of a chrysene anion peak in the mass-spectrum (see Fig. 2) implies that the EA of this molecule is positive. The peak one mass larger than the chrysene peak (see the molecular peak in the inset of Fig. 2) is due to the  $^{13}C_1$ -isotopomer of chrysene. Its intensity corresponds to its natural isotopic abundance. The mass-spectrum also shows that no fragmentation takes place with this kind of ionisation method. The occurrence of a weakly bound van der Waals complex of molecular nitrogen and chrysene indicates good vibrational cooling conditions in the jet. Excited molecular vibrations would lead to a dissociation of this complex.

Several PD-PES spectra were measured using different wavelengths of the detachment laser. The spectrum at 800 nm has been recorded with a Nd:YAG pumped dye laser, using styryl 11 as a dye and methanol as solvent. The dye laser produced pulses with about 8 ns length and an intensity of 3 mJ. The other spectra have been recorded by using the harmonics of a Nd:YAG laser. These pulses had energies of about 3 mJ and a length of 3 ns. The spectra due to detachment wavelengths of 800 and 532 nm

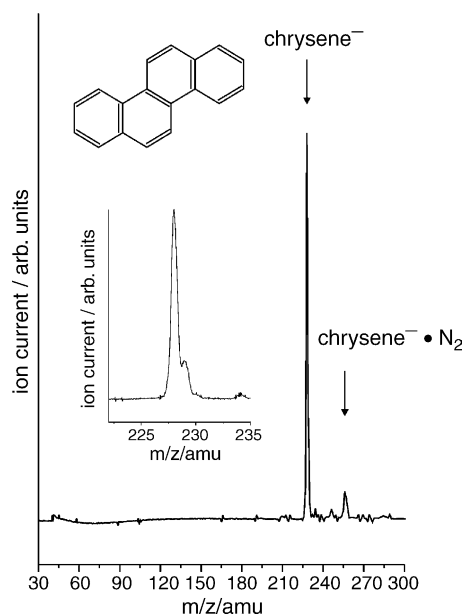


Fig. 2. Mass-spectrum of chrysene anion. The inset shows a second peak one mass larger, which is due to the  $^{13}C_1$ -isotopomer and corresponds to its natural isotopic abundance. The occurrence of the weakly bound complex  $chrysene^- \cdot N_2$  is a hint for good cooling conditions in the jet.

Download English Version:

<https://daneshyari.com/en/article/1194332>

Download Persian Version:

<https://daneshyari.com/article/1194332>

[Daneshyari.com](https://daneshyari.com)