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International Journal of Mass Spectrometry 249–250 (2006) 364–369

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Photodetachment-photoelectron spectroscopy of jet-cooled chrysene

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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 ± 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 ± 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.

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 carcinogenity. Since, their health effect differs from harmless to highly carcinogen [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.

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1387-3806/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.ijms.2005.11.024

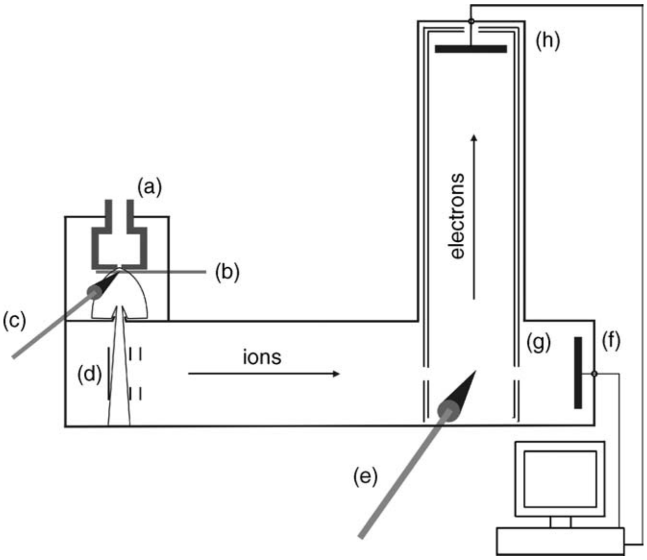

Fig. 1. Experimental set-up. Molecules are introduced into the MS by a solenoid valve (a). Anions are formed by attachment of photoelectrons, created by a laser beam (c) focused onto a hafnium-wire (b); anions are accelerated in the ion optics (d) and recorded by a detector (f). Photoelectrons are produced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

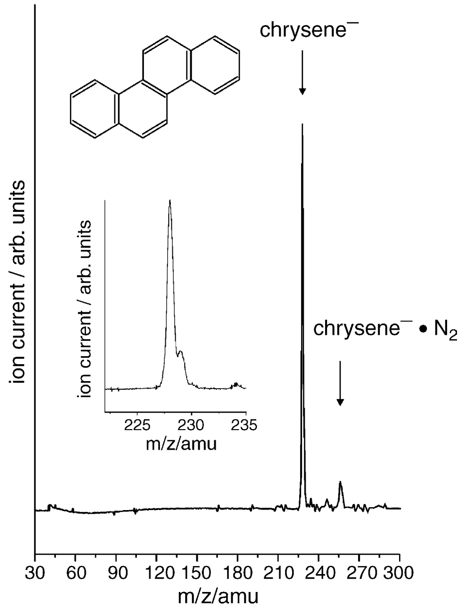

Fig. 2. Mass-spectrum of chrysene anion. The inset shows a second peak one mass larger, which is due to the $^{13}C_1$-isotopomer and corresponds to its natural isotopic abundance. The occurrence of the weakly bound complex chrysene$^-\cdot N_2$ is a hint for good cooling conditions in the jet.

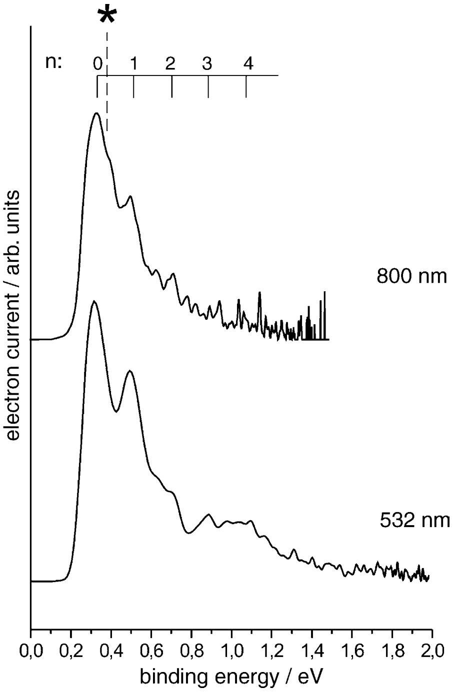

Fig. 3. PD-PES spectra of chrysene at the wavelengths of 800 and 532 nm. Both spectra show a progression of a symmetric stretching mode of the aromatic ring system. The first peak is due to the vertical detachment energy at 0.32 ± 0.01 eV, which here also equals the adiabatic electron affinity. The spectrum recorded at 800 nm shows a shoulder (*) of the first peak, indicating a second symmetric vibration mode of the ring system.

are shown in Fig. 3. The most intense peak in the spectra at 0.32 ± 0.01 eV corresponds to the vertical detachment energy of chrysene. Since, this peak is also that at lowest binding energy, we can conclude that the geometry of the anionic state does not differ too much from the neutral one. Because of this only small difference in the geometries between neutral and anionic state, the vertical detachment energy equals the adiabatic electron affinity of chrysene.

The EA of chrysene was first determined by Wentworth and Becker [24] using electron capture detection (ECD). This however, is an indirect way of determining EAs. The values for the EA of chrysene obtained by this method [24–26] are in the same order of magnitude but larger than our value of 0.32 ± 0.01 eV. Looking at other PAHs (see Table 1), one finds that ECD measurements tend to supply too high values with respect to those determined by PD-PES. This tendency of ECD-values obviously is a general effect and is found for other types of molecules such as oxygen, too [27].

Table 1
Comparison of values of EA determined by using two different methods: photodetachment-photoelectron spectroscopy (PD-PES) and electron capture detection (EDC)

Substance	$EA_{(PD\text{-}PES)}$ (eV)	$EA_{(ECD)}$ (eV) [26]
Naphthalene	−0.200 ± 0.050 [28]	0.15 ± 0.05
Anthracene	0.5300 ± 0.050 [19]	0.66 ± 0.08
Pyrene	0.406 ± 0.010 [21]	0.56 ± 0.06
Chrysene	0.32 ± 0.01[*]	0.42 ± 0.04

ECD, values are usually larger than the PD-PES-values; [*], this work.

The spectra in Fig. 3 shows a dominant progression of a mode with 0.18 ± 0.01 eV (1450 ± 80 cm^{-1}) energy. According to theoretical work [29], there is a set of five possible vibration of a_g-symmetry. Two of them were found by Raman spectroscopy of chrysene powder [29] (1431 and 1382 cm^{-1}) and by fluorescence measurements in a Shpolskii matrix [30] (1439 and 1385 cm^{-1}). One of these two vibrations (1385 cm^{-1}) was also observed by measuring phosphorescence in a Shpolskii matrix [31]. In the 800 nm spectrum a shoulder of the first peak (marked by * in Fig. 3) arises that could possibly result from a second mode of an energy of 0.06 ± 0.01 eV (480 ± 80 cm^{-1}). This second vibration is most likely due to another totally symmetric mode also found by phosphorescence measurements in a Shpolskii matrix [31].

In analogy to other PAHs [19,21,32] these two vibrations (1450 ± 80 and 480 ± 80 cm^{-1}) can be assigned to symmetric in-plane breathing modes of the aromatic ring system. The significant progression of one of these vibrations indicates that the "extra"-electron, which is released during photodetachment, is delocalised over the whole aromatic ring system and the little change of anion-geometry with respect to the neutral system (as mentioned before) is only due to small atomic displacements in the horizontal mirror plane. The progression of the totally symmetric breathing mode is also visible in the spectrum recorded at 355 nm detachment wavelength (Fig. 4). The resolution of this progression is somewhat worse, which is due to the additional excess energy of electrons at higher detachment energies. At

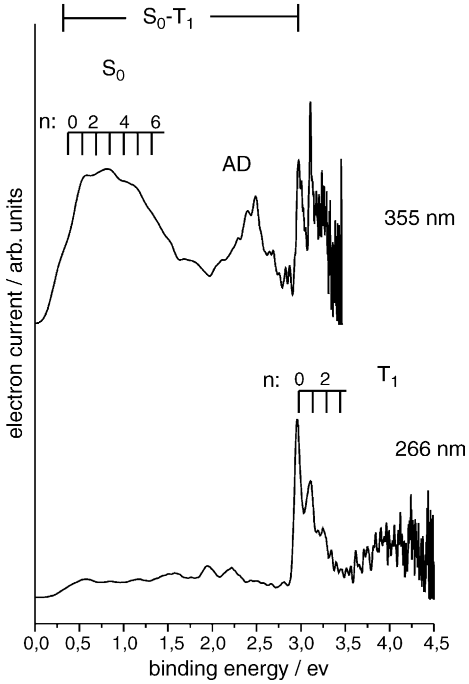

Fig. 4. PD-PES spectra of chrysene at the wavelengths of 355 and 266 nm. Here, a second electronic state with a vibrational progression appears. This state can be assigned to the first excited triplet state of neutral chrysene. The 355 nm-spectrum exhibits an additional structure at 2.5 eV, which is marked with AD (autodetachment).

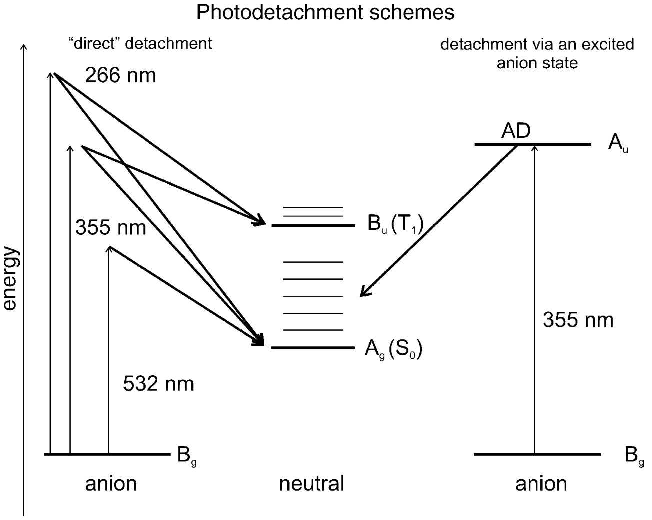

Fig. 5. Schematic excitation diagram for chrysene. At detachment wavelength of 532 nm the neutral molecule ends up in the singlet state. At excitation with 266 nm the neutral molecule can end up either in the S_0 (A_g-symmetry) or in the T_1 state (B_u-symmetry) of the neutral chrysene. At 355 nm there is an alternative excitation into an anionic state of chrysene possible that will undergo autodetachment (AD) and also ends up in the singlet state of the neutral molecule. However, different Franck Condon factors will involve different vibrational states. B_g and A_u are the symmetries of the involved anionic states.

266 nm the situation is even worse and the vibrations of the S_0-state cannot be resolved anymore. However, the spectra obtained using 355 and 266 nm show the occurrence of a second electronic state of neutral chrysene. This state is located 2.64 ± 0.01 eV (21,290 ± 80 cm^{-1}) above the singlet state and can be assigned to the first excited triplet state of the neutral molecule. Its value is in agreement with that measured by Murov et al. [33] for chrysene in CCl_4 (239 kJ/mol = 2.48 eV = 20,000 cm^{-1}) if a significant red shift of the solvent is taken into account. The triplet state also shows a progression of 0.15 ± 0.01 eV (1210 ± 80 cm^{-1}). This progression is probably due to a mode also found by CARS spectroscopy of the triplet state [29] (1240 cm^{-1}).

In the 355 nm (3.49 eV) spectrum an additional band system arises which cannot be assigned to a neutral electronically excited state. The binding energy is smaller than that of T_1, the lowest excited state. The appearance of this spectral feature in a small wavelength range of the photodetachment laser (at 355 nm but not at 266 nm) is a strong hint for an anion resonance as illustrated in Fig. 5. While 532 and 266 nm photodetachment results in neutral chrysene molecules in the S_0 or S_0 and T_1-state, respectively, 355 nm photodetachment may additionally lead to absorption into an excited anionic state A^{-**}. Autodetachment from this excited anion state then is due to Franck Condon factors, which differ from those of direct photodetachment and may result in the enhancement of particular neutral-ground-state vibrations in the photodetachment photoelectron-spectrum.

However, the binding energy of the additional spectral feature at 2.5 eV is much too large for a single vibrational mode or a combination band. It may rather be due to a vibrationally highly excited neutral ground state. It is very improbable, that such highly excited states are populated by single-step autodetachment. We therefore propose that internal conversion between two excited anion states takes place giving rise to high vibrational population in the lower excited anion state. Further on, it is fairly probable that this high vibrational population is preserved in the final neutral ground state during autodetachment. This is illustrated in Fig. 6 where internal conversion between the two excited anion states A^{-**} and A^{-*} is indicated. Such an internal conversion process seems fairly probable since the number and density of excited anion states increases with larger and larger PAHs. Several electronic anion states have been calculated by Bauschlicher Jr. [34] for chrysene in the gas phase and in solution. He found an excited anion state at 3.34 eV, which has been confirmed in experiments by Shida [35]. Another state has been calculated to lie at an energy of 3.54 eV. This state has not been found experimentally. Bauschlicher Jr. gives an error of less than 0.3 eV for his theoretical values. Therefore, it is possible that the anion resonance found at 355 nm (marked as $A^{-**} \leftarrow A^{-}$-transition in Fig. 6) is due to one of these two states within the above-mentioned error limit. Both states have A_u symmetry and are therefore symmetry-allowed final states of excited anion ← ground state anion transitions.

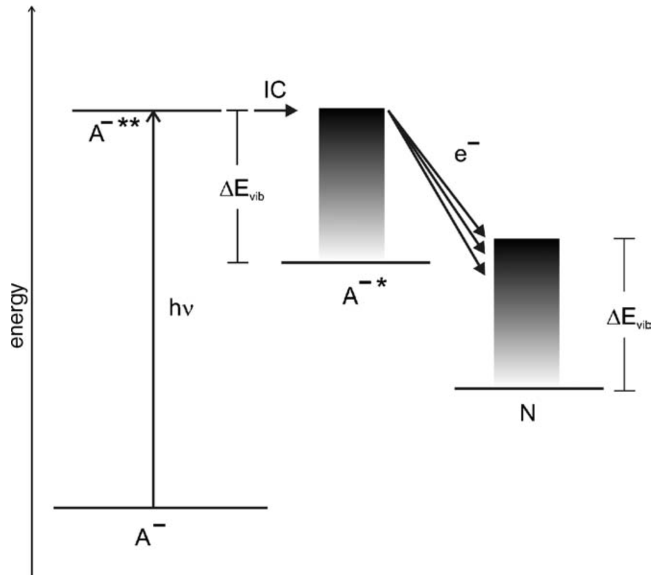

Fig. 6. Suggested scheme for the resonant excitation at 355 nm. The anion (A^{-}) is excited into an anionic state of higher energy (A^{-**}). An internal conversion step (IC) to another anionic state (A^{-*}) leads to autodetachment into a vibrationally hot neutral molecule.

If the above suggestion is valid then even for the second excited anion state (marked A^{-*} in Fig. 6) information will be supplied by the PD-PES-spectrum. The excess vibrational energy ΔE_{vib} which is getting available during the internal conversion and is preserved in the neutral chrysene during autodetachment represents a measure for the energy gap of both excited anion states A^{-**} and A^{-*}. ΔE_{vib} is a good measure for this energy gap if a vibrationally low or not-excited A^{-**} state is involved. Otherwise, ΔE_{vib} is an upper limit of the energy gap A^{*}–A^{**}. Fig. 4 (355 nm-spectrum) supplies a value for ΔE_{vib} of about 2 eV (binding energy-EA: 2.5–0.3 eV = 2.2 eV). According to measurements of Shida [35] and calculations of Bauschlicher Jr. [34] there are at least three states of A_u symme-

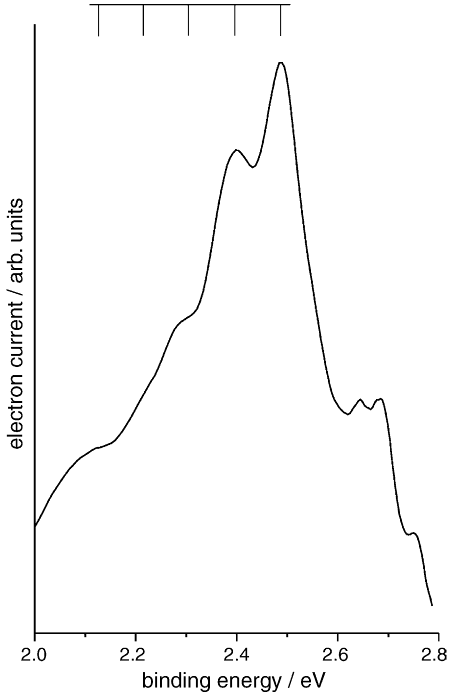

Fig. 7. The band at 2.5 eV appearing in the 355 nm-PD-PES-spectrum (see Fig. 4) on an enlarged energy scale. The spectrum shows a progression of a mode at the low-energy side of the maximum.

try below the above-mentioned states at 3.34 and 3.54 eV. Their existence supports our proposal of the process: resonant excitation of a higher anionic state—internal conversion to a lower anion state—autodetachment to a vibrationally highly excited neutral ground state.

Table 2
Summary of all results

State	Assignment	EBE (eV)	ΔE (eV)	$\bar{\nu}$ (cm^{-1})
S_0	EA	0.32	–	
	a_g-Mode	0.38	0.06[a]	480
	a_g-Mode	0.50	0.18[a]	1450
S_0 (vib $\gg$ 1)	Band maximum	2.49	–	
	ΔE_{vib}	–	$\leq$2.2[b]	$\leq$17700
	a_g-mode	2.39	0.10[c]	810
T_1	T_1	2.96	–	
	T_1–S_0	–	2.64	21290
	a_g-mode	3.11	0.15[d]	1210
A^{-**}	A^{-**}–A^-	–	$\leq$3.49	$\leq$28270
A^{-*}	A^{-*}–A^-	–	$\leq$1.3[e]	$\leq$10500

EBE, electron binding energy; S_0 and T_1, states of neutral chrysene; S_0 (vib $\gg$ 1), vibrationally highly excited neutral state; A^-, ground state of the anion; A^{-*}, low-lying excited anion state; A^{-**}, excited anion state of higher energy; ΔE_{vib}, vibrational energy of S_0 (vib $\gg$ 1); ΔE_{vib}, represents an upper limit of the A^{-**}–A^{-*} energy gap (see Fig. 6). The accuracy of all values is better than ±80 cm^{-1} (=±0.01 eV).

[a] EBE−EBE(EA).

[b] EBE(band maximum)−EBE(EA).

[c] EBE(band maximum)−EBE.

[d] EBE−EBE(T_1).

[e] $\Delta E(A^{-**}–A^-)-\Delta E_{vib}$.

Concerning the structure of the anion resonance at 355 nm (see this band on an enlarged energy scale in Fig. 7), a well-resolved vibrational sub-structure is observed. The frequency of this vibration is 0.10 ± 0.01 eV (810 ± 80 cm^{-1}) and equals a vibration of neutral chrysene in the singlet state with a_g-symmetry, as found in Raman [36] (770 cm^{-1}), fluorescence [30] (771 cm^{-1}) and phosphorescence [31] (776 cm^{-1}) spectroscopy. The appearance of this new vibration may be possible due to a change in Franck Condon factors during the internal conversion process and may give some information on the geometry of the involved anionic states. However, further experiments are necessary to verify this suggestion. A summary of all results is given in Table 2.

4. Conclusion

The adiabatic electron affinity of chrysene equals the vertical detachment energy due to only small geometric changes between anionic and neutral geometries, it is 0.32 ± 0.01 eV. The photodetachment-photoelectron spectra show a vibrational progression of the symmetric stretching modes of the aromatic ring system. Therefore, we can conclude that the "extra" electron of the anion is located over the entire aromatic ring system and the rings are somewhat enlarged with respect to the neutral geometry. Using smaller wavelengths for the detachment process, the triplet state of neutral chrysene becomes visible. Here, again, a progression of a vibrational mode can be seen. We determine a singlet–triplet energy gap of 2.64 ± 0.01 eV. Finally, at 355 nm excitation wavelength, an anion resonance occurs. The excited anionic state should have A_u symmetry due to symmetry selection rules. This anion resonance is correlated with a vibrationally highly excited neutral ground state. We suggest an internal conversion process between two excited anion states to explain the appearance of this band in the photodetachment-photoelectron-spectrum. Similar features of anion resonances are also found in other PAHs [20,21,32] and in C_{60} [37]. Our suggestion of anionic internal conversion may also be applicable to these cases.

References

[1] S.J. Harris, A.M. Weiner, Combust. Sci. Technol. 31 (1983) 155.
[2] M. Frenklach, J. Warnatz, Combust. Sci. Technol. 51 (1987) 265.
[3] M.L. Lee, M.V. Novotny, K.D. Bartle, Analytical Chemistry of Polycyclic Aromatic Compounds, Academic Press, New York, 1981 (Chapter 2).
[4] Y. Yürüm (Ed.), New Trends in Coal Science, NATO ASI Series, Series C: Mathematical and Physical Sciences, vol. 244, Kluwer Academic Publishers, Dordrecht, 1988.
[5] R.G. Harvey (Ed.), Polycyclic Hydrocarbons and Carcinogenesis, American Chemical Society, Washington, DC, 1985.
[6] E.A. Silinsch, Organic Molecular Crystals, Springer-Verlag, Berlin, 1980.
[7] A. Devos, M. Lannoo, Phys. Rev. B 58 (1998) 8236.
[8] G.I. Nemeth, H.L. Selzle, E.W. Schlag, Chem. Phys. Lett. 215 (1993) 151.
[9] J.W. Hager, S.C. Wallace, Anal. Chem. 60 (1988) 5.
[10] M. Shahbaz, I. Akiyama, P. LeBreton, Biochem. Biophys. Res. Commun. 103 (1981) 25.

[11] F. Salama, C. Joblin, L.T. Allamandola, J. Chem. Phys. 101 (1994) 10252.

[12] D.K. Bohme, Chem. Rev. 92 (1992) 1487.

[13] T. Henning, F. Salama, Science 282 (1998) 2204.

[14] T.P. Snow, A.N. Witt, Science 270 (1995) 145.

[15] S. Wilson, K. Jones, Environ. Pollut. 81 (1993) 229.

[16] S. Wise, B. Benner, G. Burd, S. Chester, R. Rebbert, M. Schantz, Anal. Chem. 60 (1988) 887.

[17] M.B.C. Leão, A.C. Pavão, J. Mol. Struct. 539 (2001) 297.

[18] A.C. Pavão, C.A. Taft, T.C.F. Guimarães, M.B.C. Leão, J.R. Mohallem, W.A. Lester Jr., Chem. Phys. A 105 (2001) 5.

[19] J. Schiedt, R. Weinkauf, Chem. Phys. Lett. 266 (1997) 201.

[20] M.A. Duncan, A.M. Knight, Y. Negishi, S. Nagao, Y. Nakamura, A. Kato, A. Nakajima, K. Kaya, Chem. Phys. Lett. 309 (1999) 49.

[21] N. Ando, S. Kokubo, M. Masaaki, A. Nakajima, Chem. Phys. Lett. 389 (2004) 279.

[22] G. Drechsler, C. Bäßmann, U. Boesl, E.W. Schlag, J. Mol. Struct. 348 (1995) 337.

[23] C. Bäßmann, W. Boesl, D. Yang, G. Drechsler, E.W. Schlag, Int. J. Mass Spectrom. Ion Proc. 159 (1996) 153.

[24] W.E. Wentworth, R.S. Becker, J. Am. Chem. Soc. 84 (1962) 4263.

[25] R.S. Becker, E. Chen, Chem. Phys. 45 (1966) 2403.

[26] R.S. Ruoff, K.M. Kadish, P. Boulas, E.C.M. Chen, J. Phys. Chem. 99 (1995) 8843.

[27] K.M. Ervin, I. Anusiewicz, P. Skurski, J. Simons, W.C. Lineberger, J. Phys. Chem. A 107 (2003) 8521.

[28] J. Schiedt, W.J. Knott, K. Le Barbu, E.W. Schlag, R. Weinkauf, J. Chem. Phys. 113 (2000) 9470.

[29] C. Jung, A. Lau, H.J. Weigmann, W. Werncke, M. Pfeiffer, Chem. Phys. 72 (1982) 327.

[30] A. Olszewski, Z. Kubiak, Bull. Acad. Polon. Sci. (Ser. Math. Astron. Phys.) 23 (1975) 921.

[31] A. Olszewski, Z. Kubiak, Bull. Acad. Polon. Sci. (Ser. Math. Astron. Phys.) 23 (1975) 641.

[32] J.K. Song, N.K. Lee, J.H. Kim, S.Y. Han, S.K. Kim, J. Chem. Phys. 119 (2003) 3071.

[33] S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, Marcel Dekker Inc., New York, 1993.

[34] C.W. Bauschlicher Jr., Chem. Phys. Lett. 409 (2005) 235.

[35] T. Shida, Electronic Absorption Spectra of Radical Ions, Physical Science Data, Elsevier, Amsterdam, 1988.

[36] B. Schrader, W. Meier, Z. Naturforsch. 21 (1960) 480.

[37] X.B. Wang, C.F. Ding, L.S. Wang, J. Chem. Phys. 110 (1999) 8217.