ABSOLUTE PHOTODETACHMENT CROSS-SECTION MEASUREMENTS FOR HYDROCARBON CHAIN ANIONS

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ABSTRACT

Absolute photodetachment cross sections have been measured for the hydrocarbon chain anions C_nH^- , n = 2, 4, and 6, which are relevant for an understanding of molecular clouds in the interstellar medium. Data have been obtained for different photon energies within approximately 1 eV of the detachment threshold. With our recently developed method we have achieved a precision of better than 25% on these absolute cross sections. The experiments have been carried out by means of photodetachment tomography of the mass-selected molecular anions in a multipole radio-frequency ion trap. The measured absolute cross sections are in accordance with the empirical scaling law of Millar et al. and have allowed us to determine its free parameters. These results are important for predicting the photostability and thus the abundance of carbon chain anions in planetary atmospheres, in circumstellar envelopes, and in photon-dominated regions of interstellar molecular clouds.

Key words: astrochemistry - ISM: molecules - molecular data - molecular processes

Online-only material: color figures

1. INTRODUCTION

1.1. Astrophysical Relevance of Molecular Anions

The abundance of negative ions in the interstellar medium and in planetary ionospheres and their role in the chemistry of these environments has been one of the long-standing discussion subjects in astrochemistry. The possible importance of negatively charged ions in the synthesis of interstellar molecules was first thoroughly investigated by Dalgarno & McCray (1973), although the involvement of H⁻ in the build-up of molecular hydrogen in astronomical regions where atomic hydrogen is in the neutral state had already been pointed out by McDowell (1961). Anions and dipole-bound states have also been made responsible for some of the diffuse interstellar bands (Sarre 2000; Tulej et al. 1998), but a definite proof for this assumption has not yet been accomplished.

1.2. Observational Evidence

Nevertheless, it was not until 2006 that the first molecular anion was detected outside the solar system, in the envelope of a carbon-rich star (IRC +10216; McCarthy et al. 2006). This identification triggered intensive searches for anions in different astronomical objects and in the last years anions have been observed in a dark core (TMC-1) and a protostar (IRAS 04368+2557 in L1527). The negatively charged species that so far have been identified include the linear hydrocarbons C_nH^- of chain length n = 4, 6, and 8, as well as the nitrogencontaining species CN^- and C_3N^- (Cernicharo et al. 2007; Sakai et al. 2007, 2008; Agúndez et al. 2008, 2010; Remijan et al. 2007; Brünken et al. 2007; Kasai et al. 2007; Kawaguchi et al. 2007; Thaddeus et al. 2008; Gupta et al. 2009). C_6H^- and C_8H^- have also been detected in a starless core in the Lupus molecular cloud (Sakai et al. 2010). Furthermore, a tentative detection of C_5N^- has been reported (Cernicharo et al. 2008), which still has to be verified through comparison with hitherto unavailable laboratory spectroscopic data. The presence of carbon chain and nitrile anions is not restricted to extrasolar environments. The Cassini Plasma Spectrometer has allowed their identification in Titan's ionosphere, where they may greatly influence aerosol formation (Vuitton et al. 2009).

1.3. Formation and Destruction of Cosmic Anions

These observations have generated a lot of interest in the formation and destruction mechanisms of negatively charged ions. Anions will mostly be produced by dissociative attachment (Snow et al. 2009), reactions with H^- (Cordiner et al. 2008), and radiative association. The efficiency of the latter process was predicted by Herbst (1981) to increase with molecular size and electron affinity of the neutral, thus favoring the formation of the observed long-chain carbon and carbon-nitrogen anions now observed. For degradation of anions three major destruction mechanisms exist under interstellar conditions: photodetachment, associative detachment with H, C, N, and O atoms, and mutual neutralization with cations (e.g., C⁺). Anion reactions are not only significant in determining the abundances of these species themselves, they also considerably affect the densities of some neutrals. Model calculations of dark clouds (Walsh et al. 2009) showed considerable augmentation of the abundances of larger C_n, C_nN, and C_nH molecules upon addition of anion chemistry because some of these species can be partly generated via anions.

In dark clouds, anions might even replace electrons as the main carrier of negative charges (Wakelam & Herbst 2008). This in turn can affect the ionization fraction of astronomical environments, since cations should recombine much faster with anions than with electrons. Inclusion of anion reactions into model calculations also influences the abundances of different

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Figure 1. Simplified schematic view of the experimental setup. Ions are produced in a discharge from precursor gas entering the setup through the pulsed valve (PV), extracted using the Wiley–McLaren electrode configuration (W), gated via the mass-selection deflector (MSD), and stored in the 22-pole trap (T). A laser illuminates the trapped ions at a radial position selected via a movable lens (ML), thereby inducing trap loss due to photodetachment. The remaining ions are then detected on the microchannel plate (MCP), and the signal is recorded by a digital storage oscilloscope.

(A color version of this figure is available in the online journal.)

species predicted by models of star-forming regions (Harada & Herbst 2008). Obviously, knowledge of exact rates and product branching ratios of the formation and degradation pathways of anions is crucial for the validity of such models. Furthermore, all three anion destruction pathways (photodetachment, associative detachment, and mutual neutralization) are predominant in different astronomical environments. In the circumstellar envelope IRC +10216, where many anions have been detected so far, radiative association with H atoms is predicted to be the prevalent anion loss mechanism in the inner part, whereas mutual neutralization with C⁺ dominates in intermediate regions and photodetachment in the outer parts of the envelope (Millar et al. 2007). Theoretical calculations of reaction rates of these processes leading to results that are at odds with observed anion abundances are not rare (Herbst & Osamura 2008). Laboratory experiments are therefore necessary to verify the input parameters of these computations.

1.4. Experimental State-of-the-art

Chemical processes involving gas-phase anions have been studied for a long time (Gronert 2001; Ervin 2001). Drift tubes, guided ion beams, supersonic beams, and ion traps have been successfully employed to study anion reactions (see, e.g., Mikosch et al. 2010 and references therein). Still, despite the astrophysical significance of anionic processes, experimental investigations of astrophysically relevant anion reactions are scarce. Whereas state-of-the-art measurements of associative detachment reactions of C_nH^- ions have been carried out using a selected ion flow-tube apparatus (Eichelberger et al. 2007), much less data are available for photodetachment and mutual neutralization processes. This is unfortunate, since the outcome of model calculations greatly depends on the quality of these input data. While photodetachment spectra of the C₄H⁻, C₆H⁻, and C₈H⁻ ions have been obtained by Pino et al. (2002), no measurements of the absolute photodetachment cross sections of the observed C_nH^- ions have, to the best of our knowledge, been reported.

Model calculations (Millar et al. 2007) therefore have adopted the empirical formula

$$\sigma(\epsilon) = \sigma_{\infty} \sqrt{1 - \frac{\mathrm{EA}}{\epsilon}} \tag{1}$$

for the dependence of the photodetachment cross section σ on the photon energy ϵ . The numerical value of the asymptotic empirical cross section for large photon energies σ_{∞} has been assumed to be 10 Mbarn (10⁻¹⁷ cm²). The electron affinity of the corresponding neutral is denoted by EA. In the limit when the photon energy approaches the electron affinity, this empirical formula converges to the Wigner threshold law for s-wave photodetachment $\sigma \propto \sqrt{\epsilon - EA}$.

Due to the paucity of experimental data, the general validity of this relation and the magnitude of the factor σ_{∞} may well be questioned. Ion traps have recently been successfully employed to study absolute photodetachment cross sections (Hlavenka et al. 2009). Here, we present an investigation of absolute cross sections of the hydrocarbon chain anions C₂H⁻, C₄H⁻, and C₆H⁻. Possible impacts of these new findings on the predictions of model calculations of circumstellar envelopes and photondominated regions will be discussed.

2. EXPERIMENTAL METHODS

The experimental setup is based on a new tandem-time-offlight 22-pole-ion trap configuration. A previous version of the setup has been presented elsewhere (Mikosch et al. 2008). A simplified schematic representation can be found in Figure 1.

All measurements were performed in the 22-pole radiofrequency ion trap under ultra-high vacuum conditions. Anions are first produced in a pulsed DC discharge from a gas jet consisting of acetylene, carbon dioxide, and argon. Negative ions are extracted using a Wiley–McLaren time-of-flight mass spectrometer. Individual molecular species can be selected according to their time of flight using switched electrostatic deflector elements. The selected anions are then stored for a time t_s in the 22-pole trap, where they thermalize with helium buffer gas. The temperature of the trap setup, and thereby of the buffer gas, can be set between 8 and 300 K using a closed-cycle refrigerator in combination with ohmic heating. Measurements on C₄H⁻ and C₆H⁻ have been carried out at temperatures around 150 K, while the data for C₂H⁻ have been obtained at room temperature.

After the storage time, the ions are extracted from the trap by means of a DC potential gradient and enter a time-offlight mass spectrometer with mass resolution $m/\Delta m > 10^3$. They are then detected on a microchannel plate detector. The corresponding signal is recorded on a digital oscilloscope and stored for evaluation.

Photodetachment can be observed during storage time if a laser beam is allowed to pass through the trap. The beam propagation direction is parallel to the longitudinal symmetry axis of the trap. The optical axis can be moved in the radial plane. To this end, a long-focal-length lens is positioned in front of the vacuum chamber, such that the focal point is located inside the trap volume. Any transversal movement of the lens then translates into a shift of the position at which the laser beam intersects the trapping volume in the radial plane. Ideally, we obtain a unit magnification ratio, i.e., the transversal shift of the focus is identical to the movement of the lens. In practice, the magnification ratio is measured to take values between 0.85 and 1.15, due to non-ideal alignment of the longitudinal distance between the lens and the trap, as well as the wavelength dependence of the effective focal length of the lens. If the laser beam passes through the trapped ion cloud, it may neutralize the anions via photodetachment

$$C_nH^- + h \nu \rightarrow C_nH + e^-,$$

provided that the photon energy overcomes the threshold for this process. The neutral molecules are subsequently lost from the trap. By varying the storage time, we measure the loss rate of trapped anions. In the experimental setting, the trap fillings are kept sufficiently low such that ion–ion interactions can be neglected. The density distribution of the ions therefore only depends on the trap geometry, the applied potentials, the buffer gas temperature, and the ion mass. The distribution is thus preserved in the loss process, which thereby takes the form of a simple exponential decay, characterized by a rate constant k. For photodetachment-induced decay, this rate is given by

$$k_{pd}(x, y) = \sigma \Phi \rho(x, y), \qquad (2)$$

where (x, y) is the center position of the laser beam in the radial plane, $\rho(x, y)$ denotes the ion column density along the beam propagation direction, σ is the photodetachment cross section, and Φ is the photon flux. For a continuous-wave laser, this flux is given by

$$\Phi = P/(h\nu), \tag{3}$$

with *P* the emitted power and h v the photon energy of the laser light, while for a pulsed laser with pulse energy ϵ and repetition rate f_{rep} ,

$$\Phi = f_{\rm rep} \,\epsilon/(h \,\nu),\tag{4}$$



Figure 2. Trap loss induced by photodetachment. Comparison of the exponential decay of the measured ion signal with increasing storage time with and without photodetachment laser light. The inset shows a tomography of laser-induced decay rates revealing the ion density distribution in the radial plane. The observed structures in the density distribution are caused by imperfections in the trapping potential (Otto et al. 2009).

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as long as a single pulse is sufficiently weak not to locally deplete the ion distribution. In addition to this photodetachment-induced loss rate, a background loss rate of ions from the trap k_{bg} can be observed in the absence of laser light, resulting in the total observed loss rate

$$k_{\text{tot}}(x, y) = k_{pd}(x, y) + k_{bg}.$$
 (5)

A typical decay measurement with and without laser radiation is shown in Figure 2.

By varying the position at which the laser beam traverses the ion cloud, we scan the entire density distribution. The absolute cross section for the photodetachment process can then be expressed as (Trippel et al. 2006)

$$\sigma = \frac{\int \int (k_{\text{tot}}(x, y) - k_{bg}) \, dx \, dy}{\Phi}.$$
 (6)

Note that this equation still holds when taking into account the extended transverse intensity distribution of the focused laser. Fluctuations in the laser power can be counteracted by normalizing by Φ for every single point. To this end, the time evolution of the laser intensity is monitored and interpolated where necessary. In practice, the integral in Equation (6) is approximated by discrete summation over an equally spaced rectangular grid of laser positions. The typical grid spacing for these measurements is slightly larger than the waist of the laser beam, yet more than an order of magnitude smaller than the trap diameter, which allows us to resolve all relevant details of the ion density distribution. The inset of Figure 2 shows an example of the resulting tomographies.

In this work, we have investigated hydrocarbon anions $C_nH^$ for n = 2, 4, and 6. C_2H^- can be photodetached with blue light, which can be derived from continuous-wave Blu-ray diode lasers, with typical output powers on the order of 100 mW. The heavier hydrocarbon anions have larger electron affinities and need ultraviolet light for photodetachment, which in our case is provided by a frequency-doubled nanosecond pulsed dye laser, with a pulse energy of typically 1 mJ and a repetition rate of 10 Hz.



Figure 3. Spectral variation of the measured absolute photodetachment cross sections for C_2H^- (diamonds, green), C_4H^- (squares, red), and C_6H^- (circles, blue). The previous model assumptions according to Equation (1) (based on the literature values for the threshold energies given in Table 1) are shown as dashed lines. For n = 4 and 6 the data have been used to fit the asymptotic cross section (solid lines); no fit is given for n = 2, where an effective threshold energy needs to be taken into account (see Figure 4).

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3. RESULTS AND DISCUSSION

3.1. Absolute Photodetachment Cross Sections above Threshold

For all three hydrocarbon anions, we have measured the absolute photodetachment cross sections according to the procedure outlined above, at various photon energies. Figure 3 shows the cross section as a function of photon energy (points). The measured values are contrasted with the simple model given by Equation (1) (dashed lines). The model threshold energy has been taken from Pino et al. (2002) for n = 4, 6 and Ervin et al. (1990) for n = 2, respectively. For n = 4 and 6 we have performed a fit with the same functional form and threshold energies, using the asymptotic cross section σ_{∞} as a free parameter. The fit results are shown as solid lines. For n = 6this one-parameter fit agrees well with the measured points; for n = 4 the functional form does not fit well. For n = 2 the known electron affinity does not agree with the observed photodetachment threshold. This together with an improved fit for n = 2 is discussed in the next section (see Figure 4).

The measurements and fit results for the asymptotic cross sections are summarized in Table 1, together with the corresponding statistical errors. The employed threshold energies are listed in the table's caption. The fit result for n = 2, which uses a different apparent threshold energy as discussed below, is already included for completeness. It can be seen that all asymptotic cross sections are smaller than the previously assumed value of 10^{-17} cm². In the case of C₆H⁻ the difference even amounts to a factor of approximately two. The relevant sources of systematic errors and their contribution to the total systematic error budget are listed in Table 2. As listed in the table, the total systematic error is estimated to be smaller than 25% for the pulsed laser measurements, and smaller than 20% for the continous-wave (CW) laser measurements. It is dominant over all statistical errors for the individual measurements. Thus the deviations from the previously assumed value are expected to be significant, in particular for C₆H⁻, and it is recommended to use the asymptotic cross sections presented here in future simulations of the interstellar negative ions.



Figure 4. Near-threshold spectral dependence of the photodetachment cross section for C_2H^- . Absolute (tomographic) measurements and relative measurements are represented by full and empty symbols, respectively. The dashed line represents the model defined in Equation (1) with the asymptotic cross section assumed in Millar et al. (2007) and the known electron affinity as threshold energy. The solid line represents the fit of the same model with both the threshold energy and the asymptotic cross section as free parameters (see Table 1). The dotted line results when only the asymptotic cross section is varied in the fit. (A color version of this figure is available in the online journal.)

Photon energy (eV)

 Table 1

 Measured Cross Sections and Fitted Asymptotic Cross Sections for the Molecular Anions C_nH^- , n = 2, 4, and 6

n	Photon Energy	σ	$\Delta \sigma$ (Stat.)
2	3.04	0.70	0.01
2	4.03	5.05	0.12
2	∞	8.8	0.2
4	3.79	1.60	0.01
4	4.03	7.72	0.08
4	∞	7.7	1.6
6	3.86	0.86	0.02
6	4.03	1.04	0.11
6	∞	4.8	0.7

Notes. Photon energies are given in eV, cross sections are in Mbarn (10^{-18} cm^2) . Statistical accuracies are given for each value, estimated systematic accuracies are listed in Table 2. The asymptotic cross sections are derived from fits to Equation (1) using the literature electron affinities 3.561 eV and 3.796 eV for C₄H⁻ and C₆H⁻, respectively (shown in Figure 3), and the derived effective threshold energy 3.019 eV for C₂H⁻ (see Figure 4).

3.2. Photodetachment near Threshold

To provide a useful fit for the photodetachment cross section of C_2H^- , we have studied the cross section near threshold in more detail. For small variations of the photon energy near threshold, which are within the tuning range of a single laser, the spectral variation of the cross section is obtained based on a single absolute cross-section measurement at one laser wavelength. For the other close-by wavelengths, it is then sufficient to scan the laser only over a relatively small fraction of the full density distribution. The spatial structure observable in the distribution allows us to verify that variations of the laser beam pointing with the wavelength are negligible. Absolute values for the cross section are then derived indirectly by the scaling relation

$$\sigma(\epsilon_2) = \sigma(\epsilon_1) \times \frac{\sigma'(\epsilon_2)}{\sigma'(\epsilon_1)}$$

Table 2

Error Budget for Absolute Photodetachment Cross-section Measurements with Pulsed (Photon Energies above 3.7 eV) or cw (Photon Energies below 3.1 eV) Lasers, as Percentages of the Full Cross Section

Cause of Uncertainty	Pulsed/cw
Pulse energy/intensity	10/5
Ions outside field of view	15
Background loss rate	3
Imaging aspect ratio	3
Vacuum window absorption	3
Laser repetition rate	1/
Interpolation error	≪1
Residual power fluctuations	≪1
Mass spectrum peak positions	≪1
Wavelength measurement	≪1
Total (assuming independence)	<13/8
Total (worst case)	<25/20

Note. Note that the most important contributions are constant for all measurements with the same molecular species, allowing much more accurate measurements of relative cross sections (e.g., spectral variations) within one species.

where the prime version denotes the value obtained by integration over the restricted area.

Figure 4 shows the measurement for C_2H^- over the tuning range of our blue diode laser. With these data we have performed a fit according to Equation (1), using the asymptotic cross section and the threshold energy as the two free parameters. In this way the cross-section result is obtained that is listed in Table 1. In the same fit we obtain an apparent threshold energy of $3.019(1)_{\text{stat}}(5)_{\text{syst}}$, where the systematic error arises from an uncertainty in the wavelength measurement. In contrast, previous measurements (Ervin et al. 1990) and coupled cluster calculations (Natterer & Koch 1995; Woon 1995) have provided a value for the electron affinity of C_2H of 2.969(6) eV.

The deviation of our measured apparent threshold energy from the measured electron affinity is likely related to the symmetry of the wavefunction of the emitted photoelectron. For the $X^{1}\Sigma^{+}$ ground state of C₂H⁻ the photodetachment transition to the $X^2\Sigma^+$ ground state of C₂H by an s-wave electron is symmetry forbidden for a one-electron transition (Reed et al. 1976). The empirical formula, Equation (1), which represents s-wave photodetachment near threshold, therefore does not represent the correct scaling in this spectral region. However, the excited $A^2\Pi$ electronic state of the neutral product, which lies about 0.46 eV above the ground state (Taylor et al. 1998), can be formed together with an s-wave electron. Furthermore, the A-state is known to exhibit strong vibronic coupling to the $X^2\Sigma^+$ state even for photon energies below the A-state detachment threshold (Taylor et al. 1998). This coupling may well be expected to modify the energy dependence of the cross section near threshold to a functional form that comes close to the energy dependence for s-wave detachment. Therefore, sufficiently high above threshold, Equation (1) is still a useful approximation, as long as the apparent threshold energy derived from our measurements is used. Note that for neutral C₄H the X-state to A-state energy splitting is an order of magnitude smaller than for C₂H and is even reversed in C₆H (Taylor et al. 1998), which allows for s-wave photodetachment already much closer to threshold (for C₄H) or directly at threshold (for C_6H), making the empirical scaling law of Equation (1) a valid approximation.



Figure 5. Near-threshold spectral dependence of the photodetachment cross section for C_6H^- . The open circles represent our relative cross-section measurements, while the solid line above the shaded area represents data taken from Pino et al. (2002). The filled circles are our tomographic absolute cross-section measurements. The scaling to absolute cross sections for the latter data is achieved using a fit of the model given by Equation (1) to the nonresonant part of the above-threshold photodetachment spectra (dashed line).

(A color version of this figure is available in the online journal.)

The near-threshold photodetachment of the heavier hydrocarbon anions C_nH^- with n = 4, 6, and 8 has been investigated previously by Pino et al. (2002) with high spectral resolution, revealing a lot of resonant structure, which has been attributed to vibronic transitions. These spectra represent only relative measurements, yielding no information on the absolute value of the photodetachment cross section. Using a similar approach as described above for C_2H^- , keeping the laser position fixed to a local maximum in the ion density distribution, we have remeasured this spectral variation. Although we do not reach the same spectral resolution as Pino et al. (2002), mainly due to the temporal overhead of an ion trap experiment compared to a beam experiment, the correspondence of the coarse structure is obvious from Figure 5, while the hot band resonant features observed in Pino et al. (2002) are strongly suppressed in our buffer gas cooled ensemble. Our results allow us to pull the previous spectra to an absolute cross-section level, by matching the shape with our own relative measurements, which in turn are referenced to our result for the absolute cross section presented in Table 1. The shape matching is done by fitting a model according to Equation (1) to the above-threshold part of the spectra, leaving out all resonant structures.

4. ASTROPHYSICAL IMPLICATIONS

All three major anion loss mechanisms (photodetachment, associative detachment, and mutual neutralization) play a role in different astronomical objects. It is therefore necessary to have correct values of rate constants and their dependence on physical parameters as temperature, and, in the case of photodetachment, photon wavelengths. For example, associative detachment is predicted to be the major loss mechanism in the inner region of the circumstellar envelope IRC+10216 up to a radius of 8×10^{16} cm, whereas mutual neutralization takes over this role at distances from the star between 1.8×10^{17} and 1.3×10^{18} cm. At other radii photodetachment is predicted to dominate (Cordiner et al. 2007). It will be interesting to see how the new cross sections affect the abundance of anions in simulations of these objects. This especially holds for C₆H⁻ whose asymptotic cross

section is found in this work to be a factor of two smaller than the value of 10 Mbarn $(10^{-17} \text{ cm}^{-1})$ used in models. This might also be the case for other large anions like deprotonated polycyclic aromatic hydrocarbons (PAHs) and PAH anions.

Measurements of absolute photodetachment cross sections like those reported in the present paper are also crucial for the understanding the chemistry of ionospheres of planets and their satellites. Model calculations of Titan's ionosphere (using the empirical formula by Millar et al. 2007) mentioned above, however, predict that photodetachment is only a minor destruction mechanism of anions in Titan's atmosphere, although its relative importance increases with the altitude. In the case of CN^- it is predicted to be the second most important loss pathway after associative detachment at an altitude above 1100 km (Vuitton et al. 2009).

Since irradiation by the interstellar or, in the case of planets and moons, solar radiation field covers a broad range of wavelengths, it is important to have measurements of *absolute* cross sections of the photodetachment of anions over at least a large part of the spectral range of the incident light. Furthermore, it is important to gauge the asymptotic cross section at infinite incident photon energy, which, as the present experiment has shown could show considerable variations with different anions. Thus, only exact knowledge of absolute cross sections over a wide wavelength range will allow for reliable anion abundance predictions by models.

5. CONCLUSION

We have obtained laboratory data for the photodetachment cross section of several hydrocarbon chain anions that are of relevance for the interstellar medium. The measured data are well described with an empirical scaling law combined with our experimentally determined parameters. Our results are summarized in Table 1 and are suggested to be used together with Equation (1). The estimated overall relative precision of the determined cross sections is about 25%. The provided cross sections now allow one to predict the stability of the studied molecular anions in interstellar radiation fields, in particular in circumstellar envelopes and in photon-dominated regions.

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