

Absolute Dissociative Electron Attachment Cross Sections in Acetylene and its Deuterated Analogue

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Abstract: An instrument for the measurement of absolute dissociative electron attachment cross sections was constructed and applied to two prototype molecules, acetylene (C₂H₂) and deuterated acetylene (C₂D₂). The isotope effect at the first dissociative electron attachment band at 3 eV was determined – the cross section for C₂D₂⁻ / C₂H₂⁻ is 14.4 times smaller than that for C₂H₂⁻ / C₂H₂. The results play a central role in validating recent theoretical work of Chourou and Orel. The dominant fragments at the second dissociative attachment band around 8 eV are the light fragments H⁻ or D⁻. These bands exhibit weaker isotope effects.

Keywords: Absolute cross section · Dissociative electron attachment · Isotope effect

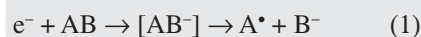
Introduction

A large majority of readers is likely to consider electron-driven chemistry as an exotic field of questionable relevance and usefulness – and it is true that it is of little use as a synthetic tool for fine chemicals. It does, however, play a major role in a surprisingly wide range of natural and man-made environments. In the gas phase it is the principal channel of chemical change in plasmas, both natural as found in the interstellar space and the upper atmospheres of planets (including the earth), and technological, such as those used to provide reactive intermediates in many production steps in microelectronics.

Electron-driven chemistry is also found in the condensed state. Examples are radiation damage to living tissue, important for radiation therapy, and the recent technology to produce nano-sized devices by EBID – electron-beam induced deposition.

The present study is concerned with isolated molecules, but gas phase data are often used in the simulation of condensed phase. The list of examples is far from being exhaustive – electron-driven processes are important in plasma-disinfection, cleaning, modification of surface properties, toxic waste disposal, satellite propulsion, electron-beam induced polymerizations and other applications.

Dissociative electron attachment (DEA):



the topic of the present article, is, together with neutral dissociation and dissociative ionization, the major electron-driven process leading to reactive intermediates. It proceeds in nearly all cases *via* a short-lived (ps range) anion called a resonance. There is a large body of literature on the study of resonances and of dissociative attachment, extending over a long period of time (see, for example, the early review by Schulz^[1]), but two considerations motivated us to continue this research. The first is that a majority of the existing data is qualitative, the yield of the fragments is given only in relative units. Quantitative, absolute, data were measured already early, but they are scarce, and discrepancies between the results from different laboratories are sometimes found. The second motivation is that the new applications, and recent developments of theory, created the need for data on compounds for which no data exists, like on metalorganic compounds, used as precursors in EBID, or acetylene, the subject of the present paper, interesting

primarily from the point of view of theory. The broader scope of the current work in Fribourg, of which this paper constitutes a part, is thus improvement of the instrumental techniques to measure high-quality absolute cross sections and to apply them to compounds of current interest.

Interest in electron-driven chemistry of acetylene is motivated in part by the fact that it has been detected in upper planetary atmospheres where free electrons are also found,^[2] by the recent interest in its chemistry in plasma, where it was found to trigger nucleation of nanoparticles^[3] and by its occurrence in flames.

Additional interest stems from astronomy: the molecular anions C₆H⁻, C₄H⁻^[4] and C₈H⁻^[5] were recently identified in the interstellar space – as the first anions in outer space. The identification is done *via* comparison of laboratory and space microwave spectra. In the laboratory, the anions were prepared in the glow discharge in the mixtures of acetylene and diacetylene, and electron-driven chemistry of acetylene is important to understand this environment.

Perhaps the most important motivation of the present work lies in the fact that it permits validation of a new theoretical description of DEA – which is generally much more difficult and less advanced than the description of thermal chemistry or photochemistry of neutral molecules. This is primarily due to the fact that the dissociation proceeds in competition with autodetachment, the fast spontaneous loss of an electron from the anion (resonance) [AB⁻] in Eqn. (1). This has the consequence that the variational principle does not apply and the standard quantum chemi-

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cal codes cannot be used to calculate the potential surface of the resonance. Instead, computationally intensive and less precise scattering calculations, yielding not only the energy but also the autodetachment width Γ for each geometry, must be used. This, in turn, has the consequence that the majority of existing calculations of absolute DEA cross sections are for diatomic molecules, and the few calculations on polyatomic molecules treat the problem as pseudo-diatom. An important current goal of the theory is thus development of true polyatomic methods, treating the problem in more than one dimension of nuclear coordinates.

A pioneering progress in this direction is the work of Chourou and Orel,^[6] who, using acetylene as a prototype, calculated absolute DEA cross sections taking into account three dimensions (the C–H and C≡C distances, and the C≡C–H angle). They first used the *ab initio* complex Kohn variational method to derive the complex potential surface (*i.e.* both its real and imaginary parts) of the π^* resonance as a function of the three dimensions. Then they calculated the temporal development of the nuclear wave packet on this potential surface. Their calculations show that the dissociation involves first bending and then stretching of the C–H bond, and can thus not be described by a one-dimensional model.

Since the dissociation channel is in competition with autodetachment in the course of the motion of the nuclear wave packet, the resulting DEA cross section is a very sensitive test of the model used to calculate the resonant potential surface. A second important test of the theory is the isotope effect: the heavier deuterium moves slower making the dissociation time longer and thus favouring the autodetachment channel and substantially reducing the DEA cross section.

This paper briefly describes the recently constructed instrument to measure DEA cross section, which by-passes many of the problems of earlier instruments by several new design principles and by combining three modes of operation with complementary characteristics: active and passive ion collection and quantitative time-of-flight (TOF) mass spectrometer. It then presents the results for C_2H_2 and C_2D_2 and compares them to the theoretical results of Chourou and Orel.

Experimental

The present instrument^[7] combines two basic principles of operation: The ‘total ion collection’ (TIC) tube^[8,9] and a time-of-flight (TOF) mass spectrometer. Two different modes are possible for the TIC,

with either passive or active ion collection. None of these principles is new, but the fact that all can be used in one instrument in a complementary way, and careful design in detail, improved the accuracy and the range of sensitivity which can be reached.

The instrument uses an axial magnetic field of about 300 Gauss to collimate the electrons and a trochoidal electron monochromator to reduce the energy-spread of the incident electrons. It has a target chamber connected to a capacitance manometer used to determine the absolute density of the target molecules. The side walls of the target chamber can be relatively easily removed and replaced – either two walls with three ion current collectors each for the TIC mode, or, for the TOF mode, one wall with three ion current collectors (one of them used as an ion ‘pusher’ in this case) and one wall with a rectangular ion exit slit.

The ‘total ion collection’ mode has been described in detail in ref. [8]. The cross section σ is determined as

$$\sigma = \frac{I_i}{I_e n_g l} \quad (2)$$

where I_i is the current of ions, n_g is the number density of the gas, I_e is the electron current, measured behind the target chamber, and l is the length of the interaction path.

The most difficult part is the measurement of the ion current and the collision chamber used for this purpose is shown schematically in Fig. 1. One difficulty is the separation of the generally very small (1 fA–100 pA) ion current from the much larger current of scattered electrons. It is based on the fact that the ions have much larger gyroradii than electrons, are not confined by the magnetic field, and are collected at electrodes surrounding the electron beam in the collision chamber. The separation is not complete, however, and a small current of multiply scattered electrons reaches the collection electrodes, limiting the sensitivity of the device. The

chamber can be operated in two modes that differ in the way in which the ions are collected: i) passive collection mode with a field-free chamber and ii) active collection mode where ions are extracted with an electric field. Consistent results have been obtained with both modes, which is a useful test of quality of the data.

The first mode is similar to that used by Burrow and coworkers.^[10] All six sheets are grounded, the chamber is field-free and the collection relies on the kinetic energy release and the thermal energy of the fragment ions to reach the collection electrodes.

In the second mode, a symmetric extraction voltage is applied across the inner sheets and the ion current is measured on the positive sheet. This mode is similar to that used by Rapp, Briglia, and co-workers.^[8]

The collection electrodes are split into three sections, 1, 2, and 1 cm long, and current is collected only on the centre section. This compensates, to a large degree, the loss of ions formed with substantial axial kinetic energies, as indicated by arrows in Fig. 1. Applying alternate extraction voltages to the three segments in the active collection mode compensates the lateral cycloidal drift of the electrons in crossed magnetic and electric fields.

An important advantage of the total ion collection tube is low discrimination with respect to the kinetic energy of the anions and the fact that it is an inherently absolute measurement – no calibration reference is required. Serious drawbacks are the absence of mass resolution and a limited sensitivity due to the already mentioned background electron current. The limited sensitivity was a serious problem in the present case, the TIC tube could measure the cross section for C_2H_2 , but not the smaller cross section of C_2D_2 .

To remove these limitations we added a controlled-transmission TOF ion mass analyser to our experimental apparatus.^[7] In this mode one wall of the collision

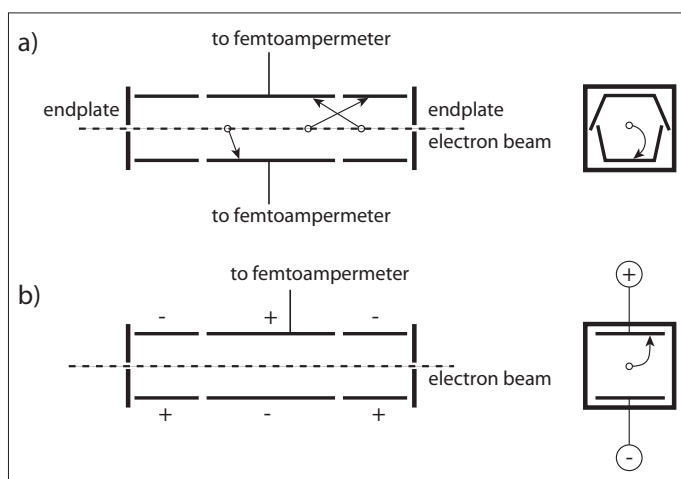


Fig. 1. Schematic view of the collision chamber in the a) passive collection mode and b) the active collection mode. The left-hand side shows the longitudinal, the right-hand side are the cross sectional view of the chamber.

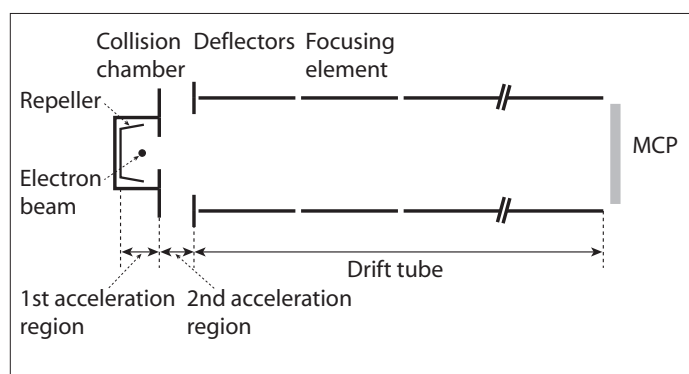


Fig. 2. Scheme of the time-of-flight tube. The orientation of electron beam is perpendicular to the paper plane.

chamber is replaced by one having an exit slit through which ions enter the time-of-flight tube (Fig. 2). The collectors on the opposite wall are used as ion repellers. A short (200 ns) pulse of electrons is sent through the interaction region while the ion repellers are on the potential of the chamber. A 4 μ s long pulse with an amplitude of -300 V is applied to the repellers about 200 ns later, after the electrons have left the collision chamber. The experiment is repeated at a rate of 10–100 kHz. The TOF tube consists of a three-cylinder electrostatic lens, which images the ion exit slit onto the MCP detector (anion impact energy 3 keV). The first section of the TOF tube is split into two electrostatic deflectors, used to compensate the effect of the magnetic field. The second section of the TOF tube is used to control the focusing. The third section of the TOF tube consists of a field free flight tube. The design of the target chamber, the exit slit, and the TOF tube were guided by ion trajectory calculations to achieve minimum discrimination with respect to ion mass and initial kinetic energy. The TOF mode yields only relative cross sections and we used the cross section of 14 pm^2 for the 4.4 eV band of O^- production from CO_2 for calibration.

For all three modes, the entire experimental setup was always verified by measuring the DEA cross sections for O^- formation from N_2O , O_2 , and CO_2 . The pressure in the collision chamber is measured by a capacitance manometer and was kept typically in the range $3\text{--}6 \times 10^{-4}$ mbar. The energy scale was calibrated on the onset of O^-/CO_2 DEA band at 3.99 eV. The electron beam current was typically 20–80 nA and the resolution 200 meV.

Results

The 3 eV band in C_2H_2 consists of only one mass and is sufficiently intense to be measured in the TIC mode.^[11] The 3 eV band in C_2D_2 was too weak for the TIC mode, and the bands around 8 eV consists of several fragments, making the TOF measurements necessary. The cross section value for producing C_2H^- from C_2H_2

at 3 eV obtained by using the TOF mode is $3.45 \pm 0.8 \text{ pm}^2$, in good agreement with the measurements in the total ion-collection setup with the result of $3.8 \pm 0.9 \text{ pm}^2$ (average of the cross sections from the active and passive ion collection modes). The measurements were repeated several times and the averages of the TOF peak cross sections are given in Table 1, typical spectra are shown in Fig. 3. The results of Azria and Fiquet-Fayard for C_2H_2 ^[12] are somewhat lower, both at 3 eV and at 8 eV. Low signal permitted Azria and Fiquet-Fayard only the determination of an upper limit for the 3 eV band in C_2D_2 – it is consistent with the present results.

The absolute value of the cross section is very small. This has been explained by a large value of Γ of the $^2\Pi_g$ resonance mediating DEA at 3 eV, which results in fast autodetachment and thus an unfavourable competition between dissociation and autodetachment – most of the $[\text{C}_2\text{H}_2^-]$ formed decays by autodetachment, only a minority dissociates. The large isotope effect, *i.e.* the $15\times$ lower value of the 3 eV cross section in C_2D_2 , is understood qualitatively as the consequence of the slower motion of the heavier D, resulting in a longer dissociation time permitting more autodetachment.

Concerning quantitative calculations of the cross sections, the original results of Chourou and Orel^[6] were applied to target molecules in their vibrational ground states (*i.e.* at 0 K) and predicted a value of

3.44 pm^2 for the 3 eV band in C_2H_2 . This value was very close to our initial TIC experimental value^[11] of 3.8 pm^2 and is even closer to the TOF value of 3.45 pm^2 . In fact, the agreement is much better than expected in view of the fact that the DEA cross section is a very steep function of the primary theoretical result – the autodetachment width Γ of the resonance – and the fact that Γ is very hard to calculate *ab initio*. Our later measurement of C_2D_2 revealed, however, a discrepancy between the calculated ($30\times$) and measured ($15\times$) isotope effects. We proposed that the discrepancy could be due to finite temperature of the target gas.

Later calculations^[13] confirmed that this discrepancy can be removed by taking thermal vibrational excitation of the target into account. In particular a substantial population of the bending vibrations in the target molecule (there are two such modes, π_g and π_u , each doubly degenerate), together with the calculated rapid rise of the DEA cross section with initial vibrational quantum. By adding the four lowest bending vibrational states into the calculation Chourou and Orel have found the resulting ratio $\sigma(\text{C}_2\text{H}_2)/\sigma(\text{C}_2\text{D}_2)$ to be 17.9, which is in good agreement with the experiment value.^[13] However, the better agreement of the isotope effect came at the price of worsening the agreement of the absolute values of the cross section, which became almost a factor of two higher than the measured value.^[13] This disagreement is, however, less serious than the disagreement of the isotope ratios, because of the already mentioned steep dependence of the cross section on the hard-to-calculate width Γ .

These results confirm the prediction that the bending modes of acetylene play a dominant role in the dissociation process. This is in line with the prediction of the calculation that the $^2\Pi_g$ resonance needs to bend before it can dissociate. This is understandable already on a qualitative level, the dissociation of the resonance is symmetry forbidden in the linear geometry, but is made possible by vibronic coupling be-

Table 1. DEA peak cross sections [pm^2]. The present values are reliable within $\pm 25\%$.

Target	Energy	Ion	This work	Literature
C_2H_2	3.0	C_2H^-	3.45	3.8 ± 0.9 , ^[11] 2.2 ± 0.3 ^[12] 3.4 ^[6] (calc.)
	7.9	H^-	3.94	4.4 ± 1 ^{[11]a} , 3.1 ± 0.4 ^{[12]a}
	8.3	C_2^-	0.8	
C_2D_2	3.0	C_2D^-	0.24	≤ 0.19 ^[12] 0.119 ^[6] (calc.)
	7.7	D^-	1.45	
	8.4	C_2^-	0.17	

^aTotal cross section measurement; sum of H^- and C_2^- .

tween the π^* and the σ^* resonances which makes the π^* resonance bent.^[10,13] 'Pre-bending' it by exciting one of the bending vibrations accelerates the process.

Chourou and Orel carried out similar electron scattering calculations on HCN and DCN.^[14] They found out that the isotope effect is comparable to that observed in the case of the isoelectronic acetylene, but the dissociation mechanism is different. The dynamics in these systems proceeds predominantly *via* tunnelling through the barrier rather than a reaction path that bends to avoid the barrier. The excitation in the bending mode is much less important in the dissociation for HCN and DCN. Absolute partial cross sections for dissociative electron attachment to HCN and to the deuterated target are being measured in our laboratory in order to verify the theoretical description of the DEA process in these two molecules.

Concerning the 8 eV band, our partial cross sections show that the dominant fragment is H^- . The observed isotope effect is generally much smaller than for the 3 eV band: the cross section ratio is 2.7 in the production of H^- or D^- and 4.7 for the production of C_2^- . This is an indication that the resonances involved have narrower autodetachment widths Γ , making the competition between autodetachment and dissociation less critical. This conclusion is in line with the assignment of the 8 eV band to Feshbach resonances, with a hole in a valence orbital and a double occupation of a Rydberg-like orbital.^[15,16]

Conclusions

Absolute cross sections for dissociative electron attachment to C_2H_2 and C_2D_2 have been measured in three different modes using a modified trochoidal electron spectrometer coupled once with a total ion collection tube and once with a time-of-flight mass filter. The mass resolved experiment confirms that at 3 eV the C_2H^- fragment is observed and reveals that the H^- fragment dominates above the C_2^- fragment at 8 eV.

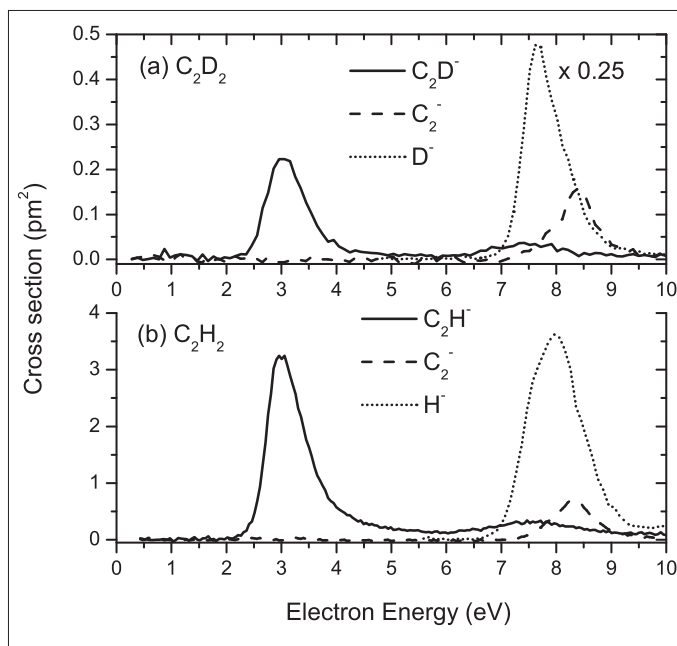


Fig. 3. Dissociative electron attachment cross sections for (a) C_2D_2 and (b) C_2H_2 .

The TOF measurements quantified the pronounced isotope effect at the first dissociative electron attachment band, with the cross section for $\text{C}_2\text{D}^-/\text{C}_2\text{D}_2$ being 14.4 times smaller than that for $\text{C}_2\text{H}^-/\text{C}_2\text{H}_2$. The recent calculations by Chourou and Orel, at 0 K, are in good agreement with our experimental values for $\text{C}_2\text{H}^-/\text{C}_2\text{H}_2$ but underestimate values for $\text{C}_2\text{D}^-/\text{C}_2\text{D}_2$, their ratio $\sigma(\text{C}_2\text{H}^-)/\sigma(\text{C}_2\text{D}^-)$ being 28.9.^[6] A later calculation of Chourou and Orel^[13] showed that the DEA cross section rises rapidly with initial excitation of bending vibrations and has removed the discrepancy in the isotope ratio by repeating the calculation at 333K, the temperature of the experiment. The contribution of the vibrationally excited bending modes plays an important role in the production of the C_2H^- ions in the 3 eV energy range.

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