Dissociative Electron Attachment To Unstable Molecules And Slow Fragmentation Of Metastable Molecular Anions

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Abstract. Recent experimental investigations of dissociative electron attachment to unstable molecules and free radicals are reviewed along with observations of metastable negatively charged ions. Measurements have been made with a time-of-flight mass spectrometer in Belfast and also, for metastable ions, with a double focussing twin field mass spectrometer in Innsbruck. Electron attachment to unstable CS, for example, was found to be similar to electron attachment to the valence isoelectronic CO molecule with observation of S⁻ and C⁻ ions just above the thermodynamic threshold for S⁻ + C (³P) at 5.43 eV, C⁻ + S at 6.40 eV and S⁻ + C(¹D) at 6.70 eV with peak cross sections of ~ 0.025 Å², 0.002 Å² and 0.003 Å² respectively. Slow fragmentation of metastable SF₆⁻ ion formed in low energy electron attachment to SF₆ has been observed on microsecond timescales in competition with autodetachment; processes SF₆⁻ → SF₅⁻ + F and SF₆⁻ → SF₆ + e⁻ respectively. Fragmentation of metastable anions of benzene derivatives, such as 2,4-dinitro-toluene [CH₃C₆H₃(NO₂)₂], has also been observed on microsecond timescales.

1. Introduction
This progress report reviews some recent experiments that have been performed with a new electron attachment apparatus ERIC, ‘Electron Radical Interaction Chamber’, which has been designed to investigate electron attachment to unstable molecules and free radicals [¹, ²]. Collisions between electrons and molecules are fundamental molecular processes, which occur in lightning, plasmas, lasers, the upper atmosphere, astrophysical environments. In many of these environments highly reactive unstable molecules, and particularly free radicals, are present and yet there are relatively few experimental studies of electron interactions with such molecules. There are, of course, difficulties in preparing samples of unstable molecules and free radicals for experimental investigations. Past experimental investigation of unstable molecules includes electron attachment to OCIO [³] and electron impact ionization of OH [⁴]. Theoretical work includes calculations of low energy electron collisions with CFₙ radicals (n = 1 – 3) [⁵] and CS [⁶].

The new instrument, ERIC, has also been used to investigate the ‘slow’ fragmentation of metastable negatively charged molecular anions, such as the well known SF₆⁻ ion [⁷], and
benzene derivatives, such as 2,4-dinitro-toluene \([\text{CH}_3\text{C}_6\text{H}_3(\text{NO}_2)_2]\) in a joint project with complimentary measurements in Innsbruck made with a twin field mass spectrometer. Here ‘slow’ refers to microsecond timescales, which are orders of magnitude slower than nuclear vibrational motion timescales, femtoseconds, and electronic motion timescales, attoseconds.

The first step in the formation of a negatively charged molecular ion, or anion, in an electron molecule collision is electron attachment, which can be represented for a general molecule, \(AB\), by

\[
\text{AB} + e^- \rightarrow \text{AB}^{-*}
\]

where \(\text{AB}^{-*}\) is a metastable superexcited state of the anion \(\text{AB}^-\). This metastable anion is ‘superexcited’ because it necessarily has more energy than the energy of the neutral molecule and a free electron. The superexcited state may autodetach on the attosecond timescale of electronic motion thus;

\[
\text{AB}^{-*} \rightarrow \text{AB} + e^-
\]

If a resonance occurs, however, the superexcited state may have a lifetime which is sufficiently long for the molecule to dissociate, which occurs typically on the vibrational femtosecond timescale, to give dissociative electron attachment overall, which can be represented by

\[
\text{AB} + e^- \rightarrow \text{AB}^{-*} \rightarrow \text{A}^- + \text{B}
\]

Alternatively, the superexcited anion \(\text{AB}^{-*}\) can be collisionally stabilized by a ‘third body’, \(M\), thus

\[
\text{AB}^{-*} + M \rightarrow \text{AB}^- + M
\]

or it can also lose energy by emission of a photon. When a photon is emitted the overall process is radiative attachment

\[
\text{AB} + e^- \rightarrow \text{AB}^{-*} \rightarrow \text{AB}^- + h\nu
\]

‘Slow’ dissociation of ‘metastable’ molecular ions is well known for positive ions, see e.g. [8], but some examples of metastable negatively charged ions are known, perhaps because autodetachment lifetimes are generally orders of magnitude shorter than typical micro- and milli-second observation time windows of mass spectrometers.

2. ERIC, Electron Radical Interaction Chamber

The spectrometer ERIC is shown schematically in Figure 1 and has been described elsewhere [1]. Briefly, sample gas is passed to the differentially pumped interaction region through a glass inlet system, which includes the Evenson 2.45 GHz microwave cavity shown in Figure 2, which is used to generate unstable molecules. A 1 µs pulse of low energy electrons from a trochoidal monochromator enters the interaction source region of a small linear time-of-flight mass spectrometer. When all the electrons have left the ion source a pulse applied to the ion repeller generates a large electric field of typically 200 V/cm. This electric field is the first of a two electric field Wiley-McLaren type linear time-of-flight mass spectrometer designed for second order space focussing [9]; the second electric field is in the acceleration region and the drift region is field free. The voltages of the mass spectrometer can be set for detection of negative or positive ions. The pulse repetition rate is \(~12\) kHz.

3. CS, carbon monosulphide

A spectrum of dissociative electron attachment to CS, carbon monosulphide, generated in the microwave discharge is shown in Figure 3. The vertical ordinate axis represents electron energy and the horizontal abscissa represents ion time-of-flight. The identities of the fragment ions
formed in dissociative electron attachment are indicated at the top of the figure. The signals have been integrated to give the spectrum given in Figure 4. The S$^-$ and C$^-$ ions appear at their thermodynamic thresholds; S$^- + C$ ($^3P$) at 5.43 eV, C$^- + S$ at 6.40 eV and S$^- + C$($^1D$) at 6.70 eV. The cross sections for formation of these ions are $\sim 0.025 \text{ \AA}^2$, 0.002 \text{ \AA}^2 and 0.003 \text{ \AA}^2 respectively. The electron attachment bands are remarkably similar to those found in electron attachment to the valence isoelectronic CO molecule, although the thermodynamic thresholds for negative ion formation that are $\sim 5$ eV lower in CS than for CO, which is mostly due to the significantly weaker bond strength of CS compared to CO.

Generally, many different molecules are present in the gas stream when the microwave discharge is used to generate unstable molecules, as was the case for SO, S$_2$O and S$_2$O$_2$ [1]. In the case of CS, however, it was possible to generate a relatively pure sample of CS with a microwave discharge of carbon disulphide diluted in helium. This purity enabled the spectrum of CS shown in Figure 3 to be observed without interference from other molecules. Cleaner methods of radical production are being examined; the generation of unstable molecules and free radicals presents many experimental challenges.

4. Metastable fragmentation of SF$_6^-$

Most metastable negatively charged molecular ions formed in electron attachment are too short-lived to be observed on the microsecond timescales of mass spectrometry. A famous exception is, of course, SF$_6$ and many experiments have been performed to determine the lifetime of SF$_6^-$ ions with respect to autodetachment, see e.g. [10, 11]. The threshold for formation of SF$_5^-$ + F from SF$_6$ is very close to zero, however, and fragmentation of metastable SF$_6^-$ ions had been observed in mass spectrometers some time ago [12, 13], but lifetimes had not been determined for SF$_6^-$ ions with respect to fragmentation.

SF$_6^-$ has been investigated in Belfast with ERIC and Innsbruck with a twin sector field mass spectrometer. In Innsbruck, SF$_6^-$ ions were mass selected with the magnetic sector of the mass spectrometer and then passed along a field free drift tube before they entered the electric sector,
Figure 3. Colour online. A two dimensional spectrum of dissociative electron attachment to CS. The ordinate is electron energy and abscissa ion time-of-flight (see text).

Figure 4. Integrated intensities of $S^-$ and $C^-$ formed in dissociative electron attachment as a function of electron energy.
which analyses ion kinetic energy. The pass energy of the electric sector is varied to observe any fragment ions with lower kinetic energy than the $\text{SF}_6^+$ parent ion peak; this is a MIKE scan. A MIKE spectrum recorded in Innsbruck is shown in Figure 5; a weak peak four orders of magnitude smaller than the $\text{SF}_6^+$ signal is observed due to formation of $\text{SF}_5^-$. Analysis of this weak peak shows that little kinetic energy is released in fragmentation; the kinetic energy distribution has a FWHM (full width half maximum) of 18 meV.

A two dimensional dissociative electron attachment spectrum of $\text{SF}_6$ measured with ERIC is shown in Figure 6. The main peaks are due to $\text{SF}_6^{-*}$ and $\text{SF}_5^-$ ions which do not dissociate as they are accelerated in the interaction and acceleration regions of the time-of-flight mass spectrometer. There is weak signal between these peaks due to $\text{SF}_6^{-*}$ ions that dissociate into $\text{SF}_5^-$ whilst they are being accelerated; if an ion is accelerated for some time as $\text{SF}_6^{-*}$ and for some time as $\text{SF}_5^-$ then its final speed, and hence time-of-flight, will be intermediate between the speeds of $\text{SF}_6^{-*}$ and $\text{SF}_5^-$. If the $\text{SF}_6^{-*}$ ion dissociates soon after the application of the extraction pulse to the interaction region then it will be accelerated mostly as $\text{SF}_5^-$ and its time-of-flight will be close to that of the $\text{SF}_5^-$ peak. Alternatively, if an $\text{SF}_6^{-*}$ ion dissociates close to the end of the acceleration region then its flight time will be close to that of the main $\text{SF}_6^{-*}$ peak. Indeed two zones of metastable signal are identifiable, zones 1 and 2, which are due to dissociation in the interaction region and acceleration region respectively. Monte-Carlo simulation has confirmed that the difference in intensities observed between these two zones are not artificial; the intensity is lower in the acceleration region’s zone 2 because ions are accelerated more rapidly in the acceleration region and spend less time in it. Experiments have been performed at a variety of different sample gas pressures to ensure no collisional effects contributed to the observed metastable signal in zones 1 and 2.

Comparison of the data with Monte-Carlo simulations has enabled lifetimes of $\text{SF}_6^{-*}$ ions to be estimated as a function of electron impact energy and, thus also, as a function of the internal energy of the $\text{SF}_6^{-*}$ ion. The details of this analysis are beyond the scope of this progress report, but Figure 7 is presented to show the results obtained; full details are presented elsewhere [7].

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Figure 6. Colour online. A two dimensional spectrum of dissociative electron attachment to SF$_6$. The main peaks are due to SF$_6^-$ and SF$_5^-$ ions passing from the interaction region to the detector. Signal in zones 1 and 2 is due to SF$_6^-$ ions that dissociate to give SF$_5^-$ ions whilst they are being accelerated in the interaction and acceleration regions respectively.

Figure 7. Lifetimes of SF$_6^-$ ions as a function of electron impact energy determined with data from ERIC (see text).
References
[1] Field T A, Slattery A E, Adams D J and Morrison D D 2005  *J. Phys. B* **38** 255
[2] Graupner K, Field T A and Feketeova L 2006  *New J. Phys.* **8** 314
[3] Senn G, Drexel H, Marston G, Mason N, Märk T D, amd C Schmale M M, Tegeder P, Rühl E and Illenberger E 1999  *J. Phys. B* **32** 3615
[4] Tarnovsky V, Deutsch H and Becker K 1998  *J. Chem. Phys.* **109** 932
[5] Rozum I, Limao-Vieira P, Eden S, Tennyson J and Mason N J 2006  *J. Phys. Chem. Ref. Data* **35** 267
[6] Sobrinho A M C and Lee M T 2005  *Int. J. Quantum Chem.* **103** 703
[7] Field T A, Graupner K, Mauracher A, Scheier P, Bacher A, Denifl S, Zappa F and Märk T D 2007  *submitted* to  *J. Chem. Phys.*
[8] Cooks R G, Beynon J H, Caprioli R M and Lester R G 1973  *Metastable Ions* (Amsterdam: Elsevier)
[9] Eland J H D 1993  *Meas. Sci. Technol.* **4** 1522
[10] Compton R N, Christophorou L G, Hurst G S and Reinhardt P W 1981  *J. Chem. Phys.* **45** 4634
[11] Liu Y, Suess L and Dunninga F B 2005  *J. Chem. Phys.* **122** 214313
[12] Ahearn A J and Hannay N B 1953  *J. Chem. Phys.* **21** 119
[13] Lifshitz C, Peers A M, Grajower R and Weiss M 1970  *J. Chem. Phys.* **53** 4605