Electron Attachment to Radicals and Unstable Molecules

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Abstract. Experimental investigation of electron attachment to unstable molecules is considered. Recent results of electron attachment to CS, S₂O and S₂O₂ are reviewed. The challenges of this work are highlighted with respect to ongoing experiments to investigate electron attachment to NH and NH₂ radicals.

1. Introduction

In low temperature technological plasmas the majority of free electrons have kinetic energies below the ionization thresholds of gas molecules present. These electrons can excite the gas molecules rotationally, vibrationally and electronically, which may lead to molecular dissociation. Low energy electrons can also attach to gas phase molecules to form ‘Temporary Negative Ions’, which are unstable with respect to loss of the electron. Temporary negative ions formed may dissociate to give neutral and negatively charged fragments; this process, dissociative electron attachment, can be represented for a general molecule AB by

\[ AB + e^- \rightarrow AB^{--} \rightarrow A + B^- \]  \hspace{1cm} (1)

where \( AB^- \) is the temporary negative ion. Temporary negative ions are generally formed at quite specific electron energies because the energy of the electron must be equal to the difference in energy between the initial state of the neutral molecule and the temporary negative ion state.

Many investigations of dissociative electron attachment to stable molecules and clusters have been reported, see e.g. [1, 2], but there have been few studies of electron attachment to unstable molecules. Graves et al. [3] have highlighted the desirability of information about dissociative electron attachment to radicals for plasma modelling, not least because radicals are key reactive chemical species in technological plasmas. Dissociative electron attachment has been observed experimentally to some stable free radicals, such as NO [4], and partially stable ones, such as OCIO [5, 6], which has also been investigated theoretically [7]. Experiments have also been performed to investigate electron attachment to the diatomic molecules S₂ [8] and Na₂ [9]. Other unstable species that have been studied include electronically excited molecules such as SO₂ in the \( ^1\text{B}_1 \) state [10, 11]. There have also been calculations of electron scattering of low energy electrons by unstable molecules such as ClO, CF, CF₂ and CF₃ [12, 13, 14, 15] for which there are no experimental data.

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A new experiment, ‘Electron Radical Interaction Chamber’ (ERIC), has been developed to investigate dissociative electron attachment to unstable molecules. Experimental investigations of electron attachment to CS [16], S\textsubscript{2}O and S\textsubscript{2}O\textsubscript{2} [17] performed with ERIC are discussed here. Challenges of this experimental technique are also presented with respect to experiments to investigate electron attachment to NH and NH\textsubscript{2}.

2. Experiment

![Figure 1. Schematic diagram of ERIC](image)

The spectrometer ERIC is shown schematically in Figure 1. ERIC includes a trochoidal monochromator [18] and a time-of-flight mass spectrometer [19]. The electron energy resolution is $\sim 200$ to 250 meV determined from the full width half maximum (FWHM) of the SF\textsubscript{6} peak at zero energy. The time-of-flight mass spectrometer has a mass resolution ($\Delta M/M$, FWHM) of $\sim 100$ to 200. For optimum electron energy resolution close to zero electric fields are required in the interaction region whereas large electric fields are required for optimal mass resolution. To satisfy these contradictory requirements the experiment is pulsed at $\sim 10$ kHz; a short pulse of electrons passes through the interaction region with close to zero electric field. Ions are pushed down the mass spectrometer with a large electric field generated by the application of a pulse to the ion repeller after the electron pulse has passed through the interaction region.

The interaction region is differentially pumped from below to minimize the pressure in the electron monochromator and time-of-flight mass spectrometer. Sample gas is introduced through a glass inlet system which includes a Evenson microwave cavity for the generation of unstable molecules. Typical microwave powers of 40 to 100 W at 2.45 GHz are applied to generate unstable molecules from precursor molecules diluted in helium. In general, it is not possible to obtain a pure sample of the desired unstable molecule with the microwave discharge, but instead a mixture of molecules are formed. Some control over the gas mixture in the interaction region is possible, however, by variation of the helium and precursor molecule pressures in the microwave discharge and the microwave input power level.

The voltages of the mass spectrometer are reversible so that it is possible to detect both negative and positive ions with the mass spectrometer. When the microwave plasma is running positive and negative ion mass spectra are taken alternately. Positive mass spectra are taken at low electron energies where parent ions are formed without fragmentation to characterize the gas in the interaction region. Negative ion spectra are taken to observe electron attachment to the gas in the interaction region.

The time-of-flight mass spectrometer is ideal for this work on unstable molecules where a mixture of molecules is frequently present in the interaction region. Time-of-flight mass
Figure 2. Mass spectrum at 20 eV of gas formed in discharge of He, N₂ and H₂.

Figure 3. Two dimensional spectrum of positive ions formed as a function of electron energy ionizing gas formed in a microwave discharge of He, N₂ and H₂.

spectrometers are ‘multiplex’, that is to say that they are sensitive to more than one mass at any time, unlike quadrupole and magnetic sector mass spectrometers which filter the ions so that only one mass is observed. The benefit of the multiplex time-of-flight mass spectrometer is that one sees all the positive ions and all the negative ions formed at each electron energy when scanning for positive and negative ions. It is particularly valuable to see all the ions when a mixture of gases is present, which may give a variety of negative ions; it is not necessary to scan the mass spectrometer through all possible negative ion masses at each electron energy. Thus, with the time-of-flight mass spectrometer it is simply necessary to scan the electron energy and all masses are observed.

3. results
3.1. Generation of NH and NH₂
Experiments have been performed to generate NH and NH₂ in a microwave discharge of helium, nitrogen and Hydrogen gas. Previously, Jauberteau et al. reported formation of NH and NH₂ in a 2.45 GHz microwave discharge of nitrogen, hydrogen and argon gas [20]. Helium replaced argon for the present work because argon metastables have been found to reduce the gain of the multichannel planes in the mass spectrometer previously.

A mass spectrum taken at 20 eV electron energy of the gas mixture formed in a microwave
discharge of helium, nitrogen and hydrogen is shown in Figure 2. Many ions are observed including \( \text{NH}_2^+ \). A scan was taken of positive ions formed whilst the electron energy was varied to find the appearance energy of \( \text{NH}_2^+ \). This scan is shown as a two dimensional spectrum in Figure 3. In this two dimensional spectrum each horizontal line represents an individual mass spectrum recorded at the electron energy indicated on the vertical axis.

Integrated intensities of \( \text{NH}_2^+ \) and \( \text{NH}_3^+ \) ions in Figure 3 are shown in Figure 4 as a function of electron energy. The appearance energy of \( \text{NH}_3^+ \), \( \sim 10 \text{ eV} \), is at the ionization energy of \( \text{NH}_3 \), 10.070 \( \pm \) 0.020 eV [21], confirming the presence of \( \text{NH}_3 \) in the interaction region. The appearance energy of \( \text{NH}_2^+ \), \( \sim 15 \text{ eV} \), is, however, significantly higher than the ionization energy of \( \text{NH}_2 \), 11.46 \( \pm \) 0.01 [22], and is rather close to the appearance energy of \( \text{NH}_2^+ \) in dissociative ionization of \( \text{NH}_3 \), 15.60 \( \pm \) 0.02 [23]. Therefore, the radical \( \text{NH}_2 \) was not observed in this experiment and \( \text{NH} \) was not observed either. Thus, it was not possible to investigate electron attachment to \( \text{NH} \) and \( \text{NH}_2 \).

This example is given to illustrate the challenges in the preparation of unstable molecules. The most obvious difference is between the present experiment and the experiment of Jaubertau et al. [20] is that helium was used instead of argon as a buffer gas. Furthermore, as noted by Jaubertau et al. surface reactions are critical and their apparatus had steel walls whereas in ERIC unstable molecules pass along glass tubes. Further experiments to investigate electron attachment to \( \text{NH} \) and \( \text{NH}_2 \) are planned.

### 3.2. Electron attachment to \( \text{SO}, \text{S}_2\text{O} \) and \( \text{S}_2\text{O}_2 \)

Unstable \( \text{SO}, \text{S}_2\text{O} \) and \( \text{S}_2\text{O}_2 \) were formed in a microwave discharge of \( \text{SO}_2 + \text{He} \), however, there was always a mixture of these products and undissociated \( \text{SO}_2 \) in the gas stream. Figure 5 shows two integrated spectra of negative ions formed as a function of electron energy with the microwave discharge turned off, (a), and on, (b). Figure 5 (a) is simply a spectrum of electron attachment to \( \text{SO}_2 \), of course, because there is no dissociative electron attachment to helium; there is a clear window between 0 and 4 eV electron energy where there is no electron attachment to \( \text{SO}_2 \). In Figure 5 (b) several new resonances are observed due to electron attachment between 0 and 4 eV electron energy, which are, clearly, due to the unstable molecules in the interaction region formed by the microwave discharge.

The mixture of gases complicated the assignment of each new dissociative electron attachment processes to either \( \text{SO}, \text{S}_2\text{O} \) or \( \text{S}_2\text{O}_2 \). The assignment was made by variation of the relative pressure of each molecule in the gas stream and comparison with the attendant variation in intensity of the new dissociative attachment bands. The relative pressures of the different molecules in the gas stream were varied indirectly by variation of the pressure of He and \( \text{SO}_2 \).
Figure 5. Dissociative electron attachment spectra observed (a) to SO\(_2\) and He and (b) to SO\(_2\), He, SO, S\(_2\)O and S\(_2\)O\(_2\) from [17]. Several new resonances are present in (b), which have been assigned to S\(_2\)O and S\(_2\)O\(_2\). No new resonances were observed due to SO. The same spectra are presented in panels (a) and (b) with both linear (top) and logarithmic (lower) vertical scales. The results for the negative ions are split between two logarithmic plots in (a) and (b) for clarity.

Entering the microwave discharge. The new features observed in Figure 5 (b) have been assigned to S\(_2\)O and S\(_2\)O\(_2\) [17] as summarized in Table 1.

Absolute cross sections have been estimated for the new electron attachment processes of S\(_2\)O and S\(_2\)O\(_2\) observed by comparison of the intensities of positive and negative ions formed from S\(_2\)O and S\(_2\)O\(_2\) with a reference molecule, SO\(_2\), with known cross sections for electron impact formation of positive and negative ions [17]. These estimates are shown in Table 1.

3.3. Electron attachment to CS, carbon monosulphide

Dissociative electron attachment to CS gives S\(^-\) at 5.43 ± 0.15 eV, C\(^-\) at 6.40 ± 0.15 eV and S\(^-\) 6.70 ± 0.15 eV [16], as shown in Figure 6. The thresholds of these bands lie at the thermodynamic limits for production of S\(^-\) + C, C\(^-\) + S and S\(^-\) + excited C (\(^1\)D) respectively. There are similarities between the electron attachment spectra of CS and CO. These interactions of CS with low energy electrons will play a role in technological plasmas containing carbon and sulphur used, for example, to deposit n-type semiconducting diamond-like carbon films and in extraterrestrial environments where electrons are present with 5 to 7 eV energy [16].

CS was formed in the microwave discharge of CS\(_2\) and He. One set of conditions was found where only CS contributed to the electron attachment spectrum. Further negative ion spectra were recorded, however, with a variety of conditions where several different molecules contributed
| radical | Ion    | $E_{\text{peak}}$ (eV) | $\sigma$ ($\text{Å}^2$) | Confidence |
|---------|--------|-------------------------|--------------------------|------------|
| S$_2$O$_2$ | S$^-$  | 0.0                     | 30                       | Medium     |
| S$_2$O$_2$ | SO$^-$ | 0.8                     | 2.7                      | High       |
| S$_2$O$_2$ | SO$^-$ | 1.2                     | 1.9                      | High       |
| S$_2$O$_2$ | SO$^-$ | 3.0                     | 0.48                     | High       |
| S$_2$O$_2$ | SO$^-$ | 3.7                     | 0.53                     | High       |
| S$_2$O$_2$ | S$_2$O$^-$ | 3.7 | 0.31 | High |
| S$_2$O | S$^-$  | 1.6                     | 0.30                     | High       |
| CS | S$^-$  | 5.4                     | 0.025                    | High       |
| CS | C$^-$  | 6.4                     | 0.003                    | High       |
| CS | S$^-$  | 6.7                     | 0.002                    | High       |
| S$_2$O$^+$ | S$^-$  | 1.8                     | 0.09                     | High       |

Table 1. Summary of new resonances observed with estimated absolute cross sections for First results obtained with ERIC are presented for S$_2$O, S$_2$O$_2$ and CS [17, 16]. Confidence in the table refers to the confidence of the assignment of the ion observed to the unstable molecule. † Note that the second listing for S$_2$O was obtained from the CS experiment where S$_2$O was formed in small quantities (see text).

Figure 6. Dissociative electron attachment to CS

electron attachment resonances. In some of these measurements a small quantity of S$_2$O was observed, which had already been investigated, as described above, with SO and S$_2$O$_3$. The same electron attachment process was observed from S$_2$O with the formation of O$^-$ at 1.8 eV.

Absolute cross sections for electron attachment to CS have been determined in the same way as for S$_2$O and S$_2$O$_2$. These estimates are also shown in Table 1 along with a new estimate for the cross section of dissociative electron attachment to S$_2$O based on the CS spectra where S$_2$O was observed. Although there is some discrepancy between the values of absolute cross section they agree to within the expected uncertainty of these estimates [16].

4. Conclusions
A new spectrometer, ‘Electron Radical Interaction Chamber’ (ERIC), has been developed to investigate dissociative electron attachment to unstable molecules. Results have been reported for S$_2$O, S$_2$O$_2$ and CS [17, 16]. These measurements are challenging, as described here in the case of experiments to investigate electron attachment to NH and NH$_2$. Confidence in the reliability of this method to observe electron attachment to unstable molecules is reinforced by the observation of the same dissociative electron attachment process of O$^-$ formation from S$_2$O.
in two separate experiments. The peak electron energy and estimated absolute cross section derived from the two different observations of the process, shown in Table 1, are not identical, but agree within the experimental uncertainty.

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