A new technique to study plasma chemistry kinetics

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Abstract. Accurate kinetics of plasma processes are necessary for modeling of the chemistry occurring in the upper atmosphere, re-entry, combustion, and discharges. While a great deal of data exists in the literature for most types of plasma chemistry processes, there remain gaps for reactions less amenable to traditional measurements. In particular ion-ion mutual neutralization reactions have received relatively little study, and essentially no detailed product branching fractions are known. Similarly, while hundreds of electron attachment rate constants to stable species have been reported, only a handful of measurements of electron attachment rate constants to unstable radical species exist in the literature. We report several measurements involving these classes of reactions using a novel flowing afterglow technique: Variable Electron and Neutral Density Attachment Mass Spectrometry (VENDAMS). The technique takes advantage of these processes occurring as secondary and tertiary chemistry in high density plasmas, and uses excess electrons as chemical ionization agents to monitor neutral product concentrations. Systems starting with a variety of neutrals have been studied over a temperature range of 300 to 550 K. We report several novel measurements including: the first temperature dependences of electron attachment rate constants to radical species; the first complete neutral product distributions of ion-ion mutual neutralization reactions along with the associated temperature dependences; evidence of a novel plasma chemistry process \((A^+ + B^- \rightarrow \text{neutrals} + e^-)\), which we term electron catalyzed mutual neutralization.

1. Introduction

Hundreds of reaction rate constants for plasma chemistry processes have been derived from flow tube measurements.\cite{1} Typically rate constants are determined by maintaining pseudo-first order conditions while varying either reactant concentration or reaction time.\cite{2} As long as a single reaction dominates the chemistry in the flowtube, extracting a reaction rate constant from this type of measurement requires only trivial analysis. However, these conditions are difficult to create for certain types of reactions. In particular, little reliable data exists for ion-ion mutual neutralization rate constants due to the challenge of accurately measuring initial ion concentrations in the flow tube, and, with the exception of the results reported here, no complete neutral product distributions exist. Additionally, while hundreds of thermal electron attachment rate constants to stable species have been reported,\cite{3} only two measurements of electron attachment rate constants to unstable radical species exist in the literature.\cite{4}

We have recently begun using a flowing afterglow Langmuir probe (FALP) apparatus in a novel manner (a technique dubbed variable electron and neutral density mass spectrometry (VENDAMS))\cite{5} that trades the simplicity of the analysis described above for the ability to study other types of chemistry, including ion-ion mutual neutralization and electron attachment to radical species, which occur when an electron attaching neutral species is introduced to a weakly ionized plasma. The method has also yielded evidence that electrons act as third bodies to enhance the rate of ion-ion mutual neutralization; this plasma chemistry loss process has not been previously reported in the literature.

To date VENDAMS measurements have been made using a range of neutral precursors. These include several sulfur fluorides (SF\(_6\), SF\(_2\)Cl, SF\(_2\)C\(_6\)H\(_5\), SF\(_4\), SF\(_2\)CN, SF\(_3\)C\(_6\)F\(_5\)) as well as POCl\(_3\), PSCl\(_3\), (COCl)\(_2\), and

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Fe(CO)$_3$. The processes for which VENDAMS yields well-defined kinetic data are highly dependent on the specifics of the system being studied, but fall into the three broad categories outlined above. The remainder of this paper will detail the VENDAMS experimental technique, the method of analysis used to extract kinetic information from the data, and an overview of the results on systems studied to date ordered into each of those three categories of plasma chemistry processes.

2. Experimental

FALP apparatuses have been in use for several decades,[6] and the details of the instruments in general and the particular apparatus in use by the plasma chemistry group at Air Force Research Laboratory have been well-documented.[7] Briefly, a flow of helium gas is introduced to a stainless-steel lined, glass, 1m long, 7 cm diameter flow tube through an upstream mass-flow controller and removed downstream by a Roots pump. Shortly after being introduced, a portion of the helium passes through a microwave discharge cavity producing a weakly-ionized plasma consisting primarily of He$^+$, He$_2^+$, He$^*$, and e$^-$. Ar gas is flowed downstream of the microwave cavity at approximately 5% of the He flow, effectively converting He$_2^+$ and He$^*$ to Ar$_2^+$. By the time the flow has reached a glass inlet port 20 cm downstream of the Ar inlet (roughly 2 ms at a typical ion velocity of $10^4$ cm s$^{-1}$), an Ar$^+/e$ plasma has been established with Ar$^+$ accounting for roughly 95% of the positive charge. The electron density is measured using the Langmuir probe over a dynamic range of $10^7$ to $5 \times 10^{10}$ cm$^{-3}$. The full range of initial electron densities ($N_e(0)$) at the downstream glass inlet is achievable by moving the microwave cavity further away or closer to the inlet and, to a lesser degree, by vary the microwave power. Charge densities are a small fraction of the neutral He density, which is typically $3.2 \times 10^{16}$ cm$^{-3}$ (1 torr at 300 K). At these pressures, ions undergo numerous collisions with the buffer gas and are, in most cases, assumed to be thermalized to the temperature of the flowtube. The flow is sampled 46 cm downstream of the neutral gas inlet by a 1mm on-axis aperture leading to a differentially pumped chamber and a quadrupole mass spectrometer with which to monitor the relative concentrations of ionic species. The Langmuir probe is used to measure the ambipolar diffusion rate of the plasma by monitoring the electron density as a function of distance along the flow tube for a known ion flow velocity. The velocity is also measured using the Langmuir probe, by pulsing the microwave discharge and noting the arrival time of the pulse on the probe as a function of the probe’s distance along the flow tube.

Either one or two neutral gases are added through the downstream glass inlet at known rates via mass-flow controllers. A single gas is typically added in concentrations on the order of $10^5$ to $10^7$ cm$^{-3}$, typically in a 0.1% to 1% concentration mixture in He at a flow rate of 1 to 10 std. cm$^{-3}$ min$^{-1}$. Product anion abundances after the known reaction time (generally 4.6 ms) are monitored using the quadrupole mass spectrometer while varying $N_e(0)$ from well below to well above the neutral reactant density. At very low $N_e(0)$, the primary electron attachment to the neutral species quickly depletes the electron density, inhibiting all subsequent chemistry. These data yield product branching fractions of the primary electron attachment by measuring the relative abundance of product ions (the total electron attachment rate constant may be measured in the usual manner of measuring the decrease in the electron density above that of ambipolar diffusion as a function of reaction time). In the case of dissociative electron attachment, each ionic product is accompanied by a neutral co-product, generally an unstable radical species. At higher $N_e(0)$, sufficient concentrations of electrons survive to react with these radicals, assuming the attachment is energetically accessible. The ions resulting from the “secondary” chemistry are also monitored using the mass spectrometer and allow rate and product information of attachment to the radical species to be determined. At still higher $N_e(0)$, the anions produced in the primary attachment neutralize with Ar$^+$ present in the flowtube at a significant rate. If the resulting neutral products are exothermic for attachment, excess electrons in the flowtube act as chemical ionizing agents allowing for a sensitive probe of the concentrations of those products.

A second electron attaching gas may be added as well (a “2-gas” experiment) serving two purposes: 1) it is convenient to produce a monatomic anion from a primary attachment because the mutual neutralization of that anion with Ar$^+$ will proceed at a negligible rate, and as a result the concentration of the anion acts as an internal standard against which to measure the mutual neutralization rate constant of polyatomic anions with Ar$^+$. The
second gas may be chosen to yield the monatomic anion in cases where attachment to the first species does not. 2) adding a large concentration of a fast electron attaching gas quickly depletes the electron density in the flowtube, inhibiting all of the “secondary” chemistry described above with the exception of mutual neutralization and allowing for a much simplified analysis in order to accurately determine mutual neutralization rate constants. Electron attachment to CCl$_4$ yields only Cl$^-$ at the collisional rate constant. When added as the second gas in low concentrations ($<10^{10}$ cm$^{-3}$), CCl$_4$ serves purpose 1) above, and when added in high concentrations ($>10^{10}$ cm$^{-3}$) serves both purposes 1) and 2) above.

3. Analysis

Modeling the experimental anion abundances as a function of $N_e(0)$ in order to extract total and partial reaction rate constants requires accounting for the numerous reactions that can occur between all the species known (ions observed on the mass spectrometer) or inferred (corresponding product neutrals) to be present in the flowtube. The rate constant of each of these reactions is a parameter in the modeling. Product anion abundances may be calculated simply by iteratively solving the coupled differential equations describing the production and destruction of species as indicated by all the possible reactions. However, many of the reaction rate constants are largely or completely unknown. This creates concern that the data may be underdetermined.

The set of possible reactions is greatly reduced by maintaining experimental conditions in which only the fastest reactions affect the anion abundances outside of uncertainty. Specifically, neutral concentrations are held sufficiently low (generally less than $10^{10}$ cm$^{-3}$) that ion-molecule reactions, with typical upper limit rate constants of $10^{-9}$ cm$^3$ s$^{-1}$, are negligible relative to electron attachment and ion-ion mutual neutralization processes. The reduced set of relevant reactions may still number as high as 10-20 unknown rate constants depending on the system, creating a large parameter space. The full parameter space is explored by a Monte Carlo optimization in which 1) a set of reaction rate constants is randomly guessed; 2) the kinetics of the system are calculated from the known initial conditions throughout the known reaction time; 3) the resulting calculated anion abundances are compared to the experimental abundances via a weighted least-squares characterized by a goodness-of-fit ($0$ being a perfect fit); 4) the best-fit and uncertainty limits for each rate constant are determined by plotting the goodness-of-fit as a function of that rate constant. In some cases the goodness-of-fit may be a strong function of a particular rate constant, and that rate constant is then well-defined by the data. In other cases, the goodness-of-fit may be independent of a particular rate constant, and that rate constant is left completely undefined by the data.

4. Results and Discussion

Data derived from VENDAMS measurements fall across several disparate types of plasma processes. The remainder of this paper will discuss each of the types of processes studied in turn.

4.1 electron attachment to unstable radical species

Prior to the VENDAMS technique, only two reaction rate constants to unstable radical species had been reported in the literature. Each of those measurements (on CCl$_3$ and CH$_2$Br)[4] were derived by monitoring the electron depletion in a FALP as a function of reaction time above that explained by primary attachment to a neutral precursor, and each measurement was performed at room temperature. VENDAMS measurements to date on several systems have yielded electron attachment rate constants to several radical species: SF$_5$, SF$_3$, PSCl$_2$, and POCl$_2$. With the exception of POCl$_2$, each of these measurements extends across the temperature range of 300 K to 550 K, allowing for determination of the temperature dependence of the attachment. Reported rate constants appear in Table 1.

In this temperature range, most attachment rate constants to stable species show either no temperature dependence or a positive temperature dependence.[8] The exceptions are species which attach electrons with
near unit efficiency, and are limited by the collision rate constant with an electron, which decreases as $T^{-1/2}$. For most species for which dissociative attachment is energetically accessible, this decrease along with the increase in the electron autodetachment rate with temperature is offset or swamped by an increased rate of stabilization through dissociation of the excited anionic species produced by electron capture.

Table 1. Measured electron attachment rate constants to the indicated radical species at the indicated temperatures

| Species | 300 K     | 400 K     | 500 K     | 550 K     |
|---------|-----------|-----------|-----------|-----------|
| SF$_5$  | $2.5 \pm 1 \times 10^8$ | $1.1 \times 3 \times 10^8$ | $9 \pm 3 \times 10^9$ | -         |
| SF$_3$  | $4 \pm 3 \times 10^9$ | $8 \times 3 \times 10^9$ | $8 \times 3 \times 10^9$ | -         |
| PSCl$_2$| $1.4 \pm 0.6 \times 10^8$ | $1.1 \pm 0.4 \times 10^7$ | - | $9.1 \pm 5 \times 10^8$ |
| POCl$_3$| $1 \pm 2 \times 10^8$ | - | - | -         |

Both electron attachment to SF$_5$ and to PSCl$_2$ show possible steep negative temperature dependences (in both cases, a temperature dependence of zero is just within the experimental uncertainty). It is unclear if these dependences, if real, suggest a physical distinction between attachment to radical species and stable species, or if these happen to be two exceptional cases. Both SF$_5^-$ and PSCl$_2^-$ are bound (although non-dissociative attachment is not observed for either system), and no differences in the potential surfaces between these species and those of other measured systems that could lead to different dynamics are immediately obvious.

4.2 ion-ion mutual neutralization

The dynamics of ion-ion mutual neutralization (MN) reactions involving only atomic species are fairly well-understood.[9-10] The likelihood of neutralization is a function of the location of curve crossings between the ionic potential and excited electronic states of the neutral atoms, with the large excess energy of the neutralization ending up in the only available degree of freedom: the kinetic energy of the separating neutrals. If either of the species is polyatomic, the situation is greatly complicated. Each curve crossing involves a quasi-continuum due to internal modes of the polyatomic species, and the exothermicity of the reaction has numerous degrees of freedom to be distributed amongst. VENDAMS measurements provide precise total MN rate constants and the first reported complete MN neutral product distributions against which theory of MN dynamics may be evaluated.

4.2.1 total rate constants

MN rate constants may be reasonably predicted from parameterized formulas based on the Landau-Zener model of curve crossings.[11] Comparison of measured MN rate constants to those from theory has shown that the predicted dependences on electron binding energy (EBE) of the anion and on system temperature appear to generally hold.[12] However, the comparison suffers from two concerns: 1) rate constants for MN involving at least one structured species vary by less than an order of magnitude, requiring rather high precision in measurements in order to test theory and 2) many of the reported rate constants rely on ion concentrations measured using a Langmuir probe, a technique that has been shown to be unreliable.[13]

Using the “2-gas” procedure described above, VENDAMS yields MN rate constants to uncertainties as low as 10%. Importantly, the determination does not rely on determining the absolute concentrations of ions present in the flowtube, but rather on the relative concentrations of two anionic species, which may be measured much more precisely. In the condition where primary electron attachment to two neutral attaching gases depletes the electron density, all higher order chemistry is inhibited and only the anions produced by the initial attachment are observed in the flowtube. The ratio of the anions as a function of N$_e$(0) varies almost solely as a function of the relative MN rate constants (in all cases here, the positive charge in the plasma is dominated by Ar$^+$, and any MN must occur with that species). If one of the anions undergoes MN with Ar$^+$ with a negligible rate constant,
as Cl\(^{-}\) is known to do, the change in the relative abundance of the other anion yields the absolute MN rate constant.

MN rate constants have been measured for SF\(_6\)\(^{-}\), SF\(_5\)\(^{-}\), SF\(_4\)\(^{-}\), PSCI\(_5\)\(^{-}\), PSCI\(^{-}\), POCl\(_5\)\(^{-}\), POCl\(_5\)\(^{-}\), c-C\(_6\)F\(_5\)\(^{-}\), c-C\(_6\)F\(_14\), Fe(CO)\(_6\)\(^{-}\), Cl\(_2\), FCI, and CN\(^{-}\) across the temperature range from 300 K to 550K. Rate constants appear in Table 2. In agreement with prior results, MN rate constants appear to follow the theoretical T\(^{-0.5}\) dependence.[12] The dependence on EBE appears somewhat weaker than previously predicted, although larger EBE are weakly correlated with lower MN rate constants. MN involving a polyatomic species appear to have predictable rate constants in the range of 4-6 x10\(^{-8}\) cm\(^3\) s\(^{-1}\). Measured MN rate constants for three systems involving a diatomic anion and a monatomic cation are nearly identical and are lower than those involving a polyatomic species. That these reactions involving simpler systems are slower is expected because they involve fewer curve crossings, and the likelihood of a curve crossing favorable to MN is proportionally lower. For the same reason, however, we would expect the simpler systems to have less predictable rate constants than those involving polyatomic species, but this is not borne out by the current data.

**Table 2. Measured mutual neutralization rate constants of the indicated anions with Ar\(^{+}\) at the indicated temperatures**  

| Species | 300 K | 400 K | 500 K | 550 K |
|---------|-------|-------|-------|-------|
| SF\(_6\)\(^{-}\) | 5.0 ±0.5 | 3.8 ±0.5 | 3.4 ±0.5 | - |
| SF\(_5\)\(^{-}\) | 3.5 ±0.5 | 2.9 ±0.6 | 2.6 ±0.6 | - |
| SF\(_4\)\(^{-}\) | 4.0 ±0.8 | 3.3 ±0.7 | 2.9 ±0.7 | - |
| POCl\(_5\)\(^{-}\) | 5.6 ±0.6 | 4.5 ±0.6 | 4.1 ±0.7 | - |
| POCl\(_5\)\(^{-}\) | 4.6 ±0.7 | 3.8 ±0.7 | 3.0 ±0.6 | - |
| PSCI\(_5\)\(^{-}\) | 4.5 ±0.7 | 3.3 ±0.5 | - | 2.6 ±0.5 |
| PSCI\(^{-}\) | 5.4 ±1.1 | 4.3 ±0.8 | - | 3.9 ±0.8 |
| c-C\(_6\)F\(_5\)\(^{-}\) | 5.5 ±1.3 | - | - | - |
| (COCl)\(_2\)\(^{-}\) | 5.3 ±1 | 4.3 ±0.9 | - | - |
| Fe(CO)\(_6\)\(^{-}\) | 5.0 ±0.7 | - | - | - |
| Cl\(_2\) | 3.0 ±0.6 | 2.4 ±0.5 | - | 1.8 ±0.5 |
| FCI | 3.0 ±0.7 | 2.4 ±0.7 | 1.5 ±0.5 | - |
| CN\(^{-}\) | 3.0 ±1.0 | - | - | - |

4.2.2 product branching fractions

While overall reaction rate constants of MN appear reasonably predictable, the dynamics of the MN process are not. MN reactions are typically very exothermic, as typical ionization energies (8-20 eV) are much larger than typical electron affinities (0-5 eV). It is unclear what fraction of that available energy is funneled to internal modes of the products, what fraction remains in the kinetic energy of the separating products, and what aspects of the potential surface affect those fractions. The neutral product distributions of MN are clues to the dynamics; a larger amount of fragmentation indicates more energy placed in the internal modes of the neutralizing species. Prior to the VENDAMS technique, no complete product distributions were reported in the literature.

The MN reactions SF\(_n\)\(^{-}\) + Ar\(^{+}\) \rightarrow SF\(_m\) + (n-m)F + Ar (n=6,5,4) each have several energetically accessible product channels,[14] each of which may be characterized by the number of S-F bonds broken and the resulting SF\(_m\) neutral. Because the electron attachment rate constants of SF\(_m\) (m=2-6) are known (m=2,3,5 via VENDAMS, m=4,6 from the literature) the fraction of each SF\(_m\) neutral product may be quantified by measuring
the amount of electron attachment product to each species. VENDAMS measurements using neutral precursors \( \text{SF}_6, \text{SF}_5\text{Cl}, \) and \( \text{SF}_4 \) each yield neutral product distributions of MN of the dominate anion produced by electron attachment \( (\text{SF}_6^-, \text{SF}_5^-, \) and \( \text{SF}_4^- \) respectively) with the dominate cation present in the flowtube, \( \text{Ar}^+ \).

Measured product distributions appear in Figure 1. The distributions of both \( \text{SF}_6^- \) MN and \( \text{SF}_5^- \) MN were measured over the temperature range of 300 K to 500 K, and no dependence was found. The fraction of fragmented product varies significantly between the three reactions. Differences in the product distributions are apparent, with a greater fraction of product from \( \text{SF}_5^- + \text{Ar}^+ \) undissociated than from \( \text{SF}_6^- + \text{Ar}^+ \), with \( \text{SF}_4^- + \text{Ar}^+ \) likely falling in between. The ordering is correlated to the total exothermicities of the three reactions \( (14.8 \text{ eV SF}_6^- + \text{Ar}^+; \, 11.8 \text{ eV SF}_5^- + \text{Ar}^+; \, 14.4 \text{ eV SF}_4^- + \text{Ar}^+) \). While it may be initially unsurprising that the degree of fragmented product scales with available energy, in all three cases the available energy is well in excess of that needed to break several S-F bonds, and the energy in excess of that needed to break a single S-F bond is nearly identical in all three reactions \( (10.2, 10.1, 10.3 \text{ eV respectively}) \). This suggests that factors beyond the total available energy dictate the likelihood of transferring a large amount of energy to the internal modes of the neutral products.

![Figure 1](image)

**Figure 1.** Product branching fractions of MN of the indicated anions with \( \text{Ar}^+ \). Product channels are defined by the number of S-F bonds broken in the reactant anion to yield the product neutral; i.e. channel 1 indicates \( \text{SF}_n + \text{Ar}^+ \rightarrow \text{SF}_{n-1} + \text{F} + \text{Ar}^+ \).

4.3 electron catalyzed mutual neutralization

The effects of neutral third bodies enhancing the rate of plasma loss processes (radiative recombination, dissociative recombination, and mutual neutralization) have been well-documented and are important in understanding the chemistry of plasma at elevated pressures.\[15-17\] Electron third bodies have also been found to enhance the rate of radiative recombination,\[18-19\] and likely have a small, but difficult to measure, effect on much faster dissociative recombination processes. However, electron third bodies have not been previously suggested to increase the rate of mutual neutralization reactions. Despite the above observations, an enhancement would not be expected in MN because the previously recognized three-body processes all proceed by a collisional mechanism wherein the third body removes a significant amount of kinetic energy from the
system, trapping the charged species in the attractive well, which can then only be exited by neutralization. Due to the extreme mass difference, an electron is a poor collisional energy sink for a system composed of two ions.

As stated above, the “2-gas” VENDAMS experiment determines an MN rate constant to within an uncertainty of 10-25% (Figure 2A). Surprisingly, modeling “1-gas” VENDAMS data using the measured MN rate constants consistently underestimates the loss-rate of the anion, with the magnitude of the underestimation scaling linearly with \( N_e(0) \) (Figure 2B). This suggests that a plasma loss process unaccounted for in the modeling contributes significantly to the observed chemistry at higher \( N_e(0) \). The negative charge can only be removed by neutralizing with \( \text{Ar}^+ \) (no other positive species is present in the flowtube in sufficient concentrations to have the measured effect, and any polyatomic positive species will show a decreasing effect with increasing \( N_e(0) \) due to competing dissociative recombination). The only third bodies whose concentration scales appropriately with \( N_e(0) \) are \( \text{Ar}^+ \) and \( e^- \), and only assuming an \( e^- \) third body is consistent with both the “1-gas” and “2-gas” data. We suggest that the unaccounted for loss process is

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M^- + \text{Ar}^+ + e^- \rightarrow \text{ neutrals } + e^-
\]

which we term electron catalyzed mutual neutralization (ECMN). The process appears general; measured rate constants for \( M^- = \text{SF}_6^-, \text{POCl}_3^-, \text{and POCl}_2^- \) are on the order of \( 10^{-18} \text{ cm}^6 \text{ s}^{-1} \) and are non-zero outside of uncertainty as well as showing steep negative temperature dependences typical of three-body processes. Measured ECMN rate constants for several other species are similar in magnitude, but are not non-zero outside of uncertainty.

![Figure 2](image)

*Figure 2.* Measured (points) and best-fit calculated (lines) anion abundances from addition of \( 2 \times 10^9 \text{ cm}^{-3} \) \( \text{SF}_6 \) along with the indicated concentration of \( \text{CCl}_4 \) as a function of \( N_e(0) \). The high \( [\text{CCl}_4]_0 \) condition (A) determines \( k_{\text{MN}} \). The low \( [\text{CCl}_4]_0 \) condition (B) is only fit by including a non-zero \( k_{\text{ECMN}} \).

A mechanism by which ECMN can occur is not obvious. Because ECMN is additive above MN, the mechanism must occur at inter-ion distances that would not otherwise lead to neutralization. While an \( e^- \) can not effectively remove kinetic energy of the system through collisions, if interaction with the \( e^- \) transfers kinetic energy of the system to the internal modes of the anion (the only readily available energy sink), the rate enhancing effect would be similar. Electrons loosely bound to a dipole have been shown to excite vibrations in the resulting neutral species when leaving the complex.[20] The leaving electron causes a fluctuation in the potential seen by the dipole, resulting in a time-dependent change in the dipole moment (a transition dipole) resulting in some probability of exciting a vibration, much as though a photon was interacting with the system. A similar effect could occur here as a third body electron passes between the anion and cation, shielding the ionic attraction and causing a fluctuation in the potential as the ionic attraction is decreased and then
reestablished. For electrons moving at thermal velocities, the frequency of that fluctuation is on the order of hundreds of cm$^{-1}$, similar to the energy of low frequency vibrations. Although this is entirely speculative, the measured ECMN rate constants do show a correlation with the calculated IR strength of low frequency modes of the anion, as would be expected from the proposed mechanism.

5. Conclusions

A new flowing afterglow technique to study the kinetics of several plasma chemistry processes that are difficult or impossible to measure by other means has been described. The method, variable electron and neutral density attachment mass spectrometry, exploits the higher order chemistry that occurs when an electron attaching neutral species is added to a weakly ionized plasma. Unlike traditional FA methods, which maintain conditions where this other chemistry is negligible simplifying analysis, VENDAMS allows for a wide range of chemistry to contribute and relies on kinetic modeling of the system in order to extract rate constants and product branching fractions from the data. Several types of novel measurements are reported. Rate constants and product branching of electron attachment to unstable radical species along with temperature dependences are reported. Rate constants for mutual neutralization reactions are reported with uncertainties as low as 10%; importantly the measurements do not rely on unreliable determinations of the ion concentrations in the flowtube. The first complete product branching fractions for mutual neutralization reactions are reported. Finally, VENDAMS measurements yielded evidence of a new plasma loss process, electron catalyzed mutual neutralization.

Acknowledgments

This work has been supported by the Air Force Office of Scientific Research. N S S received funding through the National Research Council’s Research Associateship Program.

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