RICE UNIVERSITY

The Effect of Internal Energy on the Lifetime of SF₆ Negative Ions

by

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Abstract

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The lifetimes of SF$_6^-$ ions produced in K(np)/SF$_6$ collisions at high $n$ are being investigated as a function of target temperature over the range 300K to 600K. At room temperature collisions are found to lead predominantly to the formation of long-lived SF$_6^-$ ions with lifetimes $\tau \approx 1$ms. As the target temperature is raised long-lived ($\tau \approx 0.5$ms) ions are still observed but their mean lifetime is reduced. In addition, the growth of a short-lived ion signal ($\tau \leq 10$ $\mu$s) is evident which, by 600K, accounts for $\sim 45\%$ of the total SF$_6^-$ ion signal. These lifetimes are compared with those obtained using quasi-equilibrium theory and calculated SF$_6^-$ vibrational frequencies.
Acknowledgements

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Chapter 1

Introduction

1.1 Electron Attachment to Molecules

Free electrons are present in many different environments: plasmas, atmospheres, inter-stellar space, and irradiated cells to name a few [1, 2]. Also present in these environments are atoms and molecules. Collisions between free electrons and molecules are therefore a common occurrence in nature and understanding these reactions is important for understanding the environments in which they take place. Knowledge of such collisional behavior is also important for many practical applications. For example, the microchip industry makes use of gas-phase electron-molecule collisions to generate free radicals (extremely reactive molecular fragments) which are then used to reactively etch silicon oxide substrates [2, 3]. Many electronegative gases (such as sulfur hexafluoride – the focus of the present study) are used as gaseous dielectrics, for which a quantitative understanding of the effects of temperature on the electron attachment and detachment processes becomes important [4].

Free electron attachment to molecules can lead to reactions of the form:

\[ \rightarrow XY + e^{-}, \]  
\[ e^{-} + XY \rightarrow XY^{--} \rightarrow X + Y^{-}, \]  
\[ \rightarrow XY^{-}. \]

In reaction 1.1.1, the transient negative ion \( XY^{--} \) quickly reverts back to a neutral molecule and a free electron (autodetachment). In reaction 1.1.2, attachment of the electron results in fragmentation of the intermediate ion producing a neutral and a
charged fragment, a process termed dissociative capture. In reaction 1.1.3, the intermediate is temporarily stabilized by internal processes leading to the formation of a long-lived metastable negative ion. This last reaction is of primary interest in the present work and is described briefly as follows.

Low energy electron attachment usually proceeds via a resonance with the neutral molecule, forming a negative-ion resonant state [5]. Unlike bound electrons in a molecule which are characterized by a stationary state, negative-ion resonant states are non-stationary (time dependent) and will decay with a characteristic autodetachment lifetime, τ. It has been shown [5-7] that many large polyatomic molecules capture thermal electrons via a nuclear-excited Feshbach resonance to form long-lived (τ > 10−6s) negative ions. This type of resonance involves the coupling between the kinetic energy of the captured electron and the vibrational degrees of freedom of the molecule. There is no electronic excitation of the target molecule, and the negative ion is produced in a state of high vibrational excitation. If the excess energy (which is comprised primarily of the molecule’s electron affinity, any initial internal molecular vibrational energy, and the kinetic energy of the captured electron) is not removed by radiative or collisional processes, however, the negative ion will ultimately decay through autodetachment.

Immediately following initial resonant capture the excess energy is localized in the attaching mode. This is then redistributed among the many other degrees of freedom, a process termed intramolecular vibrational energy redistribution (IVR). This redistribution of energy prolongs the time required for the metastable negative ion to return to a configuration for which autodetachment is favorable. Consequently, long-lived metastable negative ions formed through a nuclear-excited Feshbach resonance tend
to possess a large number of vibrational degrees of freedom, the lifetime against autodetachment typically increasing with the complexity of the molecule [5].

Though quantitative calculations of the lifetimes of long-lived metastable ions are challenging and depend on the input parameters, simple qualitative statistical arguments predict a decrease in the lifetime as the internal energy is increased. This can be achieved by either increasing the energy of the captured electron or by increasing the vibrational energy of the neutral target.

1.2 Interactions between Neutral Molecules and Rydberg Atoms

As will be discussed in the following sections, Rydberg atoms provide a valuable source of quasi-free low energy electrons. This use has been described in detail theoretically and has been employed experimentally with success for many years [2, 5, 8-12].

1.2.1 Rydberg Atom Properties

A Rydberg atom is an atom with one or more electrons excited to a high principal quantum number \( n \). (The potassium atoms used in the present study have only a single valence electron, so complexities that arise from multi-electron excitation are not introduced.) The physical characteristics of Rydberg atoms differ appreciably from those of atoms in ground or low-lying states. Some of these differences are exemplified in Table 1.1 which lists several atomic properties, the scaling of the property with \( n \), and representative values of the properties at various \( n \). One of the most prominent characteristics of a Rydberg atom is its large physical size. With a mean orbital radius of
\( n^2 a_o \), (where \( a_o \) is the Bohr radius), it is possible to produce atoms with macroscopic dimensions. For example, a hydrogen atom excited to \( n = 1000 \), would have a mean diameter of \( \sim 0.1 \) mm.

<table>
<thead>
<tr>
<th>Property</th>
<th>Scaling (a.u.)</th>
<th>( n = 1 )</th>
<th>( n = 15 )</th>
<th>( n = 30 )</th>
<th>( n = 45 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Radius</td>
<td>( a_o n^2 )</td>
<td>0.053 nm</td>
<td>12 nm</td>
<td>48 nm</td>
<td>107 nm</td>
</tr>
<tr>
<td>Orbital Period</td>
<td>( T_o n^3 )</td>
<td>0.15 fs</td>
<td>0.5 ps</td>
<td>4.1 ps</td>
<td>13.7 ps</td>
</tr>
<tr>
<td>Binding Energy</td>
<td>( \frac{R}{2n^2} )</td>
<td>13.6 eV</td>
<td>60 meV</td>
<td>15 meV</td>
<td>6.7 meV</td>
</tr>
<tr>
<td>Radiative Lifetime</td>
<td>( \tau_o n^3 )</td>
<td>6.78 ns</td>
<td>22.9 ( \mu )s</td>
<td>183 ( \mu )s</td>
<td>618 ( \mu )s</td>
</tr>
</tbody>
</table>

Table 1.1 Properties of Rydberg atoms for selected principal quantum numbers \( n \).

1.2.2 Rydberg Atom-Molecule Collisions

If the principal quantum number of a Rydberg atom is sufficiently high (\( n \gtrsim 10 \)) the separation between the excited electron and the ion core is such that there is little overlap of their wavefunctions. In this situation the atomic behavior can be discussed using the classical Bohr model, and it is in this regime that Rydberg atoms can be employed as electron donors in collisions with molecules. Classically, the excited valence electron can be viewed as being in a distant near-Keplerian orbit around a stationary ion core. If, when a target molecule encounters such a system, the range of the excited electron-target interaction is much less than the atomic dimension, the electron-
molecule interaction time will be short in comparison with the electron orbital period. Thus the Coulomb field from the ion core may be regarded as constant during the electron-molecule interaction. Furthermore, because of the large atomic size, the electron and ion core act as independent scattering objects during collisions with neutral targets. At thermal velocities, the calculated rate constants for electron capture from highly excited Rydberg atoms to polyatomic molecules using this “free” electron model (neglecting the Coulomb attraction between charged collision products) have been shown to be equal to the rate constants for capture of free electrons having the same velocity distribution [8].

Two major factors that influence the lifetime of metastable negative ions are the kinetic energy of the incident electron and the initial internal energy in the target molecule. The use of Rydberg atoms as a source of free electrons allows these two variables to be studied independently. The present experiments are conducted at high-$n$ for two reasons. When $n$ is large the electron is typically captured far from the ion core and the effects of post-attachment electrostatic interactions between the charged collision products are very small. For intermediate values of $n$, the product negative ions are formed in close proximity to the Rydberg core and post-attachment electrostatic interactions can influence both the lifetime of the product negative ions and the number that is observed. The second reason to use high $n$ values is to achieve lower electron energies. The mean kinetic energy of the electron is equal to its binding energy and scales as $1/n^2$. Typical energies range from $\sim100\text{meV}$ at intermediate $n$ values ($n \sim 12$) to just a few $\text{meV}$ at higher $n$ values ($n \gtrsim 30$). By keeping the kinetic energy of the incident
electron small, its contribution to the total excess energy is negligible, allowing detailed study of the influence of internal molecular vibrational energy on negative ion lifetime.

The simplest method of adding internal energy to a molecule is to increase its temperature. However, in many experiments (such as electron swarm studies) the energy distribution of the free electrons is also increased as the target temperature is raised making it difficult to study directly the effect of internal energy on target lifetime. Rydberg atoms provide a controlled temperature-independent source of near mono-energetic low-energy electrons. As stated in [13], the study of long-lived negative ions requires good control and measurement of the temperature and electron energy, and the facility to measure anion lifetimes over a significant range. Indeed, these are the key features of the experiments presented in this work.

1.3 Introduction to $SF_6^-$

The present studies focus on the lifetime of negative ions formed by free electron attachment to Sulfur Hexafluoride ($SF_6$) through collisions with Rydberg atoms. Because of its many uses and a high rate constant for free electron attachment ($\sim 4 \times 10^{-7}$ cm$^3$/s) [14], $SF_6$ has been the subject of numerous negative ion studies over the past several decades, see [2] for an extensive review. Electron collision processes involving $SF_6$ find applications in electrical discharge devices, in plasma etching, and in low-energy electron-scavenging techniques.

At near zero electron energy metastable $SF_6^-$ ions are formed by s-wave attachment, with the electron coupling strongly to the Raman-active $v_1$ symmetric stretch
(or "breathing") mode [15, 16]. It is possible this mode is favored because of the molecule's high degree of symmetry ($O_h$). The energy deposited in this mode is then rapidly redistributed throughout the other modes in the molecule (IVR). The probability that the energy will be reconcentrated in a mode in which autodetachment is favorable is small, leading to the formation of a long-lived metastable negative ion.

Reported lifetimes of $SF_6^-$ vary widely and usually fall into one of two groups depending on the experimental method employed. Time-of-flight techniques typically yield lifetimes of a few tens of microseconds [5, 17-19], while ion-cyclotron and Rydberg atom studies yield lifetimes in the millisecond range [20-23]. Because statistical arguments predict a decrease in negative ion lifetime as the internal energy of the target is increased (as will be shown in the following sections), it is plausible that variations in measured lifetimes can be attributed to differences in the target gas temperature or the mean kinetic energy of the captured electron. Such differences would lead to the population of a different distribution of negative ion states when using different experimental methods.
Chapter 2

Statistical Theory

2.1 Reaction Scheme

A theoretical description of negative ion lifetimes has been proposed [18, 24] based upon the principle of detailed balance and quasi-equilibrium theory (QET). In the context of this statistical treatment the following reaction scheme is considered:

\[ e(E_i) + SF_6(E_{vib}) \xrightarrow{\sigma} SF_6^{*-} (E^*) \xrightarrow{\tau} e(E_f) + SF_6^* (E_{ex}) . \]  
(2.2.1)

In this expression, \( E_i \) represents the initial kinetic energy of the incident electron and \( E_{vib} \) is the internal vibrational energy (above the zero-point energy) of the neutral molecule before attachment. \( E^* \) is the total internal energy of the excited \( SF_6^{*-} \) metastable ion after collisional attachment. Following autodetachment, the electron is ejected with an energy \( E_f \) while \( E_{ex} \) remains in the neutral \( SF_6 \) molecule as internal energy. In this reaction scheme, the lifetime for autodetachment of electrons with a velocity \( \nu \) undergoing unimolecular electron attachment with cross section \( \sigma(\nu) \) is given by

\[ \tau = \frac{\rho_*(E^*)}{\rho_o(E_{ex}, E_f) \nu \sigma(\nu)} , \]  
(2.2.2)

where \( \rho(E^*) \) is the density of states of the reactant negative ion and \( \rho_o(E_{ex}, E_f) \) the density of states of the product electron-molecule system.

Anion lifetime calculations using Eq. 2.2.2 require reliable values for the electron affinity, absolute cross sections for associative electron attachment, and vibrational frequencies for both the neutral molecule and the anion. Recently improved values of
these parameters for the $SF_6^-$ anion have become available, allowing improved calculations compared to those performed previously [18, 24]. The most notable advance comes from new calculated values for the vibrational frequencies of the $SF_6^-$ ion [25, 26] which are supported by recent measurements of the $v_3$ gas-phase vibrational frequency [26, 27]. Prior to their availability lifetime calculations were carried out under the assumption that the anion and neutral frequencies were the same, which (as will be discussed) resulted in anomalously short calculated lifetimes.

Absolute cross sections for electron attachment to $SF_6$ have been reported by several authors [2] and depend strongly on electron energy, $E_t$, varying approximately as the inverse of electron velocity at low energies (consistent with an s-wave capture process). In Rydberg electron transfer (RET) processes the electron velocity is well defined because the time-averaged kinetic energy of the electron is equivalent to its binding energy. The remaining parameters of Eq. 2.2.2 (internal energy and density of states) are discussed in detail the following sections.

2.2 Vibrational Energy

A fundamental assumption of QET is that all of the internal energy of the excited anion is randomized, the total internal energy being simply

$$E^* = EA + E_t + E_{vib},$$

(2.2.3)

where the adiabatic electron affinity, $EA$, is defined as the energy difference between the ground states of the anion and the neutral. Early measurements of the adiabatic electron affinity ranged from 0.0eV to ~1.5eV [2, 5], but the value of 1.05eV [28] has been widely
accepted for more than 20 years. As previously stated, $E_i$ is the energy of the captured electron ($\sim 1$ meV) and contributes negligibly to the total internal energy.

The vibrational energy depends on temperature and can be calculated using basic statistical thermodynamics as can be found in just about any statistical mechanics textbook [29, 30]. The probability that a molecule is in a particular energy state $j$ is given by

$$P_j = \frac{1}{Z} e^{-\frac{E_j}{k_B T}} ,$$

where $E_j$ is the energy of the system when it is in state $j$, $k_B$ is Boltzmann's constant, and $T$ is the temperature of the system. The exponential term in Eq. 2.2.4 is known as the Boltzmann factor and gives the probabilistic weighting of each state. The probability is normalized by dividing by the partition function, which is a sum over all the Boltzmann factors

$$Z = \sum_j g_j e^{-\frac{E_j}{k_B T}} ,$$

where $g_j$ is the degeneracy of the state. (Because the number of molecules is fixed and in constant thermal equilibrium with the environment the partition function is known as the *canonical* partition function.) $E_j$ refers to the vibrational energy of a single mode. Therefore, the total vibrational energy is simply the sum of the energies in each mode

$$E_{\text{vib}} = E_{\nu_1} + E_{\nu_2} + E_{\nu_3} + \cdots$$

In view of this, the total vibrational partition function can be written as

$$Z_{\text{vib}} = (Z_{\nu_1}) \cdot (Z_{\nu_2}) \cdot (Z_{\nu_3}) \cdots = \prod_i^n (Z_i)^{g_i} .$$
where $N$ is the number of vibrational modes. $Z_i$ is the partition function of a single vibrational mode $i$ with degeneracy $g_i$

$$Z_i = \sum_{n=0}^{\infty} e^{-\frac{h\nu_i n}{k_B T}}. \quad (2.2.7)$$

where $h$ is Planck's constant and $\nu_i$ is the frequency of the mode. The total number of vibrational modes in a nonlinear molecule with $m$ atoms is $N = 3m - 6$. Therefore $SF_6$ has 15 vibrational modes (along with 3 rotational and 3 translational modes). Using the series expansion

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

the partition function in Eq. 2.2.6 can be written as

$$Z_{vb} = \prod_i^{N} \left(1 - e^{-\frac{h\nu_i}{k_B T}}\right)^{-g_i}. \quad (2.2.8)$$

The frequencies of the vibrational modes of $SF_6$ are shown in Table 2.1 along with their corresponding degeneracies. The partition function can be used to determine the average vibrational energy as a function of temperature through the relation

$$\langle E_{vb}\rangle = -\frac{\partial}{\partial \beta} \ln(Z_{vb}), \quad (2.2.9)$$

where

$$\beta = \frac{1}{k_B T}.$$ 

As shown in Figure 2.1, the average vibrational energy increases with temperature. Raising the temperature of the molecules from 300K to 600K increases the average vibrational energy from 74meV to 347meV (above the zero-point energy).
<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$ ($A_{1g}$)</td>
<td>774</td>
<td>1</td>
</tr>
<tr>
<td>$\nu_2$ ($E_g$)</td>
<td>642</td>
<td>2</td>
</tr>
<tr>
<td>$\nu_3$ ($T_{1u}$)</td>
<td>948</td>
<td>3</td>
</tr>
<tr>
<td>$\nu_4$ ($T_{1u}$)</td>
<td>616</td>
<td>3</td>
</tr>
<tr>
<td>$\nu_5$ ($T_{2g}$)</td>
<td>525</td>
<td>3</td>
</tr>
<tr>
<td>$\nu_6$ ($T_{2u}$)</td>
<td>347</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 2.1 Vibrational frequencies of SF$_6$ with the corresponding mode degeneracy.

The population in the vibrational ground state can be easily obtained by noting that when $E_{vib} = 0$, the Boltzmann factor goes to 1. Therefore, the probability is simply

$$p_{vib}^{ground} = \frac{1}{Z_{vib}},$$

(2.2.10)

which is ~30% and ~1% at 300K and 600K, respectively.

It should be noted that the rotational energy has not been included in the internal energy calculations. This is justified because the electron attachment is an s-wave capture process ($\ell = 0$), so the resonance between the electron and the molecule is primarily a vibrational coupling.
Figure 2.1 Vibrational energy (above the zero-point energy) in the SF₆ molecule as the temperature is increased.

2.3 Density of States

Lifetime calculations using QET are statistical in nature and depend on the density of states available to the anion compared with the density of states available to the detached electron and neutral molecule. The density of states for the $SF_6^-$ ion, $\rho(E^*)$, is calculated according to the Marcus-Rice approximation as modified by Whitten and Rabinovitch [31]. In this approach, the sum of states $G(E)$ for a molecule with $s$ degrees of freedom and excess internal energy $E$ above the zero-point energy $E_z$ is given by the expression
\[
G(E) = \frac{(E + aE_s)^s}{s! \prod_{i=1}^s h\nu_i}. \tag{2.2.11}
\]

The parameter \(a\) in Eq. 2.2.11 is an empirical factor ranging from 0 to 1 that is used to modify the amount of zero-point energy included in the sum of states calculation. This factor is a function of both the dispersion of the vibrational frequencies and the quantity \(E' = E/E_s\),

\[
a = 1 - \beta \omega(E') \tag{2.2.12}
\]

where

\[
\beta = \frac{s-1}{s} \frac{\langle \nu^2 \rangle}{\langle \nu \rangle^2} \tag{2.2.13}
\]

and

\[
\omega = \begin{cases} 
[5.00E' + 2.73(E')^{0.50} + 3.51]^{-1}, & 0.1 < E' < 1.0 \\
\exp[-2.4191(E')^{0.25}], & 1.0 < E' < 8.0 
\end{cases} \tag{2.2.14}
\]

The value of \(\beta\) varies from about unity for molecules with a narrow spread of vibrational frequencies to about 2 for molecules with a wide distribution of frequencies. For \(SF_6\), which has a relatively narrow frequency distribution, \(\beta = 1.03\).

The density of states can be obtained by differentiating the sum of states with respect to \(E\) leading to the expression

\[
\rho(E) = \frac{(E + aE_s)^{s-1}}{(s-1)! \prod_{i=1}^s h\nu_i} \left[1 - \beta \frac{d\omega(E')}{dE'} \right]. \tag{2.2.15}
\]
When applied to the reactant anion system, Eq. 2.2.15 is a function of the total internal energy, \( \rho(E) = \rho(E^*) \), and the zero-point energy is evaluated using the vibrational frequencies of the negative ion with mode degeneracies \( g_i \),

\[
E_z = \sum_{i=1}^{N} g_i (\frac{1}{2} \hbar \nu_i).
\]

Calculated frequencies for \( \text{SF}_6^- \) [25, 26] are shown in Table 2.2. Apart from the \( v_4(T_{1u}) \) mode there is fairly good agreement between the various computational models, indicating that the calculated frequencies should provide at least a reasonable estimate of the expected negative ion lifetimes. Further credence is given to the calculated anion frequencies by the measured values of \( v_3 \) of 685(5) cm\(^{-1}\) reported by Bopp et al. [25] and 670(10) cm\(^{-1}\) obtained by Steill et al. [26].

<table>
<thead>
<tr>
<th>Computational Approach</th>
<th>( v_1 (A_{1g}) )</th>
<th>( v_2 (E_g) )</th>
<th>( v_3 (T_{1u}) )</th>
<th>( v_4 (T_{1u}) )</th>
<th>( v_5 (T_{2g}) )</th>
<th>( v_6 (T_{2u}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gutsev MP2/6-311+G(s:2df,F:2d)</td>
<td>595</td>
<td>425</td>
<td>686</td>
<td>291</td>
<td>319</td>
<td>225</td>
</tr>
<tr>
<td>Schaefer DZP++ B3LYP</td>
<td>568</td>
<td>423</td>
<td>627</td>
<td>111</td>
<td>313</td>
<td>216</td>
</tr>
<tr>
<td>B3LYP/aug-cc-pVDZ</td>
<td>564</td>
<td>440</td>
<td>645</td>
<td>174</td>
<td>306</td>
<td>213</td>
</tr>
<tr>
<td>B3P86/aug-cc-pVDZ</td>
<td>585</td>
<td>456</td>
<td>666</td>
<td>176</td>
<td>311</td>
<td>218</td>
</tr>
<tr>
<td>CCD/aug-cc-pVDZ</td>
<td>607</td>
<td>474</td>
<td>678</td>
<td>135</td>
<td>319</td>
<td>227</td>
</tr>
<tr>
<td>MP2/aug-cc-pVDZ</td>
<td>606</td>
<td>459</td>
<td>709</td>
<td>305</td>
<td>317</td>
<td>223</td>
</tr>
<tr>
<td>MP2/6-311+G(S:3df,F:2d)</td>
<td>606</td>
<td>424</td>
<td>679</td>
<td>272</td>
<td>323</td>
<td>232</td>
</tr>
<tr>
<td>MP2/6-311+G(3df)</td>
<td>602</td>
<td>422</td>
<td>673</td>
<td>265</td>
<td>323</td>
<td>229</td>
</tr>
</tbody>
</table>

Table 2.2 Calculated frequencies (in cm\(^{-1}\)) for the \( \text{SF}_6^- \) ion with \( \text{O}_h \) symmetry [25,26].

The density of states for the \( \text{SF}_6^- \) + electron product system is determined by the partitioning of the energy available upon autodetachment, \( E^* - EA \), between the internal
energy remaining in the neutral molecule, $E_{ex}$, and the kinetic energy of the detached electron, $E_f$. Since the energy in the product system must equal the available energy,

$$E_{ex} + E_f = E^* - EA.$$  \hspace{1cm} (2.2.16)

Therefore, the sum of states for the product system, $G_o(E)$, can be written as the product of the number of neutral molecular states and the number of free electron states,

$$G_o(E) = G_o(E_{ex} + E_f) = G_n(E_{ex})G_e(E_f).$$  \hspace{1cm} (2.2.17)

The density of states for the product system is obtained by differentiating Eq. 2.2.17,

$$\rho_o(E_{ex}, E_f) = \rho_e(E_f)G_n(E_{ex}) + \rho_n(E_{ex})G_e(E_f).$$  \hspace{1cm} (2.2.18)

However, for the present conditions

$$\rho_e(E_f)G_n(E_{ex}) \gg \rho_n(E_{ex})G_e(E_f),$$

reducing Eq. 2.2.18 to

$$\rho_o(E_{ex}, E_f) = \rho_e(E_f)G_n(E_{ex}).$$  \hspace{1cm} (2.2.19)

The molecular sum of states, $G_n(E_{ex})$, is obtained by Eq. 2.2.11, and the free electron density of states is

$$\rho_e(E_f) = \frac{m_e^2v}{2\pi^2\hbar^3}.$$  \hspace{1cm} (2.2.20)
2.4 Lifetime Calculations

Using the density of states for the product and reactant systems as obtained in section 2.2.3, the expression for the lifetimes of the negative ion given in Eq. 2.2.2 can now be written as

\[
\tau = \frac{2\pi^2 \hbar^3}{m_e^2 v^2 \sigma(v)} \frac{\rho_-(E^+)}{G_n(E_{ex})}.
\]

(2.2.21)

Using Eq. 2.2.21, the lifetimes of \(SF_6^-\) were calculated over the temperature range 300K to 600K. The assumption is made that the energy of the detached electron is equal to the initial electron energy prior to attachment, i.e. \(E_f = E_i\) and \(E_{ex} = E_{vib}\). An increase in temperature results in an increase of \(E_{vib}\) and therefore \(E^+\), causing a growth of both \(\rho_-\) and \(G_n\). The growth of the calculated sum of states is shown in Figure 2.2.

![Figure 2.2](image)

**Figure 2.2** Calculated sum of states, \(G_n(E_{vib})\), for \(SF_6\) as the temperature is increased.
Figure 2.3 Calculated $SF_6^-$ ion lifetimes using the vibrational frequencies listed in Table 2.2 for temperature ranges of (a) 300K to 600K and (b) 480K to 600K.
While $\rho$ also increases, its growth is much less rapid than that of $G_n$ leading to an overall reduction in the calculated anion lifetimes, as shown in Figure 2.3. The different lifetime curves correspond to the different computational methods used to calculate the vibrational frequencies of the anion, listed in Table 2.2. All of the predicted lifetimes demonstrate similar behavior, decreasing rapidly from a few milliseconds at 300K to a few tens of microseconds at 600K.
Chapter 3

Experimental Apparatus

Measurements of negative ion lifetimes are conducted using the apparatus shown schematically in Figure 3.1. Potassium atoms from an effusive beam are excited to a high Rydberg state using the crossed output of an extracavity-doubled ring dye laser. Excitation occurs in the presence of a target gas in a heated interaction region over a temperature range ~300–600K. The interaction region is defined by two resistively heated electrodes which contain small apertures to allow entrance and exit of the laser and potassium beams and extraction of collision products.

Experiments are conducted in a pulsed mode. Following each laser pulse, negative ions formed through collisions are extracted from the interaction region by a pulsed electric field. Depending on the polarity of the field, ions are accelerated either up or down through a series of fine-mesh copper grids. If the ions exit through the upper extraction grid they enter a drift region where their flight time to a position sensitive detector (PSD) is controlled by selectively adjusting the electric potential applied to the meshes. If the ions exit the interaction region through the lower extraction grid they are accelerated through a drift region into a permanent-magnet Penning ion trap where they can be stored for times >100 ms before extraction to the bottom detector. Time-of-flight spectra obtained from the top PSD are used to evaluate ion behavior on short (≤50μs) timescales, whereas the Penning trap is used to determine ion behavior on long (>50μs) timescales. The probability of ion formation following any laser pulse is low and data are accumulated over many laser shots.
Figure 3.1 Schematic of the experimental apparatus.

3.1 Vacuum System

Photo-excitation of potassium atoms in an effusive beam and detection of collision products requires a high vacuum environment. The vacuum system is
comprised of three differentially-pumped stainless steel chambers: the main chamber (which contains the apparatus shown in Figure 3.1), the oven chamber, and the trap chamber. The background pressure in the main chamber is typically $\sim 1 \times 10^{-7}$ Torr. A gas manifold is used to introduce the target gas into the main chamber, the pressure of the gas being controlled by a needle valve. Due to limitations of the detectors, target gas pressures are kept below $\sim 10^{-5}$ Torr.

The potassium beam originates from the oven chamber which is separated from the main chamber by a 0.3mm diameter circular aperture. The small dimension of this aperture provides isolation of the relatively high pressure oven chamber from the main chamber. Both the main chamber and oven chamber are pumped by diffusion pumps. The ion trap is differentially pumped by a turbo molecular pump. The trap is separated from the main chamber by a 1cm diameter entrance aperture to admit the negative ions. The background pressure inside the trap cannot be directly measured; however, it should be less than that of the main chamber considering the low outgassing rate of the materials used to build the trap ($< 10^{-8} \text{ mbar} \cdot \text{L/cm}^2 \cdot \text{s}$) [32].

3.2 Potassium Beam

Alkali metals have a single $ns$ valence electron which can be photoexcited to a high-lying $np$ state. An effusive beam of ground-state potassium atoms is created by heating a 1 g ampoule of potassium metal in a stainless steel oven. The body of the oven is resistively heated to a temperature of 300°C, well above the melting point of potassium (63.38°C). The emerging vapor is collimated by a 0.5 mm exit aperture which is kept 20°C above the temperature of the oven body. This prevents potassium atoms from
condensing on the aperture and clogging the oven. Once the atoms have exited the oven they are further collimated by the 0.3 mm aperture separating the oven chamber from the main chamber. The combination of these two apertures restricts the beam divergence to <1°. A hot wire detector in the main chamber is used to measure the beam density, which is estimated to be \( \sim 10^9 \text{ cm}^{-3} \) in the center of the interaction region.

3.3 Laser System

For potassium, the ionization potential of the 4s electron is 4.34 eV, which corresponds to a wavelength of 286 nm. Photoexcitation of ground-state atoms to the selected np Rydberg levels used in this work requires radiation with wavelengths in the range 286-295 nm. This is obtained by using a frequency-doubled dye laser.

The laser used in this work is a frequency-stabilized Coherent CR699-21 ring dye laser. The use of Rhodamine 6G dye provides a tuning range of \( \sim 560-640 \text{ nm at } \sim 1 \text{ W} \). The dye laser is pumped by 7.5 W of 532 nm light provided by a Coherent Verdi V8\textsuperscript{®} solid state laser. Single frequency operation of the dye laser is achieved through the use of three optical tuning elements: a 3-plate birefringent filter with a passive bandwidth of 380 GHz, a thin etalon with a free-spectral-range (FSR) of 200 GHz, and a thick etalon with a 10 GHz FSR. This combination provides an effective output line width of \( \lesssim 500 \text{ kHz} \) [33].

Though the line width of the CR699-21 laser is sufficiently narrow, the \( \sim 40 \text{ GHz/hr} \) [33] drift of the center frequency is unacceptable. To correct the long-term frequency drift the output of the dye laser is actively stabilized by locking it to a frequency stabilized Helium-Neon (HeNe) laser by the use of a Fabry-Perot etalon. The
dye and HeNe beams are superposed and directed through the etalon which is scanned at 50 Hz using a piezoelectric transducer. As the length of the cavity changes, two series of transmission peaks are detected corresponding to the resonant frequency of each of the input lasers. Any deviation in frequency by the dye laser will result in a shift of its transmission peak relative to the HeNe laser, i.e., in the peak separation. The difference in relative peak spacing is used to generate an error signal which then returns the dye laser to its original frequency. This active stabilization reduces the long-term frequency drift of the dye laser to <1 MHz/day [34].

The frequency-stabilized output of the dye laser is directed into a Spectra-Physics WAVETRAIN® tunable frequency doubler. The beta-Barium Borate (BBO) crystal inside the WAVETRAIN® utilizes nonlinear second harmonic generation to produce an output beam at twice the frequency of the input beam. The BBO crystal is cut for optimum phase matching of 600 nm light. The active stabilization of the WAVETRAIN® keeps the resonator cavity locked to the input frequency as it is scanned providing a tunable frequency-doubled output. Typical conversion efficiencies are ~5–10%, giving an output power in the range of 50-100 mW.

The continuous output of the WAVETRAIN® is chopped into pulses of duration ~150 ns–2 μs using an acousto-optic modulator (AOM). The pulsed light then enters the main chamber through a quartz window oriented at Brewster's angle.

3.4 Interaction Region

The interaction region is comprised of two resistively heated electrodes separated by ~1 cm which enclose a cylindrical volume measuring ~5 cm in diameter. Apertures
are cut into the sides of the electrodes to allow entrance and exit of the crossed laser and potassium beams. Apertures covered with fine mesh copper grids in the top and bottom of the interaction region allow extraction of charged collision products. Target gas can freely enter the interaction region because it is open to the main chamber; however, the sizes of the apertures are kept small to help maintain thermal equilibrium between the target gas and the walls of the interaction region. (As a consequence of the small apertures, Rydberg atoms begin to pass out from under the extraction aperture ~6 μs after their formation.) Few collisions are needed for most large polyatomic molecules to reach thermal equilibrium. For SF₆, which has a thermal accommodation coefficient of 0.77 [35], (translational) thermal equilibrium with the walls is reached within 2 or 3 collisions, see Figure 3.2.

Figure 3.2 Calculated increase in target SF₆ temperature vs. collisions with the walls of the interaction region heated to 600K.
Target gas pressure is measured using an ion gauge connected to the main chamber. It is important to note, however, that a difference in temperature between the gas in the interaction region and the gas in the main chamber will result in a difference in the relative densities as well (a phenomenon known as thermal transpiration). The ratio of the densities is given by:

\[
\frac{\rho_{IR}}{\rho_{Ch}} = \sqrt{\frac{T_{Ch}}{T_{IR}}},
\]

(3.4.1)

where the subscripts \( Ch \) and \( IR \) refer to the main chamber and the interaction region, respectively. Water-cooled plates are placed a short distance (~1 cm) from the top and bottom of the interaction region to prevent heating of the rest of the apparatus.

Excitation of Rydberg atoms occurs in the center of the interaction region where collisions with target gas can lead to formation of negative ions through dissociative and non-dissociative electron capture. Ions are created in either zero field or a uniform dc electric field in the interaction region. When collisions occur in zero electric field Rydberg atoms are allowed to interact with the target gas for times ranging from ~150 ns to ~2 µs before any collision products are extracted from the interaction region. However, when collisions take place in a uniform dc field the product ions immediately begin acceleration en route to exiting the experimental volume.

3.5 Time-of-Flight Spectrometer

A time-of-flight spectrometer is used to analyze the decay of metastable negative ions on timescales of a few tens of microseconds. The spectrometer is located above the interaction region, as shown in Figure 3.1. Ions are extracted upward into the top drift
region where they pass through a series of apertures containing fine mesh copper grids which isolate the fields in the different drift regions. Charged particles are detected upon exit from the spectrometer by a position sensitive detector (PSD). The PSD is comprised of two microchannel plates and a resistive anode which supplies position information. The PSD has an approximately circular active area with a ~25 mm diameter. The arrival time distribution of the signal is used to determine the decay (or build up) of the ion population, whereas the position distribution is used to ascertain various properties of the ion flight path (focusing, clipping, etc.).

3.6 Permanent-Magnet Penning Trap

To measure lifetimes on timescales longer than a few tens of microseconds the ions are stored in a trap for a controlled amount of time whereupon those that survive are extracted and detected by the bottom PSD. The trap used in the present work is a Penning trap comprised of cylindrically symmetric electrodes immersed in a uniform magnetic field. The trap can be used to store ions for times >100ms, providing a useful tool for the measurement of long-lived ion lifetimes.

3.6.1 Ion Motion in an Ideal Penning Trap

In an ideal Penning trap, the electrode surfaces are revolved hyperboloids contained in a uniform magnetic field pointing along the axis of revolution (defined to be the z axis). A cross section of this configuration is shown in Figure 3.3. For trapping negative ions, the end cap electrodes are negatively biased with respect to the ring electrode. This provides axial confinement of the ions which oscillate harmonically
along the axis of the trap. Since the ions move in a magnetic field they also experience cyclotron motion as they oscillate [36]. The near-circular cyclotron orbit results in ion confinement in the radial direction. The crossed electric and magnetic fields, however, also introduce another motion, magnetron motion. The superposition of the magnetron motion and the cyclotron motion is shown in Figure 3.4.

The magnetic field in the trap is simply $B = B_0 \hat{z}$, whereas the electric field is defined as $E = -\nabla \Phi$, with the scalar potential given by:

$$\Phi(x, y, z) = \frac{V_0}{2z_0^2 + r_0^2}(2z^2 - x^2 - y^2),$$

(3.6.1)
where $2z_0$ is the separation of the end cap electrodes, $r_0$ is the radius of the ring electrode, and $V_0$ is the potential difference between the end cap and ring electrodes [37]. A charged particle moving in this configuration experiences a Lorentz force,

$$F = qE + q(v \times B)$$  \hspace{1cm} (3.6.2)

The motion of the particles is described by the Newtonian equations, $F = ma$, which can be explicitly written as:

$$\ddot{x} - \omega_c \dot{y} - \frac{1}{2} \omega_2^2 x = 0,$$  \hspace{1cm} (3.6.3)

$$\ddot{y} - \omega_c \dot{x} - \frac{1}{2} \omega_2^2 y = 0,$$  \hspace{1cm} (3.6.4)

$$\ddot{z} + \omega_2^2 z = 0,$$  \hspace{1cm} (3.6.5)

The equations of motion are in terms of the axial frequency,
\[ \omega_z = \sqrt{\frac{4qV_0}{m(2z_0^2 + r_0^2)}} \]  

(3.6.6)

and the cyclotron frequency,

\[ \omega_c = \frac{qB_0}{m}, \]  

(3.6.7)

where \( q \) and \( m \) are the charge and mass of the trapped particle, respectively. From these equations it is apparent that the axial motion in the \( z \) direction is decoupled from the motion in the \( x-y \) plane. However, the coupling of the cyclotron and magnetron oscillations lead to a modified cyclotron frequency,

\[ \omega_c = \frac{1}{2}(\omega_c + \sqrt{\omega^2_c - 2\omega_z^2}) \]  

(3.6.8)

with the modified magnetron frequency written as

\[ \omega_\perp = \frac{1}{2}(\omega_c - \sqrt{\omega^2_c - 2\omega_z^2}). \]  

(3.6.9)

Not all values for the applied electric and magnetic fields will result in stable trapping of the ion. Since the frequencies must be real-valued numbers, it is evident from the expressions for \( \omega_\perp \) and \( \omega_c \) that the trapping condition is

\[ \omega^2_c - 2\omega^2_z > 0. \]  

(3.6.10)

Typical trapping conditions are such that

\[ \omega_\perp \approx \omega_c \gg \omega_z \gg \omega_\perp. \]  

(3.6.11)

By substituting the definitions of \( \omega_c \) and \( \omega_\perp \) into Eq. 3.6.10 the trapping condition can be written in terms of experimental parameters as

\[ V_0 < \frac{B_0^2 qd_0^2}{2m}, \]  

(3.6.12)
where \( d_0 \) is the characteristic trap dimension defined as \( d_0^2 = \frac{1}{4}(2z_0^2 + r_0^2) \). Table 3.1 lists several masses with the associated maximum applied trapping voltage. The limiting voltages assume \( d_0^2 = 12.4 \text{cm}^2 \) and \( B_0 = 0.3 \text{T} \).

<table>
<thead>
<tr>
<th>Mass (amu)</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5346</td>
</tr>
<tr>
<td>50</td>
<td>107</td>
</tr>
<tr>
<td>100</td>
<td>53</td>
</tr>
<tr>
<td>150</td>
<td>36</td>
</tr>
</tbody>
</table>

Table 3.1 Maximum trapping voltages of selected masses. The listed voltage refers to the potential difference between the end cap and ring electrodes.

3.6.2 Cylindrical Penning Traps

The hyperbolic electrodes of an ideal Penning trap are difficult to realize in the laboratory; however, a suitable substitution can be made by using planar end cap electrodes and a cylindrical ring electrode. This design has been implemented in the present trap.

In a cylindrical Penning trap with a ring electrode radius of \( r_0 \) and an end cap separation of \( 2z_0 \), the electric potential near the center of the trap can be expanded in terms of even-ordered Legendre polynomials, \( P_k(\cos \theta) \), as [32, 38, 39]

\[
V(r, \theta) = \frac{1}{2} V_0 \sum_{k, m=0}^{\infty} D_k \left( \frac{r}{d_0} \right)^k P_k(\cos \theta)
\]

(3.6.13)

where \( V_0 \) is the potential difference between the end caps and the ring electrode, and \( d_0 \) is the characteristic trap dimension defined in section 3.6.1. The expansion coefficients \( D_k \) can be written as a series expansion of Bessel functions,

\[
D_k = \frac{(-1)^{\frac{k+1}{2}} \pi^{k-1}}{k! 2^{k-3}} \left( \frac{d_0}{z_0} \right)^k \sum_{n=0}^{\infty} \frac{(-1)^n (2n + 1)^{k-1}}{J_0(i \pi (n + \frac{1}{2}) \frac{z_0}{z_0})}.
\]

(3.6.14)
In a purely quadrupole field (as in an ideal trap) $D_2$ would be the only surviving term in the expansion of the electric potential in 3.6.13. However, in a cylindrical geometry other surviving terms must be taken into account. Excepting $D_0$, which is negligibly small, the lowest order coefficients are most important, since $r \ll d_0$. $D_2$, the quadrupole term, relates the axial oscillation frequency $\omega_z$ for a trapped particle of charge $q$ and mass $m$ to the trapping potential $V_0$ [32, 39]:

$$\omega_z = \sqrt{\frac{qV_0}{md_0} D_2}.$$  \hspace{1cm} (3.6.15)

![Figure 3.5](image)

**Figure 3.5** Ratio of the dominant anharmonic term, $D_4$, to the quadrupole term, $D_2$, in the polynomial expansion of the trapping potential.

The higher order coefficients describe the anharmonicities in the trap, the most dominant term being $D_4$. The presence of $D_4$ introduces an energy-dependent shift in the axial frequency
\[
\frac{\Delta \omega_z}{\omega_z} = \frac{3}{2} \frac{E_z}{m \omega_z^2 d_0^2} \frac{D_4}{D_2},
\]

where \(E_z\) is the axial energy and \(m \omega_z^2 d_0^2\) is the axial well depth. The ratio of the axial energy to the well depth is typically very small; therefore, the size of the anharmonicity is largely determined by the ratio of \(D_4\) to \(D_2\). Figure 3.5 shows a graph of \(\frac{D_4}{D_2}\) as a function of \(\frac{a}{z_0}\), which goes to zero when \(\frac{a}{z_0} \approx 1.2\). In the present trap \(r_0 \approx 1.05z_0\), suggesting that trap anharmonicities should be minimal.

Simulations of ion behavior in the cylindrical trap were carried out using SIMION 3D v7.0, a three-dimensional electrostatic lens analysis program developed at the Idaho National Engineering Laboratory. Simulations of an ion of mass 146 amu (corresponding to that of \(SF_6\)) under typical trapping conditions of +3 V on the ring electrode and -5 V on the top and bottom end cap electrodes are shown in Figure 3.6. The graphs show (a) the kinetic energy, (b) the electric field at the location of the ion, (c) the electric potential at the location of the ion, (d) the velocity of the ion, and (e) the position of the ion as a function of time (injection into the trap occurs 48\(\mu\)s after ion creation).
Figure 3.6 Simulated ion properties under typical trapping conditions.
3.6.3 Trap Design and Operation

Penning traps require the use of a strong uniform magnetic field. Fields of this nature are often created using a specific geometry of current-carrying wire, such as a solenoid. Many of the complexities of such an arrangement can be simplified by using permanent magnets to produce the desired field. The Penning trap in the current experiments employs a series of rare-earth-permanent-magnets (REPMs) which have a number of favorable properties. Specifically, REPMs have very large intrinsic magnetic moments per unit volume along with a high resistance to demagnetization by external or internal fields [40]. Consequently, REPMs can be shaped into a variety of arrangements which would cause demagnetization in traditional magnets. This makes it possible, through the use of cladding magnets, to construct a geometry of permanent magnets which produces a strong uniform magnetic field inside a desired volume while limiting the stray fields outside this region.

![Cross section of the trap electrodes.](image)

Figure 3.7 Cross section of the trap electrodes.
In the present apparatus, the trap electrodes are comprised of a cylindrical copper ring of radius \( r_0 = 4.2 \text{ cm} \) with planar end disc electrodes separated by \( 2z_0 = 8.0 \text{ cm} \), see Figure 3.7. The end disc electrodes have 1 cm diameter apertures which contain fine mesh grids (70 lines per inch) to allow ions to be injected into and extracted from the trap. These electrodes are immersed in a 0.3T magnetic field provided by an arrangement of seven NdFeB REPMs and two iron discs. Each of the magnets have a radial symmetry and is magnetized in the direction indicated in Figure 3.8.

![Figure 3.8 Magnetization of the cladding magnets surrounding the trap electrodes.](image)

The magnetic field inside the trap is provided primarily by the central cylindrical magnet. Magnetic equipotential surfaces are created at either end of the trapping volume by a set
of iron discs, and the remaining cylindrical and conical cladding magnets aid in confinement of the field.

Because the voltages required for trapping ions also precludes their entrance into the trap, the top and bottom electrodes are connected to fast voltage switches. When the ions are created, the bottom electrode is biased negative, while the entrance grid is positively biased to help draw them into the trap. When the ions are near the center of the trap the bias on the entrance grid is switched from positive to negative, providing axial confinement of the ions. Once the trap has been closed a series of short (~500 ns duration) extraction pulses is applied to the top electrode to remove any free electrons produced by autodetachment. These pulses, which do not affect the trap's heavy ion storage characteristics, prevent negative ion formation in the trap through free electron attachment to any residual target gas. Ions are extracted from the trap by the application of a large positive voltage to the bottom electrode.

3.6.4 Detached Electron Behavior in the Trap

When a free electron is produced in the trap through autodetachment there is a possibility of reforming a negative ion through reattachment. At the low pressures in the trap (<$1 \times 10^{-7}$ Torr), the period of the free electron extraction pulses is sufficiently short (~15 $\mu$s) to prevent attachment to another molecule present in the trap. However, because the period of the cyclotron motion in the trap (~0.1 ns) is short, the possibility of the autodetached electron revisiting its parent molecule and being reattached must be examined.
The electric field from the detached electron induces a dipole moment in the parent molecule. The electron is then in the presence of both an electric field from the trap electrodes and a dipole field from the molecule. The magnitude of the induced dipole field depends on the molecule’s polarizability, \( \alpha \),

\[
E_{\text{dip}} = 2\alpha \frac{k^2 q}{r^5},
\]

(3.6.17)

where, \( k = (4\pi\varepsilon_0)^{-1} \), \( q \) is the electron charge, and \( r \) is the electron-molecule separation. Figure 3.9 shows the induced dipole field for \( SF_6 \), which has a polarizability of \( 44.1 \ a_0^3 \).

![Figure 3.9 Induced dipole field of \( SF_6 \).](image)

The values of \( r \) in Figure 3.9 are chosen such that the dipole field is approximately of the same magnitude as the field produced by the trap electrodes (as shown in Figure 3.6b). The diameter of the cyclotron orbit of a free electron with an energy of 1 meV in a 0.3 T magnetic field is 7114 \( \text{Å} \), resulting in average electron-molecule separation of \( r_{\text{rms}} = \)
5030Å. At these distances the dipole field is negligible and we consider only the electric fields from the trap electrodes.

The electric field in the trap causes an axial displacement of a free electron in addition to the cyclotron orbit, producing a helical motion. Because the electric field is not constant throughout the trap, there are two primary regimes to which we direct our attention: maximum field and zero field. The electric field is at a maximum at the turning points of the axial oscillation where the ion velocity is \( \sim 0 \text{ m/s} \), see Figure 3.6. If the electron undergoes autodetachment at these points the molecule, which is now neutral, feels no influence from the electric and magnetic fields. However, in one cyclotron orbit the electron experiences an axial displacement

\[
z = \frac{2\pi^2 mE}{qB_0^2},
\]

(3.6.18)

where \( E \) is the electric field in the trap. Under typical trapping conditions this amounts to a distance of \( \sim 1200 \text{ Å} \), which is much greater than the radius of the electron capture cross section for \( SF_6 (\sigma \sim 25 \text{ Å}) \) at electron energies of \( \sim 1 \text{ meV} \).

In the center of the trap the electric field is near zero and the ion velocity is at a maximum. An electron that detaches at this point still experiences a helical trajectory because it has a nonzero velocity (resulting from the \( \sim 1 \text{ meV} \) dissociation energy). In order for recapture to occur, the \( z \)-component of the velocity (which is parallel to the magnetic field) must be sufficiently small for the axial displacement during the cyclotron orbit to be within the radius of the capture cross section,

\[
v_z \leq \frac{\sigma}{T}.
\]

(3.6.19)
For $SF_o$, this corresponds to $v_z \approx 25 \text{ m/s}$. An electron released with an energy of 1 meV has a velocity of $\sim 2 \times 10^4 \text{ m/s}$, resulting in a $\sim 0.14^{\circ}$ spread of velocities which revisit the molecule within its capture radius. Assuming an isotropic electron velocity, the probability of a detached electron having a velocity suitable for reattachment is <0.1%.

### 3.7 Data Acquisition System

In addition to the installation of a new interaction region, a significant portion of the effort in this work went towards upgrading the data acquisition (DAQ) system. The implementation of the new DAQ system provides increased flexibility and convenience during both data acquisition and analysis.

Previously, data had been acquired using a Macintosh Quadra 800 system interfaced with a CAMAC (Computer Automated Measurement and Control) bus. Ion arrival time information was gathered and returned to the computer by a quad-event timer mounted in the CAMAC rack, which was limited to a collection window of 41 $\mu$s. The DAQ program, written in C, triggered a Stanford Research Systems (SRS) DG535 pulse generator which controlled the timing sequence of the experiment.

The new data acquisition system implements a LabVIEW-based program on an IBM ThinkCentre® PC with a 3.20GHz Pentium 4 processor and 2GB of RAM running on a WindowsXP platform. The pulse sequence is provided by firmware encoded on a field programmable gate array (FPGA) chip. Simply stated, an FPGA is a semiconductor device containing programmable logic components and interconnects. The elements on the chip can be programmed to duplicate the functionality of simple logic components (AND gates, OR gates, etc.) or even more complex operations such as decoders and
simple math functions. The National Instruments PCI-7831R board utilizes the Xilinx Vertex® series FPGA chip on NI reconfigurable input/output (RIO) hardware providing 8 analog inputs, 8 analog outputs, and 96 digital input/output pins. In the current experiments, the FPGA (among other tasks) is programmed to control the pulse sequence to the apparatus. Each pulse is sent to a different output on the chip, providing truly parallel operation.

Timing information is collected using the National Instruments PCI-6602 Counter/Timer card. The card has 8 independent 32-bit counters with an 80MHz clock, providing a resolution of 12.5ns over a possible 53s collection window. As indicated by their product numbers, both the FPGA and timing boards are seated on the PCI bus of the computer. A control flow diagram for the DAQ system can be found in the Appendix.
Chapter 4

Lifetime Measurements

4.1 Experimental Procedure

Metastable $SF_6^{-*}$ ions are created through collisions between $SF_6$ molecules and 30p and 45p Rydberg atoms. The Rydberg atoms are created in the presence of $SF_6$ target gas ($\rho \approx 10^{10} - 10^{11} \text{ cm}^{-3}$) near the center of a heated interaction region. The influence of target temperature on $SF_6^{-*}$ lifetime was studied over the temperature range 300K to $\sim$600K, which corresponds to an increase in vibrational energy from 74meV to $\sim$350meV. The vibrational energies over these temperatures are large compared to the mean kinetic energy of the captured Rydberg electron, which is $\sim 3(1.3)$ meV at $n = 30(45)$.

To examine the behavior of $SF_6^{-*}$ ions on the timescale of a few tens of microseconds, negative collision products were directed into the upper drift region and their arrival time distribution at the top position sensitive detector (PSD) was observed. Position data are used to confirm that all ions are collected independent of their initial velocity. Typical position data are shown in Figure 4.1. Signals associated with free electrons produced by photoionization from blackbody radiation were identified through measurements with no target gas and are subtracted. For measurements at $n = 30$, ions
were created in the presence of a small $\sim 5$–$10$ V/cm dc electric field in the interaction region. This causes the ions to begin acceleration out of the interaction region at the time of formation. However, because of Stark effects, the presence of such a field at $n = 45$ greatly reduces Rydberg atom production. Consequently, atoms were excited to $n = 45$ in zero field and the extraction field was applied immediately following the $\sim 150$ ns laser pulse. Ion flight time to the upper PSD was controlled by adjusting the bias on the meshes in the drift region.

To examine the lifetime of $SF_{6}^{-*}$ ions on timescales greater than that of the flight time to the top PSD, ions were directed into the lower drift region and injected into the Penning trap where storage times can be in excess of 100 ms. Excitation of atoms to both $n = 30$ and $n = 45$ in the interaction region occurred in zero field. Following a $\sim 2$ μs laser
pulse, collisions were allowed to take place for \( \sim 1 \) \( \mu \)s before extraction into the lower drift region by a small (<5 V/cm) electric field. The entrance grid to the trap was maintained at a positive bias (\( \sim +20 \)V) during the ion’s flight through the drift region to allow entrance into the trap. At a selected time the bias to the entrance grid was switched from positive to negative, trapping the ions until an extraction pulse (typically +200–400V) applied to the exit grid accelerated them towards the lower PSD. Using the trap, detection times at the PSD were varied from \( \sim 75 \) \( \mu \)s (straight through the trap) to >5 ms.

Because the PSDs have a “dead time” of \( \sim 10 \) \( \mu \)s following detection of an ion, the probability of detection is kept low, \(< \sim 0.1\), and data are accumulated over thousands (or even millions) of laser pulses.

### 4.2 Time-of-Flight Spectra

Using the time-of-flight spectrometer located above the interaction region, arrival time distributions at the upper PSD for ion products following K(30p)/\( SF_6 \) and K(45p)/\( SF_6 \) collisions at room temperature were recorded and are shown in Figure 4.2. The spectra show sharp increases in the measured signal at flight-times corresponding to those anticipated for \( SF_6^- \). Following these onsets the ion signals decay exponentially, emulating the decay of the Rydberg atom population in the interaction region. However, this decay becomes much more rapid at later times as the Rydberg atoms begin to move from under the extraction aperture. Because excitation to the \( n = 45 \) state occurs in zero field, product ions resulting from collisions prior to the pulsed extraction field accumulate in the interaction region. These appear in the time-of-flight spectra as a sharp peak at the onset of the ion signal. Inspection of Figure 4.2 provides no evidence of a
significant decrease in the size of the onsets associated with the arrival of $SF_6^-$ ions for flight times in the range $\sim18-32 \mu s$, indicating that product ions are very long-lived ($\tau \gg 30 \mu s$). The observation of only long-lived $SF_6^{-\ast}$ ions following room-temperature collisions is consistent with earlier Rydberg atom measurements [41].

![Graphical representation](image)

**Figure 4.2** Time-of-flight spectra of collision products between $SF_6$ and K(30p) (a, b) and K(45p) (c, d) at 300K.

Significant differences in the arrival time distribution are observed when the interaction region is heated. Figure 4.3 shows the time-of-flight spectra for product ions following K(30p)/$SF_6$ and K(45p)/$SF_6$ collisions at 300°C ($\sim573K$). The most prominent difference between the room temperature and high temperature spectra is the growth of the early-time signal at high temperatures. This signal initially grows with time and does
Figure 4.3 Time-of-flight spectra of collision products between $SF_6$ and K(30p) (a, b) and K(45p) (c, d) at 573K.

not simply follow the exponential decay of the Rydberg atom population. This indicates that it is associated with the collection of electrons resulting from the decay of short-lived $SF_6^-$ ions while still in the interaction region or enroute to the PSD. (Ancillary tests indicated that, for the present operating conditions, the PSD detects $SF_6^-$ ions with an efficiency $\sim 75\% - 80\%$ that of electrons.) Though these short-lived ions have a range of lifetimes, an estimate of a representative value can be obtained by assuming a single lifetime, $\tau$. With this assumption, the time evolution of the parent Rydberg atom population, $N^*$, and short-lived $SF_6^-$ ion population, $N_{\text{short}}$, is described by
\[
\frac{d}{dt} N^* = -\frac{N^*}{\tau_{\text{eff}}}
\]  

(4.2.1)

and

\[
\frac{d}{dt} N_{\text{short}} = N^* \rho k_{\text{short}} - \frac{N_{\text{short}}}{\tau}
\]

(4.2.2)

where \( \rho \) is the target gas density and \( k_{\text{short}} \) is the rate constant for the formation of short-lived \( \text{SF}_6^- \) ions. The lifetime of the parent Rydberg population is described by an effective lifetime, \( \tau_{\text{eff}} \), because it is reduced from that of the natural lifetime of the Rydberg state through collisions with the target gas. This effective lifetime can be obtained directly from the data as the initial decay of the ion signal, which mirrors the decay of the parent Rydberg atoms. Solving the coupled 1st-order differential equations in (4.2.1) and (4.2.2) provides the short-lived \( \text{SF}_6^- \) ion population as a function of time,

\[
N_{\text{short}}(t) = N^*(0) \frac{\rho k_{\text{short}}}{1/\tau_{\text{eff}} - 1/\tau} \left( e^{-t/\tau} - e^{-t/\tau_{\text{eff}}} \right).
\]

(4.2.3)

Fits of the this function to the early-time signal in several different high temperature time-of-flight spectra yield lifetimes in the range of 1 – 10 \( \mu \)s.

The total rate constant for the formation of \( \text{SF}_6^- \) ions can be written as the sum of the rates for the formation of short and long-lived ions

\[
k_{\text{total}} = k_{\text{short}} + k_{\text{long}}.
\]

A fit to a typical data set at 573K produces rate constants of \( k_{\text{long}} = 2.03 \times 10^{-7} \text{cm}^3/\text{s} \) and \( k_{\text{short}} = 1.89 \times 10^{-7} \text{cm}^3/\text{s} \), which is in good agreement with the accepted value for the total rate constant (for a 1 meV electron) of \( k_{\text{total}} = \sim 4 \times 10^{-7} \text{cm}^3/\text{s} \) [14]. From the rate constant
fits it is evident that formation of short-lived $SF_6^-$ ions accounts for $k_{\text{short}}/k_{\text{total}} \approx 48\%$ of the total ion signal at 573K.

![Graph showing ion signal versus arrival time at different temperatures](image)

**Figure 4.4** Time-of-flight spectra for collision products following K(30p)/$SF_6$ collisions at selected temperatures.

A more direct approach to determining the ratio of short-lived ions to the total ion production is to simply take the ratio of counts recorded at the PSD before the onset of the $SF_6^-$ ion arrival (adjusted for the variation in detection efficiency between electrons and ions) compared to the total number of counts. Figure 4.4 shows a composite of the time-of-flight spectra for collision products following K(30p)/$SF_6$ collisions at selected temperatures. Though the attachment rate of low energy free electrons to $SF_6$ does not vary significantly over the temperature range 300K – 600K [2, 42, 43, 44], the total

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measured ion signal decreases with temperature because the target density in the interaction region decreases with temperature due to thermal transpiration.

![Graph showing the fraction of total signal against temperature](image)

**Figure 4.5** Growth of the ratio of short-lived $SF_6^-$ ions to the total ion signal with increasing temperature.

As illustrated in Figure 4.5, the short-lived ion signal grows rapidly with temperature above $\sim 300K$. By 600K the short-lived component accounts for $\sim 44\%$ of the total $SF_6^-$ ion production, which is within error of the value obtained from comparing the fitted rate constants at $T = 573K$.

Inspection of the time-of-flight spectra in Figure 4.3 provides another difference between the arrival time distributions following collisions at room and high temperatures. At 573K the onsets in the long-lived ion arrival features occur with two distinct thresholds, a larger peak preceded by a smaller peak. The first peak is attributed to
collection of $\text{SF}_3^-$ ions produced by dissociative capture (reaction 1.1.2). In this reaction, capture of the electron results in fragmentation of the intermediate $\text{SF}_6^-$ ion producing a neutral fluorine atom and an $\text{SF}_3^-$ ion.

Measurements of the $\text{SF}_3^-$ and $\text{SF}_6^-$ step heights at the onset of the ion signals (which are proportional to the total number of ions that survive to the PSD) indicate that the $\text{SF}_3^-$ ions, which are known to be stable, account for ~30\% of the long-lived negative ion signal at 573K. Similar step height measurements were carried out at various temperatures and the ratio of the $\text{SF}_3^-$ signal to the total ion signal with increasing temperature is shown in Figure 4.6.

![Graph showing the ratio of the $\text{SF}_3^-$ signal to the total ion signal with increasing temperature.]

**Figure 4.6** Ratio of the $\text{SF}_3^-$ signal to the total ion signal measured on the top detector with increasing temperature.
The growth of the $SF_5^-$ signal was also examined using the lower PSD by allowing ions to pass directly through the Penning trap. The longer flight path through the trap provides better time resolution between the two ion species, as shown in Figure 4.7.

![Arrival time graph](image)

**Figure 4.7** Separation of the $SF_5^-$ and $SF_6^-$ ion signals at the lower PSD after passing through the Penning trap for a target temperature of 573K.

With adequate separation, the ratio of the two populations can be obtained by comparing the relative areas of the two peaks. The absolute growth of the $SF_5^-$ ion signal from measurements obtained using the top and bottom PSDs is displayed as an Arrhenius plot in Figure 4.8. The two methods indicate activation energies of 286 meV and 378 meV, which is consistent with the range of values (120 meV – 430 meV) reported by other low pressures experiments [13, 44, 45, 46].
Figure 4.8 Arrhenius plot of the $\text{SF}_5^-$ signal obtained on the top and bottom detectors. The solid and dashed lines correspond to exponential fits and indicate activation energies of 286meV and 378meV, respectively. The two curves are normalized to the highest temperature data point.

Measurements of the step height from the (stable) $\text{SF}_5^-$ peak to the $\text{SF}_6^-$ peak indicate that, even at target gas temperatures of ~600K, many product ions are still very long-lived, $\tau >> 30 \, \mu s$. The lifetime of these long-lived ions was studied using the Penning trap.

4.3 Trapped Population Data

The Penning trap was used to examine the decay of long-lived $\text{SF}_6^-$ ions on timescales greater than that of the flight time to the top PSD. At higher temperatures
stable $SF_5^-$ ions are also produced and injected into the trap, and their contribution to the trapped population, shown in Figure 4.9, is subtracted from the long-lived ion signal.

![Graph showing the fraction of trapped population vs. temperature](image)

**Figure 4.9** Temperature dependence of the ratio of the $SF_5^-$ signal to the long-lived signal as measured using step heights on the top PSD and ion counts on the bottom PSD.

The time evolution of the $SF_6^{**}$ population in the trap following K(45p)/$SF_6$ collisions is shown in Figure 4.10 for selected target gas temperatures in the range 300K – 423K. Ion populations are normalized to the signal obtained at the earliest extraction time. As with the short-lived ion signal, the decay of the long-lived ion signal is not characterized by a single exponential, rather the data indicate a range of lifetimes. At 300K the lifetimes extend from $\sim$1 ms to >10 ms. The longer lifetimes, however, are most likely influenced by radiative stabilization. The rate of decrease in the ion population at room temperature is consistent with previous Rydberg atom studies.
involving the Penning trap [41]. Heating the interaction region leads to a decrease in the average lifetime of the long-lived ions, the shortest lifetimes extending down to \(~\)400 \(\mu\)s.

**Figure 4.10** Time evolution of the (trapped) long-lived SF\(_6^-\) population at 300K (\(\triangle\)), 330K (\(\circ\)), 373K (\(\bullet\)), and 423K (\(\bullet\)). The solid lines indicate exponential decay corresponding to lifetimes of 400 \(\mu\)s and 1 ms.
The trapped long-lived ion population shows no significant decrease in measured lifetimes as the temperature is further increased from 423K to 623K, as shown in Figure 4.11. Interestingly, the temperature range over which the trapped ion population shows significant reduction in lifetime, 300K – ~450K, is very similar to the range over which the growth of the short-lived ion signal is most rapid.

![Graph showing normalized ion signal vs. arrival time](image)

**Figure 4.11** Time evolution of the (trapped) long-lived $\text{SF}_6^-$ population at 423K (●), 493K (○), 573K (•), and 623K (▼).

It has been shown [47] that metastable negative ions created through Rydberg electron transfer (RET) can have increased lifetimes at low $n$. This is due to post-attachment interactions between the product $\text{K}^+$ and $\text{SF}_6^{-*}$ ions in which internal energy is transferred from the $\text{SF}_6^{-*}$ ion to translational energy of the product ion pair. These interactions, however, become negligible for $n \gtrsim 30$. The influence of target temperature
on post-attachment interactions was examined by observing the trapped ion population following K(12p)/SF₆ collisions.

![Graph](image)

**Figure 4.12** Time evolution of the SF₆⁻ population in the Penning trap at 300K following K(νp)/SF₆ collisions at n = 12, 30, and 45.

As seen in Figure 4.12, the lifetimes of the trapped ion populations are the same for n = 30 and n = 45, whereas at n = 12 they are significantly increased. These results are consistent with those observed during earlier studies involving (RET) at room temperature [47]. Figure 4.13 shows that when the interaction region is heated to 573K the lifetimes of the ion population in the trap are the same for n = 12 and n = 45. As before, the SF₅⁻ contribution to the total trapped ion population was determined by allowing the incoming ions to pass directly through the trap to the lower PSD and is subtracted. The fraction of the long-lived ion signal attributed to SF₅⁻ at n = 12 is ~25% at 573K.

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Figure 4.13  Time evolution of the SF$_6^-$ population in the Penning trap at 573K following K(σp)/SF$_6$ collisions at $n = 12$ and 45.

The data in Figure 4.13 indicate that, in contrast to collisions at room temperature, post-attachment interactions are not significant at higher temperatures.
Chapter 5

Conclusions

5.1 Conclusions

The lifetimes of $SF_6^-$ ions formed by attachment of low energy electrons depend strongly on the target temperature, i.e. on the internal energy in the neutral $SF_6$ molecule. At room temperature only long-lived ions are observed, whereas when the target temperature is increased above room temperature the lifetime of the long-lived ions is seen to decrease and the production of a short-lived ion signal is observed. The measured lifetimes at room temperature support the results of experimental methods which yield lifetimes in the millisecond range, i.e., ion-cyclotron and previous Rydberg atom studies.

Calculated lifetimes at room temperature using quasi-equilibrium theory (QET) are in good agreement with the present results. As the temperature is increased, however, the calculated values predict a monotonic decrease in ion lifetime that is much more rapid than is experimentally observed. In addition, the appearance of an independent short-lived ion signal produced at higher temperatures is not predicted by QET which calls into question its central assumption, namely that the excitation energy in the anion is completely randomized. Indeed, there is further experimental evidence [48] that casts doubt on this assumption from recent studies of dissociative electron attachment to $SF_6$. In these studies, the effect of thermal excitation on $SF_5^-$ production was compared to that of laser-induced excitation of the $v_3$ mode. The results indicate that vibrational energy pumped into the $v_3$ mode through laser-excitation remained there for times on the order
of ~1 μs. This suggests that intramolecular vibrational energy redistribution (IVR) following photoabsorption must be slow, i.e., that not all of the internal vibrational modes are strongly coupled.

If indeed the vibrational modes are not all strongly coupled and the additional internal energy is not randomly distributed throughout the molecule, then an appealing speculation is that the long-lived and short-lived ions might be associated with population of two semi-independent groups of anion states resulting from different initial vibrational configurations prior to electron attachment.

5.2 Future Work

A natural extension of this work is to apply these experimental and computational methods to other molecular species known to attach low energy free electrons. Possible interesting targets include C₆F₆, c-C₇F₁₄, C₁₀F₈, and C₂Cl₄. Future experiments could also further explore the effect of internal energy on post-attachment interactions, only briefly considered in this work.

The present apparatus is equipped with a gas line that feeds directly into the interaction region which leads to much higher target densities than when the gas is admitted through the main chamber. It was not needed in the present work because of the high attachment rate of SF₆. However, through the use of this gas line, future work could also include the study of electron attaching targets with small cross sections, such as O₂.
References


[34] B. Lindsay, "Superlock Manual", Rice University.


Appendix A

DAQ Control Flow Diagram

Position Sensitive Detector
- Micro-Channel Plate
- Resistive Anode

Timing Preamp

Discriminator

Level Adaptor
- Stop Clock
- Strobe

Timing Card
- Time Data

FPGA Card

Superlock

Computer
Appendix B

Selected Derivations

B.1 Free Particle Density of States

Imagine a volume expanding from the origin into the positive octant of momentum space \((k_x, k_y, k_z > 0)\). The number of particles that can fit into this volume is

\[
N(k) = \frac{1}{8} \frac{4 \pi k^3}{(\frac{2\pi}{k_x})(\frac{2\pi}{k_y})(\frac{2\pi}{k_z})} = \frac{k^3}{6\pi^2} (L_x L_y L_z), \tag{B.3.1}
\]

where \(L_x L_y L_z\) is the quantum volume a particle occupies in momentum space. The number of states per unit volume is then simply

\[
G(k) = \frac{k^3}{6\pi^2}. \tag{B.3.2}
\]

The density of states is found by differentiating the number of states with respect to energy,

\[
\rho(E) = \frac{d}{dE} G(E). \tag{B.3.3}
\]

To convert the number of states from a function of momentum to a function of energy we employ the relation

\[
k = \sqrt{\frac{2mE}{\hbar^2}}. \]

G(k) then becomes

\[
G(E) = \frac{1}{6\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{1}{2}} E^{\frac{3}{2}} \tag{B.3.4}
\]

and

\[
\rho(E) = \frac{1}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{1}{2}} E^{\frac{1}{2}}. \tag{B.3.5}
\]
This expression can be written in terms of the velocity using $E = \frac{1}{2}mv^2$,

$$\rho(v) = \frac{1}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \left( \frac{mv^2}{2} \right)^{\frac{1}{2}},$$  \hspace{1cm} (B.3.6)

which reduces to

$$\rho = \frac{m^2v}{2\pi^2 \hbar^3}.$$ \hspace{1cm} (B.3.7)
B.2 Anion Lifetime Calculations

Written using Maple version 10.0

> restart; with(plots)

1. Find Excess Energy in the Neutral

Average Energy (summing over first 10 oscillator levels)

\[
\text{Evib} := T \rightarrow \sum_{i=1}^{15} \left( \sum_{m=0}^{10} \frac{h c \nu_i \left( m + \frac{1}{2} \right) e^{-\frac{h c \nu_i (m + 1/2)}{k T}}}{\sum_{n=0}^{10} e^{-\frac{h c \nu_i (n + 1/2)}{k T}}} \right)
\]

SF6 Vibrational frequencies (from Jacox)

> nu:=[774, 642, 642, 948, 948, 948, 616, 616, 616, 525, 525, 525, 347, 347, 7, 347];

Constants and unit conversions

> h := 6.626e-34; c := 2.9979e10; k := 1.38e-23; me := 9.11e-31; meV := 1000/(1.6e-19);

\[
h := 0.6626 \times 10^{-33}
\]

\[
c := 0.29979 \times 10^{11}
\]

\[
k := 0.138 \times 10^{-22}
\]

\[
me := 0.911 \times 10^{-30}
\]

\[
meV := 0.6250000000 \times 10^{22}
\]

Find zero-point energy

> Ez := add(1/2*h*c*nu[i], i=1..nops(nu));
> Ez*meV;

\[
Ez := 0.9302351194 \times 10^{-19}
\]

581.3969496

Adiabatic Electron affinity

> EA := 1050/meV;

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Assume a 1meV electron energy
> $E_e := 1/\text{meV}$;

Find excess energy in the molecule
> $E_{\text{int}} := (T) \rightarrow \text{evalf} (E_{\text{vb}}(T) - E_z);$  
> $E_{\text{star}} := (T) \rightarrow E_A + E_e + E_{\text{int}}(T);$  

\[ E_A := 0.1680000000 \times 10^{-18} \]
\[ E_e := 0.1600000000 \times 10^{-21} \]
\[ E_{\text{int}} := T \rightarrow \text{evalf} (E_{\text{vb}}(T) - E_z) \]
\[ E_{\text{star}} := T \rightarrow E_A + E_e + E_{\text{int}}(T) \]

Room temp vibrational energy in meV
> $E_{\text{int}}(300)$*meV;

73.73808788

> plot($E_{\text{int}}(T)$*meV, T=300..600, title="Internal Vibrational Energy (Above Zero-Point Energy)", labels=["Temperature (K)", "Energy (meV)", labeldirections=[horizontal, vertical], axes=boxed);
2. Density of States for the Neutral + Free Electron System (The Product System)

-- The density of states for the product system is \( \rho(SF6 + e) = \rho(e) G(SF6) \) --

Electron velocity
\[ \text{ve} = \sqrt{2*\text{e}/\text{me}}; \quad \text{ve} := 18741.99426 \]

Density of States for a free electron (neglecting spin -- spin degeneracy shows up in the density of states for the product channel and the reactant channel, so they cancel in the lifetime ratio)
\[ \text{rho}_e := \text{evalf}(\text{me}^2*\text{ve}/2/\text{Pi}^2/(\text{h}/2/\text{Pi})^3); \]
\[ \text{rho}_e := 0.671905388510^{45} \]

Sum of States for Neutral SF6
\[ G := E \rightarrow \frac{(E + a1(E) E_z)^{\text{nops}(\nu)}}{\text{nops}(\nu)! \left( \prod_{i=1}^{\text{nops}(\nu)} \frac{\text{h c v}_i}{\text{h}_i} \right)} \]

Rabinovitch's parameters with neutral SF6 vibrational frequencies
\[ \text{al} := (E) \rightarrow 1 - \beta 1 * \omega 3 (E); \]
\[ \beta 1 := 1.028748196 \]
\[ \omega 1 := E \rightarrow \frac{1}{5.00 \frac{E}{E_z} + 2.73 \left( \frac{E}{E_z} \right)^{0.50} + 3.51} \]
\[ \omega 2 := E \rightarrow e^{-2.4191 \left( \frac{E}{E_z} \right)^{0.25}} \]
\[ \omega 3 := E \rightarrow \text{piecewise}(0.1 \text{ E}_z < E \text{ and } E < 1.0 \text{ E}_z, \omega 1(E), 1.0 \text{ E}_z < E \text{ and } E < 8.0 \text{ E}_z, \omega 2(E)) \]
Compare the approximation method to direct counts at $T = 300K$ (count = 7) and $T = 350K$ (count = 28)

\[
\begin{align*}
&G(E_{\text{int}}(300)) \quad G(E_{\text{int}}(350)) \\
&7.151424519 \\
&25.07429513
\end{align*}
\]

Plot sum of states for SF6 (neutral) as a function of temperature (assuming an electron energy of 1meV)

\[
\begin{align*}
&SOS:=\text{seq}([T*5+300, \quad G(E_{\text{int}}(T*5+300))], T=0..60): \\
&\text{plot1:=pointplot}(\{SOS\}, \text{title}="\text{Sum of States for SF6}", \text{labels}=\{\text{"Temperature (K)"}, \text{"Number of Vibrational States"}\}, \text{labeldirections}=\{\text{horizontal, vertical}\}, \text{axes=boxed}): \text{display}(\text{plot1});
\end{align*}
\]

The density of states for the product system is then

\[
\begin{align*}
&\text{rho1:=(E)\rightarrow rho_e*G(E);} \\
&\rho 1 := E \rightarrow rho\_e \ G\(E\)
\end{align*}
\]

Room temp density of states for product system

\[
\begin{align*}
&\text{rho1}(E\_{\text{int}}(300)); \\
&0.4805080670 \times 10^{46}
\end{align*}
\]
3. Density of States for the SF6 Anion System (The Reactant System)

Calculated anion vibrational frequencies (defined as methods 1-12) as given by J. Steill, 2007

> Gutsev_MP2:=

> Schaefer_DZP:=
[568, 423, 423, 627, 627, 627, 111, 111, 111, 313, 313, 313, 216, 216, 216, 216]:

> B3LYP_VDZ:=

> B3RP86_VDZ:=
[585, 456, 456, 666, 666, 666, 176, 176, 176, 311, 311, 311, 218, 218, 218, 218]:

> CCD_VDZ:=
[607, 474, 474, 678, 678, 678, 135, 135, 135, 319, 319, 319, 227, 227, 227, 227]:

> MP2_VDZ:=

> MP2_3df_2d:=

> MP2_3df:=
[602, 422, 422, 673, 673, 673, 265, 265, 265, 323, 323, 323, 229, 229, 229, 229]:

> nu2:=
[Gutsev_MP2, Schaefer_DZP, B3LYP_VDZ, B3RP86_VDZ, CCD_VDZ, MP2_VDZ, MP2_3df_2d, MP2_3df]:

Density of states is given by differentiating sum of states: \( \rho(E) = \frac{d}{dE} G(E) \), also included is a factor of 2 to account for the "doublet" anion density of states, which has an unpaired electron that can be spin up or spin down.

> rho2:=(E,method)->((E+a2(E,method)*Ez2(method))^1/(nops(nu)-1))!*product(h*c*nu2[method,i],i=1..nops(nu)))*(1-beta2(method)*domega6(E,method));

\[
\rho_2 := (E, \text{method}) \rightarrow \frac{(E + a2(E, \text{method}) \cdot Ez2(\text{method}))^{(\text{nops}(\nu)-1)}}{(\text{nops}(\nu) - 1) \left( \prod_{i=1}^{\text{nops}(\nu)} \frac{h \cdot c \cdot v^2_{\text{method},i}}{1 - \beta2(\text{method})} \right)}
\]

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Rabinovitch's parameters with anion frequencies

\[ a_2 := (E, \text{method}) \rightarrow 1 - \beta_2(\text{method}) \cdot \omega_6(E, \text{method}) \]

\[ \beta_2 := \text{method} \rightarrow \text{evalf} \left( \frac{(nops(v) - 1) \left( \sum_{i=1}^{nops(v)} \frac{v^2_{\text{method},i}}{nops(v)} \right)^2}{nops(v) \left( \sum_{i=1}^{nops(v)} \frac{v^2_{\text{method},i}}{nops(v)} \right)^2} \right) \]

\[ \omega_4 := (E, \text{method}) \rightarrow \frac{1}{5.00 \frac{E}{\text{Ez2(\text{method})}} + 2.73 \left( \frac{E}{\text{Ez2(\text{method})}} \right)^{0.50} + 3.51} \]

\[ \omega_5 := (E, \text{method}) \rightarrow E \]

\[ \omega_6 := (E, \text{method}) \rightarrow \text{piecewise}(0.1 \ \text{Ez2(\text{method})} < E \ \text{and} \ E < 1.0 \ \text{Ez2(\text{method})}, \ \omega_4(E, \text{method}), 1.0 \ \text{Ez2(\text{method})} < E \ \text{and} \ E < 8.0 \ \text{Ez2(\text{method})}, \ \omega_5(E, \text{method})) \]

\[ \text{Ez2} := \text{method} \rightarrow \text{add} \left( \frac{1}{2} h c v^2_{\text{method},i}, i = 1..\text{nops(v)} \right) \]

\[ \text{domega6 := (Energy, method) \rightarrow evalf} \left( \text{subs}(E = \text{Energy, } \frac{d}{dE} \omega_6(E, \text{method}) \text{Ez2(\text{method})}) \right) \]
4. Find the lifetime of the SF6 anion

\[ \tau := (E_{\text{int}}, E_{\text{star}}, \text{method}) \rightarrow \frac{\rho_2(E_{\text{star}}, \text{method})}{\rho_1(E_{\text{int}}) \vee \sigma} \]

The attachment cross section for a 1meV electron is \(~2e-17 \text{ } m^2\) \cite{Christophorou2000}

\[ \sigma := 2e-17; \]

List the lifetimes for the various methods at \(T = 300\text{K} \text{ and } 600\text{K}\)

\[ \text{for } j \text{ from } 1 \text{ by } 1 \text{ to } 8 \text{ do} \]
\[ \text{print(evalf(tau(E_int(300),E_star(300),j))*1000,} \]
\[ \text{evalf(tau(E_int(600),E_star(600),j))*1000} \) \text{ end do;} \]

\begin{align*}
1.209891144, & 0.01199698183 \\
23.06000456, & 0.2448906010 \\
6.573134240, & 0.06829940785 \\
5.000913450, & 0.05132743650 \\
7.750583130, & 0.07950343785 \\
0.9223976425, & 0.009020940055 \\
1.298653179, & 0.01291452860 \\
1.477893688, & 0.01476402578.
\end{align*}

\[ \text{for } j \text{ from } 1 \text{ by } 1 \text{ to } 8 \text{ do Lifetime[j]:=seq([T*10+300,} \]
\[ \text{evalf(tau(E_int(T*10+300),E_star(T*10+300),j))*1000],T=0..30} \) \text{ end do;} \]

\[ \text{LifetimePlot:=pointplot([LifeTime[1],LifeTime[2],LifeTime[3],LifeTime[4],LifeTime[5],LifeTime[6],LifeTime[7],LifeTime[8]],title="Lifetimes of SF6 Anion by Various Methods",labels=["Temperature (K)","Lifetime (ms)"]},\text{labeldirections=[horizontal,vertical],axes=box):display} \text{({LifetimePlot});} \]
Lifetimes of SF6 Anion by Various Methods

Temperature (K)

Lifetime (ms)
B.3 Thermal Transpiration

The number of particles passing through a hole of area $A$ is:

$$N = \frac{1}{4} \rho v A,$$

(B.1.1)

where $\rho$ is the number of particles per unit volume and

$$v = \sqrt{\frac{8kT}{m\pi}}$$

is the mean molecular velocity. In equilibrium the number of particles passing through the hole from side A is equal to the number passing through from side B,

$$N_A = N_B.$$

(B.1.2)

Substituting Eq. B.1.1 in the equilibrium condition, Eq. B.1.2,

$$\rho_A v_A = \rho_B v_B$$

$$\rho_A \sqrt{\frac{8kT_A}{m\pi}} = \rho_B \sqrt{\frac{8kT_B}{m\pi}}$$

$$\rho_A \sqrt{T_A} = \rho_B \sqrt{T_B}$$

Therefore,

$$\frac{\rho_A}{\rho_B} = \sqrt{\frac{T_B}{T_A}}.$$
B.4 Differential Equation Solution

To find the population of the short-lived $SF_v^{*+}$ ions as a function of time given in Eq. 4.2.3, it is necessary to solve the two coupled differential equations given in Eqs. 4.2.1 and 4.2.2, which are written here as

$$\frac{d}{dt}N_a(t) = -\frac{N_a(t)}{\tau_a} \tag{B.2.1}$$

$$\frac{d}{dt}N_b(t) = N_a(t)\rho k_b - \frac{N_b(t)}{\tau_b}. \tag{B.2.2}$$

The solution to B.2.1 is straightforward and is given by

$$N_a(t) = N_a(0)e^{-\frac{t}{\tau_a}}. \tag{B.2.3}$$

Substituting Eq. B.2.3 into Eq. B.2.2 and rearranging terms gives

$$\frac{d}{dt}N_b(t) + \frac{N_b(t)}{\tau_b} = \rho k_b N_a(0)e^{-\frac{t}{\tau_a}}. \tag{B.2.4}$$

This is a single 1st-order differential equation of the form

$$y'(x) + P(x)y(x) = Q(x), \tag{B.2.5}$$

which has a well-known solution:

$$y(x) = Ce^{-\int P(x)dx} + e^{-\int P(x)dx}\int Q(x)e^{-\int P(x)dx}dx. \tag{B.2.6}$$

Noting that

$$y(x) = N_b(t),$$

$$P(x) = \frac{1}{\tau_b}, \text{ and}$$

$$Q(x) = \rho k_b N_a(0)e^{-\frac{t}{\tau_a}},$$
the solution takes the form

$$N_b(t) = Ce^{\frac{t}{\tau_b}} + N_a(0)\frac{\rho k_b}{1/\tau_a - 1/\tau_b} \left( e^{\frac{t}{\tau_a}} - e^{\frac{t}{\tau_b}} \right). \quad (B.2.7)$$

The arbitrary constant $C$ is determined through initial conditions: $N_b(0) = 0$, indicating that $C = 0$. Therefore $N_b(t)$ is given by

$$N_b(t) = N_a(0)\frac{\rho k_b}{1/\tau_a - 1/\tau_b} \left( e^{\frac{t}{\tau_a}} - e^{\frac{t}{\tau_b}} \right), \quad (B.2.8)$$

which is the solution given in Eq. 4.2.3.
B.5 Rate Constants for Formation of Short- and Long-Lived Ions

Written using Maple version 10.0

```
> restart; with(plots): with(Statistics):
with(LinearAlgebra): 

Define the equations describing the time evolution of the Rydberg atom population (with blackbody-reduced lifetime \( \tau \) 2) and short-lived ion population (with lifetime \( \tau \)), \( \rho \) is the target gas density, \( k_s \) is the rate constant for short-lived ion formation, and \( kl \) is the rate constant for long-lived ion formation:
> EQ1 := diff(Nr(t), t) = -Nr(t) * rho * (ks + kl) - Nr(t) / tau2;
> EQ2 := diff(Ns(t), t) = Nr(t) * rho * ks - Ns(t) / tau;

\[
\begin{align*}
EQ1 & := \frac{d}{dt} Nr(t) = -Nr(t) \rho (ks + kl) - \frac{Nr(t)}{\tau^2} \\
EQ2 & := \frac{d}{dt} Ns(t) = Nr(t) \rho ks - \frac{Ns(t)}{\tau}
\end{align*}
\]

Define the initial conditions:
> IC1 := Nr(0) = No;
> IC2 := Ns(0) = 0;

\[
IC1 := Nr(0) = No \\
IC2 := Ns(0) = 0
\]

Solve the coupled differential equations (the time evolution of the long-lived ion population is simply proportional to the Rydberg atom population by \( \rho kl \)):
> soln := dsolve([EQ1, EQ2, IC1, IC2]):
> assign(soln):
> Nryd := simplify(Nr(t));
> Nlong := Nryd * rho * kl;

\[
\begin{align*}
Nryd & := No e^{-\left(\frac{\rho \tau^2 ks + \rho \tau^2 kl + 1}{\tau^2}\right)t} \\
Nlong & := No e^{-\left(\frac{\rho \tau^2 ks + \rho \tau^2 kl + 1}{\tau^2}\right)t} \rho kl
\end{align*}
\]

Import the data for the long-lived ion signal:
> LateData := readdata("C:/Documents and Settings/Trap Control/My Documents/DAQ System/Analysis/SF6 Analysis/Early Electron Signal/SF6(30p) 600K 1e-5 Torr Late signal.txt", 2):
> MLate := Matrix(LateData):
> TimeLate := (1e-6) * Column(MLate, 1):
> CountsLate := Column(MLate, 2):
> DataMLate := Matrix([[TimeLate, CountsLate]]):
```

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Fit the data to Nlong:
> **LateFit:=Fit(Nlong,TimeLate,CountsLate,t);**

\[
\text{LateFit} := 175.69144736552 e^{(-114740.69293980 t)}
\]

\[
\sigma := 5.8948368051843
\]

Plot the data and the fit:
> **A1:=pointplot(DataMLate);**
> **B1:=plot(LateFit,t=0..7e-6,color=blue,thickness=3);**
> **display({A1,B1},view=[0..7e-6, 0..200]);**

> **unassign('Nr(t)'); unassign('Ns(t)');**

Now define the time evolution of the Rydberg atom and short-lived ion populations using the numerical value for \( \rho (ks + kl) + \frac{1}{\tau^2} \) obtained from the fit to the long-lived ion signal:

> **EQ1:=diff(Nr(t),t)=-Nr(t)*(-1/t)*op(1,op(2,LateFit));**
> **EQ2:=diff(Ns(t),t)=Nr(t)*rho*ks-Ns(t)/tau;**

\[
\text{EQ1} := \frac{d}{dt} Nr(t) = -114740.69293980 Nr(t)
\]

\[
\text{EQ2} := \frac{d}{dt} Ns(t) = Nr(t) \rho ks - \frac{Ns(t)}{\tau}
\]
Solve the differential equations (the time evolution of the early-time electron signal is simply \( \frac{N_{\text{short}}}{\tau} \)):

\[
> \text{soln} := \text{dsolve}([\text{EQ1}, \text{EQ2}, \text{IC1}, \text{IC2}])
> \text{assign(soln)}:
> \text{Nryd} := \text{evalf} \left( \text{simplify}(N_{\text{r}}(t)) \right):
> \text{Ns} := \text{simplify}(N_s(t)):
> \text{Nelec} := \frac{N_{\text{short}}}{\tau} = \frac{5000000 \left( \frac{e^{-\frac{t}{114740.6929\tau}}}{573703.464699 \tau - 5000000} \right) - 1}{573703.464699 \tau - 5000000}
\]

Import the data for the early-time electron signal:

\[
> \text{EarlyData} := \text{readdata}("C:/\text{Documents and Settings/Trap Control/My Documents/DAQ System/Analysis/SF6 Analysis/Early Electron Signal/SF6(30p) 600K 1e-5 Torr Early signal.txt"),2):
> \text{MEarly} := \text{Matrix}(\text{EarlyData}):
> \text{TimeEarly} := (1e-6)*\text{Column(MEarly,1)}:
> \text{CountsEarly} := \text{Column(MEarly,2)}:
> \text{DataMEarly} := \text{Matrix}([[\text{TimeEarly}, \text{CountsEarly}]]):
\]

Fit the data to Nelec:

\[
> \text{EarlyFit} := \text{Fit}(\text{Nelec, TimeEarly, CountsEarly, t})
> \text{sigma} := \text{Fit}(\text{Nelec, TimeEarly, CountsEarly, t, output=residualstandarddeviation})
\]

\[
\text{EarlyFit} := 196.7606326868 \left( e^{\frac{564656.104017221}{t} - 1} \right) e^{-679396.796957031t}
\]

\[
\sigma := 8.3065275861661
\]

Plot the data and the fit:

\[
> \text{A2} := \text{pointplot}(\text{DataMEarly})
> \text{B2} := \text{plot}(\text{EarlyFit, t=0..30e-6, color=blue, thickness=3})
> \text{display}([\text{A2, B2}, \text{view}=[0..30e-6, 0..200]])
\]
Get the coefficient $C$ to the exponential terms in Nelec:

\[ C := \text{op}(1, \text{Nelec}) / \text{denom}(\text{Nelec}); \]

Determine $\tau$ directly from the $e^{-\frac{t}{\tau}}$ term in the Nelec fit:

\[ \tau := \frac{1}{\text{op}(1, \text{op}(1, \text{op}(3, \text{EarlyFit})))}; \]

Determine the ratio of the rate constants from the ratio of the coefficients in the Nelec and Nlong fits, $C N_o \rho \, k_s$ and $N_o \rho \, k_l$, respectively:

\[ \frac{\text{ks_to_kl_Ratio}}{\text{C}} := \frac{\text{op}(1, \text{EarlyFit}) / C}{\text{op}(1, \text{LateFit})}; \]

\[ C := \frac{5000000}{\tau} \]

\[ \tau := 0.1471893898 \times 10^{-5} \]

\[ \text{ks_to_kl_Ratio} := 0.9307823125 \]

Solve for $k_l$ using the ratio of $k_s$ to $k_l$ and the numerical value for $\rho (k_s + k_l) + \frac{1}{\tau_2}$ obtained from the fit to the long-lived ion signal (the blackbody-reduced lifetime $\tau_2$ is determined by extrapolation down to zero density of a graph of the Rydberg decay rate vs. target gas density):

\[ k_l := ((-1/t) * \text{op}(1, \text{op}(2, \text{LateFit}))) - (1/\text{tau2})) / \rho / (1 + \text{ks_to_kl_Ratio}); \]

\[ \rho := (9.66e18) * (0.46) * (1e-5) / (573); \]

\[ \text{tau2} := (1/0.085) * 10^(-6); \]
\[ kl := \frac{0.5179247778 \left( 114740.69293980 - \frac{1}{\tau^2} \right)}{\rho} \]

\[ \rho := 0.7754973822 \times 10^{11} \]

\[ \tau^2 := 0.00001176470588 \]

Display the rate constants:
> \texttt{Digits:=3;}  
> \texttt{kl:=kl;}  
> \texttt{ks:=ks_to_kl_Ratio*kl;}  

\[ kl := 0.203 \times 10^{-6} \]

\[ ks := 0.189 \times 10^{-6} \]