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Characterizing Fluorine and Chlorine Atom Flow Rates Using Iodine Atom Spectrometry

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The production of F and Cl atoms in an electrical discharge of F2 or Cl2 has been examined in a flow reactor. A tunable diode laser was used to probe the concentration and translational temperature of I atoms produced by F and Cl atom reactions with HI. Kinetic modeling codes were used to determine the discharge efficiencies from the titration plots and the observed trends for atom concentration as a function of F2 or Cl2 and pressure. These calculations indicate that the dc discharge used in these experiments is 100% efficient for F2 flow rates \( \geq 0.5 \text{ mmol s}^{-1} \) and reactor pressure \( \leq 20 \text{ torr} \). The highest \( F_2 \)-free \( F \) atom flow rate that we can generate is \( 1.0 \text{ mmol s}^{-1} \). Preliminary data for the Cl2 discharge indicate that this is a much less efficient source of Cl atoms with yields of less than 50%.

Introduction

SINCE their invention in the mid 1960s, the most widely studied class of chemical lasers has been the hydrogen halide systems.† These lasers operate on an exothermic energy release whereupon the liberated energy is deposited into newly formed hydrogen halide bonds to produce a population inversion between vibrational levels. The following three-atom exchange reactions typify the pumping reaction for producing upper vibrational levels in hydrogen halides:

\[
X + H_2 \rightarrow HX (v) + H \quad (1)
\]

\[
X + HY \rightarrow HX (v) + Y \quad (2)
\]

\[
H + X_2 \rightarrow HX (v) + X \quad (3)
\]

where \( X \) and \( Y \) are the halogens F, Cl, Br, I, and \( H \) can be replaced by deuterium D. In some cases, more than 50% of the available exothermicity is channeled into product vibration and high vibrational levels, up to \( v = 10 \), can be populated. However, lasing usually occurs on \( \Delta v = -1 \) and -2 transitions between the low-lying vibrational levels. For example, the prominent rovibrational laser lines for the HF laser lie in the \( (v'' = 2 \rightarrow v' = 1) \) and \( (v'' = 1 \rightarrow v' = 0) \) bands between 2.5 and 3.0 \( \mu \text{m} \).

Recently, a population inversion and lasing were reported by this laboratory on the atomic iodine \( I^*(2\Pi_{3/2})-I^*(2\Pi_{1/2}) \) transition at 1.315 \( \mu\text{m} \) using the following energy transfer process:

\[
\text{NCI}(a^1\Delta) + I^*(2\Pi_{3/2}) \rightarrow \text{NCI}(X^3\Sigma^-) + I^*(2\Pi_{1/2}) \quad (4)
\]

This system is analogous to the well-known chemical oxygen iodine laser (COIL).8 The NCI(a^1\Delta) metastable \( (T_0 = 1.1 \text{ eV}) \) is isovalent to singlet oxygen in COIL and undergoes an efficient energy transfer reaction similar to the \( O_3(a^1\Delta) + I^*(2\Pi_{3/2}) \) reaction in COIL. However, in this scheme the NCI(a^1\Delta) is generated through a purely gas-phase chemical reaction mechanism

\[
\text{Cl} + \text{HN}_3 \rightarrow \text{HCl} + \text{N}_2 \quad (5)
\]

Cl + N3 \( \rightarrow \) NCI(a^1\Delta) + N2

and, as such, represents a significant breakthrough in chemical laser technology.

It should be noted that reactions (1-6) are preceded by a complex set of chain chemistry where the free radicals \( X \) and/or \( H \) are generated in the initial steps. There are many methods for generation of these radicals, including electrical and microwave discharges, photolysis, and purely chemical means such as high-temperature combustors. The coupling of high-enthalpy flows found in chemical lasers with these radical generator schemes produces large amounts of heat in the active medium. Thus, extracting efficient continuous wave laser operation involves managing homogeneous reagent mixing times and thermal budgets of the active medium with respect to the kinetics of the system. Through optimization of several flowfield parameters such as gas temperature, velocity, and species density, an appropriate laser resonator and sub- or supersonic nozzle design can be fashioned to accommodate the extreme heat release and mixing requirements found in these systems. Because these parameters are variable, the laser output power/efficiency will fluctuate accordingly, and a systematic choice of operational conditions is required for efficient operation. This is especially true of the hydrogen halide lasers because the vibrational distribution and small signal gain can vary widely with operating conditions. The NCI(a^1\Delta)/I^*(2\Pi_{1/2}) laser system is also sensitive to operating conditions. For example, to optimize the NCI(a^1\Delta) and I^*(2\Pi_{1/2}) generation, complete dissociation of \( F_2 \) or \( Cl_2 \) is essential because IF and IFCl, which are generated by

\[
I + X_2 \rightarrow IX + X \quad (7)
\]

where \( k_p = 4.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) (Refs. 9 and 10) rapidly quench NCI(a^1\Delta) (Ref. 11) and I^*(2\Pi_{1/2}). Note that \( k(I + Cl_2) \) is estimated to be the same as \( kI^*(2\Pi_{1/2} + Cl_2) \) (Ref. 10).

Indeed, most chemical lasers and other high-temperature reacting flows contain complex chemical and fluid dynamical processes that require facile temporal and spatial resolution. Before the advent of tunable diode lasers, the data required to fully characterize these systems were difficult to obtain. However, a species' concentration and temperature can now be readily characterized through its spectral absorption features using commercial narrow-line tunable diode lasers. The resulting spatially resolved, high-fidelity, and high-resolution data are particularly useful for characterizing the complex environment found in chemical lasers.

In this paper, we expand on our earlier report of a versatile titration technique that measures F atom densities by using a laser-based absorption technique.12 The data reduction methodology has been refined, and a one-dimensional computational fluid mechanics analysis has been applied. Although this methodology is a general
technique for characterizing F or Cl atom concentrations produced from combustion or electrical discharge devices, our specific interest is to find conditions where large F2 and Cl2 free flows of F or Cl atoms could be generated using an electric discharge because molecular halogenes and interhalogenes are deleterious quenchers of NCl(a'\Delta) and I*(2P1/2).

Experimental Methods

A. X + HI Atom Titration

In these experiments, F and Cl atoms are generated by a commercial electric (dc) discharge (Helios, Inc.) in F2 or Cl2. Optical absorption methods for determining absolute concentration of these atomic species is difficult because the lowest energy allowed transitions for F and Cl atoms lie in the vacuum UV.13,15 The 2P3/2-2P1/2 spin-orbit transitions16 for F and Cl, 404 and 881 cm⁻¹, respectively, can be probed directly, but the signals are quite weak and difficult to discern. A source for a 404-cm⁻¹ laser no longer exists. To circumvent these problems, titration methods have been developed, where a chemical reagent that reacts with X is added to the flow to produce a species that can be readily detected and converted into absolute concentration. For example, a sensitive technique for detecting F atoms in a flow tube involves monitoring the intensity of HF (ν' = 3 → ν'' = 0) chemiluminescence at 880 nm generated by F + Cl2H2 reactions while adding CF3I as an F atom titrant.17 This method is well suited for small flows of F, but would be quite expensive and difficult to implement in our large flow reactor. The most common methods for detecting the presence of Cl in a flow are resonance fluorescence and Cl2 afterglow. Unfortunately, the titrants CN2O and Cl2HBr are not appropriate or cost effective for our conditions (high flow rates and high pressure). In addition, these methods do not allow for simultaneous concentration and temperature measurement, as well as two-dimensional spatial resolution of the F and Cl density in the flow.

Unlike most techniques that involve the removal of a halogen-dependent chemiluminescent signal as a function of added titrant concentration, we monitor the generation of I atoms from the reaction between a halogen atom (X = F or Cl) and hydrogen iodide using an 1.315-μm diode laser to probe the I*(2P3/2) → I*(2P1/2) spin-orbit transition:

\[ X + HI \rightarrow HX + I \]  

(8)

[where \( k_e = 4.1 \times 10^{-11} \) and \( k_C = 1.6 \times 10^{-10} \) cm³ molecule⁻¹ s⁻¹ (Ref. 20)]. The I atom absorption increases linearly with HI concentration [HI], until all of the X atoms have been consumed. On continued addition of HI, the I atom absorption reaches a maximum and levels off to a constant value. Ideally, there are no X or I atom loss processes, and the initial X concentration [X]₀ is given by the maximum [I] observed. Typically, however, at least one or more X or I atom loss processes are present, and [X]₀ is determined by analysis of the I vs HI plots measured at a variety of experimental conditions. In our case, one-dimensional fluid mechanics calculations were used to determine [X]₀ and the F and Cl atom production efficiency of our dc discharge.

B. Flow Reactor

A schematic of the stainless-steel flow reactor hardware is shown in Fig. 1a. The reactor is pumped by two Kinney 850 pumps in parallel, each equipped with a Roots blower. The main reactor channel is 5.08 cm wide by 1.91 cm high by 30.5 cm long in the flow direction. A 2.4-cm-diam dc discharge tube is mounted at its entrance. A noise levels are achieved by 30-50 scans, and I atom number densities as low as 3-5 × 10¹⁰ cm⁻³ can be routinely detected. Multiple passes through the reactor can easily lower this limit: Densities as low as 1 × 10¹⁰ cm⁻³ can be detected with a 2-m path length (private communication, S. J. Davis, Physical Sciences, Inc., Andover, Massachusetts, 1998).

The iodine atom number density is derived from Beer's law:

\[ I = I_0 e^{-\gamma(v)L} \]  

(10)

The path length L (two passes) is 10 cm, and \( \gamma(v) \) is given by

\[ \gamma(v) = \left( \frac{1}{2} \right) (2A_{3,9}/8\pi) f(v) [I^*-1/4] \]  

(11)
Fig. 1a Schematic diagram of the flow reactor; side view of the flow reactor shows the injection points for He (~130 mmol s⁻¹), F₂/Cl₂ (0.5–1.5 mmol s⁻¹), N₂, and HI (0.0–6.0 mmol s⁻¹).

Fig. 1b Optical path for the I atom laser probe.

Fig. 1c Flow tube hardware and the computational domain used in the one-dimensional model; see text.

\[ A_{34} \text{ is the Einstein coefficient for the 3,4 hyperfine transition (5.08 s⁻¹), } \lambda \text{ is wavelength (1.3145 } \mu \text{m), and } f(\nu) \text{ is the line shape function. For our conditions, } [I^*] = 0, \text{ the inversion number density reduces to } \frac{2}{3} [I], \text{ and the ground-state density is obtained by integrating the gain over frequency:} \]

\[ \text{spectral area} = \int_{0}^{\infty} y(\nu) \, d\nu = -\frac{7 \lambda^2 A_{34}}{24 \pi^3} \]  

The I atom spectra are fit by a Voigt function:

\[ y = \text{spectral area} \times \frac{2 \mathcal{L}(2)}{\pi^3} \times \frac{w_L}{w_G^2} \times \int_{-\infty}^{\infty} \left[ e^{-t^2} \left/ \left( \sqrt{\mathcal{L}(2)} \times \frac{w_L}{w_G} \right) \right. \right] dt \]

where \( w_G \) and \( w_L \) are the Gaussian and Lorentzian linewidths (full width at half maximum), respectively. If collisions with He are assumed to be the main source of broadening, the I atom translational temperature is calculated by

\[ \text{temperature (K)} = M \left( \frac{w_G}{7.16 \times 10^{-7} v_0} \right)^2 = 295/ w_L \times 3.1 \times P_{\text{He}} \]  

where \( v_0 \) is the line center of the transition (7607.5 cm⁻¹) and \( M \) is the atomic weight (126.9 g mol⁻¹). Example spectra and fits are shown in Fig. 2.

Based on the overall signal-to-noise ratio and the scatter of repeated temperature measurements at the same conditions, the relative error of the temperature measurement is assigned as ±30 K. The I atom density is given directly by the spectral area, and the error is quite small (<5%).
energy transfer reactions of HF, the energy transfer from HF(v) to I, by Kota et al. for any surface was 0.10 at 80 K, which indicates

I + atoms via the reaction F + HI, the interhalogen reactions F + I2 and value of

Hence, these aspects of the model are described in detail. The finite-

changes are assumed to be continuous, and the gas is assumed to be range 200-323 K and is assumed to hold for the temperature range

D. Fluid Mechanics Simulations: Methods

The model used in this investigation to analyze the experiment data is based on the generalized one-dimensional flow development of Shapiro.22 This model describes the flow through a channel with changes in area and chemical composition, secondary mass injection, wall friction, and heat exchange with the duct walls. The flow changes are assumed to be continuous, and the gas is assumed to be real, with temperature-dependent specific heats. All chemical reactions are modeled with Arrhenius-type rate expressions for the forward rate. The equilibrium constant for each reaction is determined via the Gibb's free energy method (see Ref. 23), and the backward rate is calculated from the forward rate and the equilibrium constant.

The primary aspects of the model center on its ability to predict the changes in F atom number densities by three-body recombination, wall recombination, and reactions of F and I2 with I and I2. Hence, these aspects of the model are described in detail. The finite-rate chemistry and reactions used by our model are shown in Table 1 (see Refs. 24–31). The primary reactions are the production of I atoms via the reaction F + HI, the interhalogen reactions F + I2 and I + F2, and the atom recombination reactions. The vibrational distribution within HF produced by the F + HI reaction, the vibrational energy transfer reactions of HF, the energy transfer from HF(v) to I, and the deactivation of I* and HF(v) are listed for completeness, but

\[ \text{Table 1} \]

\begin{tabular}{|c|c|c|}
\hline
Reaction & \( k \), cm³ molecule⁻¹ s⁻¹ & Reference \\
\hline
I atom production & & \\
F + HI \rightarrow HF(0) + I & 1.59 \times 10⁻¹¹ & 9 \\
F + HI \rightarrow HF(1) + I & 1.91 \times 10⁻¹¹ & — \\
F + HI \rightarrow HF(2) + I & 2.39 \times 10⁻¹¹ & — \\
F + HI \rightarrow HF(3) + I & 2.55 \times 10⁻¹¹ & — \\
F + HI \rightarrow HF(4) + I & 3.03 \times 10⁻¹¹ & — \\
F + HI \rightarrow HF(5) + I & 3.98 \times 10⁻¹¹ & — \\
F + HI \rightarrow HF(6) + I & 2.55 \times 10⁻¹¹ & — \\
\hline
Interhalogen reactions & & \\
F + I₂ \rightarrow IF + I & 4.3 \times 10⁻¹⁰ & 9 \\
I + F₂ \rightarrow IF + F & 1.9 \times 10⁻¹⁴ & 24 \\
\hline
Three-body recombination & & \\
F + F + F \rightarrow F₂ + F & 1.9 \times 10⁻⁸ \text{exp}(629/T) & — \\
F + F + F \rightarrow F₂ + F₂ & 1.9 \times 10⁻⁸ \text{exp}(629/T) & — \\
F + F + M \rightarrow F₂ + F₂ + M & 7.8 \times 10⁻⁸ \text{exp}(629/T) & — \\
I + I + I \rightarrow I₂ + I & 5.0 \times 10⁻³³ \text{exp}(2120/T) & 9 \\
I + I + HI \rightarrow I₂ + HI & 3.8 \times 10⁻²³ \text{exp}(2120) & 9 \\
I + I + I₂ \rightarrow I₂ + I & 3.5 \times 10⁻³³ \text{exp}(2120/T) & 9 \\
I + I + M \rightarrow I₂ + M & 5.5 \times 10⁻³⁴ \text{exp}(575/T) & 9 \\
\hline
Wall recombination reactions & & \\
F + F + wall \rightarrow F₂ + wall & \gamma_F = 0.05 & 25 \\
I + I + wall \rightarrow I₂ + wall & \gamma_I = 1.0 & 26, 27 \\
\hline
Energy transfer reactions & & \\
\Gamma + HF(0) \rightarrow I + HF(2) & 1.1 \times 10⁻¹² & 28 \\
\Gamma + HF(0) \rightarrow I + HF(1) & 1.5 \times 10⁻¹³ & — \\
\Gamma + HF(0) \rightarrow I + HF(0) & 1.8 \times 10⁻¹² & — \\
\Gamma + F₂ \rightarrow I + I₂ & 5.0 \times 10⁻¹⁴ & 29 \\
\Gamma + I₂ \rightarrow I + I₂ & 3.6 \times 10⁻¹¹ & 30 \\
\Gamma + IF \rightarrow I + IF & 1.5 \times 10⁻¹¹ & 31 \\
HF(v) \rightarrow HF(0) \rightarrow HF(v' - 1) & v(5.0 \times 10⁻¹⁰ T⁻¹) & 1 \\
\quad + HF, v = 1-6 & + 5.8 \times 10⁻²² T⁻₂ & 26, 27 \\
HF(v) + He \rightarrow HF(v - 1) & v(2.6 \times 10⁻²⁰ T⁻²) & — \\
\quad + He, v = 1-6 & — & — \\
HF(v) + F₂ \rightarrow HF(v - 1) & v(1.3 \times 10⁻³⁰ T⁻⁵) & — \\
\quad + F₂, v = 1-6 & — & — \\
HF(v) + HF(v') \rightarrow & v(2.7 \times 10⁻¹¹ \text{exp}(-1360/T)) & — \\
HF(v + 1) + HF(v' - 1) & + F, v = 1-6 & — \\
\quad, v = 1-6, v' ≥ v + 2, & — & — \\
\quad, v'(v + 1) ≤ 40 & — & — \\
\hline
\end{tabular}

where \( y_A \) is the recombination efficiency of species A, the subscript \( W \) pertains to properties in the gas at the wall, and the subscript \( eq \) indicates equilibrium conditions in the main body of the flow. The value of \( y_F \) used here is 0.05, the maximum value determined by Kota et al.34 at room temperature for all surfaces investigated including stainless steel. Note that the maximum value of \( y_F \) reported by Kota et al. for any surface was 0.10 at 80 K, which indicates

\[ J_A = y_A \sqrt{R_A T_A / 2\pi M_A [\rho_{AW} - \rho_{AW} (\rho_A / \rho_A)_{eq}]} \]

\[ J_A \]

Fig. 2 Sample I atom spectra showing F = 3 - F = 4 hyperfine component of the I atomic (5p⁺²P₁/₂-5p⁻²P₁/₂) spin orbit magnetic dipole transition; signal-to-noise ratio is excellent and both spectra are well fit by a Voigt function.

The I atom flow rate is calculated by

\[ \dot{I} = [I] V * A \] (15)

where \( V \) is given by Eq. (9) and \( A \) is the cross-sectional reactor area. Note that Eq. (15) can only be used if \([I]\) is uniform along the vertical axis of the reactor. Because the velocity depends on both the temperature (±30 K) and total molar flow rate, we estimate that the I atom flow rate is reliable to within 15%. This is consistent with the systematic uncertainty normally associated with flow tube measurements.21

The primary aspects of the model center on its ability to predict the changes in F atom number densities by three-body recombination, wall recombination, and reactions of F and I2 with I and I2. Hence, these aspects of the model are described in detail. The finite-rate chemistry and reactions used by our model are shown in Table 1 (see Refs. 24–31). The primary reactions are the production of I atoms via the reaction F + HI, the interhalogen reactions F + I2 and I + F2, and the atom recombination reactions. The vibrational distribution within HF produced by the F + HI reaction, the vibrational energy transfer reactions of HF, the energy transfer from HF(v) to I,
that surface catalysis of F atom recombination is a relatively inefficient process. Kota et al. also report temperature dependent relations for Cl and Br atoms. (see Ref. 27). The I atom recombination coefficient used in this model is 1.0, based on the recommendations of Perram and Hager\textsuperscript{26} and the work of Fisk and Hays.\textsuperscript{27} This value is also consistent with the recombination coefficients recently reported by Kota et al. for Cl and Br atoms\textsuperscript{28} (also see Ref. 26).

The computational domain for the physical space within the experiment simulated with this model extends from the exit of the discharge tube to the point at which the I atom measurements are taken in the streamwise direction, from wall to wall and shroud to shroud in the lateral direction, and from wall to wall in the vertical direction, see Fig. 1c. The discharge tube is treated as a black box entity, for which only the exiting mass flow is known; the pressure, temperature, and the F\textsubscript{2} dissociation fraction of the flow exiting the discharge tube are unknown quantities that are determined by matching the model predictions to measured quantities downstream. For the range of pressures, temperatures, and mass flow rates considered here, the flow exiting the discharge tube is subsonic, and in all simulations of the experiment, the flow is treated as subsonic throughout.

An important simplifying assumption of our calculations is that the HI/He flow is modeled with instantaneous mixing at the same streamwise position relative to the discharge tube exit at which the actual flow is injected. Secondary He is injected at the position of the second row of injectors, consistent with the experiment. Because the pressure across the injector orifices is always greater than 2:1, the sonic conditions are used to specify the temperature and pressure for each injectant flow.

The numerical technique used to solve the governing equations of the model is a first-order Adams–Bashfouth–Moulton method (see Ref. 35). In this numerical integration, the nominal step size $\Delta x$ is 0.05 cm. This value was chosen by iteration until changes in the integrated solution were <1%. The step size after gas injection locations was decreased to $\Delta x/200$ and returned to $\Delta x$ over a distance of 4$\Delta x$. The solution is marched through the channel in the flow direction giving only upstream dependence and not directly capturing the elliptic nature of the subsonic flow. The calculated downstream pressure is determined by varying the inflow pressure until the model prediction and measurement agree. This technique is also used to match the experimentally determined temperatures. Reactant flow rates are input to the model as fixed quantities and are not affected by the pressure/temperature iterations.

Each titration represents a series of experiments where all parameters and flow rates are held constant except [HI]. As the HI flow rate approaches 0, the heat release of the F+HI reaction is minimized, and the flow conditions approach those for the flow without HI. Hence, the initial temperature exiting the discharge is determined by matching the temperature and pressure with the model for the lowest HI flow rate in the titration. On the other hand, because the F\textsubscript{2} dissociation fraction exiting the discharge tube is also unknown, this quantity is determined by matching the I atom number density measured for the highest HI flow in each titration series. The high [HI] data are used because they have the highest signal-to-noise ratio and are the least kinetic model dependent. With the dissociation fraction, pressure, and temperature fixed, the model is run for the remaining HI flow rates in the titration.

![Fig. 3 Vertical profiles at various positions along the reactor; I atom laser probe can be translated along the transverse and vertical axis of the reactor. Profiles are flat for d ≥ 5.5 cm.](image)

![Fig. 4 Typical F+HI titration plots, I atom densities, I atom flow rates, and temperatures as a function of added HI at $F_2 = 0.45$ mmol s$^{-1}$: (a) $P = 12$ torr; (b) $P = 15$ torr; and (c) $P = 20$ torr.](image)
temperature profiles are no longer peaked. As the distance between the reagent inlet and the observation point increases, the temperature decreases and the temperature profiles are peaked in the center and fall off toward the edges. Clearly, a constant velocity distribution should be exhibited, indicative of a constant velocity distribution along the vertical axis. The data measured 2.5 cm from the HI inlet are peaked in the center and is -1-00 K lower at the edges. The I atom flow sured values. The agreement between the predicted temperatures via line shape analysis and the model.

Future reactor designs will resolve this problem. Figure 3b shows the theoretical line and the problem described earlier, the error is only ~20%, and the problem is not serious. In general, however, the agreement between the model and the experiment is very good, with the values and slopes of the agreement between the predicted temperatures via the line shape analysis and the model predictions tend to validate both the line shape analysis and the model.

Figures 6 and 7 summarize the titration results as a function of F2 flow rate and pressure. In all three panels, the data points represent

Experimental Results

A. Vertical Profiles

An important advantage of our experimental technique is the ability to measure I atom concentrations and temperatures along both the transverse and streamwise directions of the flow reactor. Figure 3a shows the vertical profiles of the I atom flow rate measured at F2 = 0.45 mmol s\(^{-1}\) with excess HI, P = 15 torr, and five different positions along the reactor. A uniform concentration profile should be exhibited, indicative of a constant velocity distribution along the vertical axis. The data measured 2.5 cm from the HI inlet are peaked in the center and fall off toward the edges. Clearly, a uniform flowfield has not been established and these data are not useful for determining \[I\] and T. The presence of at least one I atom loss process seems evident by the factor of 2 loss of I atoms at \(d = 5.5\) cm and 15.5 cm. However, subsequent chemiluminescent measurements indicated significant flaring of the flow and leakage around the 10.5- and 15.5-cm flow containment shrouds. Consequently, only the 5.5 cm datum is considered to be reliable. Future reactor designs will resolve this problem. Figure 3b shows the I atom temperature profiles. At \(d = 2.5\) cm, the temperature peaks in the center and is ~100 K lower at the edges. The I atom flow data violate mass balance, which indicates that the plug flow has not been established. As the distance between the reagent inlet and the observation point increases, the temperature decreases and the temperature profiles are no longer peaked.

The calculated temperature for \(d = 5.5\) cm is 488 K, and is consistent with the measured values. The agreement between the predicted temperatures via the line shape analysis and the model predictions tend to validate both the line shape analysis and the model.
both the is inversely proportional to the with larger increased F2, and although the corresponding titration curves. Figure 6 demonstrates the effect of in- 

\[ E = 375 \text{ kcal mol}^{-1} \]

\[ F_2 \text{ dissociation fraction, } \alpha = \frac{I \text{ atom yield}}{I \text{ atom flow rate}} \]  

\[ F_2 = 0.44 \text{ mmol s}^{-1} \]

\[ F_2 = 0.87 \text{ mmol s}^{-1} \]

\[ F_2 = 1.30 \text{ mmol s}^{-1} \]

the average I atom flow rate from the plateau region of the corresponding titration curves. Figure 6 demonstrates the effect of increased F2, and although the I atom flow rate is shown to increase with larger F2 flow rates, the I atom yield given by

\[ \alpha = \frac{I \text{ atom yield}}{2\text{F}_2 \text{ flow rate}} \]  

is inversely proportional to the F2 flow rate. These data indicate that both the F2 flow rate and reactor pressure affect the performance of the dc discharge. The highest F2-free flow rate of F atoms that we are capable of generating is 1.0 mmol s\(^{-1}\). As shown in Fig. 7, for \( F_2 \leq 0.44 \text{ mmol s}^{-1} \) and \( P \geq 20 \text{ torr} \), 100% dissociation is achieved. At higher F2 flow rates and pressures, the dissociation efficiency decreases linearly.

C. Cl + HI Titrations

A set of typical Cl + HI titrations are shown in Fig. 8. The atom flow rate generated by the Cl2 discharge is significantly smaller than that obtained from F2. In addition, the temperature is slightly lower, \( T = 400 \text{ K} \). Increasing the Cl2 flow rate does not generate more Cl atoms and increasing the pressure also degrades the discharge performance. The highest Cl atom flow rate that we can generate is 0.3 mmol s\(^{-1}\) independent of the initial flow rate of Cl2, and the average temperature is \( -380 \text{ K} \). The best dissociation efficiency, \( \alpha = 50\% \), is achieved for Cl2 = 0.5 mmol s\(^{-1}\) and \( P = 15 \text{ torr} \). This cursory analysis clearly indicates that Cl2 is inferior to F + HCl/DCI as a Cl atom source. As a result, no model calculations were performed.

Conclusions

The present results demonstrate the utility of the diode laser as a probe of atom flow rates and temperatures. Based on the experimental data and one-dimensional fluid mechanical modeling results, we have established the efficiency of our dc discharge for generation of large F and Cl atom densities. The X + HI titration reactions effectively convert the F and Cl atoms to iodine atoms, which are detected by near IR laser absorption. This method has clear advantages over alternative techniques such as resonance fluorescence or absorption, Cl2 recombination afterglow, and HF (\( \Delta v = 3 \)) chemiluminescence. Specifically, the laser probe technique gives both atom densities and temperatures and can give two-dimensional spatial resolution when the beam is translated along the vertical and streamwise axes of the reactor. When the path length is increased, extremely low concentrations can be measured.

References


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