EXCIMER LASER RESEARCH

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#### Abstract

This quarterly report describes experimental investigations of interhalogen molecules. These molecules are under consideration to achieve high power scalable laser action in the near UV and visible portion of the spectrum.

The report includes a description of fluorescence experiments for these molecules and an analysis of formation kinetics. A
A theoretical model has been developed to describe the excited ion-pair state structure of the interhalogens. The predictions of this theory are borne out by fluorescence experiments.
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I. INTERHALOGEN RESEARCH

This report discusses interhalogen research carried out under this contract. The primary accomplishments are summarized in Table 1. The section will first develop the motivation for interhalogen research and proceed to describe the analytical model and experimental results.

A. CRITERIA FOR LASER CANDIDATES

Experience gained from the rare gas and mercury monohalide lasers suggests several important criteria by which new laser candidates can be considered. These criteria are summarized in Table 2.

- Molecular excited states which are ionic in character provide the advantage of formation via long range reactive collisions which efficiently channel into the upper laser level.

For example, formation processes for the ionic states of HgCl* and KrF* include ion-ion recombination:

\[ \text{Kr}_2^+ + F^- \rightarrow \text{KrF}^* + \text{Kr} \]
\[ k \approx 2-3 \times 10^{-6} \text{ cm}^3/\text{sec} \]

\[ \text{Hg}^+ + \text{Cl}^- + \text{Ar} \rightarrow \text{HgCl}^* + \text{Ar} \]
\[ k \approx 2 \times 10^{-6} \text{ cm}^3/\text{sec} \]

Neutral reactions:

\[ \text{Kr}^* + \text{F}_2 \rightarrow \text{KrF}^* + \text{F} \]
\[ k = 8 \times 10^{-10} \text{ cm}^3/\text{sec} \]

\[ \text{Hg}^* + \text{Cl}_2 \rightarrow \text{HgCl}^* + \text{Cl} \]
\[ k = 3.8 \times 10^{-10} \text{ cm}^3/\text{sec} \]
and also replacement collisions:

\[ \text{Kr} + \text{ArF}^* \rightarrow \text{KrF}^* + \text{Ar} \]
\[ k = 5 \times 10^{-10} \text{ cm}^3/\text{sec} \]

\[ \text{Hg} + \text{XeCl}^* \rightarrow \text{HgCl}^* + \text{Xe} \]
\[ k \approx 3 \times 10^{-10} \text{ cm}^3/\text{sec} \]
TABLE 1. SUMMARY OF INTERHALOGEN RESEARCH

- **FORMATION OF INTERHALOGEN SPECIES** **ICl**, **IBr**, **BrCl**, **BrF**
  **IN ARGON/HALOGEN DONOR MIXTURES**
  - **EXCITED SPECIES DENSITY** $10^{13} - 10^{14}$ cm$^{-3}$
  - **EMISSION WAVELENGTHS** 300 nm - 450 nm
  - **FLUORESCENCE EFFICIENCY** 1 - 3%

- **INTERHALOGEN IONIC MODEL CALCULATED**
  - **TRANSITION WAVELENGTHS ESTIMATED**
  - **EXPERIMENTAL AGREEMENT WITHIN 10%**

- **NEUTRAL FORMATION CHANNEL OBSERVED IN ARGON MIXTURES**

- **ION-ION FORMATION CHANNEL PREDICTED FOR NEON MIXTURES**
TABLE 2. CRITERIA FOR NEW LASER CANDIDATES

- **IONIC UPPER LASER LEVEL**
  - EFFICIENT FORMATION CHARACTERIZED BY LARGE CROSS SECTIONS AND NEAR UNIT BRANCHING RATIOS

- **COVALENT/REPULSIVE OR SLIGHTLY BOUND LOWER LASER LEVEL**
  - DEPLETION BY THERMAL DISSOCIATION (XeF)
  - IF SLIGHTLY BOUND \( T_g \geq \frac{1}{20} D_e \)
  - LARGE DIFFERENCE IN INTERNUCLEAR SEPARATION (HgCl)
    VIBRATIONAL RELAXATION

- **POSITION OF ATOMIC/MOLECULAR STATES RELATIVE TO IONIC POTENTIAL CURVE**
  - IONIC STATE PREDISSOCIATION (ArI*, ArBr*)
  - FORMATION VIA METASTABLE REACTIONS

- **POSITION OF HIGHER LYING ELECTRONIC LEVELS OF THE MOLECULE**
  - LOW SELF ABSORPTION
The reaction rates shown above have been determined for both KrF* formation processes (1-3) and for HgCl* formation (4-6). The reaction branching ratios into the ionic excited state of KrF* are near unity for all of the above formation channels.

- Molecular ground states which are repulsive or characterized by a strong covalent bond avoid rapid bottlenecking during the laser pulse.

The lower state need only be repulsive enough for rapid molecular dissociation and may even be relatively flat as in the case of KrF shown in Figure 1. In fact, a strongly repulsive lower state, such as the Xe₂ ground state, may not be desirable since this could broaden the transition bandwidth and hence decrease the gain.

A strong covalent ground state may be acceptable for candidate molecules having a bound-bound transition. As a rule, covalent bonds exhibit much smaller internuclear equilibrium separations than ionic bonds. As shown in Figure 2 for HgCl, this results in a lower laser level which is a high lying vibrational level. In the case of HgCl, the lower level, \( v'' = 22 \), has been observed to be rapidly relaxed in high-pressure laser gas mixtures during laser pulses of 100 nsec. If the well depth is adequately large the manifold of lower state vibrational levels can be large enough to maintain a negligible population in the lower laser level even in the presence of rapid relaxation. In this way, bottlenecking of a bound lower laser level may be avoided for pulses the order of 1 µsec. This constraint on the lower laser level eliminates the alkaline earth monohalides as scalable laser candidates since the ground state as well as the first excited state are ionic character. For example, in CaCl the internuclear separations for the ground and excited states are identical. In this case, the most intense transition in a high pressure laser medium is \( v' = 0 \rightarrow v'' = 0 \) and this would incur rapid bottlenecking.
Figure 1. Estimated Potential Curves for KrF
Figure 2. Estimated Potential Curves for HgCl.
The position of molecular states below the ionic excited state is critical to both formation and quenching of this excited state via potential curve crossing. States whose potential curve cross the ionic potential curve far above the minimum may be useful in the formation of the ionic molecular state via neutral, or harpoon reactions. As shown in Figures 1 and 2, metastable Kr* and Hg* atoms open the respective formation channels:

\[
\text{Kr}^* \left( ^3P_2 \right) + \text{F}_2 \rightarrow \text{KrF}^* + \text{F} \\
\text{k} = 8 \times 10^{-10} \text{ cm}^3/\text{sec}
\]

\[
\text{Hg}^* \left( ^3P_2 \right) + \text{CCl}_4 \rightarrow \text{HgCl}^* + \text{CCl}_3 \\
\text{k} = 2 \times 10^{-10} \text{ cm}^3/\text{sec}
\]

It should be cautioned that excited states which cross the ionic potential curve near its minimum can lead to rapid dissociation of the ionic molecule. An example of this is indicated by the potential curves for ArI shown in Figure 3. In fact, ArI* emission is totally quenched by this predissociation and every ArI* simply leads to the creation of an excited iodine atom, I*. A similar situation occurs for ArBr*, resulting in Br* production. In fact this predissociation has been suggested\(^{(7)}\) as the primary formation process for the Br\(_2^*\) laser.

Clearly, if the ionic curve minimum is far enough above lower molecular states, branching into these lower states can be avoided. This condition can be satisfied in molecules composed of atoms have a ground state configuration which is closed shell, \(^1S_0\), namely the rare gases, Zn, Cd, and Hg, and the alkaline earths; or atoms with one electron less than a closed shell, the halogens. With the exception of iodine, these atomic species do not contribute states lying several
Figure 3. Estimated Potential Curves for ArI
electron volts above the ground states from which lower molecular potentials can be formed. Thus, the excited state ionic molecular curve can extend down to an energy of several eV without crossing many lower molecular curves. Transitions from the lowest vibrational levels of such ionic potentials result in visible and near UV wavelengths. In contrast, (np) \(^4\) outer shell electron configurations such as oxygen, selenium and sulfur have \(^1\)D and \(^1\)S states which lie within 1-3 eV of the ground state. These will lead to molecular potentials which cross the ionic excited state curves and possibly incur predissociation in a species such as ClO.
The existence of ionic excited states in the homonuclear halogen molecules is well established. The halogen lasers Br$_2$, I$_2$, and F$_2$ have ionic upper levels and are generally consistent with the candidate criteria discussed previously. The larger class of interhalogens should also be considered as laser candidates since the presence of ionic excited states in these molecules provides the possibility of efficient formation, visible laser transitions, and room temperature operation. The similarity of the excited ionic states of the interhalogens to the ground state alkali halides derives from the fact that an excited halogen atom has a tightly bound core similar to that of the neighboring ground state alkali atom. For example, the electron configuration of excited Br*:(4p)$^4$5s and ground state Rb:(4p)$^6$5s both include a core of tightly bound 4p electrons and a loosely bound 5s valence electron. The ionization potential of the 5s electron, 3.98 eV for Br* and 4.18 eV for Rb, are quite close as well as the second ionization potential of a 4p electron, 27.5 eV for Rb and 19.2 eV for Br*. This will result in a chemistry which is kinetically and generically similar for Br* and Rb. One consequence of this is the ability to form an excited ionic state via the neutral or harpoon reaction:

\[ \text{Br}^* + \text{ACl} \rightarrow \text{Br}^+ \text{Cl}^- + \text{A} \]

which occurs via the Br$^* + \text{Cl}$ curve crossing with the Br$^+ + \text{Cl}^-$ potential curve. This crossing is ensured since the Br$^*$(4P$_{5/2}$) metastable energy of 7.86 eV is below the asymptote of the lowest ionic curve for Br$^+$(3P$_2$) + Cl$^-$($^1S_0$) at 8.23 eV.

The interhalogen ground electronic state 1$\Sigma^+$ has been well characterized as shown in Table 3. There is much less information about the low lying excited molecular $^3\pi_{0,1,2}$ states resulting from combination of halogen atoms in the ground spin-orbit states $^3P_{1/2}$ and $^3P_{3/2}$. Figures 4, 5, and 6
### TABLE 3. INTERHALOGEN GROUND STATE $^1\Sigma^+$ PARAMETERS

<table>
<thead>
<tr>
<th></th>
<th>$R_O''$ (Å)</th>
<th>$\omega''$ (cm$^{-1}$)</th>
<th>$D_O''$ (eV)</th>
<th>References</th>
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<tr>
<td>BrCl</td>
<td>2.14</td>
<td>443</td>
<td>2.25</td>
<td>(12)</td>
</tr>
<tr>
<td>IC</td>
<td>2.33</td>
<td>382</td>
<td>2.19</td>
<td>(13)</td>
</tr>
<tr>
<td>IBr</td>
<td>2.49</td>
<td>267</td>
<td>1.84</td>
<td>(14)</td>
</tr>
<tr>
<td>FCl</td>
<td>1.63</td>
<td>784</td>
<td>2.59</td>
<td>(15)</td>
</tr>
<tr>
<td>FBr</td>
<td>1.76</td>
<td>673</td>
<td>2.42</td>
<td>(12)</td>
</tr>
<tr>
<td>FI</td>
<td>1.91</td>
<td>612</td>
<td>2.91</td>
<td>(12)</td>
</tr>
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</table>

$R_O''$: equilibrium internuclear separation  
$\omega''$: vibrational level separation  
$D_O''$: dissociation energy
Figure 4. Morse Potential Energy Functions for ICl

\[
\begin{align*}
CI(2P,\downarrow) + I(2P) &\rightarrow 3Cl(1P) + I(1S^+,0) \\
CI(2P,\downarrow) + I(2P) &\rightarrow \text{other configurations}
\end{align*}
\]

The diagram illustrates the potential energy functions as a function of internuclear distance, \( r(\text{Å}) \). The labels \( ^3\Pi_1 \), \( ^3\Pi_0 \), and \( \Sigma^+ \) represent different energy levels or states, with \( \nu = 0 \) and \( \nu = 1 \) indicating vibrational states.
Figure 5. Morse Potential Energy Functions for BrC1 (Broken Lines Indicate the Estimated Positions of Unobserved States.)
Figure 6. Approximate Potential Energy Curves for IBr
show these lower excited molecular states for I Cl, \(^{(16)}\) Br Cl \(^{(16)}\) and I Br. \(^{(17)}\) The excited ion-pair states of these molecules has not been considered previously.

The following analysis predicts the features of the interhalogen ion-pair excited states and the wavelengths of expected laser transitions. It is assumed for these purposes that the lowest ion-pair states correlating with the lowest halogen positive ion states \(X^+ (^3P_{2,1,0})\) have the same shape and are separated at the potential minima by the \(^3P_{2,1,0}\) level separations.

The excited state ion-pair potential curve for interhalogen diatomics has been approximated by a truncated Rittner potential \(^{(18)}\) with a repulsive term of the Born-Mayer form. \(^{(19)}\) This approximation includes the ion-ion polarization terms which are important for the interhalogen \(X^+ Y^-\) pairs due to the sizeable positive ion polarizability. These polarizabilities for halogen atoms can be estimated from the negative ion polarizabilities by methods discussed elsewhere. \(^{(20)}\) A comparison of these polarizabilities in Table 4 shows the halogen positive ion polarizabilities are a factor of \(-2\) greater than those of the corresponding alkali atoms. \(^{(18)}\) As an example, the polarization terms contribute \(-16\%\) to the calculation of the ion-pair binding energy for \(Cl^+ F^-\).

Table 5 lists the results of these calculations and compares the interhalogen ion-pair state features to those of the alkali halides. \(^{(18)}\) In general, note that the interhalogen equilibrium separation is small and the binding energy is greater than the corresponding alkali halide. This is a result of the stronger ion-ion polarization interaction between halogen ion pairs.

To estimate the interhalogen wavelengths expected to exhibit strong lasing transitions, assumptions concerning the lower levels are necessary. Analogous to the identification \(^{(21)}\) of the lasing transitions in \(I_2\) and \(Br_2\), it will be assumed that the strong interhalogen transitions will also occur between \(^3\pi_2 \rightarrow ^3\pi_2\) molecular states. As shown in Section III, the \(I_2\)
TABLE 4. HALOGEN POLARIZABILITIES

<table>
<thead>
<tr>
<th></th>
<th>$\alpha_-(\text{Å}^3)$</th>
<th>$\alpha_+(\text{Å}^3)$</th>
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<tr>
<td>F$^-$</td>
<td>1.28</td>
<td>0.456</td>
<td>Na$^+$</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>3.00</td>
<td>1.51</td>
<td>K$^+$</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>4.50</td>
<td>2.56</td>
<td>Rb$^+$</td>
</tr>
<tr>
<td>I$^-$</td>
<td>7.00</td>
<td>4.05</td>
<td>Cs$^+$</td>
</tr>
<tr>
<td>INTERHALOGEN</td>
<td>ALKALI HALIDE</td>
<td>Re (Å) (a)</td>
<td>E_B (ev) (b)</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------</td>
<td>------------</td>
<td>--------------</td>
</tr>
<tr>
<td>FCl</td>
<td>NaCl</td>
<td>2.13</td>
<td>6.52</td>
</tr>
<tr>
<td>FBr</td>
<td>NaBr</td>
<td>2.34</td>
<td>6.09</td>
</tr>
<tr>
<td>F1</td>
<td>NaI</td>
<td>2.40</td>
<td>6.22</td>
</tr>
<tr>
<td>ClF</td>
<td>KF</td>
<td>2.16</td>
<td>6.32</td>
</tr>
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<td>IF</td>
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<td>IBr</td>
<td>CsBr</td>
<td>2.89</td>
<td>5.08</td>
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(a) Re is the equilibrium internuclear separation
(b) E_B is the ion-pair binding energy
lower laser level $^{3}g$ is a low lying excited state nested within the ground electronic state manifold. The low lying excited states shown in Figures 4-6 indicate similar nested states for the interhalogens. It will be assumed that the $^{3}g$ and $^{3}u$ curves are as close for interhalogens as they are (8) for I$_{2}$ (~1 eV) and this difference will be neglected here.

Table 6 lists the predicted laser wavelengths for the interhalogen molecules. The wavelengths have been indicated for transitions originating from the two lowest ion-pair states which correlate with the separate atoms $X^{+}(^{3}P_{2}) + Y^{-}(^{1}S_{0})$ and $X^{+}(^{3}P_{1,0}) + Y^{-}(^{1}S_{0})$. Also listed are the strongest fluorescence bandheads observed in our e-beam pumping experiments and also the demonstrated laser transitions. The largest variation is < 10% and results from the uncertainty in estimating the lower state of the transition. In these calculations the lower energy level is taken to be the $^{3}g_{2}$ potential minimum. The observed transitions appear to be originating on the higher ion-pair state. This is consistent with possible formation channels and will be discussed below in the kinetics section.

Figure 7 shows an estimated potential curve for I Cl based upon the analysis of this section. Figures 8 and 9 show microdensitometer traces of I Cl* and Br Cl* spectra for different gas mixture compositions. Note that the strong interhalogen bands overlap the weaken Br$_{2}$* and I$_{2}$* bands. Fluorescence data was also obtained for I Br* and BrF*.
TABLE 6. COMPARISON OF PREDICTED/OBSERVED INTERHALOGEN SPECTRA

- ESTIMATE TRANSITION BAND WAVELENGTHS

\[
\begin{align*}
X^+ (^3P_{1,0}) + Y^- (^1S_0) & \rightarrow ^3\Pi_{1,2} \\
X^+ (^3P_2) + Y^- (^1S_0) & \rightarrow ^3\Pi_{1,2}
\end{align*}
\]

<table>
<thead>
<tr>
<th>X⁺Y⁻</th>
<th>λ₁ (nm)</th>
<th>λ₂ (nm)</th>
<th>λ⁰BS (nm)</th>
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<tr>
<td>IF</td>
<td>480</td>
<td>700</td>
<td>491 (15)</td>
</tr>
<tr>
<td>ICl</td>
<td>450</td>
<td>670</td>
<td>430</td>
</tr>
<tr>
<td>IBr</td>
<td>380</td>
<td>510</td>
<td>390</td>
</tr>
<tr>
<td>BrF</td>
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<td>270</td>
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</tr>
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Figure 7. Estimated Potential Curves for ICl
Figure 8. E-Beam Excited ICl* Fluorescence
Figure 9. E-Beam Excited BrCl* Fluorescence
C. INTERHALOGEN KINETICS

Two possible formation channels into the ionic state may be used to advantage in direct e-beam pumping of high pressure gas mixtures. These formation processes leading to the interhalogen excited ion-pair species \( XY^* = X^+ Y^- \) include ion-ion recombination

\[
X^+ + Y^- + M \rightarrow XY^* + M
\]

and the neutral reaction

\[
X^* + AY \rightarrow XY^* + A
\]

1. Ion Formation Channel

The ion pathways may be accessed through the predissociation of neon halide species into halide positive ions. It is well established\(^7\) that \( Ar^+ Br^- \) predissociates

\[
Ar Br^* \rightarrow Ar + Br^* (^4P)
\]

into the manifold of bromine \(^4P\) states. Similar processes occur for \( Ar Cl^* \), \( ArI^* \) and \( NeF^* \) to yield \( Cl^* \), \( I^* \) and \( F^* \). This predissociation follows from the curve crossings shown in Figure 10 which occurs at the minimum of the \( ArI^* \) potential curve. Similar predissociation is predictable for the neon halides \( Ne Br^* \), \( Ne Cl^* \) and \( NeF^* \). However, in this case, the predissociation should yield \( Br^+ \), \( Cl^+ \) and \( I^+ \) as indicated in Figure 11. The predicted 'interhalogen formation kinetics for Ne/AX/BY mixtures of high pressure Ne and halogen bearing molecules AX, BY is characterized by the example

\[
ed_p + Ne \rightarrow Ne^+ e_p + e_s
\]

\[
e_s + \begin{cases} AX \rightarrow X^- + A \\ BY \rightarrow Y^- + B \end{cases}
\]

\[
Ne^+ + X^- + Ne \rightarrow NeX^* + Ne
\]

\[
NeX^* \rightarrow X^+ + Ne
\]

\[
X^+ + Y^- + Ne \rightarrow XY^* + N
\]
Figure 10. Estimated Potential Curves for ArI
Figure 11. Predicted Neon Halide Predissociation
Many pathways have been ignored in this simple example, however, such a scheme can describe the recent ClF* laser demonstration\(^{22}\) in Ne/F\(_2\)/Cl\(_2\).

2. **Neutral Formation Channel**
   
   In general, the neutral reaction channel is not easily accessed in direct e-beam excitation. However, as mentioned above, mixtures excited halogen atoms may readily be formed in rare gas/halogen mixtures by
   
   \[
   \text{Ar}_2^+ + I^- + \text{ArI}* + \text{Ar} \\
   \text{ArI}* \rightarrow \text{Ar} + I^* 
   \]
   
   as indicated in Figure 3, and also by
   
   \[
   \text{Ar}_2^+ + \text{Br}^- \rightarrow \text{ArBr}* + \text{Ar} \\
   \text{ArBr}* \rightarrow \text{Ar} + \text{Br}^* 
   \]
   
   and
   
   \[
   \text{Ne}_2^+ + F^- \rightarrow \text{NeF}* + \text{Ne} \\
   \text{NeF}* \rightarrow \text{Ne} + F^* 
   \]
   
   In this case, the formation of an ionic state via the neutral reactions
   
   \[
   \text{Br}^* + \text{CF}_3\text{Cl} \rightarrow \text{BrCl}* + \text{CF}_3 \\
   \text{I}^* + \text{CF}_3\text{Cl} \rightarrow \text{ICl}* + \text{CF}_3 \\
   \text{F}^* + \text{CF}_3\text{Cl} \rightarrow \text{FCI}* + \text{CF}_3
   \]
   
   become accessible. Analogous neutral reactions have been identified\(^{7}\) as the formation channels for Br\(_2\)* excited states in Ar/Br\(_2\) and Ar/BrI mixtures. The interhalogen formation channels indicated above should comparable to those processes observed in Ref. 7. These neutral kinetics rely on finding the optimum halogen donors and mixture composition such that dissociative electron attachment forms primarily I\(^-\) and Br\(^-\). It is also important to recognize that competing neutral reactions will be present such as

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\[ \text{Br}^* + \text{HBr} \rightarrow \text{Br}_2^* + \text{H} \]
\[ \text{Br}^* + \text{CF}_3\text{Cl} \rightarrow \text{CF}_3\text{Br}^* + \text{Cl} \]

Examples of candidate molecules and gas mixture components favorable for formation via netural reactions are shown in Table 7.

The experimental results shown above in Section II.B are consistent with the neutral formation channels indicated in Tables 8 and 9. Particularly in the case of ICl* formation, the emission appears to be originating on the ionic potential curve correlating with \( \text{I}^+ (3\text{P}_0) + \text{Cl}^- (\text{S}_0) \) which is the second ion-pair state. The excited I* levels produced in the predissoiciation of ArI* have energies \( 4\text{P}_{5/2} \) (6.77 eV), \( 4\text{P}_{3/2} \) (7.66 eV), \( 4\text{P}_{1/2} \) (7.55 eV). The details of the dynamics depend on the \( 4\text{P} \) branching ratios but it is evident that selective excitation of the \( \text{I}^+ (3\text{P}_0) \) ion state is possible and also is consistent with the shorter wavelengths predicted by the ionic state model.
TABLE 7. GAS MIXTURES FOR INTERHALOGEN FORMATION VIA NEUTRAL CHANNELS

- FORMATION OF \((XY)^* = (X^+Y^-)\)

\[ X^* + AY \rightarrow (XY)^* + A \]

<table>
<thead>
<tr>
<th>IONIC STATE</th>
<th>GAS MIXTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I^+Cl^-)</td>
<td>Ar/HI/CF(_3)Cl</td>
</tr>
<tr>
<td>(I^+F^-)</td>
<td>Ar/HI/CF(_4)</td>
</tr>
<tr>
<td>(I^+Br^-)</td>
<td>Ar/HI/HBr</td>
</tr>
<tr>
<td>(Br^+Cl^-)</td>
<td>Ar/HBr/CF(_3)Cl</td>
</tr>
<tr>
<td>(Br^+F^-)</td>
<td>Ar/HBr/CF(_4)</td>
</tr>
<tr>
<td>(Br^+I^-)</td>
<td>Ar/HBr/CF(_3)I</td>
</tr>
<tr>
<td>(F^+Cl^-)</td>
<td>Ne/F(_2)/CF(_3)Cl</td>
</tr>
<tr>
<td>(F^+Br^-)</td>
<td>Ne/F(_2)/CF(_3)Br</td>
</tr>
<tr>
<td>(F^+I^-)</td>
<td>Ne/F(_2)/CF(_3)I</td>
</tr>
</tbody>
</table>

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TABLE 8. NEUTRAL FORMATION CHANNEL CONSISTENT
WITH BrF*, BrCl* FLUORESCENCE RESULTS

$\text{Ar/HBr/CC}_4$, NF$_3$: 50 PSIA/10t/2t

\[
\begin{align*}
\text{Ar} + e_p & \rightarrow \text{Ar}^+ + e_p + e_s \\
\text{Ar}^+ + 2\text{Ar} & \rightarrow \text{Ar}_2^+ + \text{Ar} \\
e_s + \text{HBr} & \rightarrow \text{Br}^- + \text{H} \\
\text{Ar}_2^+ + \text{Br}^- & \rightarrow \text{ArBr}^* + \text{Ar} \\
\text{ArBr}^* & \rightarrow \text{Ar} + \text{Br}^* (5s) \\
\text{Br}^* + \text{CC}_4 & \rightarrow \text{BrCl}^* + \text{CC}_3 \\
& \quad \quad \text{315 nm} \\
\text{Br}^* + \text{NF}_3 & \rightarrow \text{BrF}^* + \text{NF}_2 \\
& \quad \quad \text{355 nm} \\
\text{Br}^* + \text{HBr} & \rightarrow \text{Br}_2^* + \text{H} \\
& \quad \quad \text{292 nm}
\end{align*}
\]
### TABLE 9. NEUTRAL FORMATION CHANNEL
**CONSISTENT WITH ICl*/IBr* FLUORESCENCE RESULTS**

Ar/I₂/CCl₄, HBr : 50 PSIA/30t/10t

\[
\begin{align*}
\text{Ar} + e & \rightarrow \text{Ar}^{+} + e_{p} + e_{s} \\
\text{Ar}^{+} + 2\text{Ar} & \rightarrow \text{Ar}_{2}^{+} + \text{Ar}
\end{align*}
\]

\[
\begin{align*}
e_{s} + \text{I}_{2} & \rightarrow \text{I}^{-} + \text{I} \\
\text{Ar}_{2}^{+} + \text{I}^{-} & \rightarrow \text{ArI}^{*} + \text{Ar}
\end{align*}
\]

\[
\begin{align*}
\text{ArI}^{*} & \rightarrow \text{Ar} + \text{I}^{*} (6s) \\
\text{I}^{*} + \text{CCl}_{4} & \rightarrow \text{ICl}^{*} + \text{CCl}_{3} \\
\text{I}^{*} + \text{HBr} & \rightarrow \text{IBr}^{*} + \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{I}^{*} + \text{I}_{2} & \rightarrow \text{I}_{2}^{*} + \text{I}
\end{align*}
\]

\[
\begin{align*}
& \text{430 nm} \\
& \text{390 nm} \\
& \text{342 nm}
\end{align*}
\]

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