FOREATION, RELAXATION AND QUENCHING OF XeF, KrF AND XeCl

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ABSTRACT

Reactive quenching of the first two excited states of rare gas atoms, Rg(np5 n=1, s, P2 and P1), by halogens yields rare gas halide molecules in the B and C states and with high vibrational distributions. Interpretation of the bound-free emission spectra permits assignment of the initial distributions. Subsequent collisions of the rare gas halide molecules with He, Ne and Ar bath gas atoms result in transfer between the B and C states and vibrational relaxation. For high v levels the transfer rate is faster than vibrational relaxation, but the reverse holds for lower v levels. This can lead to a 300 K Boltzmann vibrational distribution but a nonequilibrium electronic state distribution of rare gas halide molecules in the B and C states. Modeling of the variation of the rare gas halide electronic and vibrational distributions with pressure gives a state-to-state view of relaxation processes. Photochemical dissociation of XeF2 yields XeF(B) in low v levels. Observation of the steady-state emission intensity from XeF(B), and XeF(C) from photodissociation in the presence of added reagents permits assignment of rate constants for B-C transfer and for quenching of XeF(B) and XeF(C) with 300 K Boltzmann vibrational distributions. Both the reactive quenching and photodissociation experiments indicate that the (C, ν = 3/2) state is lower in energy than the (B, ν = 1/2) state for XeF, XeCl and KrF. This has important implications for utilization of rare gas halide molecules for high power lasers.
The most important RgX formation processes for electrically driven lasers is either reactive quenching or ion-ion combination.

$$Rg(nP^5 + s) + X_2 \rightarrow RgX(B,C, \text{high } v) + X \quad (1)$$

$$Rg^* + X^* + M \rightarrow RgX(B,C, \text{high } v) + M \quad (2)$$

Reactive quenching is well characterized, see section II. Ion-ion combination has not been isolated and studied in the laboratory; but, the theoretical treatments for the rate constants seem reliable. Presumably ion-ion combination will yield molecules in both B and C states with high vibrational distributions. Vacuum U.V. photolysis of XeF$_2$ or KrF$_2$ provides a source of XeF(B) and KrF(B) in low vibrational levels$^7$.

$$\text{XeF}_2 + h\nu \rightarrow \text{XeF}(B, \text{low } v) + F \quad (3)$$

Since (1) and (2) give high v levels, one needs to understand the relaxation and quenching processes of RgX(B) and RgX(C) throughout the manifold of vibrational levels. Relaxation is defined to include vibrational relaxation and transfer between the B and C states. Quenching refers to collisional transfer to the RgX(X) or RgX(A) states.

The general importance of the RgX(C) state has been realized only recently. Clearly the C state must be included in any realistic modeling of lasers involving the B-X transition, and Lorents and co-workers have demonstrated that the XeF(C,3/2 - A,3/2) transition itself can be made to lase. They utilized the vacuum photodissociation of XeF$_2$ as the Xe$^*$ source. The focal point of this discussion will be the relationship between the RgX(B) and RgX(C) states. Our work only deals with heavy particle collisions, but the effects of energetic electrons on the B and C states also is of practical importance. The work that will be discussed is of practical importance to lasers; however, the opportunity to observe the state-to-state kinetics of the ionic rare gas halide molecules is of more basic interest. In the remainder of the discussion, the state-to-state kinetics will be emphasized rather than applications to lasers.

II. RARE GAS HALIDE FORMATION PROCESSES

A. Reactive Quenching of Rg$^*(nP^5)$ or Rg$^*(nP^7)$

The reactions of Xe$^*(nP^5)$, Kr$^*(nP^7)$ and Ar$^*(nP^7)$ with a variety of halogen donors X$_2$ and EX (R = polyatomic group) have been thoroughly studied by the flowing afterglow technique$^7$-$^{11}$. Total quenching rate constants, branching fractions for rare gas halide formation ($\Gamma_{RgX}$), electronic state ratios and vibrational distributions have been established. Very recently the reactions of the Xe$^*(nP^5)$ and Kr$^*(nP^7)$ resonance state atoms have been investigated by the resonance sensitization technique$^{12}$. Low pressure spectra from the reactions of Xe$^*(nP^5)$ and Xe$^*(nP^7)$ atoms with C$_2$F$_4$ are shown in Figure 1. The appearance of the spectra are virtually identical (close inspection reveals slightly more XeCl(B) and slightly more vibrational energy for the Xe$^*(nP^5)$ reactions). Within our experimental uncertainty the results from the resonance state atom reactions generally appear to be the same as for the $^{1P^5}$ metastable states of Kr and Xe. A summary of results from some common donor molecules is given in Table I. The vibrational distributions$^{10,13}$ were obtained by computer simulation of the bound free spectra; two samples are shown in Figure 2. Generally the vibrational distributions for RgX(B) and RgX(C) are the same. Despite the fact that HC$_2$I is the favored fuel for the XeCl laser, the $\Gamma_{XeCl}$ for reaction with HC$_2$I(v=0) is very small and some other formation process must be important in the laser.
medium. The results from the reactive quenching studies can be summarized as follows. The branching fractions for rare gas halide formation from diatomic halogens are nearly unity for Xe(3P₂) and Kr(3P₂) but somewhat less than unity for Ar(3P₂).

(2) Branching fractions for rare gas halide formation from diatomic halogens are nearly unity for Xe(3P₂) and Kr(3P₂) but somewhat less than unity for Ar(3P₂).

(3) Only the halides of Groups VI and V and a few carbon compounds (CCl₄, CBr₄, CF₃I) have \( \Gamma_{\text{RgX}} \) values of significance. A good correlation exists between compounds which dissociatively attach thermal electrons to give X⁻ and \( \Gamma_{\text{RgX}} \).

(i) For a given polyatomic reagent, \( \Gamma_{\text{RgX}} \) declines with increasing energy of Rg⁻

(ii) For a given Rg⁻, \( \Gamma_{\text{RgX}} \) declines with increasing complexity of RX.

(4) For nearly all reagents RgX(B)/RgX(C) is between 1.0 and 2.0

(5) The RgX vibrational distributions mainly depend upon the properties of the anion, X⁻, and Rg⁻, in accord with the models developed to explain the energy disposal for the electron transfer reactions of alkali metal atoms.

Most of these features can be explained in qualitative terms by the ionic-covalent curve-crossing mechanism developed for alkali metal atom reactions. This mechanism is presented in diagramatic form in Figure 3. The total quenching cross-sections are large and determined by orbiting radius on the lower adiabatic potential. The branching fractions may be less than unity because the lower adiabatic potential, i.e. \( V(Rg_x, X^-) \), is imbedded in a continuum of \( X^- \) or RX⁻ potentials and the interaction between \( V(Rg_x, RX^-) \) and \( V(Rg_x, X^-) \) is likely to be strong for some of the alternative channels. This likelihood increases with increasing density of states, e.g. higher energy or more complex RX molecules. Since the nature of the exit channel potential depends on the properties of the negative ion, \( \langle f_X \rangle \) strongly correlates with the nature of RX⁻. There is no fundamental explanation of why B and C are formed in approximately equal proportions. Apparently these two potentials are close in energy throughout the traversal of the exit channel and the states are strongly mixed if there is a large amount of excess energy. There is little dependence of the B and C state ratio upon whether the rare gas atom is in the 3P₂ or 1P₁-state; however, no experimental tests have been made for the 3P₀ or 1P₁ states.

Figure 2: Comparison of simulated (upper) and experimental (lower) spectra for XeC1(B-X) transition: lower set = 0.25 torr of Ar, upper set = 1.3 torr of Ar.

(1) Total thermal quenching cross-sections invariably are large, near the gas kinetic values.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Gate a</th>
<th>R a</th>
<th>e V</th>
<th>Vibrational distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr(3P₂) + F₂</td>
<td>72</td>
<td>1.5</td>
<td>0.85</td>
<td>( \lambda ) = 0.56 ( \lambda ) = 0.56</td>
</tr>
<tr>
<td>Kr(3P₂) + F₇</td>
<td>129</td>
<td>0.15</td>
<td>0.40</td>
<td>transverse ( \lambda ) = 0.56 ( \lambda ) = 0.56</td>
</tr>
<tr>
<td>Kr(3P₂) + OF</td>
<td>55</td>
<td>0.15</td>
<td>0.40</td>
<td>( \lambda ) = 0.56 ( \lambda ) = 0.56</td>
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<tr>
<td>Kr(3P₂) + CF₃OF</td>
<td>42</td>
<td>0.15</td>
<td>0.40</td>
<td>( \lambda ) = 0.56 ( \lambda ) = 0.56</td>
</tr>
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<td>Kr(3P₂) + Cl₂</td>
<td>75</td>
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<td>0.69</td>
<td>( \lambda ) = 0.56 ( \lambda ) = 0.56</td>
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<tr>
<td>Kr(3P₂) + ClF</td>
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<td>1.0</td>
<td>0.69</td>
<td>( \lambda ) = 0.56 ( \lambda ) = 0.56</td>
</tr>
<tr>
<td>Kr(3P₂) + CHCl</td>
<td>52</td>
<td>0.42</td>
<td>1.2</td>
<td>( \lambda ) = 0.56 ( \lambda ) = 0.56</td>
</tr>
<tr>
<td>Kr(3P₂) + SiCl₃</td>
<td>63</td>
<td>0.13</td>
<td>1.2</td>
<td>( \lambda ) = 0.56 ( \lambda ) = 0.56</td>
</tr>
<tr>
<td>Kr(3P₂) + CHCl₃</td>
<td>49</td>
<td>0.24</td>
<td>1.0</td>
<td>( \lambda ) = 0.56 ( \lambda ) = 0.56</td>
</tr>
</tbody>
</table>

Table 1. Summary of results for reactive quenching

a. Taken from reference 9, 10 and 11; for the \(^3P_2\) resonance states the rate constants may be \( \approx 10 \) \% larger. The uncertainty in \( \Gamma_{\text{RgX}} \) is \( \pm 10 \% \); branching fractions for the \(^3P_2\) atom are not well established but the trends are the same as for the \(^3P_2\) atom reactions.

b. For Xe(3P₂) reacting with NF₃, OF₂ and CF₃OF, \( \Gamma_{\text{XeF}} = 1.1, 0.92 \) and 0.40, respectively.

c. These are the low pressure limits.

d. These are the steady-state distributions. Correction for the variation of lifetimes with v level gives an initial distribution of slightly lower \( \langle f_v \rangle \). The linear surprisal type distribution denoted by the \( \lambda \) value is used to represent a type of distribution \( \lambda \) we do not mean that the initial distribution has a linear surprisal in the information-theoretic sense.
Figure 3: Schematic potential diagram for Rg + RX reactive quenching. The heavily lined area over the entrance channel represents the continuum of RX* or X* excited states through which the ion-pair potential must pass to reach the RgX* + X exit channel. The dotted area is the RgX* vibrational distribution. For ArCl, ArBr, ArI, and KrBr; some of the RgX* levels are predissociated to Rg + X* and this is indicated in the upper left hand corner.

B. Photodissociation of XeF₂ and KrF₂

In contrast to reactive quenching, vacuum ultraviolet photodissociation of XeF₂ or KrF₂ gives > 90% XeF(B) or KrF(B) in a very low vibrational distribution, see Figure 4. Although the quantum yield has not been measured, it must be high and may be unity. After passivation of the stainless steel cell with F₂ followed by flowing XeF₂ through the cell for several hours, the fluorescence signal from XeF₂ is very constant because XeF₂ is reformed. In contrast quantitative studies with KrF₂ are much more difficult because of the initiation of the chain reaction destroying KrF₂.

\[
\begin{align*}
\text{KrF}_2 + h\nu & \rightarrow \text{KrF}(B) + F \\
\text{KrF}(B) & \rightarrow \text{Kr} + F + h\nu \\
F + \text{KrF}_2 & \rightarrow \text{F}_2 + \text{Kr} + F
\end{align*}
\]

Therefore, steady-state photolytic studies with KrF₂ must be done by continuous flow of KrF₂ through the cell. The photodissociation method provides an important alternative method to reactive quenching for generating XeF(B) and KrF(B) and for study of the kinetics of the B state in low v levels. The photodissociation method, using either pulsed \(^{14,15}\) or steady-state technique, \(^3\) have provided the best measurements of radiative lifetimes and quenching rate constants.

The dissociative state of XeF₂ results from promotion of an electron from the 10\(\sigma_u\) to the 7\(\sigma_u\) orbital. The latter is a strongly antibonding orbital and leads to dissociation. Based upon the XeF product state distribution, this potential has no re-
lation to the potential (see Figure 3) for reactive quenching. This suggests that the reactive quenching potential does not involve insertion of Xe$^+$ between the F$_2$ atoms but rather Xe$^+$ reacts with a terminal F in the same way that an alkali metal atom reacts with X$_2$.

III. RELAXATION OF RgX(B) AND RgX(C) IN HIGH VIBRATIONAL LEVELS.

The primary data are XeF, XeCl and KrF spectra from reactive quenching obtained in the presence of various pressures of He, Ne and Ar, see Figure 5.

The photosensitization technique is especially useful because pressures from 0.1 to 3000 torr can be investigated. The flowing afterglow technique is limited to 0.1 to $\sim$ 50 torr. From these spectra the $I_B$/$I_C$ ratios (see Figure 5) and vibrational distributions (see Figure 6) can be obtained vs pressure. The vibrational distributions are obtained by computer simulation (see Figure 2 for an example). In converting from $I_B$/$I_C$ to a steady-state concentration ratio, the emission ratio must be multiplied by $t_C/t_B$, which is $\sim$ 10. Although the lifetimes increase by a factor of $\sim$ 3 for levels at $v = 100$, the ratio of lifetimes stays approximately constant. The relaxation can be discussed best by considering three pressure regimes, which for XeF* (or XeCl) in Ar are 0-5 torr, 5-50 torr and 50-2000 torr.

In the 0-5 torr regime the $I_B$ increases at the expense of $I_C$, the B state vibrational distributions change as shown in Figure 6 but only modest shifts occur in the vibrational populations of the C state. Since the lifetimes of the B state levels are shorter than the time between collisions for this pressure range, these effects must be associated with collisions with the XeF(C) (or XeCl(C).
state). Evidently molecules in the high v levels of the C state mainly are transferred to lower levels in the B state rather than being collisionally relaxed within the C state. From examination of the variation of the vibrational distribution of the XeCℓ(B) state with pressure, the distribution for molecules being transferred from C to B was obtained (see Figure 6). After the simulation of the C-A spectra has been completed, the vibrational relaxation within the C state also can be assigned.

In the intermediate pressure regime the \( \frac{I_{B-X}}{I_{C-A}} \) ratio increases slowly but the vibrational relaxation in both B and C states is quite rapid. Understanding the processes in this regime must await a full model: however, most likely transfers between B and C and vibrational relaxation within each manifold of levels occur simultaneously. These two processes have a strong dependence upon vibrational level and at some intermediate energy vibrational relaxation begins to dominate over transfer. At 10 torr, the XeCℓ(B) vibrational distributions have relaxed to approximately a very high temperature Boltzmann distribution. For such a temperature the equilibrium ratio should be \( \approx 1.5 \), which does approximately correspond to the observed steady-state concentration ratio in Figure 6. With further increase of pressure from 10-100 torr, vibrational relaxation to a 300 K Boltzmann distribution occurs with little change in electronic state population. Thus, the B/C ratio characteristic of the high vibrational temperature is frozen out.

With increase of pressure above 50 torr, the \( \frac{I_{C-A}}{I_{B-X}} \) ratio increases because the high temperature electronic state distribution is relaxing to a true 300 K Boltzmann distribution. For XeCℓ and XeF the limiting intensity ratio appears to be 0.3 and 3.2 respectively, which correspond to energy separations of 230 and 720 cm\(^{-1}\), respectively, with the C state being lower. These relaxation processes are summarized below for a rare gas bath gas; the subscripts, \( v'' \), \( v' \) and \( v \) represent high, intermediate and 300 K Boltzmann levels, respectively.

The values for the transfer rate constants for the levels are assigned from photolytic studies in the next section. Modeling should give rate constants for the intermediate levels as soon as the C state distributions vs pressure have been evaluated. There is no accepted explanation as to why the transfer rate constants have such a strong dependence upon vibrational energy. Possibly it is because the transitions for high v levels occur at the outer turning points when the potential curves are nearly coincident; this separation is larger for lower v levels.

IV. RELAXATION AND QUENCHING OF XeF(B) AND XeF(C)

Photolysis of XeF\(_2\) with the 147 nm Xe resonance line or the CO 4\(^{th}\) positive bands (160-180 nm) gives XeF(B) in low vibrational levels (\( v' = 0-15 \)). The yield of XeF(C) or the B-A emission from XeF(B) was too low to be measured. The subsequent relaxation and quenching processes in the presence of reagent, Q, are defined below.

\[
\begin{align*}
\text{XeF(B)} & \quad \stackrel{k_{B-C}}{\longrightarrow} \quad \text{XeF}(C) + Q \\
& \quad + Q \quad \stackrel{k_{B-C}}{\longrightarrow} \quad \text{XeF}(X \text{ or } A) + Q \\
\end{align*}
\]

\[
\begin{align*}
\text{XeF}(C) & \quad \stackrel{k_{C-B}}{\longrightarrow} \quad \text{XeF}(A) + h\nu \\
& \quad + Q \quad \stackrel{k_{C-B}}{\longrightarrow} \quad \text{XeF}(B) + h\nu \\
& \quad + Q \quad \stackrel{k_{C-B}}{\longrightarrow} \quad \text{XeF}(X \text{ or } A) + h\nu \\
\end{align*}
\]

For most reagents vibrational relaxation is faster than transfer or quenching, so the above scheme ap-
plies to a 300 K Boltzmann vibrational distribution. Steady-state analysis gives the ratio of emission intensities as

\[
\frac{I_B}{I_C} = \frac{k_{B-C} T_C^{-1}}{k_{B-C} T_C^{-1} + (k_{C-B} - k_Q) T_C^{-1}} \tag{7}
\]

Some sample spectra were shown in Figure 4 and plots of \(I_B/I_C\) vs \([Q]^{-1}\) are shown in Figure 7.

![Figure 7: Variation of \(I_B/I_C\) vs (reagent pressure)^{-1} for Ar, N₂, and SF₆ as reagents; XeF(B) was generated by photolysis of XeF₂.](image)

Since \(T_C^{-1}\) is known, values for \(k_{B-C}\) can be assigned from the slopes of these plots. If \(k_{C-B} > k_Q\), the intercept can be used to obtain \(k_{C-B}/k_{B-C}\), the 300 K equilibrium constant, \(K_{eq}\). The intercept was the same for all the rare gases (except Xe), N₂, CF₃, and SF₆, which implies that the intercept corresponds to \((k_{C-B}/k_{B-C}) T_C^{-1}\). Using the intercept values and \(T_C = 150\) nsec and \(T_B = 15\) nsec s⁻¹, \(11,14\) gives \(K_{eq} = 0.031 ± 0.004\). From \(K_{eq}\) and \(k_{B-C}\), the values of \(k_{C-B}\) can be obtained by detailed balance. If \(k_Q < k_{C-B}\), the intercept and knowledge of \(k_{B-C}\) and \(K_{eq}\) give \(k_Q\). If \(k_Q < k_{C-B}\), then \(K_{eq}\) can not be determined from the \(I_B/I_C\) vs \([Q]^{-1}\) plot.

Information also can be obtained from a plot of the ratio of the emission intensity of XeF(B) in the absence of added bath gas, \(I_B^0\) to the intensity in the presence of added bath gas, \(I_B\). Steady-state analysis gives

\[
\frac{I_B^0}{I_B} = 1 - \frac{k_Q [Q]}{k_{C-B} T_C^{-1} [Q] + k_{b-C} T_C^{-1} [Q]^2} \tag{8}
\]

For many cases \(k_{B-C} < k_Q [Q] < k_{C-B} T_C^{-1} [Q]\) and the term involving \([Q]^2\) can be neglected. For cases in which \(k_{B-C}, k_C\) and \(k_Q\) already are established, i.e. those reagents with \(k_Q < k_{C-B}\), fitting the above equation establishes all four rate constants.

This is the case for CClF₃, CHF₃, NF₃, CF₃, F₂, and Xe. If \(k_Q < k_{C-B}\) then the exchange of molecules in the B and C state is rapid relative to quenching and fitting the data from plots of \(I_B^0/I_B\) vs \([Q]\) only can be used to get the sum, \(k_Q + k_{C-B} T_C^{-1} = k_{B-C} (32)\). If it is assumed that \(k_Q = k_{C-B}\) then values for these rate constants can be estimated.

The rate constants are listed in Table 2.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>(k_{B-C}) (\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1})</th>
<th>(k_Q) (\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1})</th>
<th>(k_C) (\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1})</th>
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<tbody>
<tr>
<td>CClF₃</td>
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<td>(9 \times 10^{-13})</td>
<td>(1 \times 10^{-13})</td>
</tr>
<tr>
<td>CHF₃</td>
<td>(2 \times 10^{-14})</td>
<td>(9 \times 10^{-13})</td>
<td>(1 \times 10^{-13})</td>
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<td>NF₃</td>
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<td>(5 \times 10^{-14})</td>
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<tr>
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<td>(1 \times 10^{-14})</td>
<td>(1 \times 10^{-14})</td>
</tr>
</tbody>
</table>

Table 2. Rate Constants \(^a\) for XeF(B,1/2) and XeF(C, 3/2).

- a) The listed uncertainties are the standard deviations.
- b) Qualitative measurements of \(I_B^0/I_B\) for CO₂ and HF suggest that \(k_{B-C} > 1 \times 10^{-14} \text{ cm}^3\text{ mole}^{-1}\sec^{-1}\).
- c) The \(k_Q\) values were obtained by assuming that \(k_Q = k_{C-B}\); the experiments only give \(k_{B-C} + k_{Q} K_{eq}\) (see text).
- d) In contrast to other studies, \(^1\), we find no evidence for three-body quenching of XeF by Xe.

Qualitative experiments also were done for HF and CO₂; these reagents readily quench XeF(B) and XeF(C) and \(k_{B-C}\) and \(k_{Q} K_{eq}\) must be \(> 10^{-14} \text{ cm}^3\text{ mole}^{-1}\sec^{-1}\). This suggests that typical tank gas impurities readily quench XeF².

A few comments should be made about the rate constants of Table 2. Firstly the results were derived...
by assigning all of the broad band emission to XeF (C-A). If the XeF(B-A) emission makes a significant contribution then the rate constants and $K_{eq}$ will be altered. The calculated branching fraction for XeF(3 - A,1/2) is only 0.03 which is similar to the experimental uncertainty in the intensity measurements. Secondly, there was no evidence (from either the fit of the kinetic data or from the appearance of the spectra) for three-body quenching of XeF for any of the gases; the data for the rare gases extend up to three atmospheres. Thirdly, for NF₃, CF₃, F₂ and possibly Xe the quenching rate constants for the B and C states seem to differ; with $K_B$ being larger than $K_C$. This should be regarded as a preliminary conclusion.

Since the energy separation between XeF(C) and XeF(B) is only 720 cm⁻¹, the magnitude and dependence upon collision partner found for $K_{B-C}$ are normal. On the other hand, the magnitude of $K_C$ or $K_B$ seems surprisingly large for E-T or E-V transfer which must be the case for all the atoms and molecules in Table 2, except for F₂, because they have no excited electronic states below 3.57 eV.

The increase in quenching rate constant upon substitution of one F atom in CF₃ by a CF₂ or H atom is very large and suggests the importance of strong interactions with XeF(C) via dipole-dipole or dipole induced dipole attractive terms. A possible explanation of why $K_B$ appears to be larger than $K_C$ may be the extensive configuration interaction between the XeF(B) and XeF(X) states, especially at short range.

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