Competitive Channels in the Interaction of $Xe({}^{3}P_{J})$ with Cl_{2} , Br_{2} and I_{2}

Atom Transfer, Excitation Transfer, Energy Disposal and Product Rotational Alignment

Keith Johnson, Roland Pease, John P. Simons* and Peter A. Smith

Chemistry Department, The University, Nottingham NG7 2RD

Agust Kvaran

Science Institute, The University of Iceland, 107 Reykjavik, Iceland

The collision of electronically excited rare-gas atoms, e.g. $Xe[np^{5}(n+1)s]$ with the molecular halogens leads both to atom transfer (generating vibrationally and electronically excited rare gas halides) and to excitation transfer (generating electronically excited molecular halogens in a range of ion-pair excimer states). Translational energy utilisation and rotational alignment in the products of the atom transfer channel have been probed using a superthermal pulsed molecular beam technique, while the vibrational energy disposal and branching ratios determined under thermal collision conditions have been reassessed through direct inversion of the resolved chemiluminescence emission spectra. The range of halogen excimer states populated through excitation transfer has been identified by appeal to the literature.

The results confirm a steady increase in the importance of the excitation transfer channel in the series Cl_2 , Br_2 , I_2 , together with a decline in the fraction of the reactive channel vibrational exo-ergicity, and implicate the excited ionic potential $V[\operatorname{Xe}^+\cdots \operatorname{X}_2^-({}^2\Pi_g)]$ in the excitation transfer channel. In contrast to an earlier analysis, the vibrational energy disposal in XeX(B) is found to be unimodal with a linear surprisal. The rotational alignment of the XeX(B) perpendicular to the collision vector \mathbf{k} increases with increasing collision energy, but does not reach the limiting value $\langle P_2(\hat{J}' \cdot \hat{\mathbf{k}}) \rangle = -\frac{1}{2}$, implying considerable repulsion between the nascent products of atom transfer.

In addition to their intrinsic interest in the field of u.v.-visible laser systems, the chemiluminescent reactions of electronically excited atoms have many features attractive to the student of molecular reaction dynamics. Translational energy utilisation can be probed through measurements of the intensity of the chemiluminescence excited by collision of superthermal reagent beams;^{1,2} internal energy disposal and product branching ratios can be determined from the analysis of resolved chemiluminescence spectra under both static³⁻⁸ and molecular beam^{9,10} conditions; the influence of molecular spatial¹¹ or electronic orbital¹² alignment can be probed by polarised laser-beam excitation techniques; the collisional energy dependence of product rotational alignment and angular momentum disposal can be obtained through measurements of the chemiluminescence polarisation excited under molecular beam conditions;^{1,2,13-16} and dispersion of the chemiluminescence spectrum can reveal the dependence of the alignment on the product vibrational state.¹⁷ Many more measurements are possible when the electronically excited atom is itself fluorescent.

A particularly rich chemiluminescent system, still incompletely understood, is provided by the interaction of electronically excited rare gas atoms, $Rg^*[np^5(n+1)s]$ with the molecular halogens (and interhalogens).^{1,3,5,8-11} As with the alkali-metal atoms,

reactive scattering proceeds via the harpoon mechanism, generating electronically excited rare-gas halides:^{1,5}

$$Rg^{*} + X_{2} \rightarrow RgX[B(\frac{1}{2}), C(\frac{3}{2}), D(\frac{1}{2})] + X[^{2}P(\frac{3}{2}, \frac{1}{2})].$$
(1)

However, unlike the alkali-metal atoms, excitation transfer may compete with the atom transfer channels to generate fluorescence from the electronically excited molecular halogens:5,10,18

$$Rg^* + X_2 \rightarrow Rg + X_2^* [D'(2g) \cdots].$$
⁽²⁾

Despite the wealth of information that has been derived, principally by Setser and coworkers³⁻⁵ in a series of experiments probing vibrational energy disposal and product branching under thermal collision conditions³⁻⁵ and occasionally molecular beam conditions,^{9,10} many of the details of the reaction dynamics and mechanisms remain obscure. In part this has been due to the difficulty of analysing the complex chemiluminescence emission spectra which include a multitude of overlapping oscillatory continua associated with the bound-free transitions of the rare-gas halide and halogen excimer ion-pair states.3-5

In the present work these problems are re-addressed by the systematic application of direct spectral inversion procedures⁷ to obtain revised vibrational energy distributions in the rare-gas halide products and to effect the resolution of their chemiluminescence spectra from those of the overlapping halogen excimer systems. The latter are assigned to a range of ion-pair states by appeal to the literature. The results suggest a propensity rule for excitation transfer and the involvement of the excited ionic potential $V[Rg^+ \cdots X_2^- (^2\Pi_{\sigma})]$ in the excitation transfer process. The dynamics of the atom-transfer channel have been probed through measurements of the rare-gas halide fluorescence intensities and polarisations under molecular beam conditions at collision energies in the range (10-120) kJ mol⁻¹. While most of the experiments have focussed on the interactions of $Xe({}^{3}P_{2}, {}^{3}P_{1})$ with Cl_{2} , Br_{2} and I_{2} , some additional data obtained with Ar, $Kr({}^{3}P_{2})$ are also reported.

Experimental

Energy resolved, digitised chemiluminescence spectra excited through reactions of Xe, Kr, $Ar({}^{3}P_{2})$ were recorded at the University of Iceland using a discharge flow system and microcomputer data acquisition techniques,¹⁹ while those excited through reactions of $Xe({}^{3}P_{1})$ were recorded under similar conditions using a resonance radiation excitation system.¹⁶ In order to apply the spectral inversion procedures the experimental intensities were subsequently averaged at 200 cm^{-1} intervals: details of the inversion and spectral resolution procedures are described elsewhere^{7,8,16,19} and in later discussion.

The intensity and polarisation of the chemiluminescence associated with the XeX(B-X) systems were measured over a range of collision energies extending from 10 to 120 kJ mol^{-1} , by using an ultra-high-speed rotor accelerator to propel a pulsed beam of superthermal $Xe({}^{3}P_{2})$ atoms into a static halogen gas cell, maintained at a pressure of ca. 1.0 Pa.^{1,2,16} Beam-gas conditions were chosen to maximise the signal count rates and thus the experimental precision. Intensities were measured through appropriate optical filters transmitting the B-X oscillatory continua centred at 310 nm (XeCl), 280 nm (XeBr) and 250 nm (XeI). The polarisation index $R = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp})$ was determined from the intensities recorded through a u.v. polariser set parallel and perpendicular to the atomic beam axis. Since the transition moment for the $B(\frac{1}{2})-X(\frac{1}{2})$ system is directed parallel to the internuclear axis, the polarisation index

$$\boldsymbol{R} = -\frac{1}{2} \langle \boldsymbol{P}_2(\hat{\boldsymbol{J}}' \cdot \hat{\boldsymbol{Z}}) \rangle \tag{3}$$

K. Johnson et al.



Fig. 1. Chemiluminescence emission excited by interaction of $Xe({}^{3}P_{2})$ with Cl_{2} in Ar. Total pressure 80 Pa; corrected for instrument response.

where \hat{J}' and \hat{Z} are unit vectors directed along the product rotational angular momentum and beam axes.^{15,20} The cylindrical collision symmetry about the beam axis allows the factorisation^{15,20}

$$\langle P_2(\hat{\boldsymbol{J}}' \cdot \hat{\boldsymbol{Z}}) \rangle = \langle P_2(\hat{\boldsymbol{J}}' \cdot \hat{\boldsymbol{k}}) \rangle \langle P_2(\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{Z}}) \rangle \tag{4}$$

where $\langle P_2(\hat{J}' \cdot \hat{k}) \rangle$, the quantity of dynamical interest, is the average alignment of the product rotational angular momentum referenced to the relative velocity vector k of the colliding reagents. The 'blurring' factor $\langle P_2(\hat{k} \cdot \hat{Z}) \rangle$, and the dispersion of the mean collision energy introduced by the choice of beam-gas conditions can be calculated using Monte Carlo averaging techniques described elsewhere.^{15,20} Since the target gases (apart from Cl₂ at low collision energies) are heavy molecules, the blurring factors were not far below unity, lying typically in the range 0.88-0.98. The absolute precision of the measurements was confirmed by determining the polarisation of the fluorescence excited in the kinematically constrained reactions:

$$\operatorname{Xe}({}^{3}P_{2}) + \operatorname{HX} \rightarrow \operatorname{XeX}(B) + \operatorname{H}; \qquad \operatorname{X} = \operatorname{Cl}, \operatorname{Br}, \operatorname{I}.$$
 (5)

As the collision energy increased, each system generated fluorescence emission with a polarisation which rose asymptotically to the limiting value corresponding to the expected maximum theoretical alignment $\langle P_2(\hat{J}' \cdot \hat{k}) \rangle = -\frac{1}{2} \cdot \frac{15,16}{2}$

Results and Discussion

Excitation Transfer, Atom Transfer and Energy Disposal

Chemiluminescence spectra excited by the interaction of $Xe({}^{3}P_{2})$ with Cl_{2} , Br_{2} and I_{2} and recorded under discharge flow conditions are shown in fig. 1-5. In agreement with earlier studies by Setser and coworkers³⁻⁵ the rare-gas halide emission continua associated principally with the B-X, B-A and C-A systems are increasingly overlapped by halogen excimer emission bands in the sequence $Cl_{2} \ll Br_{2} < I_{2}$. Many previously unreported I_{2}^{*} emission bands have also been recorded at wavelengths in the visible, though their net contribution to the total intensity is low. Because of the problem of spectral overlap, the analysis of the chemiluminescence presents several problems, particularly



Fig. 2. Chemiluminescence emission excited by interaction of $Xe({}^{3}P_{2})$ with Br_{2} in Ar. Total pressure 80 Pa; corrected for instrument response.



Fig. 3 Chemiluminescence emission excited by interaction of $Xe({}^{3}P_{2})$ with I₂ in Ar. Total pressure 80 Pa; emission at $\lambda < 370$ nm corrected for instrumental response.

for the Xe^{*}/I₂ system, and a systematic procedure was adopted in order to overcome them. The first step in this procedure was the spectral inversion of the B-X continuum in each of the xenon halide systems, using the analytical techniques and potential-energy functions described and listed elsewhere,^{7,16} to gain a first estimate of the steady-state vibrational population histograms in XeX(B). The principal complication to overcome at this stage was the correction for the underlying contribution from the $C(\frac{3}{2})-A(\frac{3}{2})$ continuum; this peaks to the red of the $B(\frac{1}{2})-X(\frac{1}{2})$ system, but continues to shorter wavelengths. The contribution was first accommodated by subtracting a linearly decreasing background from the experimental spectrum in the region of the $B(\frac{1}{2})-X(\frac{1}{2})$ continuum; optimising the background correction greatly improved the self-consistency





Fig. 4 Resolution of overlapping band systems in $Xe({}^{3}P_{2})/I_{2}$. (Features identified as I_{2}^{*} are assigned in table 3.)



Fig. 5. Resolution of overlapping band systems in $Xe({}^{3}P_{2})/Br_{2}$. (Features identified as Br_{2}^{*} are assigned in table 3.)

| Interaction | of | $Xe(^{3}P_{2})$ | with | Cl_2 , | Br_2 and | I ₂ |
|-----------------|----|-----------------|------|-------------------|------------|----------------|
| | | | | | | |

| | $A/10^{-7}$ cm ⁻¹ | <i>В</i> /Å | $C_1/10^{-5}$ Å cm ⁻¹ | $C_4/10^{-5}$ Å ⁴ cm ⁻¹ | $C_6/10^{-5}$ Å ⁶ cm ⁻¹ | T'_{e}/cm^{-1} | $D_{\rm e}^\prime/{ m cm}^{-1}$ |
|------|------------------------------|----------------|-------------------------------------|--|--|------------------|---------------------------------|
| XeBr | 2.5806 | 0.370 23 | 0.934 95 | 5.685 47 | 2.617 61 | 36 182 | 30 740 |
| XeI | 5.6303 | 0.368 39 | 1.209 6 | 0.134 9 | | 40 818 | 30 482 |

Table 1. Rare-gas halide potential parameters and transition moment functions^a(a) Rittner potentials for upper C(3/2) states

| (b) | repulsive | e lower-state | potentials |
|--------------|-----------|----------------|---------------------|
| (i) <i>U</i> | [A(3/2)] | $= A \exp(-i)$ | $r/B) - C_6 r^{-6}$ |

| | • | · · · · · | 1 (/ / | - 0- | |
|------|------------------------------|---|-------------|--------------------------------|--------------------|
| | A/ cr | 10^{-7} n ⁻¹ | B /Å | $C_{6}/10$ Å ⁶ cm | b^{-5} |
| XeB | ir 5. | 528 | 0.311 32 | 6.034 | 2 |
| Xel | i 5. | 117 | 0.364 76 | 0 | |
| | (ii) $U''[A($ $A/10^{-7}$ | $\frac{1/2)] = A \exp \left[\frac{B}{B}\right]$ | p(-r/B) - 0 | $\frac{C_6 r^{-6} + D_e}{C_6}$ | |
| | cm ⁻¹ | /A | /A° | cm ⁻¹ | / cm ⁻¹ |
| XeBr | 5.9110 | 0.304 8 | 1 6.0 | 0342 | 3685 |
| XeI | 8.7471 | 0.337 9 | 2 1.7 | 73 | 7601 |

(c) Variation of transition moment $\mu(r)$, as a function of internuclear distance $\mu(r) = (C_0 + C_1 r + C_2 r^2 + C_3 r^3 + C_4 r^4)^{-1} \exp[\gamma(r-a)]$

| · · · · | - | | | - | | | |
|---------------------------------------|-----------------|-----------------|-----------------------|-----------------------|-----------------------|----------|-------|
| | C_0 | C_1 | <i>C</i> ₂ | <i>C</i> ₃ | <i>C</i> ₄ | γ | а |
| XeBr $C(3/2)-A(3/2)$ B(1/2)-A(1/2) | 19.96 -11.02 | -25.62 | 12.57 -4.352 | -2.799 | 0.248 | 0.3 | 3.292 |
| XeI $C(3/2)-A(3/2)$ B(1/2)-A(1/2) | 23.48 2.74 | -28.20 -1.82 | 13.01 0.731 | -2.731 -0.189 | 0.228 0.023 | 0.4 0 | 3.585 |

^a Data adapted from ref. (3). $B(\frac{1}{2})$ and $X(\frac{1}{2})$ potential parameters and the transition moment $\mu(B-X)$ are listed in ref. (16).

between the experimental spectra and those calculated from the vibrational population histograms. Subsequently, the contribution from the $C(\frac{3}{2})-A(\frac{3}{2})$ system was properly included in the full inversion procedure; to ease the computation the vibrational population distributions in the closely neighbouring $C(\frac{3}{2})$ and $B(\frac{1}{2})$ states were assumed equal. Initially, the calculation utilized the dispersion corrected parameters for the $C(\frac{3}{2})$ and $A(\frac{3}{2})$ potentials listed by Tamagake *et al.*, ³ however, the fit with the experimental data could be greatly improved by (*i*) lowering the $C(\frac{3}{2})$ potential for XeI to bring the observed and calculated peaks in the C-A continuum into coincide at 33 750 cm⁻¹ and (*ii*) reducing the steepness of the $A(\frac{3}{2})$ potential in XeBr relative to the repulsive wall of the $C(\frac{3}{2})$ potential. The parameters employed are listed in table 1. Finally, the contributions from the $B(\frac{1}{2})-A(\frac{1}{2})$ continuum were calculated from the vibrational population histograms, assuming the relative intensity ratios I(B-X)/I(B-A) given by Setser and coworkers.²¹ The resulting resolution of the overlapping continua in the Xe(³P₂)/I₂, Br₂ systems is shown in fig. 4 and 5, while fig. 6 shows the steady-state vibrational population histograms for XeX(B) generated through reactions of both Xe(³P₂) and

1287



Fig. 6. Steady-state vibrational population distributions N(v) in XeX(B) excited by atom transfer to $(a)-(c) \operatorname{Xe}({}^{3}P_{2})$ total pressure 80 Pa, $(d)-(f) \operatorname{Xe}({}^{3}P_{1})$, total pressure 13 Pa. $(a) \operatorname{Xe}({}^{3}P_{2})/\operatorname{Cl}_{2}$, $(b) \operatorname{Xe}({}^{3}P_{2})/\operatorname{Br}_{2}$, $(c) \operatorname{Xe}({}^{3}P)/\operatorname{I}_{2}$, $(d) \operatorname{Xe}({}^{3}P_{1})/\operatorname{Cl}_{2}$, $(e) \operatorname{Xe}({}^{3}P_{1})/\operatorname{Br}_{2}$, $(f) \operatorname{Xe}({}^{3}P_{1})/\operatorname{I}_{2}$.

 $Xe({}^{3}P_{1})$. The agreement between the recalculated and observed spectral contours of the B-X systems is displayed in fig. 7.

Vibrational Energy Disposal

The most striking feature of the distributions shown in fig. 6 is the steady decline in the average fraction of the total reaction exoergicity concentrated into vibration, f_v in the series $Cl_2 > Br_2 > I_2$ (table 2). This parallels the conclusion reached by Tamagake *et al.*³ on the basis of their spectral simulation procedures. The detailed vibrational distributions are very different, however; in particular the clear bimodal character reported earlier³ is not reproduced by the spectral inversion procedures employed here.

The steady decline in f_v observed in the reactions of $Xe({}^{3}P_2, {}^{3}P_1)$ [and also $Hg({}^{3}P_2)^6$] with the halogens contrasts strongly with the vibrational energy disposal in the corresponding alkali-metal atomic reactions estimated from complementary measurements of translational and rotational energy disposal in molecular beam experiments.²² The bimodal distributions obtained by Tamagake *et al.*³ led to the suggestion that the production of spin-orbit excited atoms was an important channel in the reactions:

$$Xe({}^{3}P_{J}) + X_{2} \rightarrow XeX(B, C, D) + X({}^{2}P_{3/2}, {}^{2}P_{1/2}).$$
 (6)

Even in the absence of clearly resolved bimodal distributions, the proposed branching into the spin-orbit excited channel could still be sustained, in view of the decreasing trend in the estimates of f_v in the sequence $Cl_2 > Br_2 > I_2$. The earlier bimodal distributions obtained in both the $Xe({}^{3}P_2)$ and $Hg({}^{3}P_2)/X_2$ reactions were analysed in terms of two overlapping components of which one, or sometimes both, corresponded to a linear surprisal.^{3,6} In contrast, each of the distributions obtained through the procedures adopted here can be accommodated on single, linear surprisal plots (see fig. 8), but with systematically declining slopes, though the representation is relatively poor for Xe^{*}/I₂. Taking $X(\frac{1}{2})$ rather than $X(\frac{3}{2})$ as the dominant channel in reaction (1) would barely



Fig. 7. XeX(*B*-*X*) oscillatory continua calculated from the distributions shown in fig. 6. \bigcirc , observed; \bigcirc , calculated. (a) Xe(${}^{3}P_{2}$)+Cl₂/XeCl(*B*-*X*), (b) Xe(${}^{3}P_{2}$)+Br₂/XeBr (*B*-*X*), (c) Xe (${}^{3}P_{2}$)+I₂/XeI(*B*-*X*), (d) Xe(${}^{3}P_{1}$)+Cl₂/XeCl(*B*-*X*), (e) Xe(${}^{3}P_{1}$)+Br₂/XeBr(*B*-*X*), (f) Xe (${}^{3}P_{1}$)+I₂/XeI(*B*-*X*).

Table 2. Average fractions of the total reaction exoergicity appearing as vibration in XeX(B), generated through the reaction

| $Xe(^{3}P_{J}) + X_{2} -$ | $\rightarrow XeX(B)_v + X$ |
|---------------------------|----------------------------|
|---------------------------|----------------------------|

| | XeCl(B) | | 2 | XeBr(B) | XeI(B) | | |
|----------------------------------|---------------|--|---------------|----------------------------------|------------------------------------|----------------------------------|--|
| Xe ^a | ${}^{3}P_{1}$ | ${}^{3}P_{2}$ | ${}^{3}P_{1}$ | ³ P ₂ | ³ <i>P</i> ₁ | ³ P ₂ | |
| $f_{\rm v}^{\rm ss} \ f_{\rm v}$ | 0.74 0.71 | 0.69 (0.77) ^b 0.67 (0.69) ^b | 0.60 0.50 | 0.53 (0.56) ^b 0.46 | 0.45 0.38 | 0.46 (0.46) ^b 0.40 | |

 ${}^{a} f_{v}^{ss}$ refers to the observed vibrational energy distribution under steady-state conditions; f_{v} is the corrected fraction, accommodating the vibrational state dependence of the Einstein coefficients for radiative decay, ${}^{3,8}_{v} \operatorname{XeX}(B)_{v} \rightarrow \operatorname{Xe} + \operatorname{X} + h\nu$.^b Ref. (3) and (5).

barely change the result in Xe^{*}/Cl₂, where the Cl $(\frac{1}{2}-\frac{3}{2})$ spin-orbit splitting is so small, and it would not greatly influence the plot for Xe^{*}/Br₂ either; the data for Xe^{*}/I₂ are rather scattered, but there is no obvious break in the plot at $v \approx 100$, which would mark the limiting levels accessible to the I(²P_{1/2}) channel; in any case ca. 25% of the total vibrational population distribution lies at higher energies. Thus the unexcited spin-orbit channel is clearly important and while a contribution from the X(²P_{1/2}) channel cannot be excluded, its contribution cannot be quantified or even identified on the basis of our analysis. The systematic behaviour shown in the surprisal plots of fig. 8 encourages the view that product branching in the atom transfer step (1) is unlikely to be the major cause of the decline in f_v in the series Cl₂, Br₂, I₂ and perhaps an alternative explanation should be sought. The parallel decline in f_v in the Hg(³P₂)/X₂ systems may be due to branching,⁶ but even when the data are analysed on that basis, a systematic decline in f_v and λ_v is still apparent in the X(3/2) channel from 0.85 and -16 (Cl), to 0.66 and -8





Fig. 8. Surprisal plots for the nascent vibrational energy distributions in XeX(B), based on the data shown in fig. 6(d)-(f), but accommodating the vibrational-state dependence of the Einstein coefficients A(v) for the XeX(B-X) emission: P(v) = A(v)N(v). The prior distributions are calculated assuming the RRHO approximation [R. D. Levine and J. L. Kinsey, in Atom Molecule Collision Theory, ed. R. B. Bernstein (Plenum Press, New York, 1979), chap. 22]. The arrows indicate the limiting energies for generation of spin-orbit excited atoms $X(^2P_{1/2})$. (a) XeCl(B)_v, $\lambda_v = -5.2$; (b) XeBr(B)_v, $\lambda_v = -1.8$; (c) XeI(B)_v, $\lambda_v \approx 0$.

-8 (Br) to 0.60 and -5 (I).⁶ Generation of $X({}^{2}P_{1/2})$ would imply access onto the excited $V{Xe^+ \cdots X_2^-[{}^{2}\Pi_g(\frac{1}{2})]}$ ionic potential.³ Evidence for access onto the excited potential is provided by the efficient branching into XeI* in the reaction of $Xe({}^{3}P_2)$ with ICI and IBr.^{2,5,10} Assignment of the spectral features associated with the halogen excimer states, populated through the competing excitation transfer channels in the Xe(${}^{3}P_2$)/X₂ systems, also supports the involvement of the V[Xe⁺ \cdots X_2^-({}^{2}\Pi_g)] potential(s). Where these involve X₂⁻[${}^{2}\Pi_g(\frac{1}{2})$] they would of course, deplete the yield of X(${}^{2}P_{1/2}$)—perhaps this is the origin of the difference between the results in Xe(${}^{3}P_2$) and Hg(${}^{3}P_2$), where excitation transfer has a low or zero probability.⁶

The Excitation Transfer Channels

Subtraction of the spectral intensities associated with the XeX(B-X, C-A, B-A) transitions from the total chemiluminescence intensities allows the following estimates of the branching ratios into the competing excitation transfer channels: $I_2(ca. 40\%)$, $Br_2(ca. 20\%)$, $Cl_2(<2\%)$. These are considerably larger than those reported earlier,⁵ but the disagreement is not surprising in view of the difficulties involved in separating the many severely overlapping features. Prior to the present work the only X_2^* features

| 0 | Interaction (| of Xe(| $^{3}P_{2}$) | with | Cl ₂ . | Br ₂ | and | Ŀ |
|---|---|--------|---------------|------|-------------------|-----------------|-----|---|
| | 111100100000000000000000000000000000000 | | - 77 | | U 174 | 1017 | | |

| Table 3 | Suggested assignments for hal | ogen excimer | emission | bands | excited | via | interaction | with |
|---------|-------------------------------|---------------------------|----------|-------|---------|-----|-------------|------|
| | Xe(| ${}^{3}P_{2}$) (see fig. | 4 and 5) | | | | | |

| λ/nm | | ref. |
|---------|--|--------|
| | I* | |
| 512 | $D'(2g) \rightarrow {}^{3}\Delta(2u)$ | 25 |
| 461 | | |
| 467 } | probably $\alpha(1u)$, $\beta(1g)$, $\delta(2u) [(D0_u^+)?]$ [from I ⁺ (3P ₂) manifold] | 24 |
| 4/5/ | $F(0^+) \rightarrow P(0^+)$ | 25 |
| 388 | $D(0_g) \rightarrow D(0_u)$ | 25 |
| 342.6 | $D'(2g) \rightarrow A'(2y) [B(1g) A(1y) \text{ neak may underly this}]$ | 25 |
| 288-289 | $g(0_{-}^{-}) \rightarrow {}^{3}\Pi(0_{-}^{-})$ | 23 |
| 277 | $G(1g) \rightarrow A(1u)$ | 28 |
| 248 | from $I^+({}^1D_2)$ manifold | 29 |
| 238 | $F'(0^+_u) \to \mathbf{X}[{}^1\Sigma(0^+_g)]$ | |
| | Br [*] ₂ | |
| 355 | $D'(2g) \rightarrow {}^{3}\Delta(2u)$ | 30 |
| 312 | $E(0_g^+) \rightarrow B(0_u^+)$ | 32, 33 |
| 290 | $D'(2g) \rightarrow A'(2u)$ | 31 |
| 237 | $F(0^+_{\mu}) \rightarrow X[\Sigma^1(0^+_{\mu})]$ | |
| 227 | ? associated with $Br^+({}^{3}P_{0,1})$ manifold | 34 |
| 219 | ? | |

which had been positively identified in these spectra were the well known $D'(2g) \rightarrow A'$ (2*u*) peaks lying at 258 nm (Cl₂), 290 nm (Br₂) and 342 nm (I₂).³⁻⁵ In the Xe^{*}/I₂ system particularly, many more transitions are clearly excited. The interaction of $X^{-}(^{T}S_{0})$ and $X^{+}({}^{3}P_{2}, {}^{3}P_{0,1}, {}^{1}D_{2}, {}^{1}S_{0})$ generates a total of twenty Hund's Case c ion-pair halogen excimer states. These are nested together in groups which correlate with each of the X^+ ionic states in ascending energy.²³ Almost all of the unassigned features observed in the Xe^*/X_2 chemiluminescence can be positively identified with transitions involving these halogen ion-pair states, principally those in the ${}^{3}P_{J}$ clusters. Summaries of the suggested assignments are presented in table 3. Consider first the Xe^*/I_2 system. The visible emission spectrum is very similar to that recorded by Tellinghuisen and coworkers²⁴ in Tesla discharge excited I_2 at high pressure (implying low levels of vibrational excitation in the features we observe at low pressures). The distinct peaks at 432 and 512 nm have been assigned earlier to the transitions $E(0_e^+) \rightarrow B(0_u^+)$ and $D'(2g) \rightarrow {}^{3}\Delta(2u).^{25}$ The remaining group of transitions, with peaks at 461, 467 and 475 nm, are believed to originate from three of the four remaining ion-pair states in the $I^+({}^{3}P_2)$ manifold, $D(0_u^+)$, $\beta(1g)$, $\gamma(1u)$ and $\delta(2u)$.²⁴ One of these, $D(0_u^+)$ can possibly be discounted since there is no trace of the expected $D(0^+_u) \to X(0^+_e)$ McClennan Band system at shorter wavelenths, though it could be buried beneath stronger overlapping systems: we shall return to this point subsequently. The sharp feature at 388 nm is certainly associated with I_2^* and it had been assigned to $\beta(1g) \rightarrow A(1u)$,²⁶ but the assignment has been questioned by Guy *et al.*²⁴ in view of the absence of the expected discrete structure at high pressures. Tellinghuisen²⁷ believes the transition should lie at shorter wavelengths, where it possibly underlies the intense feature $D'(2g) \rightarrow A'(2u)$ at 342 nm.

Several transitions must contribute to the fluorescence between 300 and 260 nm [apart from XeI(C-A)]. These include $g(0_g^-) \rightarrow 0_u^-$ at 289 nm²³ and possibly $G(1g) \rightarrow A(1u)$ at 277 nm;²⁸ $F(0_u^+) \rightarrow X(0_g^+)$ lies in the range 250-270 nm, but is expected to be very weak.²⁷ Finally, the shoulders at 248 and 238 nm, which are not reproduced in the spectral reconstruction of the XeI(B-X) continua, are present as

K. Johnson et al.

1291



Fig. 9. Relative excitation functions for the generation of (\bigcirc) XeBr(B) and (\bigcirc) XeI(B) in the superthermal Xe(³P₂) beam interaction with Br₂ and I₂. The data are normalised to the datum at lowest energy in each case.

clearly resolved peaks when the chemiluminescence is excited by $Kr({}^{3}P_{2})$. The peak at 238 nm has been assigned by Ishiwata *et al.*²⁹ to a transition from the $I^{+}({}^{1}D_{2})$ manifold, $F'(0_{u}^{+}) \rightarrow X(0_{g}^{+})$; the peak at 248 nm probably has a similar origin.²⁷ Notably, there is no emission from the lowest-lying D'(2g) state in the $Kr({}^{3}P_{2})/I_{2}$ system, where only the most highly excited transitions in I_{2}^{*} are detected. Excitation by $Ar({}^{3}P_{2})$, replaces the I_{2}^{*} features by emission from atomic iodine. The principal conclusions of this analysis can be summarised: (i) A broad range of I_{2}^{*} excimer states is excited through collision of $Xe({}^{3}P_{2})$ and I_{2} ; there is no evidence to suggest that $I_{2}^{*}(D0_{u}^{+})$ is among them, although it is readily accessible energetically and states lying at both higher and lower energies are populated. (ii) With increasingly energetic metastable rare-gas atoms the contribution from the lower-lying excimer states disappears.

Similar conclusions can be drawn from the analysis of the emission from the $Rg({}^{3}P_{2})/Br_{2}$ systems. The features at 355 and 290 nm can each be assigned to fluorescence from $Br_{2}(D'2g)$, terminating, respectively, on ${}^{3}\Delta(2u)^{30}$ and A'(2u), 31 while a weak feature superimposed on the XeBr(C-A) continuum at 312 nm matches the expected $Br_{2}(E-B)$ emission. 32,33 No doubt other weak features are also present in the irregular structure around this region. This is no evidence of any features attributable to emission from $Br_{2}[D(0_{u}^{+})]$, either at 340 or 275 nm, 33 where it might of course be masked by XeBr emission, or at 420 nm, 31 where there are no overlapping systems. When Xe(${}^{3}P_{2}$) is replaced successively by Kr(${}^{3}P_{2}$) and Ar(${}^{3}P_{2}$) the contribution from $Br_{2}(D')$ is successively diminished to be replaced by three stronger features at 237, 227 and 219 nm, probably associated with the $Br^{+}({}^{3}P_{0,1})$ manifold.

The Excitation Transfer Mechanism

The large cross-sections for quenching of the excited atoms,³⁵ the analogy with the behaviour of the corresponding alkali-metal atoms⁵ and the decreasing overall chemiluminescence cross-sections with increasing collision energy^{1,2,9,18} all imply an ionic-covalent curve crossing in the initial collision process.⁵ Fig. 9 shows the individual excitation functions for the atom transfer channels generating XeI(B) and XeBr(B). A similar collision-energy dependence is also obtained for the excitation transfer channels leading to I₂, Br₂(D'), but the severe problems caused by spectral overlap and the likely changes in the branching ratios/spectral contours with increasing collision energy do

not justify a quantitative analysis in view of the coarse optical filtering employed at superthermal energies. Its replacement by a system allowing the fully resolved spectra to be recorded at each collision energy will allow detailed analysis in the future.

The excitation functions shown in fig. 9 are almost identical and closely parallel those in the alkali-metal system K/Br_2 .³⁶ Trajectory calculations³⁷⁻³⁹ are able to reproduce the observed energy dependence in K/Br_2 by assuming an orbiting barrier at low collision energies and the reflection of potentially reactive trajectories from the inner repulsive wall of the lower adiabatic potential at higher energies. Surface crossings could take place at long range, at the first intersection with $V[Rg^+ \cdots X_2^-({}^2\Sigma_u)]$ or at shorter range onto the excited ionic potential(s) $V[Rg^+ \cdots X_2^-({}^2\Pi_g)]$. Alternatively, the excited potentials could be accessed via the first ionic potential, following a second one-electron jump.

Given a propensity for one-electron jump processes the involvement of the $V[Rg^+ \cdots X_2^- ({}^{2}\Pi_{g})]$ potentials is suggested by the nature of the halogen excimer states populated through the sequence

$$V(\mathrm{Rg}^* + \mathrm{X}_2) \to V(\mathrm{Rg}^+ \cdots \mathrm{X}_2^-) \to V(\mathrm{Rg} + \mathrm{X}_2^*).$$
⁽⁷⁾

The electronic configurations of $X_2^-({}^2\Sigma_u)$ and $({}^2\Pi_g)$ are, respectively, $\sigma_g^2 \pi_u^4 \pi_g^4 \sigma_u^1$ and $\sigma_g^2 \pi_u^4 \pi_g^3 \sigma_u^2$. A reverse electron jump from $X_2^-({}^2\Sigma_u)$ could generate the configurations 2440, the ground state of X₂; 2431 or 2341, generating excited intravalence states; or 1441, a major contributor to the ion-pair state $X_2(D0_u^+)$.^{27,28} A reverse electron jump from $X_2^{-}({}^{2}\Pi_{g})$, however, may populate a wide range of ion-pair, excimer states X_2^{*} associated with the electronic configurations 1432, a major contributor to $X_2(D'2g)$, and possibly $E(0_g^+)$ and $\beta(1g)$ as well, and 2332, associated with $F(0_u^+)$ and possibly $\gamma(1u)$ and $\delta(2u)$, as well as other intravalence states.^{25,27,40}

Apart from $X_2(D)$ (the one excimer state that remains undetected) all the excited states X_2^* so far identified in the chemiluminescence spectra could be populated by a one-electron, ionic-covalent jump from $V[Rg^+ \cdots X_2^-(^2\Pi_g)]$. If the $X_2(D)$ state is unpopulated it cannot be by virtue of its energetic inaccessibility since more highly excited states are clearly populated, nor by its removal through the back reaction⁴¹

$$X_2(D0_u^+) + Xe \rightarrow XeX(B) + X$$
(8)

in view of the very low partial pressures of Xe (and X_2) in the discharge flow system, <2 Pa.

Product Rotational Alignment

Fig. 10 shows the collisional energy dependence of the average rotational alignment $\langle P_2(\vec{J}' \cdot \vec{k}) \rangle$ of XeX(B) determined from the chemiluminescence polarisation recorded under superthermal beam-thermal gas conditions.[†] In each case the rate of increase of the alignment perpendicular to the relative velocity vector \mathbf{k} gradually falls to near zero, though even at the highest collision energies the alignment still lies some way below the limiting value $\langle P_2 \rangle = -\frac{1}{2}$: this would correspond to complete alignment of the rotational angular momentum J', of the rare-gas halide in a disc perpendicular to the relative

† Earlier pioneering measurements in the Xe*/Br₂ system using crossed-beam conditions¹ followed a similar trend, but indicated higher levels of alignment at the high energies; however, much lower signal levels are obtained under crossed-beam conditions and their absolute precision must now be in doubt. In particular, the attainment of maximum limiting alignments $\langle P_2(\hat{J}'\cdot\hat{k})\rangle = -0.5$ in each of the kinematically constrained reactions

$$Xe(^{3}P_{2}) + HX \rightarrow XeX(B) + H$$

confirms the absolute precision of the new measurements obtained under the much more favourable beam-gas conditions.



1293



Fig. 10. The collisional energy dependence of the rotational alignment in XeX(B) generated through the reaction Xe(${}^{3}P_{2}$)+X₂ \rightarrow XeX(B)+X. \bigcirc , XeCl; \triangle , XeBr; \blacklozenge , XeI [the data for XeI are less precise because of the low transmission of the polariser-filter combination employed to isolate XeI(B-X)].

velocity vector k. The data for XeI(B) appear consistently lower than for the other two systems; this could be due to overlapping emission from I_2^* , which is only weakly polarised, or possibly competition from the excitation-transfer channel.

Martin and his coworkers recently completed complementary measurements of rare gas halide rotational alignments in the Xe(${}^{3}P_{2}$)/X₂ and HX systems at low collision energies,⁴² typically $\langle E_{\rm CM} \rangle < 30 \text{ kJ mol}^{-1}$ selected by chopping the atomic reagent beam: beam-gas conditions were employed. Where their energy range overlaps those used here, similar relative trends were found, but the absolute alignments were uniformly lower. At the lowest collision energies, $\langle E_{\rm CM} \rangle < 5 \text{ kJ mol}^{-1}$, very small alignments were recorded, possibly even changing sign. This interesting result, if true, would imply alignment of J' parallel to k. However, the absolute precision of the polarisation measurements was unconfirmed and those found for Xe(${}^{3}P_{2}$)/HBr did not reach the kinematic limit. In view of the difficulty in measuring the absolute values of low polarisation ratios with acceptable precision, we believe some reassessment of the data may be necessary in the very low collision energy range.

The maximum limiting alignment would be obtained when there is a perfect mapping of the reagent orbital angular momentum L, into rotational angular momentum in the diatomic product $L \rightarrow J'$. This is achieved in the kinematically constrained Xe*/HX systems at high collision energies since $L \gg J$, L'. At lower energies, the exit orbital angular momentum L', generated by repulsion between the separating products, cannot be neglected and the alignment falls.^{15,16,20} Repulsion between the separating products must also be the principal cause of the less than maximal alignment at the highest collision energies in the Xe*/X₂ systems. The insensitivity of the alignment to increasing collision energy in this range indicates a preference for the angular momentum transfer $L \rightarrow L'$ rather than $L \rightarrow J'$.

The similar alignments found, particulary in the Xe^{*}/Cl₂ and Br₂ systems implies separation of the products of atom transfer on similar potentials. The repulsion would be greatest on the $V[\text{Rg}^+ \cdots X_2^-(^2\Pi_g)]$ potential which, in the isolated ion $X_2^-(^2\Pi_{1/2})$ would correlate with $X(^2P_{1/2})$. Preliminary model calculations, using the DIPR-DIP approximation⁴³⁻⁴⁶ which emphasizes the effect of product repulsion on the (assumed) collision dynamics, generated collisional energy dependences qualitatively similar to those observed here,^{2,47} though the absolute levels of alignment observed are uniformly lower than those that were predicted by the simple model (which neglects both vibration and rotation in the reagent gas molecules).

Conclusion

Any detailed analysis of the reactive and inelastic collision dynamics must include the exit channel interactions as well as the dependence of ionic-covalent surface crossings on the instantaneous atomic configuration, *i.e.* the inter-halogen separation and the collision geometry.^{39,48,49} This will be particularly important in the excitation-transfer channels, where second crossings must intervene.³ Steeply repulsive exit potentials, $V(Rg^+ \cdots X_2^-)$ for the atom-transfer channels, should favour the use of the direct interaction DIPR approximation, since it would discourage secondary encounters. However, the approximation $L \gg J$ will fail under beam-gas conditions at low collision energies and a proper account of angular momentum coupling must be included when the DIPR model is used to calculate the distributions of product angular momentum and alignment. Such calculations are currently in progress and will be reported elsewhere.⁵⁰

In order to follow the reactive, atom-transfer channel, the colliding system must remain on the ionic potential(s) $V(Rg^+ \cdots X_2^-)$, while passing through a network of intersections with the neutral potentials $V(Rg \cdots X_2^*)$.³ Leakage into this network could conceivably disturb the dynamics of the atom transfer process. This might be responsible for the low alignment of XeI(B), but the invariance in the excitation functions for XeI(B) and XeBr(B) and the rotational alignments of XeBr(B) and XeCI(B) to changes in the identity of the halogen, while the probability of excitation transfer decreases from 40 to 20 to 2% might suggest otherwise (though the excitation transfer ratios have so far been measured only under thermal collision conditions of course). The identities of the halogen excimer states populated through excitation transfer implicate the intermediacy of the excited ion-pair potential $V[Rg^+ \cdots X_2^-({}^2\Pi_x)]$ in the collision dynamics. A collisional energy dependence of the relative branching probabilities into the alternative channels would be reflected in a variation in the probabilities of leakage from this potential. Such a variation would inevitably be complex, being dependent on both the X-X and Rg-X distances, r_1 and r_2 .⁹ As r_1 increased on the ion-pair potential, the interactions of $V(Rg^+ \cdots X_2^-)$ with $V(Rg \cdots X_2^+)$ would occur at lower energies and shorter values of r_2 , since the equilibrium separation $r_1(X_2^*) \gg r_1(X_2)$. Leakage into the halogen excimer potentials will be sensitive to the relative rates of change of both r_1 and r_2 during the collision period and thus to the relative velocity and collision energy." This is the essence of the 'breathing-sphere' model for excitation transfer.⁵¹ New experiments are planned to explore this competition in more detail by recording the fully resolved chemiluminescence spectra under superthermal beam-gas conditions.

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1295