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# Interpretations of the mercury halide $(B^2\Sigma^+ - X^2\Sigma^+)$ chemiluminescence from reactive quenching of Hg( ${}^{3}P_{2}$ ) by halogen containing molecules

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The HgX( $B^2\Sigma^{+}-X^2\Sigma^{+}$ ), X = halogen, emission spectra have been recorded from Hg( ${}^{3}P_{2}$ ) atom reactions with several halogen containing molecules using a flowing afterglow reactor. The HgX\* emission intensities were compared with the HgCl\* emission intensity from Hg( ${}^{3}P_{2}$ ) + Cl<sub>2</sub> to assign rate constants for HgX(B) formation. The Hg( ${}^{3}P_{2}$ ) + diatomic halogen reactions have large  $k_{HgX*}$  and their branching fractions for HgX(B) formation are probably unity. The polyatomic reagents generally gave much smaller  $k_{HgX*}$ ; although, a few moderately good donors, e.g., CF<sub>3</sub>I, CBr<sub>4</sub>, CCl<sub>4</sub>, and NF<sub>3</sub> were identified. The experimental spectra were numerically simulated to assign HgX(B) vibrational energy distributions. A decrease in  $\langle f_{V}(\text{HgX}) \rangle$  was found for the Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub> series which is analogous to previous findings for  $\langle f_{V}(\text{XeX}) \rangle$  from reactive quenching of Xe( ${}^{3}P_{2}$ ). Possible reasons for the similarity are discussed. The HgX(B) vibrational energy disposal for polyatomic reagents is compared to analogous data for reactions of alkaline earth metal atoms and Xe( ${}^{3}P_{2}$ ).

### **I. INTRODUCTION**

Chemical and excitation transfer reactions yielding electronically excited products are important since they can provide the basis for visible or ultraviolet lasers. On a more fundamental level, such reactions provide a means of studying reaction dynamics at the state-to-state level through analysis of the product fluorescence spectra. Reactive quenching of the states in the Hg(6s6p,  ${}^{3}P$ ) multiplet, which yield HgX(B), X = F, Cl, Br, and I, are of interest for development of HgX(B-X) lasers.<sup>1,2</sup> Much of the work with the Hg(6s, 6p) states has been concerned with the spin-orbit effect on the HgX(B) yields; the cross sections for HgX(B) formation from  $Hg(^{3}P_{0,1}) + X_{2}$  are more than an order of magnitude smaller than from  $Hg(^{3}P_{2}) + X_{2}$ .<sup>3-9</sup> These small cross sections for  $Hg(^{3}P_{0,1})$  are not consistent with the simple covalent-ionic curve-crossing mechanism, although such a mechanism does generally fit the  $Hg(^{3}P_{2}) + X_{2}$  reactions. Little attention has been directed toward other dynamical features, such as the vibrational energy disposal, that could help to understand the spin-orbit effect on the product branching. Study of the reactions of the Hg(6s, 6p) states in some detail should provide knowledge about the dependence of product branching on starting state. Such understanding is needed to identify reactions with high probability of yielding excited state products.

In our previous work, a flowing-afterglow source of  $Hg({}^{3}P_{0})$  and  $Hg({}^{3}P_{2})$  atoms was described and the strong HgX(B-X) emission from reaction with the diatomic halogens was discussed.<sup>9</sup> Although approximately equal concentrations of  $Hg({}^{3}P_{0})$  and  $Hg({}^{3}P_{2})$  were present, formation of HgX(B) could be attributed almost entirely to reaction of  $Hg({}^{3}P_{2})$ . The flowing-afterglow source provides a convenient method for systematic investigation of the reactive quenching of  $Hg({}^{3}P_{2})$  and the present work reports a study of several polyatomic halogen containing molecules, as well as further details about the diatomic halogens.

 $Hg(^{3}P_{2}) + RX - HgX(B) + R(R = any group) .$ (1)

Besides reaction (1), other possible exit channels include intramultiplet relaxation to  $Hg({}^{3}P_{1,0})$ , dissociation and/or excitation of RX, and formation of HgX(A, X). Although we did not monitor the "dark" exit channels, formation of  $Hg({}^{3}P_{1})$  was observed and in some cases<sup>10</sup> was dominant over the HgX(B) channel. The present work is concerned only with reaction (1); rate constants for HgX(B) formation  $k_{HgX}^{*}$ , and vibrational distributions from the low pressure HgX(B-X) emission spectra are assigned. The HgX(B) emission intensity from Eq. (1) was compared to the  $HgCl^{*}(B-X)$  emission intensity from the  $Hg({}^{3}P_{2}) + Cl_{2}$  reference reaction to obtain  $k_{HgX}^{RX}^{*}$ :

 $Hg(^{3}P_{2}) + Cl_{2} - HgCl(B) + Cl; \quad \Delta H_{0}^{\circ} = -26.3 \text{ kcal mol}, \quad (2)$ 

 $k_{\rm HgC1}^{\rm C12} * = 3.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The  $k_{\text{HgC}T}^{\text{Cl2}}$  value was taken from the literature,<sup>3</sup> but tested for consistency in our work. The radiative lifetimes of the HgX(B) states are  $\leq 30 \text{ ns}^{11}$  and collisional relaxation does not occur at low ( $\leq 1 \text{ Torr}$ ) pressure; thus, the emission spectra can be used to assign initial HgX(B) vibrational distributions. The spectra exhibit little bound-bound structure and computer simulation of the spectra is required to assign vibrational distributions. The spectral simulations do not include rotation and no information is obtained concerning rotational energy disposal.

The computational techniques developed<sup>12-24</sup> for the rare gas halide bound-free emission spectra were employed for the HgX(B-X) simulations. Accurate knowledge of the upper and lower state potential curves, the dependence of the transition moment on internuclear distance, and the HgX(B) vibrational distribution are required. Cheung and  $Cool^{15}$  reanalyzed Weiland's data<sup>16</sup> and obtained improved vibrational constants and estimates of the rotational constants. Cheung and Cool's potentials were used in the present work and

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extended to higher vibrational levels by fitting Morse curves to the repulsive and attractive branches of their RKR curves. The calculations include a transition moment function based on *ab initio* calculation, <sup>17</sup> but modified to better match the experimental spectra. No simulations were performed for HgX(B-X) spectrum, since reliable potentials are not yet available for HgF.

Dissociative excitation reactions of methyl mercury and mercuric halide with  $N_2(A^3\Sigma_u^*)$  and  $Xe({}^3P_2)$  also yield HgX(B).<sup>18-20</sup> The computer simulation techniques developed in this work also were used to obtain the HgX(B) vibrational distributions from these reactions. These distributions are compared to photodissociation reactions of HgX<sub>2</sub> in the following paper.<sup>21</sup>

The alkali metal atom analogy has proven useful in interpreting the reactive quenching of the rare gas metastable atoms.<sup>22</sup> Those results, and studies of alkaline earth metal atom reactions, will be compared to the results for  $Hg(^{3}P_{2})$  atom reactions. The trends for  $k_{\text{HgX}}$  follow those for  $k_{\text{XeX}}$ ; only diatomic halogens and a few simple inorganic halides have large  $k_{HeX}$ \* and  $k_{XeX*}$  values. The  $\langle f_{V}(HgX) \rangle$  and  $\langle f_{V}(XeX) \rangle$  values are similar for diatomic halogens and decline in the  $Cl_2$ ,  $Br_2$ ,  $I_2$  series. Such a trend has not been reported for the alkali or alkaline earth metal atom (M) reactions. The variations in  $\langle f_{\nu}(HgX) \rangle$  for polyatomic halides are similar to those found for  $Xe({}^{3}P_{2})$  and alkaline metal atoms; but,  $\langle f_v(\text{HgX}) \rangle$  is smaller than  $\langle f_v(\text{XeX}) \rangle$ . The trend  $\langle f_{\mathbf{v}}(\mathbf{MX}) \rangle > \langle f_{\mathbf{v}}(\mathbf{XeX}) \rangle > \langle f_{\mathbf{v}}(\mathbf{HgX}) \rangle$  for the same polyatomic reagent can be interpreted in terms of the progressively smaller excergicity and the dynamics associated with the covalent-ionic curve-crossing mechanism.

#### **II. EXPERIMENTAL TECHNIQUES**

The flowing-afterglow reactor is essentially the same as used for studies of rare gas metastable atom reactions<sup>23</sup> and consists of a discharge region where the metastable atoms are generated and a reaction zone where the reagents are introduced. The discharge region consisted of a 1 cm diameter Pyrex tube containing the hollow-cathode electrodes made from rolled tantalum foil. The lowest voltage (~ 250 V) which would sustain in the discharge gave the largest Hg metastable concentrations. The reaction zone consisted of a 2.5 cm diameter flow tube separated from the discharge region by a 90° bend and Wood's horn light trap. Reactants were added to the reaction zone via a concentric inlet. Observation of emission was made through a quartz window attached to the flow tube with an O-ring seal. The pressure in the reaction zone could be varied by changing the Ar flow rate and/or throttling the pumping speed; however, all the work described here was performed at ~1 Torr.

Mercury was entrained in a prepurified Ar flow by passing the Ar through a refluxing column of Hg; the combined flow was passed through the discharge. The Hg flow rate was estimated to be  $10^{-4}$  of that for Ar (50 mmol min<sup>-1</sup>) by assuming the Ar to be saturated with Hg at the temperature (4 °C) and pressure at the top of the Hg reflux column. For maximum pumping speed and 1 Torr of Ar (the normal operating conditions), the metastable Hg atom concentrations, as measured by atomic absorption, were  $\sim 5 \times 10^9$  atom cm<sup>-3</sup> with  $[Hg(^3P_2)] \simeq [Hg(^3P_0)]$ .<sup>9</sup> The insignificant concentration of Ar( $^3P_{0,2}$ ) was demonstrated by the absence of N<sub>2</sub>(C-B) emission when N<sub>2</sub> was added to the reactor. Although some Hg<sup>+</sup> ions from the Penning ionization of Hg by Ar( $^3P_{0,2}$ ) are likely to be present, no difficulties were encountered from the Hg<sup>+</sup> ions. A more complete description of the metastable Hg atom flowing afterglow apparatus will be given elsewhere.<sup>10</sup>

The HgX\* emission spectra were observed with a 0.3 m monochromator equipped with a cooled  $(-20 \ ^{\circ}C)$ RCA C31034 photomultiplier tube and a 1200 line/mm grating blazed at 300 nm. The photomultiplier tube signal was detected with an SSR photon counter and displayed on a strip chart recorder. Both the monochromator and photon counter were interfaced to a DEC PDP-8/E computer and data was simultaneously acquired by computer and stored on magnetic tape. Subsequent data analyses and plotting of spectra, corrected for the detection system response, were performed by computer. The wavelength dependence of the detection system response was calibrated from 190-400 nm with a standard D<sub>2</sub> lamp (Optronics, model UV-40) and from 320-700 nm with a quartz-iodine lamp (Optronics, model 65). All spectra shown in this paper have been corrected for the wavelength dependence of the detection system.

For reagents with room temperature vapor pressures greater than 5 Torr, samples were prepared by diluting the vacuum distilled reagent with Ar and storing in Pyrex reservoirs; typical mole fractions were 0.05-0.20. An exception to this procedure was  $F_2$  for which a commercially (Matheson) prepared mixture (10% in Ar) was stored in a passivated stainless steel reservoir. The reagent flows were measured by timing the pressure rise in a calibrated volume. Reagents with low vapor pressures were introduced into the reaction zone by passing a flow of Ar over a sample contained in a trap. The reagent flow could be varied by adjusting the Ar flow or gently heating the trap; however, quantitative measurements of the flow rate could not be made with this technique.

#### **III. EXPERIMENTAL RESULTS**

The low pressure chemiluminescent spectra from the interaction of  $Hg({}^{3}P_{2})$  with several halogen containing reagents are shown in Figs. 1-4. Consistent with the short lifetimes of the HgX(B) states, <sup>11</sup> no change in the spectra was observed until the Ar pressure was  $\geq 4$  Torr. Assignment of the emission is evident from the bound-bound HgCl(B-X), HgBr(B-X), and HgI(B-X) spectra and from the similarities of the spectra from reagents with a common halogen. The HgX(B-X) emission and the  $Hg({}^{3}P_{1}-{}^{1}S_{0})$  253.7 nm atomic line from intramultiplet relaxation were the major features of the spectra; however, the  $F_{2}$  and  $I_{2}$  reactions did give HgX(C-X) emission at ~250 and 330 nm, respectively, with 5% of the HgX(B-X) intensity. Weak  $I_{2}^{*}$  continua at ~340 nm were observed for  $I_{2}$ ; these bands also were obtained



FIG. 1. HgF(B-X) chemiluminescent spectra from Hg( ${}^{3}P_{2}$ ) + F<sub>2</sub>, NF<sub>3</sub>, and  $N_2F_4$ . All spectra were taken at 1.2±0.2 Torr and with a resolution of ~4 nm. The emission from the  $F_2$  reaction extends to  $\sim 260$  nm; but, it is very weak below 310 nm.



FIG. 2. Comparison of simulated (---) and experimental (--) HgCl(B-X) chemiluminescence spectra from  $Hg(^{3}P_{2}) + Cl_{2}$ ,  $S_2Cl_2$ ,  $SOCl_2$ , (a) and  $SO_2Cl_2$ ,  $CCl_4$ , and  $CHCl_3$  (b). The experimental conditions were the same as for Fig. 1.



FIG. 3. Comparison of simulated (---) and experimental (--)HgBr(B-X) chemiluminescence spectra from Hg( ${}^{3}P_{2}$ ), Br<sub>2</sub>, CBr<sub>4</sub>, and CHBr<sub>3</sub>. The experimental conditions were the same as for Fig. 1.

from  $Xe({}^{3}P_{2}) + I_{2}$ .<sup>14</sup> Attempts to observe the HgX(*B*-*A*) bound-free emission, which is expected to lie at longer wavelengths than the B-X system, were unsuccessful. Theoretical calculations<sup>17</sup> and recent experiments using signal accumulation techniques<sup>24</sup> indicate that the B-Aintensity is ~0.1% of the B-X transition.

The qualitative appearances of all the HgX(B-X)spectra are similar with a gradual increase in intensity with increasing wavelength until a strong maximum occurs near the long wavelength limit. The dependence of the HgX(B-X) spectra on RX reagent is a consequence of different vibrational excitation. The distributions will be obtained by simulating the experimental spectra (see Sec. IV). As with the B-X rare gas halide spectra,  $^{13,14}$  the short wavelength limit,  $\lambda_{min}$ , can be used to set upper limits to the R-X bond energy,



FIG. 4. Comparison of simulated (---) and experimental (---) HgI(B-X) spectra from Hg( ${}^{3}P_{2}$ ) + I<sub>2</sub> and CF<sub>3</sub>I. The spectrum from I<sub>2</sub> contains contributions from HgI(C-X), unidentified I<sub>2</sub><sup>\*</sup> and  $I_2(D'-A')$  emission at 300, 325, and 340 nm, respectively.

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Reagent	$D_0(R-X)^b$ (kcal mol <sup>-1</sup> )		$E_{V_{\max}}$ (kcal mol <sup>-1</sup> )		ku~*	σ**
		$\lambda_{\min}$ (nm)	calc. °	obs.d	$(10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	(Å <sup>2</sup> )
$Cl_2$	$57.3 \pm 0.1$	303	27.7	27.8	32	90
CCl4	69.5	347	15.0	15.0	1.8	21.5
CHC13	67	390	18.3	5,9	1.6	6.2
CH <sub>2</sub> Cl <sub>2</sub>	$74 \pm 3$		11.3		0	0
CH <sub>3</sub> Cl	$81 \pm 5$		4.3		0	0
SO <sub>2</sub> Cl <sub>2</sub>	58, 5°	305	26.8	26.4	5.0	17.8
SOCI2	53, 9 <sup>e</sup>	295	31.4	29.6	3.7	12.7
$S_2Cl_2$	46.2°	298	39.1	28.6	1.2	4.3
$Br_2$	$45.45 \pm 0.01$	295	32.0	30.0	50	186
CBr4	$49 \pm 3$	335	28.7	18.5	f	
CHBr <sub>3</sub>	~ 55.5	350	22.2	14.8	f	
$CH_2Br_2$	$61 \pm 3$	$\sim 370$	16.7	~10.6	trace	
CF <sub>3</sub> Br	$68.7 \pm 2$		9.0		0	0
[ <sub>2</sub>	$35.60 \pm 0.01$	284	31.6	31.7	(large) <sup>f</sup>	
CH₂I₂	$50.3 \pm 2$		16.7		trace	
$CF_3I$	53.2 $\pm$ 2	350	14.0	12.7	11.2	44.2
$\mathbf{F}_2$	$37.0 \pm 1.0$	$\sim 360^{g} (242)^{h}$			99	222
$NF_3$	$57 \pm 2$	335 (291) <sup>h</sup>			8.1	23.3
N₂F₄	$\sim 71^{i}$	340 (339) <sup>h</sup>			5.3	17.4
sO,F,	~ 84				0	0

TABLE I. Summary of experimental data for reactive quenching of  $Hg({}^{3}P_{2})$ .<sup>2</sup>

<sup>a</sup>All data taken at 300 K.

<sup>b</sup>Unless otherwise indicated all bond energies were taken from Ref. 25.

<sup>c</sup>Calculated  $E_{V_{\text{max}}}$  determined from  $E_{V_{\text{max}}}^{\text{cale}} = E(\text{Hg}, {}^{3}P_{2}) + nRT + D_{0}(\text{HgX}, X^{2}\Sigma^{*}) - D_{0}(\text{RX}) - \nu_{0}$  where  $\nu_{0}$  is the band origin. The  $D_{0}(\text{HgX}, X^{2}\Sigma^{*})$  were taken from Ref. 26. The  $\nu_{0}$  were calculated from data given in Ref. 15.

<sup>d</sup> Determined from Eq. (4) and  $\lambda_{\min}$ .

<sup>e</sup>Reference 13. These values are upper limits.

<sup>f</sup>For these cases  $k_{\text{HgX}}$  was not determined because reagents flows were not measured.

<sup>g</sup>The HgF(B-X) spectrum shows a sharp drop in intensity at ~ 320 nm; however very weak emission does extend to ~ 260 nm.

<sup>h</sup>The value in parenthesis is the calculated  $\lambda_{\min} [=E(Hg, {}^{3}P_{2}) + nRT - D_{0}(R-X) + D_{0}(Hz-X; X)]$ . Since  $T_{0}(HgF, B)$ 

is not known,  $E_{\max}^{cale}$  cannot be determined for the fluorides. The value for  $D_0(\text{HgF}, X^2 \Sigma^*)$  was taken from Ref. 27.

<sup>1</sup>Reference 28.

$$D_0^{\circ}(R-X) \le E(\text{Hg}, {}^{3}P_2) + nRT - E(\lambda_{\min}) + D_0(\text{HgX}, X^{2}\Sigma^*) ,$$
(3)

assuming no activation energy for Eq. (1) and assuming that the transition from the highest populated HgX(B) vibrational level to HgX(X, v = 0) occurs with a significant intensity. The *nRT* term accounts for the thermal energy of the collision; if rotational and translational degrees of freedom are important, n = 5/2 and 3 for diatomic and polyatomic molecules, respectively. In the present work molecules with established bond energies were used and the  $\lambda_{\min}(\text{HgX})$  do not provide improvements for  $D_0^{\circ}(R-X)$ . A corollary to Eq. (3) gives the highest observed HgX(B) vibrational energy, which can be compared to the thermochemical limit,  $E_{\text{Vmax}}^{\text{calc}}$ 

$$E_{V_{\text{max}}}^{\text{obs}} = E(\lambda_{\min}) - T_0(\text{HgX}, B^2 \Sigma^*) .$$
(4)

Table I summarizes the observed  $\lambda_{\min}$  and compares  $E_{V\max}^{obs}$  and  $E_{V\max}^{calc}$ . For many of the reagents  $E_{V\max}^{obs}$  and  $E_{V\max}^{calc}$ . For many of the reagents  $E_{V\max}^{obs}$  and  $E_{V\max}^{calc}$  agree within the combined uncertainties of  $D_0^{\circ}$  (R-X) and  $D_0^{\circ}$  (Hg-X). In such cases all the excerption of Eq. (1) is implied to be available for HgX(B) vibrational excitation. The spectra from the CH<sub>n</sub>X<sub>4-n</sub> series were generally weak and  $\lambda_{\min}^{obs}$  was difficult to assign. However, even an unrealistic error of 10 nm would still give smaller  $E_{V\max}^{obs}$  values than  $E_{V\max}^{calc}$ . Apparently only

a portion of the excergicity is available for HgX(B) vibronic excitation for these reagents. Similar results were observed with the reactions of  $Xe({}^{3}P_{2}) + CH_{n}X_{4-n}$ ; although, the differences between  $E_{V\max}^{calc}$  and  $E_{V\max}^{obs}$  were smaller for XeX\*.<sup>14</sup>

Providing conditions are adjusted for first order kinetics and providing radiative decay is the only loss process for HgX(B), the relative emission rate is equal to the formation rate,

$$I_{\rm HgX} = k_{\rm HgX} * [\,{\rm Hg}({}^{3}P_{2})][\,{\rm RX}\,] \,.$$
(5)

A similar relationship exists for the  $Hg(^{3}P_{2}) + Cl_{2}$ reference reaction, and for experiments with constant  $[Hg(^{3}P_{2})], k_{HgX^{*}}^{RX}$  is given by

$$k_{\rm H\,g\,X}^{\rm R\,X} = \frac{I_{\rm H\,g\,X}[{\rm Cl}_2]}{I_{\rm H\,g\,C\,I}[{\rm R\,X}]} k_{\rm H\,g\,X}^{\rm Cl_2} \cdot .$$
(6)

In order to utilize Eq. (6)  $k_{\rm HgC1}^{Cl_2}$  must be known. Krause *et al.*<sup>3</sup> reported  $k_{\rm HgC1}^{Cl_2} = 3.2 \times 10^{-3}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> by comparing the relative intensities of HgCl(B-X) and Hg( ${}^{3}P_{1}-{}^{1}S_{0}$ ) from Cl<sub>2</sub> and N<sub>2</sub>, respectively, and using the absolute Hg( ${}^{3}P_{1}$ ) formation rate constants from Hg( ${}^{3}P_{2}$ ) + N<sub>2</sub>.<sup>29</sup> The major sources of error in the  $k_{\rm HgX*}$  determination, aside from the uncertainty in  $k_{\rm HgC1*}$  arise from the reagent purity, cali-

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bration of the detection system and the stability of the discharge. Experiments done on the same day with the same reagent mixtures gave <10% difference in the measured rate constants. Checks of some rate constants were made by doing experiments separated by several weeks with different mixtures; the agreement in  $k_{\rm HgX}$ \* usually was better than 20%. However, reagents with small  $k_{\rm HgX}$ \* are very sensitive to impurities and these  $k_{\rm HgX}$ \* deviated by as much as  $\pm 50\%$ . In general, the error limits that can be placed on  $k_{\rm HgX}$ \* are  $\pm 20\%$  for  $k_{\rm HgX}^{\rm RX} * / k_{\rm HgC1}^{\rm Cl_2} > 0.1$  and  $\pm 50\%$  for  $k_{\rm HgX}^{\rm RX} * / k_{\rm HgC1}^{\rm Cl_2} < 0.1$ .

The  $k_{\rm HgX}^{\rm RX}$  values are given in Table I along with the thermal cross sections. Because of low vapor pressure, reagent flow rates could not be measured for I<sub>2</sub>, CBr<sub>4</sub>, and CHBr<sub>3</sub> and these rate constants were not measured. However, the HgI\* emission from I<sub>2</sub> is quite strong and  $k_{\rm Hg1}^{\rm L_2} \approx k_{\rm HgBr}^{\rm Br_2}$ . The  $k_{\rm HgCl*}^{\rm RC1}$  values decline in the CCl<sub>4</sub>, CHCl<sub>3</sub>, CH<sub>3</sub>Cl series. Since the HgBr\* intensity decreased sharply for the CBr<sub>4</sub>, CHBr<sub>3</sub>, CH<sub>2</sub>Br<sub>2</sub> series,  $k_{\rm HgBr*}^{\rm Re}$  also probably declined. The reactive cross-sections for Br<sub>2</sub>(160 Å<sup>2</sup>), CCl<sub>4</sub>(34 Å<sup>2</sup>) and CHCl<sub>3</sub>(7.9 Å<sup>2</sup>) have been reported in a crossed-beam experiment. <sup>3,30</sup> These values are in good agreement with those determined in this work.

For each reagent listed in Table I, a qualitative estimate of the HgX(B) formation rate constant from  $Hg(^{3}P_{0})$  was made by monitoring the intensity of the HgX(B-X) emission with ~  $\mu$  200 mol min<sup>-1</sup> of N<sub>2</sub> added to the RX flow ( $\leq 5 \text{ mol min}^{-1}$ ). The N<sub>2</sub> reduces the Hg(<sup>3</sup>P<sub>2</sub>) concentration without significantly quenching the  $Hg(^{3}P_{0})$  concentration. For all reagents, the addition of  $N_2$  caused at least a tenfold reduction in the HgX\* intensity. While it was not possible to completely remove  $Hg({}^{3}P_{2})$  from the reaction zone in this manner, these experiments indicate that  $k_{\text{HgX*}}({}^{3}P_{0})/k_{\text{HgX*}}({}^{3}P_{2})$ is less than 0.1. The quenching of  $Hg(^{3}P_{1})$  by several of the polyatomic reagents listed in Table I gives little, if any, HgX(B).<sup>31</sup> The much lower  $\sigma_{\text{HgX}^*}$  for Hg(<sup>3</sup>P<sub>1,0</sub>), relative to  $Hg(^{3}P_{2})$ , reactions with polyatomic halides parallels the same trend for diatomic halogens.<sup>3-9</sup>

#### IV. SIMULATION OF THE HgX(B-X) SPECTRA

#### A. Procedure

The intensity (photons s<sup>-1</sup>) in a small frequency range from a single upper state vibrational level is given by<sup>32</sup>

$$I_{\nu}(\nu)d\nu = \frac{64\pi^4}{3h}\nu^3 \left| \int \psi_{\nu}\mu_e(R)\psi_e dR \right|^2 d\epsilon , \qquad (7)$$

where  $\mu_e(R)$  is the electronic transition moment,  $\nu$  is the frequency of the transition between level v and the lower state with energy  $\epsilon$ , and the wavefunctions are solutions to the radial Schrödinger equation,

$$\frac{d^2\psi}{dR^2} + \frac{2m}{\hbar^2} [E - U(R)]\psi = 0$$
(8)

for the molecular potential U(R). Equation (7) was evaluated for all bound vibrational levels of HgX(X) and a series of continuum energies ( $\Delta \epsilon = 50 \text{ cm}^{-1}$ ) to give the spectrum associated with HgX(B, v). The total spectrum was obtained by summing over the vibrational distribution,

$$I(\nu) = \sum_{\nu} N_{\nu} I_{\nu}(\nu) \quad . \tag{9}$$

 $N_v$  is the steady-state HgB(B) concentration in level v.  $N_v$  was varied by trial and error until a successful fit to the experimental spectrum was obtained. For actual comparison with the experimental spectra, detected as photons s<sup>-1</sup> wavelength<sup>-1</sup>, the  $v^3$  factor in Eq. (7) was adjusted to  $v^5$ . Rotational energy was not included in the calculation; however, trial computations including rotational energy were done to show that modest rotational energy had only a minor effect on the overall shape of the spectra.<sup>33</sup>

The three factors which determine the appearance of the spectrum are the relative shapes of the potential curves, the dependence of the transition moment on R, and the vibrational distribution. Thus, accurate potential curves and transition moments must be adopted before reliable vibrational distributions can be assigned. The present work employed the potentials developed by Cheung and Cool<sup>15</sup> for HgCl, HgBr, and HgI. The potentials are RKR potential curves for low ( $v \leq 30$ ) vibrational levels and Morse curve extensions to high energies. The Morse curve extensions were calculated using the known  $D_e$  and estimated  $r_e$  values.<sup>15</sup> The HgCl(B) and (X) potentials obtained by Cheung and Cool are shown in Fig. 5. For HgCl and HgBr the present calculations include contributions from the halogen isotopes weighted according to their natural abundance, i.e., Eq. (8) was evaluated for both Hg<sup>37</sup>Cl and Hg<sup>35</sup>Cl or Hg<sup>79</sup>Br and Hg<sup>81</sup>Br. The isotope effects were most important for the HgCl\* and HgBr\* spectra from the  $N_2(A) + HgX_2$  reactions, since the emission is predominantly from low v levels.<sup>21</sup> After our simulations were completed, Telluinghuisen and co-workers<sup>34,35</sup> reexamined the HgX(B-X) spectra. They favor slightly different vibrational assignments with concomittant changes in  $R_e(HgX)$ . Explicit tests, <sup>10</sup> to be published elsewhere, using Tellinghuisen's new potentials show that the vibrational distributions assigned here are still reliable.

The HgX(B-X) transition moment varies with  $R_{\bullet}^{11,17}$ Simulations of the HgX(B-X) spectra were initially attempted using the *ab initio*<sup>17</sup>  $\mu_e(R)$  approximated by Gaussian functions,

$$\mu_e(R) = a \exp\left(-2.773 \left(\frac{R-R_0}{c_1}\right)^2\right),$$
(10)

with a,  $c_1$ , and  $R_0$  being adjustable parameters. Since the *ab initio* calculations were done only for HgBr and HgCl, a similarly shaped  $\mu_{\theta}(R)$  was assumed for HgI. In general, the  $\mu_{\theta}(R)$  were similar for all the HgX with  $R_0 \approx R_e(B)$  and  $c_1 \approx 1.5$  Å. The parameter **a** was 4.0-4.3 D; but, the exact value is unimportant for simulations because only the variation of  $\mu_e(R)$  with R affects the variation of intensity vs  $\lambda$ . After obtaining  $\mu_e(R)$ , the emission intensity from individual vibrational levels,  $I_{\nu}(\nu)$  were calculated and approximate vibrational distributions, which reproduced the oscillatory structure of several HgX spectra, were obtained. In these initial assignments, only spectra from reactions which gave high vibrational distributions, e.g., Hg\* +X<sub>2</sub>,



FIG. 5. Potential energy curves for Hg<sup>35</sup>Cl. The inverted dashed curve is the "Mulliken" difference potential for HgCl (B, v'=30). Transition to the difference potential from the inner and outer turning points of the upper state and to the maximum of the difference potential are labeled A, B, and C, respectively. Transitions at A and C giving the minimum and maximum wavelengths of the spectrum. For low vibrational levels, the A-type transitions terminate on the attractive wall of HgCl(X) potential resulting in a low transition probability for  $v' \rightarrow v''=0$  transitions. Thus,  $\lambda_{\min}$  may not allow determination of  $E_{\max}$  for reactions giving low v' levels. The shape of the repulsive parts of the potentials for high v levels are not well characterized and the A-type transition may take several limiting forms depending on the two potentials.

 $Hg^* + SOCl_2$ ,  $Xe^* + HgX_2$ , *etc*. were simulated. The high vibrational levels sample a larger range of the internuclear distance and provide a better test of  $\mu_e(R)$ than low v levels. In these simulations, emphasis was placed on fitting the spacings and amplitudes of the oscillations, since these are more dependent on the vibrational distributions than on  $\mu_e(R)$ .<sup>12</sup> However,  $\mu_e(R)$ governs the overall intensity pattern and it was readily apparent that the *ab initio*  $\mu_{e}(R)$  were unsatisfactory. In particular, a vibrational distribution which gave roughly correct oscillatory spacings and amplitudes, gave too high an intensity near the short wavelength limit of the spectra. Since emission at these short wavelength occurs from the inner turning point of the B potential, the *ab initio*  $\mu_e(R)$  evidently were too large for  $R \leq R_e(B)$ . As a first modification, the  $\mu_e(R)$  were decreased in this region by simply shifting  $\mu_o(R)$  to larger R by approximately 0.1 Å. This change caused sufficient reduction in the intensity at short wavelengths

TABLE II. Transition moment coefficients for the HgX(B-X) transitions.<sup>2</sup>

	a	$c_1$	$c_2$	$R_0$
HgCl	4.3	1.5	2.0	3.10
HgBr	4.0	1.5	2.0	3.20
HgI	4.0	1.5	1.8	3.39

<sup>a</sup>The final form of  $\mu_e(\mathbf{R})$  was chosen as  $\mu_e(\mathbf{R})$ =  $a \exp(-2.773(R - R_0/c_1)^2)$  for  $R < R_0$  and  $\mu_{e}(e) = a \exp[-2.773(R - R_0)/c_2]$  for  $R > R_0$ .

that the envelopes of the calculated and experimental spectra were in good accord. However, in the wavelength region containing the oscillations, the calculated intensity was ~10%-20% lower than the distributions which gave the best fit to the spacing and amplitudes of the oscillations. The defect in this region was removed by increasing  $\mu_e(R)$  for  $R > R_0$  using a modified version of Eq. (10) with  $c_1$  increased for  $R > R_0$ . The *ab initio* and best fit  $\mu_e(R)$  are compared in Fig. 6 and the final parameters used to calculate  $\mu_e(R)$  are summarized in Table II. The modifications that we made to the  $\mu_e(R)$ are similar to those made by Cool and co-workers.<sup>36</sup> Their  $\mu_e(R)$ , which were derived independently from our work, are virtually indistinguishable from those shown in Fig. 6. Similar modifications to the *ab initio*  $\mu_e(R)$ ,



FIG. 6. Comparison of the *ab initio* () and modified (--) transition moment functions for the HgX(B-X) transitions. These transition moment functions give gradually declining Einstein coefficients with increasing v. The relative  $A_v$  values for HgC1(HgBr)[HgI] are 1.0(1.0)[1.0] for v = 0, 0.96(0.96)[0.96] for v = 30, 0.79(0.91)[0.94] for v = 60, and 0.58(0.72)[0.67] for v = 90.

i.e., shift of the maximum to larger R and an increase in  $\mu_e(R)$  at larger R, were required to successfully simulate the XeX(B-X) spectra.<sup>13,14</sup>

#### **B.** Vibrational distributions

The steady-state vibrational distributions were represented by flexible functions containing adjustable parameters. Most of the spectra from  $Hg({}^{3}P_{2})$  atom reactions could be fitted using a linear suprisal distribution, which has the following form for an atom +diatomic molecule prior in the rigid rotor harmonic oscillator limit:

$$N_{\nu} = (1 - f_{\nu})^{3/2} \exp(-\lambda_{\nu} f_{\nu}) .$$
 (11)

In Eq. (11)  $f_v$  was defined as  $E_v/E_{v_{max}}$ , where  $E_{v_{max}}$ was taken (usually) to be the same as the  $E_{V_{max}}^{obs}$  listed in Table II, and  $\lambda_{\nu}$  was adjusted until a fit to the spectrum was obtained. In the usual definition  $f_{\gamma}$  is  $E_{V}/\langle E \rangle$  and, for the cases with  $E_{V_{\text{max}}}^{\text{obs}} = E_{V_{\text{max}}}^{\text{calc}}$ , our definition corresponds to the standard form. Figures 2-4 show comparisons of the simulated and experimental spectra and the corresponding steady-state vibrational distributions are shown in Fig. 7. The steady-state distributions can be converted to the initial distribution using the calculated Eistein coefficients (see the caption of Fig. 6),  $N_{\nu}$  (initial) =  $A_{\nu}N_{\nu}$  (steady state). The  $A_{\nu}$ decline smoothly with increasing v and the difference between the steady-state and initial distributions is a slight enhancement of the lower v levels in the initial distribution. However the A, are not a strong function of v for  $v \leq 70$  and the difference between  $N_v$  (initial) and  $N_{\rm p}$  (steady-state) is within the uncertainty of the simulated steady-state distributions. A summary of  $\langle E_{\mathbf{v}} \rangle$ and  $\langle f_{\mathbf{y}} \rangle$ , both based on the steady-state  $N_{v}$ , and the description of the distributions are listed in Table III.

The  $Hg(^{3}P_{2}) + RCl$  reactions were the most extensively studied and a variety of vibrational distributions were found. The spectra from Cl<sub>2</sub>, S<sub>2</sub>Cl<sub>2</sub>, Cl<sub>2</sub>, and SOCl<sub>2</sub> (as well as SCl<sub>2</sub>)<sup>10</sup> show several oscillations and the vibrational distributions for these reagents peak in high levels  $(v \ge 40)$  with small populations in low v levels. The S<sub>2</sub>Cl<sub>2</sub> and SOCl<sub>2</sub> distributions are linear surprisal distributions with  $\lambda_{y} = -4$  and -5, respectively. The  $Cl_2$  spectrum could not be simulated with any single linear surprisal distribution and a sum of two functions was needed to describe the distribution. The spacings between the oscillations in the bound-free spectra become more widely spaced as the mean vibrational excitation increases, <sup>12,37</sup> and the oscillations become sharper for the narrower distributions. The distributions derived for  $SOCl_2$  and  $Cl_2$  spectra are consistent with these points. Examination of Fig. 2 shows that the oscillatory peaks to blue side of the main peak are at smaller wavelengths for Cl<sub>2</sub> than for SOCl<sub>2</sub> and reflects the shift of the vibrational distribution to higher energy. The oscillations are sharpest and most evident for the  $Cl_2$  reaction and the narrow high v level component was required to reproduce the spectrum.

The spectra from  $SO_2Cl_2$ ,  $CCl_4$ , and  $CHCl_3$  do not show oscillatory structure. The energy available from  $Hg(^{3}P_2) + SO_2Cl_2$  is nearly the same as for  $Cl_2$ ; but, the







FIG. 7. Steady-state vibrational distributions for (a) HgCl, (b) HgBr, and (c) HgI which were used for the best simulation of the spectra shown in Figs. 2-4. The correspondence between the vibrational level and vibrational energy is shown at the top and bottom of each plot.

Reagent	$\langle E \rangle^{2}$ (kcal mol <sup>-1</sup> )	E <sub>V max</sub> <sup>b</sup> (kcal mol <sup>-1</sup> )	$\langle E_{V} \rangle^{e}$ (kcal mol <sup>-1</sup> )	$\langle f_{\pmb{v}} \rangle^{\mathbf{d}}$	Distr	ibution type
Cl <sub>2</sub>	27.7	27.7	23.5	0,85	50%	$\lambda_{\rm V} = -16$
		23. 2	$(16, 8)^{f}$	(0, 61) <sup>f</sup>	50%	× <sub>V</sub> = - 2
CCl₄	15.3	15.0	6.0	0.40		$\lambda_{\mathbf{r}} = -2$
CHC13	18.3	7.1 <sup>8</sup>	3, 2	0.17		$\lambda_{\mathbf{v}} = -3$
$S_2Cl_2$	39.1	28.6	16.6	0.42		$\lambda_{r} = -5$
soci,	31.4	29.6	15.6	0.50		$\lambda_{\mathbf{v}} = -4$
SO <sub>2</sub> Cl <sub>2</sub>	26.8	26.4	7.9	0.29		$\lambda_{\mathbf{v}} = 0$
Br <sub>2</sub>	32. 0	30.0	21.2	0.66	55%	$\lambda_{v} = -8$
		19.5°	9.0°	0.46°	45%	$\lambda_{\nu} = -3$
			(15,7) <sup>f</sup>	(0.49) <sup>f</sup>		
CBr <sub>4</sub>	28.7	22. 2 <sup>h</sup>	10.3	0.36		$\lambda_{\rm v} = -3$
CHBr <sub>3</sub>	22. 2	18,5 <sup>h</sup>	9.1	0.41		$\lambda_{\rm p} = -3.5$
I <sub>2</sub>	31.6	31.6	18.0	0.60	75%	$\lambda_{\rm r} = -5$
-		9, 9°	4.5°	0.45 <sup>f</sup>	25%	$\lambda_v = -3$
			(14.6) <sup>f</sup>	(0.46) <sup>f</sup>		•
CF <sub>3</sub> I	14.0	12.7	6.5	0.46		$\lambda_{V} = -4$

TABLE III. Summary of vibrational energy disposal for  $Hg(^{3}P_{2}) + RX$  reactions.

 ${}^{a}\langle E\rangle$  is the mean available energy and is the same as  $E_{\max}^{eale}$  of Table I.

 ${}^{b}E_{\mathbf{v}_{max}}$  rather than  $\langle E \rangle$  was used to define  $f_{\mathbf{v}}$  in calculating the distributions of Eq. (11).

Unless otherwise noted  $E_{V_{max}}$  is the same as  $E_{V_{max}}^{obs}$  of Table II.  $c\langle E_V \rangle$  is the mean HgX(B) vibrational energy calculated from the steady-state distribution.  $d\langle E_{\mathbf{v}}\rangle/\langle E\rangle.$ 

"The second entries for the diatomic halogens refer to the exit channel leading to formation of excited halogen atoms.

<sup>t</sup>Combined  $\langle F_{\psi} \rangle$  or  $\langle E_{\psi} \rangle$  for both distributions.

 ${}^{e}E_{V_{max}}$  was chosen as 7.1 kcal mol<sup>-1</sup> in order to reproduce the short wavelength onset of the emission, see the text.

<sup>h</sup>See the text for a revision of previously reported [Ref. 13(a)]  $\langle f_{v}(\text{XeCl}) \rangle$  from Xe<sup>\*</sup>+SO<sub>2</sub>Cl<sub>2</sub>.

vibrational distributions clearly must be different based on the appearance of the two spectra. A linear surprisal distribution with  $\lambda_{v} = 0$  gave a good fit to the SO<sub>2</sub>Cl<sub>2</sub> spectrum. The spectra from CHCl<sub>3</sub> and CCl<sub>4</sub> were fitted with distributions given by  $\lambda_r = -3$  and -2, respectively; but the  $E_{V_{max}}^{obs}$  (CHCl<sub>3</sub>) was increased in the calculation. The  $E_{V_{max}}^{obs}$  (CHCl<sub>3</sub>) deduced from  $\lambda_{min}$  was tried first; however, it was impossible to reproduce the short wavelength onset of the experimental spectrum and  $E_{V_{\text{max}}}^{\text{obs}}$  was increased from 5.9 to 7.1 kcal mol.<sup>-1</sup> The reason for the discrepancy is associated with the small probability of the low vibrational levels of HgX(B) emitting to HgX(X, v = 0). The spectra from CBr<sub>4</sub>, CHBr<sub>3</sub>, and CF<sub>3</sub>I were matched by linear surprisal distributions with  $\lambda_{\nu} = -3$ , -3.5, and -4, respectively.

Linear surprisal type distributions were unsuccessful in simulating the spectra from  $Cl_2$ ,  $Br_2$ , and  $I_2$ . In fact, these spectra were very difficult to fit and numerous calculations were performed in an effort to find a simple physically acceptable distribution. A high  $E_{\rm y}$  component is required to give the large spacing between the oscillations but a low  $E_{y}$  component is also needed to "fill in" the troughs between the oscillations. The final form chosen to represent the distributions was a combination of two linear surprisal functions with different  $\lambda_{\mathbf{v}}$  and  $E_{\mathbf{v}_{max}}$ . One reason for using two components was the similarity with the  $Xe(^{3}P_{2}) + X_{2}$  reactions, for which the XeX(B, v) distributions were

associated with two exit channels corresponding to XeX\* (high  $E_v$ )+X<sub>2</sub>( $P_{3/2}$ ) and XeX\* (low  $E_v$ )+X( $^2P_{1/2}$ ). We used this idea in setting  $E_{V_{max}}$  for the low  $E_V$  component. Since the spin-orbit splitting increases in the halogen series, the bimodal shape of the distributions in Fig. 7 is more evident for the heavier halogens. In Table III, the  $\langle E_{\mathbf{v}} \rangle$  and the  $\langle f_{\mathbf{v}} \rangle$  for the two components are listed, as well as the average values for the sum of the two distributions.

The HgF(B-X) spectra were not simulated because a reliable HgF(B) potential is not yet available. Nevertheless, some information can be gleaned from the appearance of the spectra. For the  $Hg(^{3}P_{2}) + F_{2}$  reaction, the pronounced oscillations are indicative of a distribution peaking in high vibrational levels and by analogy with  $\operatorname{Cl}_2$ ,  $\langle f_v \rangle$  will be  $\geq 0.6$ . The HgF(B) distributions from  $NF_3$  and  $N_2F_4$  evidently peak in lower v levels; the situation is similar for the  $Xe({}^{3}P_{2})$  and  $Kr({}^{3}P_{2})$  reactions. 12,13()

#### V. DISCUSSION

#### A. General features of Hg( ${}^{3}P_{2}$ ) reactions with $X_{2}$

The observation of the ionic  $\operatorname{Hg} X(B)$  product with branching fractions close to unity is evidence that the quenching of  $Hg(^{3}P_{2})$  by diatomic halogens must involve the ionic-covalent curve-crossing mechanism; although, specific features remain to be explained. The total quenching cross sections of  $Hg(^{3}P_{2})$  by  $X_{2}$  have not been

reported; but, the  $\sigma_{Q}$  must be 100-200 Å<sup>2</sup> based on the  $\sigma_{H_{eX}*}$  values, which are consistent with the quenching cross sections of other spin-orbit states with Cl<sub>2</sub>,  $\sigma(\text{Hg}, {}^{3}P_{1})^{5(\text{b})} = 91 \text{ Å}^{2} \text{ and } \sigma(\text{Hg}, {}^{3}P_{0})^{5(\text{a})} = 28 \text{ Å}^{2} \text{ and for}$ Br<sub>2</sub>,  $\sigma(\text{Hg}, {}^{3}P_{1})^{6} = 100 \text{ Å}^{2}$  and  $\sigma(\text{Hg}, {}^{3}P_{0})^{8} = 44 \text{ Å}^{2}$ . The close correspondence between the ionization energies and polarizabilities of the alkali metal atoms (M) and metastable rare gas atoms (Rg,  ${}^{3}P_{2}$ ) ensures that their ionic and covalent potentials with the same reagent have close similarity.<sup>22</sup> Thus, the similar magnitudes of the reactive cross sections for  $Rg(^{3}P_{2})$  and M atoms are easily understood.<sup>22</sup> For  $Hg(^{3}P_{2})$  the correspondence is not so apparent because the polarizability<sup>38</sup> of  $Hg(^{3}P_{2})$ is 4.5 Å<sup>3</sup>, which is much less than for Xe\* or Cs(~60 Å<sup>3</sup>), and the I.P. (Hg,  ${}^{3}P_{2}$ ) is 4.97 eV vs 3.8 eV for Cs and Xe\*. Thus, for Hg\* the comparison of entrance channels is better made with Na with I.  $P_* = 5.1$  eV and polarizability of 24 Å<sup>3</sup>. Indeed,  $\sigma(\text{Na} + \text{Cl}_2) = 124 \text{ Å}^2$ which is close to  $\sigma(\text{Hg}({}^{3}P_{2}) + \text{Cl}_{2})$ ; but,  $\sigma(\text{Na} + \text{Br}_{2})$ =116 Å<sup>2 39</sup> is smaller than  $\sigma(\text{Hg}({}^{3}P_{2}) + \text{Br}_{2})$ . The diabatic crossing points of V(Hg<sup>\*</sup>;  $X_2^{-}$ ) and V (Hg,  ${}^{3}P_2$ ;  $X_2$ ) are inside the orbiting positions of  $V(Hg^*; X_2)$  and the magnitudes of  $\sigma_{\Omega}$  (Hg,  ${}^{3}P_{2} + X_{2}$ ) are expected to be determined by the orbiting position on the lowest adiabatic entrance channel potential.<sup>22</sup> This is not necessarily the case for the  $Hg(^{3}P_{0})$  potential since the diabatic crossing point falls at a smaller distance.

The  $\langle f_V \rangle$  for Hg( ${}^{3}P_2$ ) + X<sub>2</sub> decline in the Cl<sub>2</sub> (0.61), Br<sub>2</sub> (0.49), and I<sub>2</sub> (0.46) series. Although the HgF(B) spectra was not simulated, the appearance of the Hg( ${}^{3}P_2$ ) + F<sub>2</sub> spectrum suggests  $\langle f_V \rangle \ge 0.6$ . In fitting the spectra it was convenient to use a two component vibrational distribution, which suggests that the Hg( ${}^{3}P_2$ ) +X<sub>2</sub> reactions may occur via two characteristic pathways. The two pathways were taken to correspond to formation of ground and excited halogen atoms,

$$Hg(^{3}P_{2}) + X_{2} - HgX(B, high v) + X(^{2}P_{3/2}) - HgX(B, low v) + X(^{2}P_{1/2}).$$
(12)

Similar two component distributions were used<sup>14</sup> to simulate the XeX(B-X) spectra from Xe( ${}^{3}P_{2}$ ) +X<sub>2</sub> reactions. For both  $Hg(^{3}P_{2})$  and  $Xe(^{3}P_{2})$ , the exit channel associated with  $X({}^{2}P_{1/2})$  formation gave a lower  $\langle f_{v} \rangle$ (0.40-0.49 vs 0.60-0.85) than the channel yielding  $X({}^{3}P_{3/2})$ . The initial, as opposed to the steady state, XeX(B) and HgX(B) vibrational distributions from the diatomic halogens are compared in Fig. 8. Since the XeX\* distributions extend to much higher v levels, correcting the steady-state distributions for the variation of the lifetimes with v level is more important for XeX(B) than for HgX(B).<sup>13,14</sup> The shapes of the  $HgX^*$ and XeX\* distributions are very similar with a high  $E_v$ component peaking at  $f_v = 0.7 - 0.9$  and a lower  $E_v$  component, which appears to become more important for the the heavier halogens. However, the fraction assigned to the low  $E_v$  component may be decieving, since the overall distribution can be partioned in other ways. Several calculations were performed for the HgCl spectrum using either a Gaussian function or a flat distribution to represent the low  $E_{\mathbf{v}}$  component, while retaining the linear surprisal distribution (with variable  $\lambda_{\mathbf{y}}$ ) for the high  $E_{\mathbf{y}}$  component. Several equally good fits to the



spectrum could be obtained with the low  $E_{\gamma}$  component being 30% to 70% of the total distribution. Calculations for the  $Hg(^{3}P_{2}) + Br_{2}$  or  $I_{2}$  were not performed in as great a detail (only linear surprisal components were tried); but, the same situation would exist. Partitioning the vibrational distributions into two components does not prove the existence of two different exit channels for either  $Hg(^{3}P_{2})$  or the  $Xe(^{3}P_{2})$  reactions; the eariler suggestion<sup>14</sup> that the  $X(^{2}P_{1/2})$  channel becomes more important as  $X_{2}$  becomes heavier should not be regarded as conclusive. Nevertheless, the vibrational energy disposal of the  $Hg(^{3}P_{2}) + X_{2}$  reactions does strongly resemble the corresponding  $Xe(^{3}P_{2})$  reactions.

The two component HgX(B) distributions seem probable, but this had not been conclusively proven. Linear surprisal type functions tend to introduce some bias into the representation of broad distributions. Recently, Simons and co-workers<sup>40</sup> have reexamined the spectrum from Xe( ${}^{3}P_{2}$ ) + I<sub>2</sub> using least-squares histogram method to obtain the XeI(B) distribution. Although the low  $\langle f_{V} \rangle$  was confirmed, they prefer a single component, broad distribution with a maximum in lowv levels. Interpreting the XeI(B-X) spectrum is complicated because of overlap from the XeI(C-A) band.<sup>14,40</sup> Regardless of whether the distributions are one or two component in type, the Xe( ${}^{3}P_{2}$ ) and Hg( ${}^{3}P_{2}$ ) reactions do provide a strong contrast to alkali metal atom reactions with regard to vibrational energy disposal, since the



latter give  $\langle f_v \rangle \approx 0.8-0.9$  without significant change for different halogens.<sup>41</sup>

#### B. Reactions of Hg( ${}^{3}P_{2}$ ) with polyatomic halogen donors

Only a few polyatomic molecules, such as CF<sub>3</sub>I, CCl<sub>4</sub>, SOCl<sub>2</sub>, and NF<sub>3</sub>, have  $k_{\text{HgX}*}^{\text{RX}}/k_{\text{HgCl}*}^{\text{Cl}_2} \ge 0.1$ . Since  $k_O(\text{Hg}, {}^{3}P_2 + \text{RX}) \approx k_O(\text{Hg}, {}^{3}P_2 + \text{Cl}_2)$ , this statement is equivalent to one in which  $k_{\text{HgX}*}^{\text{RX}}/k_{\text{HgCl}*}^{\text{Cl}_2}$  is replaced with the branching fraction for HgX(B) formation. Thus, for both  $Xe({}^{3}P_{2})^{22}$  and  $Hg({}^{3}P_{2})$  only simple halides of groups V and VI have appreciable XeX\* or HgX\* branching fractions. The best organic donor molecules are  $CF_3I$ ,  $CCl_4$ , and  $CBr_4$  which dissociatively attach thermal electrons to give X<sup>-</sup>.<sup>42,43</sup> The decrease in  $\sigma_{HgX*}$ or  $\sigma_{RgX^*}$  for  $CCl_{4-n}H_n$  and  $CBr_{4-n}H_n$  parallels their reduced electron attachment cross sections. The generally smaller  $k_{HgX*}^{RX}$  relative to  $k_{RgX*}^{RX}$  for the same **RX** probably is associated with the higher I. P. of  $Hg(^{3}P_{2})$ , which leads to a smaller intermolecular distance for crossing to  $V(\text{Hg}^*, \text{RX}^-)$  relative to  $V(\text{Rg}^*, \text{RX}^-)$ . Therefore, access to competing channels at short range is enhanced for  $Hg(^{3}P_{2})$  reactions. The decrease in the RgX\* branching fractions as RX becomes more complex was associated with the increase in the density of alternative exit channels; although, in some cases specific features in the different RX interaction potentials may be important.<sup>44</sup> The direct formation of HgX(X) and HgX(A) may be important competing channels for Hg( ${}^{3}P_{2}$ ) reactions (and for Hg( ${}^{3}P_{1}$ ) and Hg( ${}^{3}P_{0}$ ) reactions).<sup>45,46</sup> The discussion in the following section bears on this possibility, since the diatomic halogen ion-pair potentials tend to correlate to HgX(A) and HgX(X) products. In work to be published separately, <sup>10</sup> we have shown that intramultiplet relaxation generally is not a dominant quenching channel for  $Hg(^{3}P_{2})$  by halogen containing polyatomic molecules.

As shown in Table III, a wide range of vibrational energy disposal is found for the  $Hg(^{3}P_{2}) + RX$  reactions. Comparison of the HgX\* vibrational distributions with previously reported XeX\* distributions<sup>13,14</sup> indicate that  $\langle f_{\nu}(XeX^{*}) \rangle$  is larger (0.2–0.3) than for  $\langle f_{\nu}(HgX^{*}) \rangle$  in all cases. The  $\langle f_{\nu}(XeX^{*}) \rangle$  are in turn systematically smaller than  $\langle f_{\nu}(BaX) \rangle$  from Ba +RX.<sup>14</sup> In the harpooning model, the nature of the RX<sup>-</sup> anion plays an important role in determining the reaction dynamics<sup>41</sup> and, in the first approximation, the energy disposal for Hg(<sup>3</sup>P<sub>2</sub>), Xe\* and Ba might have been thought to be similar rather than systematically different. However, the predictions of the model can be refined by considering the energy that is retained in the R fragment after the dissociative electron attachment step.

First consider CCl<sub>4</sub> for which the electron attachment step is well studied. The vertical electron affinity for CCl<sub>4</sub> is ~0 eV and the dissociation limit, CCl<sub>3</sub>+Cl<sup>-</sup>, is 0.4 eV below the ground state of CCl<sub>4</sub>. <sup>42(b)</sup> Time of flight measurements<sup>47</sup> indicate that 0.14 eV of this excess energy appears as translational energy and the remainder, 0.26 eV, is retained as internal energy of CCl<sub>3</sub>. The vibrational energy disposal of both Ba<sup>48</sup> and Xe(<sup>3</sup>P<sub>2</sub>)<sup>13</sup> reacting with CCl<sub>4</sub> has been interpreted by

assuming that this pattern is retained. For  $Ba + CCl_4$ the total available energy is 1.70 eV and, assuming that 1.3 eV (1.70-0.4 eV) is channeled into BaCl vibrational energy,  $\langle f_v \rangle = 0.76$ , which is in excellent agreement with the experimental value of 0.75.48 The same considerations predict  $\langle f_{V}(XeX) \rangle = 0.70$  for  $Xe({}^{3}P_{2})$ +CCl<sub>4</sub><sup>13</sup> and  $\langle f_V(\text{HgCl}) \rangle = 0.39$  for Hg(<sup>3</sup>P<sub>2</sub>)+CCl<sub>4</sub>, which match the experimental values of  $0.67^{13}$  and 0.40, respectively. The agreement, in part, may be fortutious because the CCl<sub>4</sub> dissociation is only approximately the same as reaction on the  $V(Hg^* \text{ (or } Xe^*); CCl_4)$  potential surface. The reduced  $\langle f_{\nu}(HgX) \rangle$  relative to  $\langle f_{\nu}(XeX) \rangle$ for several RX reactions can be explained by assuming that each reaction partitions the same amount of energy to the sum of the relative translational and internal energy of R. For example,  $\langle f_{\nu}(\text{XeI}) \rangle = 0.7$  for  $\text{Xe}({}^{3}P_{2})$ +  $CF_3I$  with an available energy of 1.14 eV<sup>13(b)</sup>; hence,  $E_{int}^{CF_3} + E_T \sim 0.34$  eV. If this remains unchanged when Xe\* is replaced by Hg\*,  $\langle f_{\gamma}(HgX) \rangle$  should be 0.44, which agrees well with the experimental value. Similar predictions for  $\langle f_{\mathbf{y}}(\text{HgX}) \rangle$  from CBr<sub>4</sub> and SOCl<sub>2</sub> give 0.40 and 0.58, respectively, and these values are in accord with those of Table III.

For remaining RX of Table III, the  $\langle f_{\mathbf{v}}(\mathrm{HgX}) \rangle$  predicted from the above rule of thumb generally differs by 30% - 50% from the experimental  $\langle f_v(\text{HgX}) \rangle$ . While the assumption that  $\langle E_{int}^{R} \rangle$  remains constant is probably approximately valid,  $\langle E_T \rangle$  and  $\langle E_V (HgX) \rangle$  may change when Xe<sup>+</sup> is replaced by Hg<sup>+</sup> for the cases with the more repulsive surfaces. Thus, the prediction should be best for RX that is known to give low  $\langle E_{\tau} \rangle$ . Such cases generally exhibit forward scattering in molecular beam experiments and examples are CCl<sub>4</sub>, CBr<sub>4</sub>, and CF<sub>3</sub>I for which  $\langle f_v(HgX) \rangle$  was predicted well. As X is replaced by H in the  $CS_{4-n}H_n$  series, increased backward scattering and a larger  $\langle E_T \rangle$  is observed in reactions with alkali metal atoms. The difference in repulsion between R and HgX\* will play a more important role in determining the vibrational energy disposal of these reactions and further refinements to the model are necessary to explain  $\langle f_{\nu}(HgX) \rangle$  for CHCl<sub>3</sub> and CHBr<sub>3</sub>.

Thionyl chloride (SOCl<sub>2</sub>) dissociatively attaches thermal electrons to give Cl<sup>-</sup> and SOC1.<sup>49</sup> The  $\langle f_{\mathbf{v}}(\text{HgCl}) \rangle$  is relatively large and in good agreement with the predicted value from considering  $\langle f_v(XeCl) \rangle$ . On the other hand,  $SO_2Cl_2^2$  is stable with the electron in a nonbonding molecular orbital made up primarily of chlorine p orbitals.<sup>59</sup> Thus, the  $Hg({}^{3}P_{2}) + SO_{2}Cl_{2}$  reaction might be expected to proceed via a complex. The HgCl\* vibrational distribution represented by  $\lambda_{y} = 0$ (but a three-body prior) is consistent with a more stable anion intermediate. The original assignment  $^{13(\omega)}$ of  $\langle f_{\mathbf{v}}(\mathbf{X}\mathbf{e}\mathbf{X})\rangle = 0.64$  from  $\mathbf{X}\mathbf{e}({}^{3}P_{2}) + \mathbf{SO}_{2}\mathbf{Cl}_{2}$  is much larger than expected based on an analogy to  $Hg(^{3}P_{2})$ . We reexamined the Xe\*+SO<sub>2</sub>Cl<sub>2</sub> reaction and  $\langle f_V(XeCl) \rangle = 0.48$ was assigned. Apparently a  $Cl_2$  impurity in the  $SO_2Cl_2$  sample studied previously, <sup>13(a)</sup> gave an erroneously high  $\langle f_{v}(XeCl) \rangle$ . The new  $\langle f_{v}(XeCl) \rangle$  for SO<sub>2</sub>Cl<sub>2</sub> relative to that for  $Xe({}^{3}P_{2}) + SOCl_{2}$  follows the trend observed for  $Hg(^{3}P_{2})$  and is consistent with the properties of  $SOCl_{2}^{-}$ vs SO<sub>2</sub>Cl<sub>2</sub>.

#### C. Comparison of the Hg\*, Rg\*, M, and M\* reactions with halogens

The reactions of the ground state alkali  $(M_1)$  and alkaline earth metal  $(M_{II})$  atoms with halogens are well understood at the microscopic level from molecular beam studies, and studies of excited  $M_{H}^*$  state atoms with halogens currently are being reported. 51-56 In this section we wish to compare those results with studies of the Rg(n+1s) and Hg(6s, 6p) excited state atom reactions. A large body of data has been accumulated for the  $Rg({}^{3}P_{2})$  and  $({}^{3}P_{1})$  atom reactions including molecular beam studies of the dependence of the cross sections on velocity, 57, 58 degree of polarization of the RgX\* product, 57-59 and the dependence of the reaction on orientation of the halogen,<sup>60</sup> as well as our own work in assignment of energy disposal.<sup>22</sup> Except for the differences in vibrational energy disposal to RgX\* vs MX and the excitation transfer channel yielding X<sup>\*</sup><sub>2</sub> there is a very

close parallel between the  $Rg^*$  and  $M_I$  reactions.<sup>22</sup> Although the interaction between the covalent entrance channel and the ion-pair potential provides the framework for discussion of the Xe<sup>\*</sup> and  $Hg(^{3}P_{2})$  reactions, many details remain to be explained with regard to the product side of the reaction. No further discussion will be given to the long range part of the  $V(Hg^*; X_2)$ potential which determines the total quenching cross sections. Instead attention will be focused on (i) the high branching fractions for formation of HgX(B). (ii) the spin-orbit effect in the reactivity of Hg(6s, 6p)states, and (iii) the similarities between  $Hg(^{3}P_{2})$  and  $Xe({}^{3}P_{2})$ , and the contrast with the  $M_{I}$  or  $M_{II}$  atoms with regard to vibrational energy disposal in reactions with the halogens.

For aid in the following discussion, schematic potentials of the Ca and Hg reaction with Cl<sub>2</sub> are shown in Fig. 9. The right-hand side of the figures represents

CI2

(<sup>1</sup>S)

٥Å



FIG. 9. Comparison of schematic potentials for (a)  $Ca^*+Cl_2$ , and (b)  $Hg^* + Cl_2$  suggesting the importance of the excited ionic surfaces during the course of the reactions. The zero on the energy scale refers to the separated M+Cl+Cl limit. The covalent  $Ca(^{3}D) + Cl_{2}$  curve has been omitted for clarity. In (c) the interaction of the spin-orbit components at the crossing of  $V(Hg^*, Cl_2)$  with  $V(Hg^*, Cl_2)$  are shown to illustrate that the trajectories from  $Hg({}^{3}P_{2})$  are more likely to reach the  $V(Hg^{*}, Cl_{2}^{*})$ potential than those from  $Hg({}^{3}P_{0,1})$ . The diagram has been drawn for C<sub>wy</sub> geometry but the same conclusions are reached for  $C_{2\nu}$  or  $C_s$  symmetry.



FIG. 10. State correlation diagram in  $C_{2\nu}$  and collinear geometry for conversion of Hg<sup>+</sup> and Cl<sub>2</sub><sup>-</sup> to HgCl+Cl. Spinorbit effects are not included in the diagram. Note that the energy scale has been skewed to permit display of all the states; the ionic Hg<sup>+</sup>, Cl<sub>2</sub><sup>-</sup> states occur at high energies ( $\geq 10.2 \text{ eV}$ ). The excited HgCl<sup>\*</sup> states are 4-6 eV above the ground state of HgCl<sub>2</sub> (0 eV) (Ref. 65).

the entrance channels which are crossed by one or more ionic curves that subsequently lead to the exit channel products on the left-hand side of the figure. The ionic curves for both  $\operatorname{Cl}_2^{-}({}^{2}\Sigma_{\mu}^{*})$  and  $\operatorname{Cl}_2^{-}({}^{2}\Pi_{\mu})$  are shown and, for Ca, an additional ionic potential corresponding to  $V(Ca^{**}; Cl_2^*, {}^{2}\Sigma_{u}^{*})$  is also included. The center portion of the figures corresponds to that part of the potentials which is generally not well known. Two important differences should be noted between Ca and Hg. First, spin-orbit interactions are much more important for Hg than for Ca. Thus, separate entrance channels for  $Hg(^{3}P_{2,1,0})$  are shown, whereas only a single curve represents the  $Ca(^{3}P)$  entrance channel. Second. although the notation for the first-three CaCl and HgCl states are the same, considerable differences exist in their bonding. All three states are ionic and strongly bound for CaCl and the excited electron in CaCl (A, B)is localized mainly on Ca.<sup>61</sup> In contrast, HgCl(A) is strictly a covalent repulsive state, and for both HgCl(B)and HgCl(X) the degree of ionic character depends on the internuclear distance.<sup>17(a)</sup> At large  $r_{\text{HgCl}}$ , HgCl(B) is primarily ionic and HgCl(X) primarily covalent and the reverse is the case at small  $r_{\text{HgC1}}$ .

Considerable differences have been found for the ground state reactions of mercury and alkaline earth atoms. The product angular distributions from both  $M_I$  and  $M_{II}$  atom reactions are similar and there is no evidence for the influence of a strongly attractive  $MX_2$  potentoal.<sup>62</sup> On the other hand, two characteristic reaction pathways were observed for  $Hg + I_2$ .<sup>63</sup> At low translational energies the reaction proceeds by insertion into  $I_2$  to give a long lived complex, the stable IHgI molecule. At higher energies direct abstraction via the collinear approach of Hg to  $I_2$  becomes more important. For both pathways a 0.7-2 eV barrier for formation of HgI was found. A similar situation is expected for  $Hg + CI_2$  and this is shown in Fig. 9. The existence of the Hg +  $I_2$  barrier is consistent with mo-

lecular orbital correlation arguments developed by Mayer *et al.*<sup>64</sup> to derive the salient features of the ground state Hg-I<sub>2</sub> potential energy surface. The point of view depends somewhat upon the geometry, but basically the barrier arises from a strongly avoided crossing between the repulsive ground-state (Hg+X<sub>2</sub>) covalent surface and an attractive ionic surface. For  $M_{II}+X_2$  the ionic surface crosses the ground-state covalent surface in the entrance channel at large distance and no barrier exists. Thus, the large differences in ionization potential, e.g., 6.1 eV for Ca vs 10.4 eV for Hg, and the product bond energies,  $D_0(CaCl)=4.3$ eV and  $D_0(HgCl)=1.1$  eV, are responsible for the very different reaction dynamics for ground state Ca and Hg atom reactions with halogens.

Perhaps the most surprising experimental result for the  $Hg(^{3}P_{2}) + X_{2}$  reactions is the very high branching fractions for formation of HgX(B). Since the branching fractions are high for all halogens with  $Hg(^{3}P_{2})$ , a rather general explanation must be sought. This result contrasts with the  $M_{11}^* + X_2$  reactions. For excited Ca\* atomic reacting with Cl<sub>2</sub> or HCl the total quenching cross sections are large, <sup>53</sup> e.g.,  $Ca({}^{3}P) + Cl_{2}(124 \text{ }^{3}A^{2})$ ,  $Ca(^{1}D_{2}) + Cl_{2}$  (51 Å<sup>2</sup>),  $Ca(^{3}P) + HCl$  (45 Å<sup>2</sup>), and  $Ca^{1}(D_{2})$ + HCl (90  $Å^2$ ). Chemiluminescent cross sections for CaCl(A, B) formation are much smaller, typically 20-30  $Å^{2}$  <sup>53</sup>; and the CaCl\* branching fractions are usually less than 30%. The data for Ca<sup>\*</sup> are consistent with transfer mainly to the ionic  $V(Ca^*; Cl_2^*, {}^2\Sigma_u^*)$  potential with small probabilities for those trajectories to escape from this potential before the predominent products, CaCl(X) + Cl, are formed. The reactions of  $Hg(^{3}P_{2})$ , but perhaps not  $Hg({}^{3}P_{1})$  or  $Hg({}^{3}P_{0})$ , differ strongly from this sequence of events because little HgX(X) is formed. Figure 10 shows a correlation diagram in  $C_{2\nu}$ symmetry of the ionic  $Hg^{+}+Cl_{2}^{-}$  states with intermediate HgCl<sup>\*</sup> electronic states which subsequently evolve to the HgCl+Cl states. The right-hand side of the figure

shows *adiabatic* correlations based on the *ab initio* calculations of Wadt<sup>65</sup> that are consistent with the photodissociation products from HgX<sub>2</sub>. The left-hand side was constructed from the energy ordering of the HgCl<sup>\*</sup> states<sup>65</sup> and the ion-pair states. The state correlation from the individual ion-pair states to the HgCl+Cl products is consistent with the orbital correlation scheme of Meyer *et al.*,<sup>64</sup> i.e., in general the ion-pair states "naturally" correlate to the HgCl(X, A) + Cl products. Only the HgCl<sup>\*</sup> states energetically accessible to the Hg(<sup>3</sup>P<sub>2</sub>) + Cl<sub>2</sub> reaction have been included in the diagram. The important point of Fig. 10 is that only one HgCl<sup>\*</sup> state,  ${}^{1\Sigma}_{u}({}^{1}B_{1})$ , correlates to HgCl(X) or HgCl(A).<sup>65</sup>

Based on the  $C_{2\nu}$  correlation diagram, the reaction of Hg(6s, 6p) atoms can produce some HgCl(B) via the  ${}^{1}B_{1}$  component of V(Hg<sup>\*</sup>; Cl<sup>\*</sup><sub>2</sub>,  ${}^{2}\Pi_{s}$ ). However, this pathway should account only for a small fraction of the reactive events, since it represents only one component from the  $V(Hg^*; Cl_2^{-, 2}\Pi_{*})$  potential. Moreover, reduction of the symmetry to  $C_s$  geometry (actual trajectories are best thought of as occurring in the lowest possible symmetry) or including spin-orbit effects will lead to avoided crossings in the Hg<sup>+</sup>-Cl<sub>2</sub><sup>-</sup> entrance channels. The net effect of these avoided crossings is that there is no obvious pathway to formation of HgX(B) from either  $V(Hg^*; X_2^-, {}^{2}\Sigma_u^+)$  or  $V(Hg^*; X_2^-, {}^{2}\Pi_g)$ , i.e., the potentials all have pathways leading to HgX(X) or HgX(A)if no other interactions are included. There are some interesting differences between  $C_{2v}$  and  $C_{wv}$  correlations. For example,  $V(Hg, 6s 6p; X_2)$  correlates to the HgX(C, D)+X and HgX<sup>\*</sup>+X<sup>\*</sup> products for  $C_{\infty \nu}$  and  $C_{2\nu}$ , respectively, and  $V(\text{Hg}^*; X_2^{-2}\Pi_r)$  correlates to  $\text{Hg}X^* + X^*$  and HgX(X)+X for  $C_{2\nu}$  and  $C_{\nu\nu}$ , respectively. However, with spin-orbit interactions included or in  $C_s$  geometry there always are symmetry allowed pathways to HgX(X, A)+X products from both ion-pair states in all orientations.

In order to account for the large branching fractions from  $Hg(^{\circ}P_2) + X_2$ , it is necessary that trajectories sampling  $V(Hg^*; X_2^{-})$  or  $V(Hg^*; X_2^{-})$  be diverted before reaching the HgX(A, X) products. The barrier to HgXformation in the  $Hg + I_2$  ground state entrance channel suggests a means by which this may be accomplished. According to the molecular orbital correlations of Mayer et al., <sup>64</sup> the barrier for  $C_{2\nu}$  approach of ground state Hg to  $I_2$  arises from the avoided crossing of the neutral Hg-X<sub>2</sub> potential and various ionic diabatic potentials. The ionic diabatic potential corresponds to the Hg<sup>\*</sup>-X<sub>2</sub><sup>-(2</sup> $\Sigma_{u}^{*}$ ) state in  $C_{\infty_{v}}$  geometry and Hg<sup>2\*</sup>-X<sub>2</sub><sup>2-(1</sup> $A_{1}$ ) or an  $A_1$  spin-orbit component from Hg<sup>\*</sup>  $-X_2^*({}^3B_2)$  in  $C_{2\nu}$ geometry. Using estimates for these potentials and a splitting of  $\sim 2 \text{ eV}$  at the crossing point, they<sup>84</sup> estimated a barrier height of 0.7 eV for broad-side approach, which is in reasonable agreement with the experimental range of 0.4-1.15 eV. For such a large splitting, the probability of a trajectory remaining on the upper  $A_1$  adiabatic curve, rather than leaking to the lower  $A_1$ potential, will be large and formation of HgX(B) starting from  $V(Hg^*; X_2)$  can have a strongly avoided crossing with  $V(Hg; X_2)$ . In order that all, or nearly all, trajectories on  $V(Hg^*; X_2)$  and/or  $V(Hg^*; X_2^*)$  be diverted

from HgX(X, A) + X, it is necessary to include additional, low energy covalent channels in Fig. 9. The most likely candidates are those potentials correlating to  $Hg + X_2^*$ . For example  $V(Hg; X_2^*, {}^{1,3}\Pi_g)$  correlates to HgX<sup>\*\*</sup> +X<sup>-</sup> in  $C_{\infty v}$  and to HgX(A) +X in  $C_{2v}$  geometry. In either case there will be surfaces of the right symmetry to intercept some of the surfaces correlating to  $V(Hg^{*}; X_{2})$  and  $V(Hg^{*}; X_{2}^{*})$ . Depending on the halogen, various other  $X_2^*$  states can be within the energy range. If X\* potentials are included, then a large fraction of the components from  $V(Hg^{*}; X_{2}^{*})$  and  $V(Hg^{*}; X_{2}^{**})$  can undergo avoided crossings before reaching HgX(A, X). However, without additional information it is not possible to discuss the interaction strengths between the  $V(Hg^{*}; X_{2})$  and  $V(Hg; X_{2}^{*})$  potentials. Before leaving this discussion, it is worth noting that the  $Rg(^{3}P_{2,1}) + X_{2}$ collisions can transfer to either  $V(Rg^*; X_2)$  or  $V(Rg^*; X_2^{*})$ , according to symmetry, and that both ion-pair potentials correlate directly to RgX(B, C, D) without need to consider  $V(Rg; X_2)$  or  $V(Rg; X_2^*)$  potentials.<sup>13,57</sup>

While the orbital correlations can suggest an explanation for the large HgX(B) branching fractions from the Hg(6s, 6p) multiplet, if sufficiently strong interactions between diabatic states are assumed, no distinction yet has been made between different spin-orbit states of Hg(6s, 6p). However, our work, as well as others, 3-6do show that the  $Hg(^{3}P_{0,1})$  states have small HgX(B)branching fractions relative to those for  $Hg(^{3}P_{2})$ . The  $Ca(^{3}P) + Cl_{2}$  chemiluminescent section also shows a spin-orbit effect with the  ${}^{3}P_{2}$  cross sections being 1.5-4 times larger than  ${}^{3}P_{1,0}$ , even though the energy separation between the spin-orbit states is very small  $(50-100 \text{ cm}^{-1})$ . <sup>56</sup> The symmetries of the relevant ionic and covalent surfaces for the Hg (or Ca) +  $X_2$  system are summarized in Table IV both with and without spinorbit interactions. According to Table IV, there are no symmetry restrictions which would prevent transfer from the  $Hg(^{3}P_{0,1})$  channels to either of the ionic potentials. However, Fig. 10 suggests that formation of HgX(B) maybe more important via  $V(Hg^*; X_2^*)$  and the trajectories originating from  $Hg(^{3}P_{2})$  with  $X_{2}$  are more likely to reach  $V(Hg^*; X_2^{*})$  than those originating from  $Hg({}^{3}P_{1,0})$ . In the  $C_{\infty y}$  approach, for example,  $V[Hg(^{3}P_{2}; X_{2})]$  has  $\Delta$ ,  $\Pi$ ,  $\Sigma^{-}$  components, whereas V(Hg<sup>\*</sup>, X<sub>2</sub><sup>-</sup>) has only  $\Pi$ ,  $\Sigma^-$ ,  $\Sigma^+$ . Thus, some Hg(<sup>3</sup>P<sub>2</sub>)-X<sub>2</sub> trajectories can reach  $V(Hg^+; X_2^{**})$  directly via the  $\Delta$ component. Even though some trajectories transfer from  $V(Hg, {}^{3}P_{2}; X_{2})$  to  $V(Hg^{*}; X_{2})$ , these trajectories must still cross the covalent surfaces arising from  $Hg(^{3}P_{1,0})$ . These surfaces give additional avoided crossings and an enhanced probability for  $Hg(^{3}P_{2})$  trajectories of the  $\Pi$  and  $\Sigma^{-}$  symmetry to continue to the  $V(Hg'; X_2^*)$  potential; see Fig. 9(c). The situation is unique for the  $Hg(^{3}P_{2})$  and  $Ca(^{3}P_{2})$  multiplet state since it lies highest in energy relative to the  $Hg(^{3}P_{1,0})$  states [see Fig. 9(c)]. However, the interactions between  $V(\text{Hg}; X_2^*)$  and  $V(\text{Hg}^*, X_2^{**})$  discussed earlier, must still be included otherwise trajectories reaching  $V(Hg^*; X_2^{*})$ would lead to HgX(X, A) and not HgX(B). In summary, the spin-orbit dependence of the HgX(B) branching ratio can be explained by the network effect [Fig. 9(c)], which has the overall effect of diverting trajectories starting

$Hg + X_2$	$C_{wv}^{a,b}$	$C_{2\nu}^{a}$	C <sub>s</sub> <sup>2</sup>
$Hg(^{3}P) + X_{2}(^{1}\Sigma_{g}^{*})$	<sup>3</sup> Σ <sup>+</sup> , <sup>3</sup> Π	${}^{3}B_{2}, {}^{3}A_{1}, {}^{3}B_{1}$	<sup>3</sup> A'(2), <sup>3</sup> A''
$Hg(^{3}P_{2}) + X_{2}(^{1}\Sigma_{g}^{+})$	Δ, Π, Σ-	$A_1, A_2(2), B_1, B_2$	A'(2), A''(3)''
$Hg(^{3}P_{1}) + X_{2}(^{1}\Sigma_{g}^{*})$	Π, Σ*	$A, B_1, B_2$	A'(2), A''
$\mathrm{Hg}(^{3}P_{0}) + \mathrm{X}_{2}(^{1}\Sigma_{\boldsymbol{\xi}}^{*})$	Σ-	$A_2$	A ''
$Hg^{+}(^{2}S) + X_{2}^{-}(^{2}\Sigma_{u}^{+})$	<sup>3,1</sup> ∑*	<sup>3,1</sup> B <sub>2</sub>	<sup>3,1</sup> A '
$Hg^{+}(^{2}S_{1/2}) + X_{2}^{-}(^{2}\Sigma_{u}^{+})$	Π,Σ <sup>-</sup> ,Σ <sup>+</sup>	$A_1, A_2, B_1, B_2$	A'(2), A''(2)
$Hg^{+}(^{2}S) + X_{2}^{-}(^{2}\Pi_{g})$	<sup>3,1</sup> П	$^{3,1}A_2$ , $^{3,1}B_2$	<sup>3,1</sup> A', <sup>3,1</sup> A''
$Hg^{+}(^{2}S_{1/2}) + X_{2}^{-}(^{2}\Pi_{\ell,1/2,3/2})$	$\Delta$ , II(2), $\Sigma^-$ , $\Sigma^+$	$A_1(2), A_2(2), B_1(2), B_2(2)$	A'(4), A''(4)
$ \begin{split} \mathbf{M}(^{2}S) + \mathbf{X}_{2}(^{1}\Sigma_{\mathbf{f}}^{*}) \\ \mathbf{M}^{*}(^{1}S) + \mathbf{X}_{2}^{*}(^{2}\Sigma_{\mathbf{\mu}}^{*}) \end{split} $	$2\Sigma^{*}$ $2\Sigma^{*}$	${}^{2}A_{1}$ ${}^{2}B_{2}$	$^{2}A'^{2}A'$
$M^{+}(^{1}S) + X_{2}^{-}(^{2}\Pi_{g})$	$^{2}\Pi$	${}^{2}A_{2} + {}^{2}B_{2}$	<sup>2</sup> A', <sup>2</sup> A''

TABLE IV. Symmetries of the relevant potentials for the  $Hg^* + X_2$  system with and without spinorbit interactions and  $M + X_2$ .

<sup>2</sup>If the spin multiplicity is not specified, the state have been decomposed into individual spin orbit states. For example, the  ${}^{3}B_{2}$  state for  $Hg({}^{2}S) + X_{2}^{*}({}^{2}\Sigma_{u}^{*})$  becomes three states of  $A_{1}$ ,  $A_{2}$ , and  $B_{1}$  symmetry (Ref. 66).

<sup>b</sup>The Hund's case C notation is represented by Greek symbols, Eq.,  $Hg(^{3}P_{2}) + X_{2}(^{1}\Sigma_{r})$  gives  $\Omega = \pm 2$ ,

 $\pm 1$ , 0° which are denoted in the table as  $\Delta$ ,  $\Pi$ ,  $\Sigma$ ° states, respectively.

on  $V(\text{Hg}, {}^{3}P_{2}; X_{2})$  to  $V(\text{Hg}^{*}; X_{2}^{*})$ , plus strong interactions between the ion-pair potentials,  $V(\text{Hg}; X_{2}^{*})$  and perhaps  $V(\text{Hg}^{*}; X_{2}^{*})$ , with repulsive potentials,  $V(\text{Hg}; X_{2}^{*})$ , correlating to excited halogen states. These interactions are likely to be of variable strengths allowing trajectories on some components to continue to HgX(A, X) and others to be diverted to HgX(B). The above discussion highlights the need for more experimental and theoretical knowledge of interaction potentials that include spin-orbit effects.

The vibrational energy disposal for the reactions of  $Hg(^{3}P_{2})$  and  $Xe(^{3}P_{2})$  with  $X_{2}$ , which were found to be similar, have a bearing on the above discussion. Although there is some uncertainty concerning the detailed shapes of the distributions, i.e., two-component vs a single broad distribution, the decline in  $\langle f_{v} \rangle$  in the Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub> series is certainly established. This behavior is in contrast to the reactions  $M_{I}$  and  $M_{II}$  atoms where  $\langle f_{v} \rangle$  is large (~0.8) and no significant differences between Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub> have been found. <sup>41,62(b)</sup> Thus, while the M, Xe<sup>\*</sup>, and Hg<sup>\*</sup> reactions show an overall similarity, reactive events leading to low  $\langle f_{v} \rangle$  for Xe<sup>\*</sup> and Hg<sup>\*</sup> are more important than for the M atom reactions.

The difference between the Hg\* or Rg\* vs M reactions probably is a consequence of the relative importance of the excited  $X_2^-(^{\circ}\Pi)$  state and/or symmetry considerations related to favored reactive geometries. The two possibilities are not necessarily independent. Based on correlation diagrams and the XeX\* vibrational distributions, the  $X_2^-(^{\circ}\Pi_g)$ , as well as the  $X_2^-(^{\circ}\Sigma_u^*)$  state, previously was suggested to be important for Xe( $^{\circ}P_2$ ) reactions.<sup>14,57</sup> The XY<sup>-</sup>( $^{\circ}\Pi$ ) state also has been invoked for alkali metal atom reactions with mixed halides XY since both MX and MY are observed as products<sup>67</sup> and

in observation of  $M^{-}$  formation in high energy  $M + X_2$ collisions.<sup>68,69</sup> Recent orientation experiments<sup>60</sup> also have been interpreted as suggesting the involvement of more than one ion-pair potential. The XeI\*+XeBr\* reaction cross section from  $Xe({}^{3}P_{2}) + IBr$  was largest for the parallel approach of Xe\* to the IBr rotation plane and smallest for perpendicular approach to the plane.<sup>60</sup> Since Xel\* and XeBr\* emission was not resolved and since they were detected with different efficiencies, the observed effect could be an orientation dependence of the reactive cross section or a change in the XeI\*/XeBr\* branching ratio. The explanation offered for either possibility involved the  $V(Xe^*; IBr^{-2}II)$ potential and the anisotropy associated with this surface.<sup>60</sup> Orientation experiments<sup>55</sup> with  $Ca({}^{1}P_{1}) + Cl_{2}(HCl)$ suggest a correlation of the product state with the alignment of the p orbital on Ca<sup>\*</sup>. CaCl<sup>\*</sup> chemiluminescence cross section for HCl was insensitive to p-orbital alignment; but, the CaCl(A)/CaCl(B) ratio did change with alignment [parallel approach favored CaCl(B) while perpendicular approach favored CaCl(A)]. The branching ratio dependence was explained as a consequence of preferred transfer of the s-electron of Ca\* at the inner crossing points, see Fig. 9, giving  $V(Ca^{+}, {}^{2}P; HCl^{-})$  or  $V(Ca^*, {}^2D; HCl^*)$  leaving an aligned p orbital on  $Ca^*$ which evolves into a molecular orbital giving CaCl(A) or CaCl(B), respectively. However, the small magnitude of the dependence on alignment is consistent with most of the reaction occurring via transfer of the pelectron at the first ionic surface crossing. In contrast with HCl, the CaCl\* chemiluminescence cross section with  $Cl_2$  was affected by alignment with both CaCl(A)and CaCl(B) being enhanced by perpendicular *p*-orbital alignment. Since CaCl(A and B) both are affected, the chemiluminescence was associated with the first crossing, namely  $V(Ca^*; Cl_2^*, 2\Sigma_u^*)$ . The enhancement for per-

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pendicular alignment suggests that broadside approach (or  $C_{2\nu}$ ) geometry is favored for formation of CaCl(A, B). The alignment studies of Ca(<sup>1</sup>P<sub>1</sub>) with Xe<sup>\*</sup> +IBr strongly imply a correlation between orientation of the reactants and probability for electron transfer at the crossing points. These two studies reinforce our suggestion that the X<sub>2</sub>(<sup>6</sup>Π<sub>e</sub>) potential has importance for Hg(<sup>3</sup>P<sub>2</sub>) and Xe(<sup>3</sup>P<sub>2</sub>) atom reactions with halogens.

If the  $X_2^*$  potentials are involved with the  $Xe({}^{3}P_{2,1})$ and  $Hg(^{3}P_{2})$  reactions, then  $X_{2}^{*}$  probably becomes relatively more important for the heavier halogens because  $EA(X_2^{-}, {}^{2}\Pi_{g})$  increase for  $Cl_2, Br_2, I_2$ .<sup>70</sup> The reactive cross sections for Hg\* and Xe\* still will be determined by the orbiting criteria on the long range potential; but, the branching of trajectories occurs at shorter range. The probability of reaching the  $X_2^{*}(^{2}\Pi_{*})$ potential may be enhanced for certain preferred collision geometries. As is well known, broadside attack of alkali metal atoms with halogens is symmetry forbidden for both  $X_2^{-}(\Sigma_{\mu}^{+})$  and  $X_2^{-}(\Pi_{\mu})$  potentials. No restrictions exist for Hg\* and Rg\* (except for certain components of the potentials) and the broad (and perhaps two component) HgX\* and XeX\* vibrational distributions may result from two different characteristic reaction geometries. The high vibrational energy component may correspond to collinear geometry and closely resemble the  $M + X_2$  reactions, while the  $C_{2\nu}$ approach, which resembles insertion into the halogen bond, may give the low vibrational energy component. It is worth noting that, although the state symmetries for  $Hg({}^{3}P_{2})$  and  $Xe({}^{3}P_{2})$  are the same, the electron leaves a 6s shell for the latter and a 6p shell for the former in the transfer to the ionic surface. Thus, the long range behavior of  $Xe({}^{3}P_{2})$  should more strongly resemble the alkali metal atoms, although the influence of the hole in the Xe<sup>+</sup> ion core may prove important with regard to the B, C, and D rare gas halide distribution.<sup>71</sup> Both the vibrational energy distributions and high HgX(B) branching fractions suggest a role for the  $X_2^{-}({}^{2}\Sigma_{u}^{*})$  and  $X_2^{-}({}^{2}\Pi_{e})$  potential with  $Hg({}^{3}P_2)$  reactions; the sampling of the  $X_2^{-}(2\Sigma_u^{+})$  and  $X_2(2\Pi_e)$  potentials probably depends on reactant orientation, and experiments to measure the orientation effects and the importance of the  $X(^{2}P_{1/2})$  exit channel are needed. In our opinion the finding of the same trends for  $Hg(^{3}P_{2})$  and  $Xe(^{3}P_{2})$  reactions greatly weakens the suggestions made by Simons<sup>44</sup> regarding the location of Rydberg states relative to the  $Xe^* + X_2$  entrance channel for explaning the difference in the  $Cl_2$ ,  $Br_2$ , and  $I_2$  reactions.

#### **VI. CONCLUSIONS**

The HgX(B-X) chemiluminescence spectra from the reaction of Hg( ${}^{3}P_{2}$ ) atoms with a series of halogen containing molecules were recorded under conditions such that HgX(B) vibrational relaxation was avoided. The emission spectra were used to determine the HgX(B) formation rate constants and to estimate the HgX(B) vibrational distributions. For the diatomic halogens the rate constants and branching fractions for HgX(B) formation are large, but the branching fractions are small for most polyatomic reagents. For the molecular halogens  $\langle f_{V}(\text{HgX}) \rangle$  decreases in the Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub> series, which also is the trend for reactions with  $Xe({}^{3}P_{2})$ . This trend has not been reported for reactions of ground state alkali or alkaline earth metal atoms with halogens. Comparison of the  $Hg({}^{3}P_{1})$  and  $Xe({}^{3}P_{2})$  results for reactions with halogens to the alignment studies of  $Ca(P_1)$ with  $Cl_2^{55}$  and  $Xe({}^{3}P_2)$  with  $BrI^{60}$  suggests the importance of broadside, as well as end-on, approach to the molecular halogen. It is likely that both  $V(Hg^*; X_2^*, {}^{2}\Sigma_{\mu}^*)$ and  $V(Hg^*; X_2^-, {}^{2}\Pi_g)$  potentials are involved in the  $Hg({}^{3}P_2)$ atom reactions and there also may be a correlation of the collision geometry with sampling of these two potentials. The trend in the vibrational energy disposal for  $Hg({}^{3}P_{2})$  reacting with polyatomic reagents is similar to that for reactions of  $Xe({}^{3}P_{2})$ ; but,  $\langle f_{\gamma}(HgX) \rangle$  is systematically smaller than for  $\langle f_{\mathbf{v}}(\mathbf{X}\mathbf{e}\mathbf{X})\rangle$ . This systematic difference can be explained by the neutral fragment product retaining a constant absolute amount of energy from the dissociation of RX<sup>-</sup> and the reduced excergicity of the  $Hg({}^{3}P_{2})$  reactions relative to  $Xe({}^{3}P_{2})$  reactions. The trends in the vibrational energy disposal to HgX(B)for the polyatomic reagents also are consistent with results from metal atom reactions with the same reagent.

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