A Flowing-Afterglow Study of the Quenching Reactions of $Hg({}^{3}P_{2})$ and $Hg({}^{3}P_{0})$ Atoms by Halogens, Interhalogens, and Polyatomic Halide Molecules

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Mercury $({}^{3}P_{1})$ and $({}^{3}P_{0})$ metastable atoms were prepared in a flowing afterglow reactor by passing He, Ne, or Ar carrier gas containing Hg through a dc discharge. The interaction of $Hg(^{3}P_{2})$ with 30 halogen-containing molecules (325 K) was studied by observation of the HgCl, HgBr, and HgI($B^2\Sigma^+ - X^2\Sigma^+$) chemiluminescent spectra. Intramultiplet relaxation to $Hg(^{3}P_{1})$ also was monitored for some of these molecules plus NH_{3} , CH_{4} , and CF_{4} and five nonreactive diatomic molecules. The addition of N₂ to the flow reactor removes the Hg($^{3}P_{2}$) atoms and the reactions of Hg($^{3}P_{0}$) can be isolated. The branching fraction for HgX(B) formation, X = Cl, Br, and I, is much lower for Hg(${}^{3}P_{0}$) than for Hg(${}^{3}P_{2}$) reactions. Computer simulation of the HgX(B-X) spectra provided nascent HgX(B) vibrational distributions. The reactions of Hg(${}^{3}P_{2}$) with halogens, mixed halogens, and ICN resemble the analogous $Xe({}^{3}P_{2})$ atom reactions with regard to product branching fractions and energy disposal. These data are discussed in terms of the covalent-ionic curve-crossing reactive quenching mechanism. Upper limits are set for the bond energies of CF₃NCl-Cl, CF₃NCl-Br, CF₂ClNCl-Cl, CF₂ClNF-Cl, CF₂N-Cl, and CF₂BrCF₂-I from the HgX(B-X) spectra. The B- and X-state potentials of HgCl, HgBr, and HgI were improved relative to our prior work to better simulate the HgX(B-X) spectra. The excitation-transfer reaction between Hg(${}^{3}P_{0,2}$) and CN was observed as a secondary reaction with BrCN and ICN.

I. Introduction

This laboratory previously reported a flowing-afterglow source for Hg(${}^{3}P_{2}$, 5.5 eV or 126 kcal mol⁻¹) and Hg(${}^{3}P_{0}$, 4.7 eV or 108 kcal mol⁻¹) metastable atoms, $HgX(B^{2}\Sigma^{+}-X^{2}\Sigma^{+})$ chemiluminescence spectra for X = F, Cl, Br, and I, branching fractions for HgX(B) formation, Γ_{HgX^*} , from reactions of Hg(³P₂) with diatomic halogens and a few polyatomic organic halides, and preliminary assignments of nascent HgX(B) vibrational distributions.¹ In the current study quenching by a broader range of Cl, Br, and I donors was investigated; polyatomic organic and inorganic mixed halides, interhalogen diatomic molecules, and ICN and BrCN were of special interest. As with the $Xe({}^{3}P_{2})$ and $Xe({}^{3}P_{1})$ reactions,²⁻⁸ the only polyatomic donors with large $\Gamma_{HgX^{*}}$ are the halides of oxygen, sulfur, and nitrogen and fully halogenated methane molecules, e.g., CCl₄, CBr₄, CF₃I, etc. The previously noted^{1b} similarity in branching fractions for $Xe({}^{3}P_{2})$ and $Hg(^{3}P_{2})$ reactions was found to apply also to the mixed halide reagents. The large spin-orbit effect on the product branching fractions for the Hg(6s,6p) atom reactions is further documented in this work by recording the HgI(B-X) and HgBr(B-X) spectra for reaction for $Hg(^{3}P_{0})$ with a few of the better halogen donors. Similar, but smaller, spin-orbit effects on the product distributions from reactions of group IIA (group 2)⁵⁴ metastable atoms also are known.^{9,10} Improved B- and X-state potentials and transition dipole functions for HgCl, HgBr, and HgI were used to simulate the HgX(B-X) chemiluminescence spectra. Although the assigned nascent HgX(B) vibrational distributions are similar to the earlier ones,^{1b} the present distributions are preferred.

Our general goal is to elucidate the covalent-ionic curve crossing mechanism and the role of the radical-ion intermediate state(s) in the quenching of $Xe({}^{3}P_{2,1})$ and $Hg({}^{3}P_{2})$ atoms by halogen-containing molecules.³⁻⁸ The principal data are the HgX(B) formation rate constants from $Hg(^{3}P_{2})$ and $Hg(^{3}P_{0})$ reactions and collision-free HgX(B-X) chemiluminescence spectra. However, several relative $Hg({}^{3}P_{2})-Hg({}^{3}P_{1})$ intramultiplet relaxation rate constants were measured and absolute values for CO, NO, and N_2 were obtained from comparison of the Hg(³P₁) emission intensity with the HgCl(B) emission intensity from Cl_2 . The intramultiplet relaxation rate constants for CO, N_2 , and NO can be related to other reports.¹¹⁻¹³ The performance of the metastable mercury atom flowing-afterglow reactor with He, Ne, and Ar as carrier gases is described in the Appendix.

The low-power discharge source gives $Hg(^{3}P_{2})$ and $Hg(^{3}P_{0})$ atoms in approximately equal concentrations ($\sim 5 \times 10^9$ atoms cm⁻³).¹ Addition of N_2 relaxes the Hg(³P₂) atoms with a rate contant¹² of 11 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹.

$$Hg(^{3}P_{2}) + N_{2} \rightarrow Hg(^{3}P_{1}) + N_{2}; \quad \Delta H^{o}_{0} = -13 \text{ kcal mol}^{-1}$$
(1)

The $Hg({}^{3}P_{1})$ atoms from (1) subsequently radiatively decay or are transferred by collisions with N₂ ($k = 3.9 \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹)¹⁴ to Hg(³P₀); quenching of Hg(³P₀) by N₂ is negligibly slow ($<6.1 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹). The removal of Hg(${}^{3}P_{2}$) can be monitored by the reduction of the CN(A,v')

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emission intensity from reaction 2. The Hg(³P₀) state has suf-

$$Hg(^{3}P_{2}) + ICN \rightarrow CN(A, v' \leq 5) + I + Hg; \quad \Delta H^{\circ}_{0} = -21 \text{ kcal mol}^{-1} (2)$$

ficient energy (by ~3 kcal mol⁻¹) to form CN(A, v'=0), but the more easily observed higher v' levels cannot be formed. Another monitor for $Hg(^{3}P_{2})$ is the nearly isoenergetic excitation-transfer reaction with NO, ^{13a} which is in competition with $Hg(^{3}P_{1})$ formation.

$$Hg(^{3}P_{2}) + NO \rightarrow NO(A^{2}\Sigma^{+}, v'=0) + Hg; \Delta H^{o}_{0} = 0.5 \text{ kcal mol}^{-1} (3)$$

The rate constants for HgX(B) formation from Hg(${}^{3}P_{0}$) + Br₂, I₂, and ICl were $\leq 7\%$, $\leq 13\%$, and $\leq 9\%$, respectively, of the combined $Hg(^{3}P_{2}) + Hg(^{3}P_{0})$ values. These were the only reagents for which the $Hg(^{3}P_{0})$ reaction made a significant contribution to the total HgX(B) emission intensity from the combined Hg(${}^{3}P_{2}$) + $Hg(^{3}P_{0})$ reactions. During the course of the study with BrCN and ICN, the excitation-transfer reaction with CN, first reported by Vikis et al.,¹⁵ was observed as a secondary reaction.

$$Hg(^{3}P_{2,0}) + CN(X) → CN(B) + Hg; ΔH^{\circ}_{0} = -52, -34 \text{ kcal mol}^{-1}$$
 (4)

Upper limits to bond dissociation energies can be obtained from the short-wavelength limits of the HgX(B-X) spectra.

$$D_0(R-X) \le E(Hg, {}^{3}P_2) + nRT - E(\lambda_{\min}) + D_0(HgX)$$
 (5)

In this equation $E(Hg, {}^{3}P_{2})$ is the energy of the $Hg({}^{3}P_{2})$ atom, $E(\lambda_{\min})$ is energy corresponding to the short-wavelength limit of the HgX(B-X) emission, and nRT represents the thermal energy of the collision. In obtaining this relationship, the reactions were assumed to have no activation energy. Because of their local availability, several molecules with N-Cl and N-Br bonds were studied and upper limits for $D_0(CF_2N-Cl)$, $D_0(CF_3NCl-Cl)$, $D_0(CF_2CINF-CI)$, $D_0(CF_2CINCI-CI)$, and $D_0(CF_3NCI-Br)$ were obtained. The λ_{min} values are upper limits for two reasons: (i) the reaction may not release the entire available energy to HgX(B)for any of the reactive collisions and (ii) the λ_{min} may be difficult to discern because the transition dipole tends to reduce the intensity of the transitions near the inner turning point for the HgX(B, high v^{γ} levels.

Our first simulations of the HgX(B-X) spectra^{1b} were based on the potential functions of Cool and co-workers.¹⁶ After our initial work was completed, Tellinghuisen and co-workers^{17,18} obtained isotopically pure spectra from which improved constants were derived for both the lower and upper states. In the present work the new spectroscopic constants were utilized to construct improved potentials, which were used for computer simulation of the HgX(B-X) spectra. The HgX(B) vibrational distributions obtained previously are generally satisfactory; but, the current work provides some refinement in detail.

II. Experimental Methods

The $Hg(^{3}P_{2})$ flowing-afterglow apparatus differs only slightly from the design used for metastable rare gas atoms.¹⁹ A diagram of the flow reactor, which was maintained at ~ 50 °C, is shown in Figure 1. The carrier gas (He, Ne, or Ar), purified by passage through cooled molecular sieve traps, was flowed through an air-cooled refluxing column of mercury to entrain Hg at a concentration of $\sim 10^{13}$ atoms cm⁻³. The flow was then passed through a heated, low power dc discharge to form $Hg({}^{3}P_{2})$ and



Figure 1. Schematic drawing of the flowing-afterglow reactor (Pyrex glass) used for generating mercury metastable atoms; the reactor and discharge were wrapped with heating tape to maintain a temperature of ~50 °C. The electrodes were made from rolled tantalum foil. The N_2 was added to remove $Hg(^{3}P_{2})$ atoms.

Hg(${}^{3}P_{0}$) atoms in the 5 × 10⁹ atom cm⁻³ range. To obtain only $Hg({}^{3}P_{0})$ atoms, N₂ was added to remove $Hg({}^{3}P_{2})$ by intramultiplet relaxation. The reagent gas flow was mixed with the metastable Hg* flow using the concentric reagent inlet design.¹⁹ The flow reactor was pumped by a 1000 L min⁻¹ rotary pump, and for an Ar flow rate of 0.05 mol min⁻¹ the pressure in the reactor was \sim 1.5 Torr. This corresponds to a bulk flow velocity of 30 m s⁻¹ in the 2.5-cm-diameter reactor. The dependence of the $Hg(^{3}P_{2})$ concentration on carrier gas (He, Ne, or Ar) pressure and mercury concentration was systematically studied, and the performance of the metastable mercury atom flow reactor is described in the Appendix. Although the design shown in Figure 1 performed satisfactorily for our studies, an apparatus based upon a higher pumping capacity with a separate prereactor section for N₂ addition, with its own observation window, followed by the reagent mixing and observation zone would be preferable.

The reagent gases were handled in glass vacuum lines fitted with glass-Teflon stopcocks. All reagents with sufficient vapor pressure at room temperature were distilled prior to use and stored in glass reservoirs as dilute mixtures in Ar. The nitrogen halide compounds were obtained from the laboratory of Professor DesMarteau. These compounds were handled in glass vacuum lines. The reagent flow rates were measured by monitoring the pressure rise in a calibrated volume with a pressure transducer. Relative emission intensity measurements were made with reagent flows sufficiently low such that the product emission intensities were first order in reagent concentration. For reagents with insufficient room temperature vapor pressure for preparation of mixtures, such as ICN, PBr₃, CBr₄, and I₂, the reagents were introduced into the reactor by passing a small flow of Ar over the pure sample. By heating the sample, sufficiently high reagent concentration could be obtained to quench all of the $Hg(^{3}P_{2})$ within the observation zone, and the relative HgX(B) formation rate constants could be estimated from the saturated product emission intensities (see the Results section).

The HgX(B-X) emission spectra were observed through a quartz window attached to the reactor via an O-ring seal in order to facilitate easy cleaning, see Figure 1. After several hours of operation, solid HgX₂ collects on the walls of the reactor and the window must be cleaned, since even minute deposits affect the optical transmission in the 200-300-nm range. Observations were made with a 0.3-m McPherson monochromator fitted with a 300-nm blazed grating and an RCA C31034 photomultiplier tube. The photomultiplier tube signal was processed by an SSR photon counter and displayed on a strip chart recorder. The SSR counter also was interfaced to a PDP-8 computer so spectra could be simultaneously recorded on magnetic tape for subsequent correction for the variation of the detector response with wavelength and also integrated to obtain total relative emission intensities. The response of the detection system was calibrated in the ultraviolet with a standard D₂ lamp and in the visible with a standard quartz $-I_2$ lamp. Spectral scans were generally reproducible (in the relative sense) within $\pm 10\%$ for the same reagent flow rate. The spectra acquired for simulation purposes were taken at ≤ 1.5

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TABLE I: HgX(B-X) Emission Intensity Ratio from Hg(${}^{3}P_{0}$) vs. Hg(${}^{3}P_{0}$) + Hg(${}^{3}P_{2}$)

reagent	excess energy, ^a kcal mol ⁻¹	emission	$\frac{I({}^{3}P_{0})/(I({}^{3}P_{2}) + I({}^{3}P_{0}))}{I({}^{3}P_{0}))}$
I ₂	32	HgI(B)	0.13
ICI	17	HgI(B)	$\leq 0.09^{b}$
	34	HgCl(B)	≤0.09
Br ₂	30	HgBr(B)	0.07
Cl_2	27	HgCl(B)	0.03
CBr₄	20	HgBr(B)	$\leq 0.04^{b}$
CCl ₄	15	HgCl(B)	< 0.02 ^c
PCl ₃	8	HgCl(B)	<0.005 ^c
CN	52	CN(B)	0.25

^a The excess energies are for the Hg(${}^{3}P_{2}$) reactions; the values must be reduced by 18 kcal mol⁻¹ for Hg(${}^{3}P_{0}$) reactions. ^b Inspection of the spectra taken in the presence of N₂ suggests that the Hg(${}^{3}P_{2}$) contribution to the observed emission was still ~50%. Note that the HgI(B) channel from ICl and the HgBr(B) from CBr₄ are nearly thermoneutral. ^cSince formation of HgCl(B) from Hg(${}^{3}P_{0}$) is endoergic for these reagents, these experiments measure the degree of removal of Hg(${}^{3}P_{2}$).

Torr so that the HgX(B) vibrational relaxation was negligible.

III. Experimental Results

A. HgX(B) and CN(A) Formation Rate Constants. The product intensities were measured relative to the HgCl(B) emission intensity from reaction 6. Krause and co-workers²⁰ assigned k_{HsCl^*}

$$Hg(^{3}P_{2}) + Cl_{2} \rightarrow HgCl(B) + Cl; \quad \Delta H^{\circ}_{0} = -26 \text{ kcal mol}^{-1}$$
(6)

$$k_{\text{HgCl}^*} = 32 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

by comparing the HgCl(B) emission intensity to the Hg(${}^{3}P_{1}$) intensity from reaction 3. We explicitly checked for intramultiplet relaxation to Hg(${}^{3}P_{1}$) by Cl₂ and it was of no importance. For reasons to be discussed below, the branching fraction ($\Gamma_{HgCl^{*}}^{Cl} = k_{HgCl^{*}}/k_{Q}$) must be very close to unity for reaction 6. The contributions to the HgX(B-X) emission from Hg(${}^{3}P_{0}$) and Hg(${}^{3}P_{2}$) must be considered before rate constants and branching fractions can be assigned to reaction 7 via comparison to (6). Sufficient

$$Hg(^{3}P_{2}) + RX \rightarrow HgX(B) + R$$
 (7)

 N_2 to remove Hg(³P₂), as monitored by the disappearance of the CN(A) emission from reaction 2, was added in order to isolate the reaction of $Hg(^{3}P_{0})$, and then the HgX(B) emission was recorded and compared to that from both $Hg({}^{3}P_{2})$ and $Hg({}^{3}P_{0})$. The chemiluminescence from the combined reactions of $Hg(^{3}P_{2})$ and $Hg(^{3}P_{0})$ atoms and that from the system with added N₂ are shown in Figure 2 for Br_2 and I_2 . The spectra differ considerably; note especially the greatly reduced intensities and the altered λ_{min} values. Examination of the λ_{min} values and the oscillatory positions from ICl and CBr_4 showed that the HgX(B-X) emission, even in the presence of the excess N_2 , still had a ~50% contribution from $Hg({}^{3}P_{2})$. For I_{2} and Br_{2} the HgX(B) emission is mainly from $Hg({}^{3}P_{0})$. The ratios of the HgX(B) emission intensities from $Hg(^{3}P_{2}) + Hg(^{3}P_{0})$ to that from $Hg(^{3}P_{0})$ are tabulated in Table I for high reagent concentrations; these values correspond to the ratio of the fractions of Hg(${}^{3}P_{0}$) and Hg(${}^{3}P_{2}$) + Hg(${}^{3}P_{0}$) converted to HgX(B).

$$[I(\text{Hg},{}^{3}\text{P}_{0})/I(\text{Hg},{}^{3}\text{P}_{0} + \text{Hg},{}^{3}\text{P}_{2})]_{\text{large}[RX]} = \left(k_{\text{Hg}X*}^{3p}/k_{Q}^{3p}\right) \times [\text{Hg},{}^{3}\text{P}_{0}]/\left\{\left(k_{\text{Hg}X*}^{3p}/k_{Q}^{3p}\right)[\text{Hg},{}^{3}\text{P}_{0}] + \left(k_{\text{Hg}X*}^{3p}/k_{Q}^{3p}\right)[\text{Hg},{}^{3}\text{P}_{2}]\right\} (8)$$

Since $[Hg, {}^{3}P_{2}] \approx [Hg, {}^{3}P_{0}]$, ^{la} the intensity ratio can be taken as approximately the ratio of the branching fractions. These ratios were the same for experiments performed at very low reagent flows, which implies that the total quenching rate constants for $Hg({}^{3}P_{2})$ and $Hg({}^{3}P_{0})$ are similar, because at low concentration the intensity ratio depends only on the k_{Hgx}^{3P} and k_{Hgx}^{3P} values. Although the $k_{Q^{0}}^{3P}$ values may be somewhat smaller^{20,21} than for



Figure 2. Plots of the emission spectra from $Hg({}^{3}P_{0,2})$ and $Hg({}^{3}P_{0})$ with (a) Br_{2} and (b) I_{2} . The spectra have been corrected for wavelength response. The bound features in the short-wavelength region of the $Hg({}^{3}P_{2,0}) + I_{2}$ spectrum are HgI(C-X) and I_{2}^{*} emission.

 $k_Q^{P^2}$, the small intensity ratios in Table I can be associated primarily with small $k_{B_0}^{P_2}$, values. Only for Br₂, I₂, and ICl was the HgX(B) formation from Hg(³P₀) significant (i.e., $\geq 5\%$) relative to that from Hg(³P₂) + Hg(³P₀). Since the contribution from Hg(³P₀) reaction to the HgCl(B) emission from Hg(³P₂) + Hg(³P₀) with Cl₂ is <3%, the Hg(³P₀) contribution will be ignored and the total HgCl(B-X) emission intensity will be associated with the quenching of Hg(³P₀). Wodarczyk and Harker^{21b} give $\Gamma_{H_gCl(B)}^{Cl_2} = 0.009$ for Hg(³P₀) in agreement with our conclusion. For all polyatomic reagents investigated, the HgX(B) yield from quenching of Hg(³P₀) was insignificant, as also has been found for the Hg(³P₁) atom reactions.²¹ In part, this is a consequence of the reduced available energy, since for most polyatomic molecules reduction of the energy by 18 kcal mol⁻¹ makes HgX(B) formation endoergic, see Table I (and Table VI, vide infra).

For reagents with room temperature vapor pressures >5 Torr, the integrated relative emission intensities from reactions 6 and 7 were compared in the first-order, low reagent concentration regime; see Figure 3. For these conditions the relative product emission intensity is equal to the relative product formation rate, since there is no HgX(B) quenching.

$$I_{\rm HgX^*} = k_{\rm HgX^*}^{\rm RX} [\rm Hg({}^{3}\rm P_2)][\rm RX]$$
(9)

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Figure 3. Plot of the relative HgCl(B-X) integrated emission intensities vs. Cl₂ and CCl₄ concentrations. The first-order regime is limited to $[RX] \le 0.5 \times 10^{13}$ molecule cm⁻³.

A similar relationship exists for reaction 6, and for constant $[Hg(^{3}P_{2})], k_{HgX^{*}}$ is given by eq 10. This method can be applied

$$k_{\text{HgX}^{*}}^{\text{RX}} = \frac{I_{\text{HgX}^{*}}}{I_{\text{HgCl}^{*}}} \frac{[\text{Cl}_{2}]}{[\text{RX}]} k_{\text{HgCl}}$$
(10)

to any product for which radiative decay is the only pathway for removal. In the present reactor the first-order concentration regime extended to $\sim 5 \times 10^{12}$ molecule cm⁻³; see Figure 3.

For reagents with low vapor pressure, eq 10 could not be used since [RX] could not be reliably measured. Instead a method developed by Golde et al.²² for measuring branching fractions for ion formation from quenching of $Ar({}^{3}P_{0,2})$ was adapted to the present work. High flows of reagent are added to convert all metastable atoms to products in the observation zone. The limiting high flow (saturated) relative emission intensities are proportional to the fraction of $[Hg(^{3}P_{2})]$ that is converted to HgX(B) or HgCl(B) products. For constant $[Hg(^{3}P_{2})]$ the saturated intensity measurements give the branching fraction ratio directly, ^{5a,22} see eq 8. A significant advantage is that Γ_{HgX*}^{RX} can be obtained without knowledge of k_Q^{RX} , if $\Gamma_{HgX*}^{Cl_2}$ is taken as unity. The difficulty for saturated emission intensity measurements, as contrasted to ion measurements,²² is that the reagent mixing (flame) geometry depends on flow rate and the emission zone viewed by the monochromator may change with flow rate or reagent. In the present work the slit height of the monochromator (the slit was parallel with the emission flame) was reduced to 3 mm to ensure that the reaction flame zone viewed by the monochromator did not change with reagent flow rate. Calibration experiments were done with Cl_2/Br_2 , Cl_2/CCl_4 ; and Cl_2/CBr_4 pairs for which the first-order, low reagent concentration regime already had been studied. Some of the results are shown in Figure 4. The intensity vs. reagent concentration plots do have the correct shape and the method seems to be successful. The Cl₂ and Br₂ experiments are of special interest; the saturated ratios imply that $\Gamma_{HgBr}^{Br_2}$ may be slightly higher than $\Gamma_{HgCl^{*}}^{Cl_{2}}$. However, the $Hg(^{3}P_{0})$ contribution to HgX(B) formation is higher for Br₂ than Cl₂ (7% vs. 3%), and $\Gamma_{\text{HgBr}}^{\text{Br}} \approx \Gamma_{\text{HgCl}}^{\text{Cl}_2} \approx 1.0$ for the Hg(³P₂) reactions. The branching factor ratio for CCl₄ vs. Cl₂ from Figure 4 (0.25) is higher than the product formation rate constant ratio (0.18) from Table II. This implies that $k_Q^{CCl_4} < k_Q^{Cl_2}$ or $\Gamma_{HgCl^*}^{Cl_2} < 1.0$; we prefer the former

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Figure 4. Plots of the HgX(B-X) integrated emission intensity vs. [RX] for high reagent flows; the plateau regions corresponding to complete $Hg(^{3}P_{2})$ quenching.

explanation. The $Xe({}^{3}P_{2})$ quenching rate constant^{4b} by CCl₄ was ~15% smaller than for Cl₂. The $\Gamma_{HgBr}^{CBr_4}$ value from the high reagent flow data is consistent with the $k_{HgBr}^{CBr_4}$ value from Table I, which implies that $k_Q^{Cl_2} \approx k_Q^{CBr_4}$.

The majority of the measurements were done using (9) and the resulting k_{HgX*} values are summarized in Table II. The weak HgI(C-X) and I_2^* emissions^{1b} from the I_2 reaction were included in k_{Hgl^*} . The reagents with low vapor pressure for which a relation similar to (8) was used are noted. For these cases, we assumed $k_Q^{RX} \cong k_Q^{Cl_2}$ and tabulated $k_{HgX^*}^{RX}$; this assumption is generally supported by the k_Q measurements²¹ for Hg(³P₁). The main uncertainties in the k_{HgX*} values are from the gas handling for these reactive reagents, impurities in the reagents, and the intrinsic difficulty of comparing two broad emission systems. We estimate uncertainties of $\pm 20\%$ for reagents with large $k_{\text{HgX}*}$ and $\pm 40\%$ for those with small k_{HgX*} . Except for SOCl₂, SO₂Cl₂, CF₃I, and CF₃Br, the entries in Table II are based upon new experiments. In general, the agreement of k_{HgX*} with our prior work is satisfactory. One exception is S_2Cl_2 for which the k_{HgCl*} value in Table II is significantly higher. More care was taken in sample purification in the present studies and the results of Table II are preferred over those of Dreiling and Setser.

Also listed in the Table II are the λ_{min} values from the HgX-(B-X) spectra and the associated upper limits to $D_0(R-X)$. As noted previously,^{1b} the λ_{min} values frequently provide reliable upper limits to the bond energies and several such demonstrations are given in Table II. Exceptions seem to be SCl₂ and S₂Cl₂ because the cited bond energies could give HgCl(B-X) emission below 290 nm. In fact, the cited bond energies are based upon λ_{min} values from the $Xe({}^{3}P_{2})$ reactions.³ The XeCl(B-X) emissions were very strong and the threshold regions could be examined in detail. If the $\lambda_{\min}(XeCl)$ values had been assigned without a scale expansion in the threshold region, bond energies very similar to those based upon the $\lambda_{\min}(\text{HgCl})$ limits in Table II would have been obtained. An experimental complication for assignment of $\lambda_{min}(HgCl)$ values in the 290-nm region was the presence of weak atomic Hg* emission lines, due to scattered light from the discharge. Discussion of the reliability of the bond energy limits for the nitrogen halide molecules will be delayed until after the vibrational distributions from these reactions are assigned. The $D_0(I-CF_2CF_2Br)$ value should be reliable. For reactions giving mixed products, the spectra were deconvoluted to make approximate k_{HgX*} and λ_{\min} assignments.

The CN(A) formation channel from ICN and BrCN is included in Table II for simplicity in presentation. The uncertainty in $k_{CN(A)}$ for ICN is larger than for k_{HgX*} value because of the inability to measure all of the CN(A-X) emission. We assigned the CN-(A,v'=2-5) distribution from the $\Delta v = -3$ and $\Delta v = -4$ sequences and then extrapolated a log $(N_{v'})$ vs. v' plot to estimate N_1 and N_0 . The distribution from ICN was 67:52:31:14:5:~1 for v' =0-5. The CN(A,v'=5) may be formed from secondary reaction or from ICN molecules having some vibrational energy. The rate constant for CN(A, v'=3, 4) formation was measured by comparing the CN emission intensity from v' = 3 and 4 to the HgCl(B-X) emission from reaction 6; the total rate constant was obtained by scaling for the other v' levels. Our value probably is a lower limit

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IABLE II: Kate Constant and Inermochemistry for High (B) Format
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		obsd	bond energy, kcal mol ⁻¹		ku ve		
reagent	product	λ_{\min} , nm	exptl ^a	lit. ^b	10^{-11} cm ³ molecule ⁻¹ s ⁻¹	σ _{HgX} •, Å ²	
Cl ₂	HgCl(B)	303	56.6	57.3 ± 0.1	32.0	91	
Br ₂	HgBr(B)	295	46.1	45.4 ± 0.1	50.0	187	
I ₂	HgI(B)	284	35.0	35.6 ± 0.1	40.0	167	
IČI	HgCl(B)	285	50.7		18.8	70.7	
	HgI(B)	~334°	51.1	49.7 ± 0.1	11.6	43.6	
IBr	HgBr(B)	290	44.4		21.2	85.1	
	HgI(B)	$\sim 318^{\circ}$	49.7	41.9 ± 0.1	10.4	41.7	
CĊl₄	HgCl(B)	347	68.9	69 ^d	5.8	21.5	
CCl ₃ F	HgCl(B)	370	74.0	73 ^d	0.59	2.1	
CHČl ₃	HgClB)	380	76.1	77 ± 2	1.6	6.2	
CH ₂ Cl ₂				79 ± 3	0	0	
CH ₃ Cl				83 ± 2	0	0	
COCl ₂	HgCl(B)	~400	79.8	76.6 ^d	0.17	0.55	
CCl ₃ Br	HgCl(B)			~69	0.74	3.0	
-	HgBr(B)	320	54.0	54.4 ± 1	1.5	6.0	
CBr ₄	HgBr(B)	330	56.7	55 ± 2	2.58	11.28	
CF ₂ ClBr	HgBr(B)	~360	63.9	64 ± 1.5	0.64	2.4	
CF_2Br_2	HgBr(B)	~360	63.9		0.18	0.72	
CF ₃ Br	HgBr(B)			67 ± 2	<0.1 ^f	<0.4	
CHBr ₃	HgBr(B)	354	62.5	~56°	<0.16	<0.67	
ICF2CF2Br	HgI(B)	346	53.3	~51	2.8	12.2	
CF₃I	HgI(B)	350	54.2	53 ± 2°	11.0	44.2 ^f	
PCl ₃	HgCl(B)	385	77.0	77 ± 2^{d}	4.2	15.1	
SCl ₂	HgCl(B)	~293	53.7	44.7 ^d	4.6	15.1	
S_2Cl_2	HgCl(B)	~295	54.4	44.2^{d}	3.7	13.2	
SOCl ₂	HgCl(B)	295	54.4	54.0	3.7 ^f	12.7 ^f	
PBr ₃	HgBr(B)	~360	~64	60.5°	<0.16 ^g	<0.69 ^g	
F ₂ CNCl	HgCl(B)	~300	56		2.3	7.4	
F ₃ CNCl ₂	HgCl(B)	~300	56		4.7	17.4	
CIF ₂ CNCIF	HgCl(B)	~294	54		5.0	18.5	
ClF ₂ CNCl ₂	HgCl(B)	~303	57		3.6	13.7	
F ₃ CNClBr	HgBr(B)	294	46.1		11.2	44.4	
ICN	CN(A)	$v' = 5^h$	77	80 ± 2	11.98	44 ^g	
BrCN	CN(A)	$v' = 3^i$	87	90 ± 2	j	j	

^a These are upper limits obtained from $D_0(R-X) \le E(Hg, {}^3P_2) + nRT - E(\lambda_{min}) + D_0(HgX)$; $D_0(HgCl) = 8200, 5406$, and 2839 cm⁻¹ for X = Cl, Br, and I with $n = {}^5/_2$ and 3 and T = 323 K for diatomic and polyatomic molecules, respectively. The $D_0(HgX(X))$ were taken from ref 17 and 18. ^b The bond energies for the diatomic halogens are from ref 24; the other values are from ref 23 unless specified otherwise. ^c The λ_{min} (HgI) were estimated by subtracting the HgCl* or HgBr* spectrum from the observed combined spectra. ^d The bond energy for SOCl₂, SCl₂, and S₂Cl₂ were assigned by scale expansion of the short-wavelength region of the XeCl(B-X) emission. From ref 3, the XeCl emission was very strong and the threshold could be studied. If the apparent threshold was assigned from spectra such as shown in Figure 2 or 7 without scale expansion, the apparent λ_{min} from the HgCl and XeCl spectra would give very similar apparent bond energies. ^eTaken from ref 1, the SO₂Cl₂ reaction gave $k_{HgCl^*} = 5.0 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. ^g These were measured by the saturation method assuming $k_{Q}^{RX} \simeq k_{Q}^{Cl^2}$ and $\Gamma_{HgCl^*}^{Cl^*} = 1.0$; then $k_{HgCl^*}^{RXCl^*} \approx \Gamma_{HgX^*}^{RX}(k_{HgCl^*})$. ^h Emission from CN(A, v' = 5) was clearly observable. The CN(A, v' = 5) could be formed by the secondary reaction with CN or from reaction 2, but with additional thermal energy provided from vibrational energy in CNI. ¹ Very weak emission from CN(A, v' = 4) was observed but this was attributed to the secondary reaction with CN. ^f Too small to measure.

to the true CN(A) formation rate constant. The low $k_{CN(A)}^{BrCN}$ value was checked and verified after all the other results were completed. The higher $D_0(Br-CN)$, relative to $D_0(I-CN)$, presumably plays a crucial role in reducing $\Gamma_{CN(A)}^{BrCN}$. Since excitation transfer to CN(B) was observed with BrCN, apparently CN(X) is a major primary product.

B. Rate Constants for $Hg({}^{3}P_{2})$ Intramultiplet Relaxation to $Hg({}^{3}P_{1})$. Since the [Hg] is relatively high, the sample is not optically thin and the observed I_{Hg*} must be corrected for radiation trapping. Fortunately, quenching by NO gives both NO(A) and Hg({}^{3}P_{1}), and the I_{Hg*}/I_{NO*} ratio can be measured as a function of [Hg]. Extrapolation to low Hg concentration gives the rate constant ratio, $k_{Hg*}^{NO}/k_{NO(A)}^{NO}$, which was 6.5 at ~ 320 K, see Appendix. Extensive searches were made for the NO($a^{4}\Pi-X^{2}\Pi$) emission, but it was not found. The $k_{Hg*}^{NO}/k_{NO(A)}^{NO}$ ratio is in good agreement with a beam study, I^{3} which gave 5.3–8.2, with the larger values corresponding to higher collision velocities. The radiation trapping factor, f, can be determined from the I_{Hg*}/I_{NO*} ratio for a given [Hg] and this is given in Figure 14 of the Appendix. The intramultiplet relaxation rate constants, k_{Hg*}^{M} , for Hg(${}^{3}P_{1}$) form eq 11. The k_{Hg*}^{Mg} values for CO, N₂, and NO were 15.4,

$$k_{\mathrm{Hg}^{*}}^{\mathrm{M}} = \left(\frac{I_{\mathrm{Hg}^{*}}^{\mathrm{M}}}{I_{\mathrm{HgCl}^{*}}}\right) \left(\frac{[\mathrm{Cl}_{2}]}{[\mathrm{M}]}\right) \left(\frac{k_{\mathrm{HgCl}^{*}}^{\mathrm{Cl}_{2}}}{f}\right)$$
(11)

TABLE III: Intramultiplet Hg(³P₁) Formation Rate Constants

			$k_{Hg^{\bullet}}^{M}, a 10^{-11}$
M	$k_{\mathrm{Hg}^{*}}^{\mathrm{M}}/k_{\mathrm{Hg}^{*}}^{\mathrm{CO}a}$	$\sigma_{\rm M}^*/\sigma_{\rm CO}^{*b}$	cm ³ molecule ⁻¹ s ⁻¹
СО	1.0	1.0	15.4
N_2	0.74	0.72	11.4
NO	0.67	0.65	10.3
O ₂	0.037	0.045	0.6
NH_3	0.62	0.79	9.5
H ₂	0.43	0.51	6.6
CCl₄	0.013		0.20
CHCl ₃	0.026		0.40
CH_2Cl_2	0.056		0.86
CH ₃ Cl	0.18		2.8
CH4	0.73	0.63	11.2
COCl ₂	0.0023		0.04
CF ₄	0.077		1.2
CF_2Cl_2	0.063		1.0
CF_2Br_2	0.048		0.74
CF_2BrCl	0.020		0.31
Cl_2	<0.005		<0.16
Br ₂	<0.015		<0.5
I ₂	<0.015		<0.5
CF ₃ NCl ₂	<0.02		<0.6

^a This work, the rate constants (~325 K) were measured relative to CO. However, the absolute rate constants were obtained from the $k_{Hg}^{N_2}$ of ref 12. ^b Reference 11, measured in a crossed molecular beam apparatus using effusive beams at ~373 K.

11.4, and 10.2×10^{-11} cm³ molecule⁻¹ s⁻¹. These relative $k_{Hg}^{CO} \cdot k_{Hg}^{N2} \cdot k_{Hg}^{N0}$, values agree with early thermal molecular beam measurements,¹¹ see Table III.

Burnham and Djeu¹² reported total quenching rate constants for Hg(${}^{3}P_{2}$) by CO and \hat{N}_{2} of 21 × 10⁻¹¹ and 11 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹, respectively, at 325 K with uncertainties of $\pm 35\%$. Our $k_{H_{2}}^{N_{2}}$ value is in close agreement with Burnham and Djeu's rate constant. This is an important consistency check because our reference rate constant, $k_{HgCl^*}^{Cl_2}$ was determined by Krause et al.²⁰ using the reverse procedure, i.e., they assumed that Burnham and Djeu's rate constant pertained only to $Hg({}^{3}P_{1})$ formation and compared $I_{Hg}^{N_{2}}$, with $I_{HgCl}^{Cl_{2}}$. Thus, the k_{Hgx}^{RX} , values of Table II, in fact, are based upon Burnham and Djeu's measurement for $Hg(^{3}P_{1})$ formation from N₂. Burnham and Djeu's quenching rate constant ratio for N₂ vs. CO is 0.49, whereas our $Hg(^{3}P_{1})$ formation rate constant ratio is 0.72. Other exit channels, presumably $Hg({}^{3}P_{0})$ formation, must exist for quenching by CO, or there is experimental error in the measurements. In order to check for exit channels other than $Hg(^{3}P_{1})$ formation, we did experiments with very high flows and compared $\Gamma_{Hg^*}^{N_2}$ and $\Gamma_{Hg^*}^{CO}$ using the saturation method. The I_{Hg*} from the high flow regime plots, such as Figure 4, were nearly equal implying that $\Gamma_{Hg^*}^{CO} \approx \Gamma_{Hg^*}^{N_2}$ and that Burnham and Djeu's total quenching rate constants need reinvestigation. There is a need for independent and systematic measurement of the total quenching rate constants for $Hg(^{3}P_{2})$.

The intramolecular relaxation rate constants for reagents other than CO, N₂, and NO were measured relative to CO for the same [Hg]. This is much easier (and more reliable) than comparison to the HgCl(B-X) emission, since $I_{Hg^*}^{CO}$ and $I_{Hg^*}^{RX}$ can be compared directly. A summary of the k_{Hg*}^{M} values is given in Table III; the relative values and the absolute values, using $k_{Hg*}^{N_2} = 11.4 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, are shown. Our relative values are in agreement with the previous work of Martin.¹¹ A CF_nCl_{4-n} and a CH_nCl_{4-n} series was selected for study of intramultiplet relaxation by chlorinated methanes. There is an inverse correlation of $k_{Hg^*}^M$ with k_{HgCl^*} , i.e., molecules with larger $k_{\text{Hg}^*}^{\text{M}}$ have smaller k_{HgX^*} . Considering the expected magnitudes for k_Q , the small $k_{Hg^*}^M$ + k_{HgX*} values suggest the presence of other exit channels,²⁵ such as HgX(X) + R, HgH(X) + R, or Hg + X(H) + R. In contrast to CH₄, intramultiplet relaxation by CF₄ is very inefficient and the quenching rate constant by CF_4 probably is small. Broad-band emission that might correspond to (Hg-NH₃*) excimer emission was not found for ≤ 10 Torr of Ar. The interaction of Hg(6s,6p) states with NH₃ involves HgNH₃* intermediates; this subject has an extensive literature²⁶ and will not be discussed.

C. Excitation Transfer from $Hg({}^{3}P_{2})$ and $Hg({}^{3}P_{0})$ to CN(X). During the study with BrCN and ICN, CN(B-X) emission was observed, see Figure 5, from excitation transfer between $Hg(^{3}P_{2})$ or $Hg(^{3}P_{0})$ with CN(X) that had been generated in the primary interaction event. In earlier work, Vikis and Leroy^{15b} reported excitation transfer to CN(B) and CN(A) from $Hg(^{3}P_{0})$. Since BrCN gave the least CN(A) emission by direct reaction, we studied the excitation-transfer step using BrCN as the CN(X)source. The CN(B-X) emission intensity from the combined $Hg(^{3}P_{2})$ and $Hg(^{3}P_{0})$ reactions was much stronger than the CN-(A-X) intensity. By comparing the CN(B)/CN(A) intensity ratio for the CN(A) vibrational levels above the thermochemical limit for the direct $Hg(^{3}P_{2}) + BrCN$ reaction, a CN(B)/CN(A) ratio of 50-100 was estimated for the excitation-transfer reaction. The CN(B) vibrational distribution from the band head intensities of the $\Delta v = 1, 0, -1$ sequences was $N_0 - N_4 = 100:80:80:60:40$. Our populations are more heavily weighted toward higher vibrational levels than those reported^{15b} for excitation by $Hg(^{3}P_{0})$, as would be expected from the greater available energy with $Hg(^{3}P_{2})$. Experiments also were done in which N₂ was added to remove $Hg(^{3}P_{2})$; the resulting CN(B-X) intensity for the same BrCN



Figure 5. CN(B-X) emission spectrum from $Hg(^{3}P_{0,2}) + CN$ at 1.5 Torr of Ar. The prereaction giving CN radicals was $Hg(^{3}P_{0,2}) + BrCN$.

flow was reduced a factor of 4. Since the CN(X) concentration also would be reduced by the removal of the Hg(${}^{3}P_{2}$), this experiment suggests that the excitation-transfer rate constants for Hg(${}^{3}P_{2}$) and Hg(${}^{3}P_{0}$) are similar. A correspondence between Hg* + CN and Hg* + X potential curves^{27,28} can be expected, although the additional HgCN* states correlating to CN(A) and CN(B) must be added. The interaction between Hg* and CN will be dominated by the ion-pair potential with the CN* distribution determined by predissociation from $V(Hg^+, CN^-)$.⁵

For halide donors with low Γ_{HgX^*} , secondary reaction between HgX(X) and $Hg(^{3}P_{0,2})$ could contribute to the observed HgX-(B-X) emission.^{15,27} Experiments were done to investigate this possibility using CH₃Cl, which gives no HgCl(B) directly. No HgCl(B-X) emission could be recorded under the same conditions for which CN(B-X) emission from BrCN could be readily observed. Tentative explanations for the absence of secondary HgCl(B-X) emission are as follows. (i) HgCl(X) is formed in the primary step but with vibrational energy above the HgCl(X)dissociation limit (23 kcal mol⁻¹). (ii) The excitation transfer with $Hg(^{3}P_{2})$ is quasi-resonant in nature and yields HgCl(B) above the predissociation limits correlating to $Hg(^{3}P_{1})$ and $Hg(^{3}P_{0})$. Thus, predissociation rather than HgCl(B-X) emission would occur. (iii) The excitation transfer with $Hg(^{3}P_{0})$ may yield a narrow distribution in very high v' levels (37800 cm⁻¹) which would give weak emission over a very wide wavelength range. The previously observed excitation transfer from $Hg(^{3}P_{0})$ to HgCl and to HgBr used high N₂ pressures, which would have caused appreciable vibrational relaxation prior to emission.^{15,27} Additional work is needed to more fully characterize the excitation transfer between $Hg(^{3}P_{0,2})$ and HgX(X); the possibility of HgX(C) and HgX(D) formation needs to be remembered.

IV. Simulation of HgX(B-X) Spectra and Assignment of Vibrational Distributions

A. Potentials and Transition Moments. The HgX(B-X) emission from high v' levels is dominated by spectral features arising from bound-free transitions, despite the fact that the mercury halides have bound ground states ($D_0(\text{HgX}) = 8200$, 5406, and 2839 cm⁻¹ for X = Cl, Br, and I, respectively). The bound-free character results from the large difference between $R_e(B)$ and $R_e(X)$, see Figure 6. The HgX(B-X) transitions also have bound-bound components with the ratio of bound-free and bound-bound components changing with v'. The emission intensity at frequency ν is given by the following equations.^{1b}

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Quenching Reactions of $Hg(^{3}P_{2})$ and $Hg(^{3}P_{0})$ Atoms

$$I(\nu) = \sum_{v}^{v_{\text{max}}} N_v I_v(\nu) \text{ photons (unit energy)}^{-1}$$
(13a)

$$I_{\rm v}(\nu) = \frac{64}{3h} \pi^4 \nu^3 |\langle \psi_v | \mu_{\rm eg} | \psi_{\rm E_g} \rangle|^2$$
(13b)

$$\nu = \nu_0 + E_v - E_g \tag{13c}$$

 N_v is the steady-state population of the vth vibrational level, $I_v(v)$ is the intensity from the vth level at frequency ν , μ_{eg} is the transition moment function, and ψ_v and ψ_{E_g} are the radial wave functions of the upper and lower electronic states, respectively. In order to completely characterize the emission spectrum it is necessary to determine the transition elements (probabilities) for all rotational-vibrational transitions, weighed by the appropriate rotational distribution function. In this work the effects of rotation were not included in the calculated transition matrix elements. In our earlier calculation we found that the calculations for J = 0 gave the same result as for the Boltzmann average J. Since the simulated spectrum is compared to the experimental spectrum in wavelength units, the ν^3 factor is adjusted to ν^5 . The simulation of a HgX(B-X) emission spectrum consists of calculating the transition matrix elements $\langle \psi_v | \mu_{eg} | \psi_{E_g} \rangle$ followed by combination with the appropriate vibrational distribution to reproduce the experimental spectra. Standard numerical methods are available to determine the radial wave functions, providing the potential curves for the electronic states are available. The wave functions and transition moment function are then numerically integrated over R to obtain the transition matrix elements. The critical factors are reliable potentials and transition dipole functions. Improved potential curves and transition dipole functions were used for HgCl, HgBr, and HgI as discussed below.

The potential curves developed by Dreiling and Setser were derived from the spectroscopic constants of Cheung and Cool,16 which were determined by a reanalysis of spectroscopic data of Wieland. Since a rotational analysis was not available, the rotational constants for the X state were based on the ab initio R_e'' (2.42, 2.62, and 2.81 Å for HgCl, HgBr, and HgI, respectively).²⁸ The R_e' values were then adjusted to reproduce the band intensities $(R_{e}' = 2.94, 3.10, \text{ and } 3.27 \text{ Å for HgCl, HgBr, and HgI, re$ spectively). The RKR potentials developed for the observed levels were extended to higher energy by addition of Morse-type attractive and repulsive branches. These curves and modified ab initio transition moment functions were used by Dreiling and Setser.^{1b} Although the overall envelopes of the calculated and experimental HgX(B-X) spectra were generally matched, some features of the experimental spectra were not exactly fitted. For example, the vibrational distributions which reproduced the relative positions of the major oscillations tended to give deeper oscillations than the experimental spectra, and distributions which best reproduced the overall envelope sometimes failed to match exactly the oscillatory positions. The most persistent difficulty was too large a calculated intensity near the short-wavelength limit.

Recently Tellinghuisen^{17,18} analyzed the HgX(B-X) transitions from single isotopic spectra and presented an unambiguous assignment of the v'' numbering for all three systems. Tellinghuisen used rotational constants based upon the ab initio R_e'' values and the improved vibrational constants to generate RKR potentials for HgCl(X, $v'' \le 31$), HgBr(X, $v'' \le 34$), and HgI(X, $v'' \le 23$); Morse attractive and repulsive branches were added to extend these potentials to higher energy. Morse potentials for the HgX(B)states were constructed by using the spectroscopic constants derived from these single isotope spectra. A Franck-Condon analysis was performed to determine the relative difference in the equilibrium internuclear distance of the B and X states, $\Delta R_e = 0.60, 0.57$, and 0.49 Å, giving R_e' values of 3.02, 3.19, and 3.30 Å, for HgCl, HgBr, and HgI, respectively. This can be compared to $\Delta R_e =$ 0.51 and $R_e' = 2.94$ Å for Cheung and Cool's analysis for HgCl. The changes in R_{e}' are significant and shift the Franck-Condon envelope upward by two v'' units for HgCl, by three v'' units for HgBr, and by one v'' unit for HgI.

The Tellinghuisen potentials, which are a Morse-RKR-Morse combined function for HgCl(X) and a Morse curve for HgCl(B),



Figure 6. Plots of the potentials, transition dipole function, and difference potentials for v' = 30 and 60 for HgCl. The Franck-Condon densities are shown for transitions from v' = 30 and 60. Note, the two calculated densities must be adjusted on the energy (frequency) axis before visualizing a coaddition. In fact, the low-energy ends start at the same approximate energy.

were used in our first attempt. However, the Morse potential for the B state did not have the proper anharmonicity to reproduce the spectroscopic constants. A truncated Rittner potential, which matched the Tellinghuisen RKR potential at intermediate R, was used at large R for the next attempt. The Morse extension to the RKR potential was used for small R. The Rittner potential, which has been used satisfactorily for the ionic states of the rare gas halides and alkali halides, has the form

$$V(R) = a + b \exp(-\beta R) - \frac{C_1}{R} - \frac{C_3}{R^3} - \frac{C_4}{R^4} - \frac{C_6}{R^6}$$
(14)

The constants b, β , and R_e' are determined from the boundary conditions for V(R) and its derivatives; a is the sum of T_e' and D_e' . C_1 represents ion-ion attraction, C_3 the ion-quadrupole term, C_4 the ion-induced dipole interaction, and C_6 the induced-dipole-induced-dipole interaction. For the second trial potential the C_3 and C_6 terms were ignored. The C_4 parameters were calculated from the ion polarizabilities²⁹

$$C_4 = \frac{1}{2}e^2(\alpha_+ + \alpha_-) = (5.807 \times 10^4 \text{ cm}^{-1})(\alpha_+ + \alpha_-) \text{ Å}^4$$
 (15)

where α_+ and α_- are polarizabilities in Å³, see Table IV. Since the polarizability of Hg⁺ was not available, it was estimated from the trend for Xe⁺ and Xe as $\alpha_{\text{Hg}^+} = 3.06$ Å³ ($\alpha_{\text{Hg}} = 5.1$ Å³). The resulting values $C_4 = 3.519 \times 10^5$ cm⁻¹ Å⁴ and $C_1 = 1.1614 \times 10^5$ cm⁻¹ Å, were used to solve for $b = 5.9753 \times 10^6$, $\beta = 2.3737$, and $R_e' = 2.6175$ for HgCl. The resulting Rittner potential, which

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TABLE IV: Parameters for Mercury Halide Potentials^a

	HgCl	HgBr	HgI
	X St	ate	A
$D_{e}'', \mathrm{cm}^{-1}$	8350	5500	2900
$\beta_{\rm S}, \rm \AA^{-1}$	2.067185	2.357788	2.458528
Res, Å	2.419106	2.617353	2.809851
RKR potential	0-31	0-34	0-23
(v'') ^b			
$\beta_{\rm L}, {\rm \AA}^{-1}$	2.5817	2.197600	1.535678
R _{eL} , Å	2.433749	2.385776	2.363526
	B Sta	ate	
$D_{a'}, cm^{-1}$	39900	39100	38300
$T_{a'}, cm^{-1}$	23451.6	23484.97	24066.4
<i>R.</i> , Å	3.01934	3.18839	3.297995
$\beta_{\rm S}, {\rm \AA}^{-1}$	0.662611	0.6527	0.631822
RKR potential	0-9	0-13	0-13
$(v')^{\bar{b}}$			
$\alpha_{X^-}, Å^3$	3.0 ^c	4.5 ^c	7.0 ^c
$b, d \text{ cm}^{-1}$	5.9753 × 10 ⁶	6.5981×10^{6}	6.3971 × 10 ⁶
β , ^d Å ⁻¹	2.3737	2.3315	2.2226
C_{1}^{d} cm ⁻¹ Å	1.1614×10^{5}	1.1614×10^{5}	1.1614×10^{5}
$C_4,^d$ cm ⁻¹ Å ⁴	3.1596 × 10 ⁵	4.2156×10^{5}	5.7541×10^{5}
$C_6,^d$ cm ⁻¹ Å ⁶	2.9934×10^{5}	1.450×10^{5}	7.2697×10^{4}
we'e	192.15	136.02	110. 97
$\omega_e x_e'^e$	-0.5033	-0.2734	-0.1893
weye'e	-0.1190×10^{-2}	-0.4981×10^{-3}	-0.5914×10^{-5}
$\omega_{e} z_{e}'^{e}$	0.2539×10^{-4}	0.1168×10^{-4}	0.2188×10^{-5}

^a The constants given here are for the potentials selected to fit the Band X-state potentials for the ranges of R; $R < R_S$, $R_S < R < R_L$, $R > R_L$. ^b This is the v' and v'' range of the RKR potentials. ^c α_{X^-} is the polarizability of the halide ions ref 29; see text for α_{Hg^+} . ^d These Rittner potentials must be shifted by 0.4025, 0.48303, and 0.50714 Å for HgCl, HgBr, and HgI, respectively, in order to match the true R_e' values (see text). ^e These are the spectroscopic constants that best reproduce the energy levels in the HgX(B) states, $G(v') = (v' + 1/2)\omega_e' + (v' + 1/2)^2\omega_e x_e' + (v' + 1/2)^3\omega_e y_e' + (v' + 1/2)^4\omega_e z_e'$ for the Cl³⁵ and Br⁷⁹ isotopes.

had the correct shape but did not match the RKR potential, was translated along the R coordinate so that the R_e' corresponded to the $R_e' = 3.02$ Å of Tellinghuisen. (The transformation is R' = R - 0.4025). After b, β , and R_e' were obtained, the Rittner potential was made first derivative continuous with the RKR potential by a final adjustment of the C_4 and C_6 coefficients. The Morse function was fitted to the RKR potential at short range with provision for first derivative continuity. The parameters describing the Morse and Rittner potentials are given in Table IV, and the results for HgCl are shown in Figure 6. The B-state energy levels were fit to a power series expansion in v + 1/2; these coefficients are given in Table IV.

The mercury halide X-state potentials were of the form

$$U(R) = D_{e}''(1 - \exp(-\beta_{\rm S}(R_{e\rm S} - R)))^2 \quad \text{for } R < R_{\rm S}$$

the RKR potential for $R_{\rm S} < R < R_{\rm L}$

$$U(R) = D_{e}''(1 - \exp(-\beta_{L}(R_{eL} - R)))^{2} \quad \text{for } R > R_{L} \quad (16)$$

 $R_{\rm L}$ and $R_{\rm S}$ are the inner and outer classical turning points corresponding to the highest v level of the RKR potential. The $\beta_{\rm L}$, $\beta_{\rm s}$, $R_{\rm eS}$, and $R_{\rm eL}$ values were adjusted to ensure continuity between the RKR potential and the Morse repulsive and attractive branches.

The transition dipole functions were obtained by translating the ones used by Dreiling to the new R_e' positions, followed by slight modifications to obtain better simultaneous fits to HgX-(B-X) spectra representative of distributions with different $\langle E_V \rangle$. The transition dipole functions used for this work tend to decline somewhat more sharply at small R than those used by Dreiling. A summary of the dipole functions is given in Table V. It should be noted that the maximum in μ_{eg} occurs for R slightly larger than R_e' .

What is the degree of reliability of the potential functions and the transition dipole functions? For the range of R covered by the RKR potential, see Figure 6 and Table IV, the results should

TABLE V: Mercury Halide Transition Dipole Function

-				
 parameters ^a	HgCl	HgBr	Hgl	
A	4.3	4.0	4.0	
В	3.14	3.24	3.42	
$E, R \leq B$	1.12	1.50	1.50	
E, R > B	2.0	2.00	1.80	
$n, R \leq B$	3	2	2	
R > B	2	2	2	

 ${}^{a}\mu_{eg} = A \exp(-2.2772589\{(R-B)^{n}/E\}).$



Figure 7. Comparison of simulated (broken lines) and experimental spectra for $Hg(^{3}P_{2})$ reactions with CF₂CINFCl, S₂Cl₂, Cl₂, CCl₃F, and PCl₃. The experimental spectra were obtained at 1.5 Torr and are free of collisional relaxation.

be reliable and, in general, we have confidence in the extensions to higher energy. Less certainty is associated with the transition dipole functions at large and small R. Our greatest effort was placed upon the HgCl system, because more reactions giving HgCl(B) had been studied. The envelopes of the calculated HgCl(B-X) spectra from Cl₂ and other reactions with high $\langle E_V \rangle$ fit better than before. But, there still are minor problems with the short-wavelength limit of the simulated spectra. For both Cl₂ and S_2Cl_2 , see Figure 7, the emission intensity (bound-bound) near 320 nm is too high, yet the calculated λ_{min} value falls slightly to the long-wavelength side of the experimental result, even though the correct experimental $E_{V,max}^{obsd}$ was entered into the calculations. These somewhat contradictory observations imply that μ_{eg} is not exactly correct for small R or perhaps that rotational transitions may need to be included explicitly. The sensitivity of the vibrational assignments to μ_{eg} was systematically investigated for HgBr. Our initial choice of μ_{eg} (HgBr) had the maximum at 3.29 Å (B = 3.29 for the equation in Table V). Appropriate vibrational distributions could be found which matched the HgBr(B-X)emission from several reactions with this choice for μ_{eg} . The resulting $\langle f_V \rangle$ value for Br₂ declined somewhat more than the $\langle f_{\rm V}({\rm HgCl}) \rangle$ from Cl₂, relative to the $\langle f_{\rm V} \rangle$ values determined by Dreiling and Setser. Simulation of the HgI(B-X) spectra did not

give a correspondingly large difference in $\langle f_{\rm V}({\rm HgI}) \rangle$, relative to those of Dreiling. Detailed examination of the HgBr transition matrix elements indicated that the large reduction in $\langle f_V(HgBr) \rangle$ could be a consequence of the position of μ_{eg} . The sensitivity of $\langle f_{\rm V}({\rm HgBr}) \rangle$ to the location of $\mu_{\rm eg}$ was examined by calculating sets of transition matrix elements for μ_{eg} with maximum at 3.15, 3.19, 3.24, and 3.42 Å. For the same vibrational distribution, systematic changes in the HgBr(B-X) simulated spectra were observed. As μ_{eg} was translated to shorter R, the intensity in the 295-360-nm region increased, while the intensity in the 420-490-nm region decreased. As μ_{eg} is translated to smaller R, the matrix elements from the classically allowed inner turning point are enhanced and concurrently the transitions from the outer turning point are reduced. In order to maintain a satisfactory fit to a given experimental spectrum, the populations in the higher vibrational levels must be increased and $\langle f_V \rangle$ becomes larger as μ_{eg} is translated to smaller R. For the Br₂ spectrum translating μ_{eg} from 3.29 to 3.24 Å increases $\langle f_V \rangle$ from 0.38 to 0.44 for a similar quality of fit to the experimental spectrum. A general result from the dipole functions used in this work was that the A_v values declined less with increasing v' than for the previous calculations.16

The HgBr results indicated that there is a range of acceptable positions for μ_{eg} , and the question that now arises is whether other aspects of the spectrum can be used to more uniquely assign the position of μ_{eg} . The smallest acceptable position for the maximum in μ_{eg} is determined by the intensity of the short-wavelength transitions, since placing μ_{eg} at too small a R would give to large an intensity in the 295-360-nm region for all reasonable vibrational distributions. If μ_{eg} is located at too large an R, the intensity in the short-wavelength region is underestimated. For the intermediate range of R, the vibrational distribution and μ_{eg} can be adjusted to compensate for one another. If several spectra of different $\langle E_V \rangle$ are used in locating the best position for μ_{eg} , the ambiguity can be minimized. In the present work we have chosen $\mu_{\rm eg}$ functions that are internally self-consistent, and trends in $\langle f_{\rm V} \rangle$ values should be reliable, even if absolute values are uncertain by $\pm 10\%$. To more precisely define the transition dipole function, fluorescence spectra are needed from selectively excited high vibrational levels.

B. HgX(B) Vibrational Distributions. The spectra were simulated by trial and error selection of the vibrational distribution in which the first estimate was a linear surprisal type distribution (three-body prior) with the maximum energy for the distribution, $E_{V,max}^{obad}$, fixed by the λ_{min} value.

$$N_v = (1 - f_V)^{3/2} \exp(-\lambda_V f_V), \quad f_V = E_V / E_{V,max}^{obsd}$$
 (12)

If a fit was not possible, then the sum of two linear surprisals was used with a smaller $E_{V,max}^{obsd}$ for the second distribution. The surprisal parameters, λ_{v} , were treated as adjustable constants, which were varied until a satisfactory fit to the experimental spectrum was achieved. The use of two linear surprisals provides a more flexible trial-and-error fitting function, and it does not imply an intrinsically two-component distribution. The $\langle f_V \rangle$ is defined as $\langle E_V \rangle / \langle E \rangle$ with $\langle E \rangle$ being the total available energy, which was taken from tabulated $D_0(R-X)$ unless the value determined from λ_{min} was thought to provide the better measure of the available energy. In general $\hat{E}_{V,max}^{obsd} = \langle E \rangle$; the notable exceptions are S_2Cl_2 (and SCl_2) for which $\langle E \rangle$ exceeds $E_{V,max}^{obsd}$, but see footnote d of Table II. Representative examples of the simulated and experimental spectra are shown in Figures 7, 8, and 9, and some distributions, N_v , are shown in Figure 10. The steady-state distributions of eq 12 can be converted into initial distributions, $\alpha N_v/A_{v'}$, using the calculated Einstein coefficients, $A_{v'}$. The $A_{v'}$ increase slowly with increasing v' and give a slight enhancement for the lower energy range of the initial distributions. A summary of $\langle E \rangle$, $E_{V,max}^{obsd}$, $\langle f_V \rangle$, and parameters describing the distributions are given in Tables VI and VII. The $\langle f_V \rangle$ values from Dreiling and Setser's assignments are shown for comparison. In some cases the fit to the experimental spectrum is not perfect; see CCl₃F in Figure 7 for example. A better match to the first oscillation with retention of the fit to the envelope could be ob-



Figure 8. Comparison of simulated (broken lines) and experimental spectra from $Hg(^{3}P_{2})$ reactions with Br_{2} , $CF_{2}ClBr$, and $CF_{3}NClBr$; spectra from CBr_{4} and $CHBr_{3}$ were given in ref 1.



Figure 9. Comparison of simulated (broken lines) and experimental spectra from reactions of $Hg({}^{3}P_{2})$ with I_{2} , IBr, and ICl; a spectrum from CF₃I was shown in ref 1b. The short-wavelength bands from the I_{2} reaction are HgI(C-X) and I_{2}^{*} emission. The dotted lines show the deconvoluted HgI(B-X) spectrum for ICl and IBr. The fit to the HgI(B-X) spectrum for a sociated with the uncertainty associated with deconvolution the HgBr(B-X) spectrum.

tained with a distribution composed of two linear surprisal components. However, the effort was judged not to be worthwhile since $\langle f_V \rangle$ hardly would be changed and, within our ability to assign the distributions, the energy disposal from CCl₃F closely resembles that for CCl₄.

TABLE VI:	Vibrational Energy	Disposal for	$Hg(^{3}P_{2})$	with RX ^a
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reagent	$\langle E \rangle$	$E_{\rm V,max}^{\rm obsd}$, kcal mol ⁻¹	$\langle E_{\rm V} \rangle$, ^b kcal mol ⁻¹	$\langle f_{\rm V} \rangle^b$ (this work)	shape of ^b distrib	$\langle f_{ m V} angle$ (ref 1b)
Cl,	26.8	27.5	14.7	0.55	$35\%, \lambda = -14$	0.61
2				(0.53)	65%, $\lambda = -2$	
CCl₄	15.4	15.4	6.0	0.39	$\lambda = -2$	0.40
CCl ₃ F	11.4	10.4	4.4	0.39	$\lambda = -2.5$	
CHCl ₃	7.4	8.3	3.3	0.39	$\lambda = -2$	0.43 ^d
PCl ₃	7.4	7.4	3.4	0.45	$\lambda = -3$	
S_2Cl_2	40.2	30.0	17.0	0.42	65%, $\lambda = -7$	0.42^{e}
				(0.41)	$35\%, \lambda = -2$	
CF ₃ NCl ₂	≥28.4 ^c	28.4	17.2	≤0.61	70%, $\lambda = -8$	
				(≥0.59)	$30\%, \lambda = -2$	
CF ₂ ClNCl ₂	≥27.4 ^c	27.4	15.0	≤0.54	$50\%, \lambda = -7$	
				(≤0.53)	$50\%, \lambda = -3$	
CF2CINFCI	≥27.4 ^c	30.4	16.4	≤0.53	$50\%, \lambda = -7$	
-				(≤0.52)	$45\%, \lambda = -2$	
CF ₂ NCl	≥28.4 ^c	28.4	14.2	≤0.50	$\lambda = -3$	
Br,	30.6	29.9	13.4	0.44	45%, $\lambda = -7.5$	0.49
-				(0.43)	55%, $\lambda = -2$	
CBr ₄	21.3	19.6	8.8	0.45	$\lambda = -3$	0.45 ^f
$CF_2ClBr(HgBr)$	12.4	12.4	6.4	0.52	$\lambda = -4^{g}$	
CCl ₃ Br(HgCl)	15	f	~7.6	$\sim 0.51^{h}$	$\lambda = -4$	
CCl ₃ Br(HgBr)	22.3	21.9	11.8	0.53	$\lambda = -4.5$	
CF ₃ NClBr(HgBr)	≥30.2°	30.2	12.6	≤0.42	$65\%, \lambda = -3.0$	
					$35\%, \lambda = -4.5$	
I ₂	31.6	31.9	12.4	0.39	55%, $\lambda = -4$	0.46
				(0.36)	$45\%, \lambda = -0.5$	
CF ₃ I	14.2	13.0	е			0.46
ICF ₂ CF ₂ Br(HgI)	~13.9	13.9	5.5	0.40	$\lambda = -2$	
				(0.39)		
ICl (HgCl)	34.4	33.4	17.5	0.51	30%, $\lambda = -12$	
				(0.48)	70%, $\lambda = -2$	
(HgI)	17.2	~15.8	7.1	0.41	50%, $\lambda = -4$	
				(0.40)	$50\%, \lambda = -2$	
IBr (HgBr)	34.4	31.9	15.8	0.46	45%, $\lambda = -9$	
-				(0.45)	55%, $\lambda = -3$	
(HgI)	25.0	24.7	9.3	0.37	$50\%, \lambda = -4$	
_				(0.35)	$50\%, \lambda = -2$	

^aCalculated entries are based on the steady-state HgX(B) vibrational distributions except for the $\langle f_V \rangle$ values in parentheses, which are for the initial distributions. The latter is given only if it differs significantly from the steady-state value. ^b The $\langle f_V \rangle$ is defined as $\langle E_V \rangle \langle E \rangle$, although $E_{V,max}^{bbd}$ was used to define the linear surprisal distribution; $\langle E \rangle = E(Hg, {}^{3}P_{2}) + nRT - D_{0}(R-X) + D_{0}(HgX(X)) - T_{0}(HgX)$. For HgCl distributions the $E_{V,max}$ for the second surprisal was always 2.5 kcal mol⁻¹ lower than $E_{V,max}^{bbd}$. The $E_{V,max}$ for the second surprisal for the HgBr distributions was 20.0, 19.4, and 21.4 kcal mol⁻¹ for Br₂, CF₃NClBr, and lBr, respectively. The $E_{V,max}$ for the second surprisal for the HgI distributions was 21.4, 14.1, and 14.1 kcal mol⁻¹ for I₂, ICl, and IBr. ^c These $\langle E \rangle$ were assigned from the λ_{min} values, which are lower limits; see text. ^d The $\langle f_V \rangle$ value quoted in ref 1b has been altered to account for the higher $D_0(CHCl_2-Cl)$; the difference in energy disposal to SOCl₂ ($\langle f_V \rangle = 0.50$) and SO₂Cl₂ ($\langle f_V \rangle = 0.29$) were assigned in ref 1b. The HgI(B) distribution from CF₃I corresponds to $\lambda_V = -4$; comparison of the current and previous^{1b} simulations for $\lambda_V = -4$. showed no significant differences. ^fThe (f_V) for CHsr₃ was assigned in ref 1b has been adjusted for the same $\langle E_V \rangle$ but an enhanced population near $f_V = 0.5$ (70% $\lambda_V = -4.5$ with $E_{V,max} = 12.4$ kcal mol⁻¹ and 3% $\lambda_V = -7.0$ with $E_{V,max} = 8.6$ kcal mol⁻¹). ^hThe HgCl(B-X) spectrum from CCl₃Br is badly overlapped by the HgBr(B-X) emission, which leads to an approximate assignment for $\langle f_V (HgCl) \rangle$.

TABLE VII: Vibrational Energy Disposal for $Hg(^{3}P_{0})$ and $Hg(^{3}P_{1})$ Reactions

reagent	$\langle E \rangle$, kcal mol ⁻¹	$\langle E_V \rangle$, ^{<i>a</i>} kcal mol ⁻¹	$\langle f_{\rm V} \rangle^a$	shape of distrib
$Br_2(Hg, {}^3P_0)$	13.5	6.1	0.45	$50\%, \lambda = -5^b$
$I_2(Hg, {}^{3}P_0)$	13.2	5.3	0.40	$50\%, \lambda = -1.5^{\circ}$ $65\%, \lambda = -5^{\circ}$ $35\%, \lambda = -2^{\circ}$
$Cl_2(Hg, {}^{3}P_1)$	14.4	7.2	0.50	$35\%, \lambda = -14$ $65\%, \lambda = -2$

^a All calculated entries are based upon the steady-state HgX(B) distribution. ^b These distributions are of the same form as those from Hg(³P₂) atom reactions, see Table VI. The first components had $E_{V,max} = \langle E \rangle$; the second components had $E_{V,max} = 12.3$ and 8.6 kcal mol⁻¹ for Br₂ and I₂, respectively.

Only Br₂ and I₂ gave sufficiently strong HgX(B-X) emission from reaction with Hg(³P₀) to merit simulation and the results are summarized in Table VII. The Hg(³P₀) spectra from Br₂ and I₂ were simulated with the same type of distributions as for the Hg(³P₂) reactions. We also simulated a HgCl(B-X) spectrum³⁰ from the $Hg({}^{3}P_{1}) + Cl_{2}$ reaction and found that the same type of distribution as used for $Hg({}^{3}P_{2}) + Cl_{2}$ gave a satisfactory fit. Thus, the HgX(B) vibrational distributions assigned from $Hg({}^{3}P_{2})$ reactions proved satisfactory for simulating the HgX(B-X) spectra from $Hg({}^{3}P_{0})$ or $Hg({}^{3}P_{1})$ reactions, providing that the difference in the available energy was recognized. This general conclusion appears to be firm even though the $Hg({}^{3}P_{0})$ experimental spectra are less reliable than for the $Hg({}^{3}P_{0})$ reactions. If better spectra are obtained in the future from the $Hg({}^{3}P_{0})$ and $Hg({}^{3}P_{1})$ reactions, some refinement to the vibrational distributions may be necessary.

Since the spectra from reactions which gave two HgX(B)products overlap, matching the calculated and experimental spectra requires deconvolution. The red-most region of the $HgBr^*$ (or $HgCl^*$) spectrum from IBr (or ICl) is free from HgI(B-X)emission; but, the HgI^* emission lies within the tail of the $HgBr^*$ or $HgCl^*$ envelopes. Therefore, the $HgBr^*$ (or $HgCl^*$) spectrum was fitted first, using only the interference-free region to ascertain

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⁽³²⁾ Alge, E.; Adams, H. G.; Smith, D. J. Phys. B. 1984, 17, 461, 3827.



Figure 10. HgX(B) initial vibrational distributions from the reactions of Hg(${}^{3}P_{2}$) with selected reagents. The XeCl(B) distribution for Cl₂ is included for comparison (this distribution is based upon new (unpublished) simulations from this laboratory); the XeBr* and XeI* distributions can be found in ref 1b, 6a,b, and 50.

the best-fit simulation with $E_{V,max}^{obsd}$ set equal to the $\langle E \rangle$ value from the bond energy. With the HgBr* (or HgCl*) simulation in hand, the HgI(B-X) spectrum was obtained by subtraction of the simulated HgBr* (or HgCl*) spectrum from the experimental spectrum. The HgI* spectra, with simulations, from IBr and ICl are shown in Figure 9. The best-fit vibrational distributions for HgBr(B) and HgCl(B) from IBr and ICl were of the type composed from two linear surprisals. The HgI* spectra also were fitted by distributions represented as the sum of two linear surprisals. The HgI* spectrum from ICl has a distinct shoulder at \sim 430 nm, which was not fitted well by any distribution. In fact, this feature in the $Hg(^{3}P_{2}) + I_{2}$ spectrum also is only approximately reproduced. The exact form of the HgI(B) vibrational distributions may not be well established because of the uncertainty associated with the deconvolution from the HgCl* and HgBr* spectra, but the $\langle E_{\rm v} \rangle$ values should be reliable. The difference between $\langle f_{\rm V}({\rm HgCl}) \rangle$ and $\langle f_{\rm V}({\rm HgI}) \rangle$ from ICl is certainly significant. We are less certain, but $\langle f_V(HgBr) \rangle$ appears larger than $\langle f_V(HgI) \rangle$ from IBr. The energy disposal for the two channels from IBr and

TABLE VIII: Electron Attachment Results (300 K) and HgX(B) Formation Rate Constants

reagent	EA,ª eV	β , ^b cm ³ s ⁻¹	$k_{\text{HgX}^{*}},^{c}$ 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹	k_{XeX}, d 10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹
CCl₄	2.0	3.9×10^{-7}	5.8	17
CCl ₃ F	~1.5	2.6×10^{-7}	0.6	5.0
CCl_2F_2	~ 0.8	3.2×10^{-9}		<0.5
CHCl,	~ 0.8	4.4×10^{-9}	1.6	
CH ₂ Cl ₂	~ 1.2	$\sim 5 \times 10^{-12} e$	~0.0	
CBr₄	~ 2		2.5	≥10
CH ₂ Br ₂		0.9×10^{-7}		1.3
CF ₃ Br	0.9	1.6×10^{-8}	≤0.1	6.0
CH ₃ Br	~0.4	0.6×10^{-11}	~0.0	≤0.7
CH ₃ I	0.3	1.2×10^{-7}		1.1
CF ₃ I	1.6		11.0	13
NF_3		2.1×10^{-11}	8.1 ^f	2.4

^aElectron affinity values are from ref 31a; these should be considered as adiabatic electron affinities. ^bThe 300 K electron attachment rate constants were taken from ref 32 unless noted otherwise. The β values for CFCl₃ and CF₂Cl₂ from ref 32 are generally larger than from other sources; see ref 31b. ^cThis work. ^dReferences 2, 3, and 4b. ^eReference 31b. ^fThe HgX* and XeX* formation rate constants for NF₃ are not so large, ref 1b, but the branching fractions are significant since the total quenching rate constants also are rather small, ref 4b.

ICl closely resembles that for the corresponding homonuclear diatomic halides.

An important point is the difference, if any, of the current vibrational distributions vs. those of Dreiling and Setser.1b Within the combined experimental and theoretical uncertainties, there is no significant change in average energies or in the shapes of the HgX(B) distributions from reactions with polyatomic reagents, see Table VI. The change in $\langle f_V \rangle$ for the CCl₃H reaction is a consequence of using a different $D_0(CHCl_2-Cl)$ and not in the $\langle E_V \rangle$ assignment. For $D_0(CHCl_2-Cl)^{23b} = 77$ kcal mol⁻¹, $\langle f_V$ -(HgCl)) is increased to ~ 0.4 and there is little difference in energy disposal between CCl₄ and CHCl₃ (which also is the case for CBr₄ vs. CHBr₃). Unfortunately, the situation for the Cl₂, Br₂, and I₂ reactions, which have large $\langle E \rangle$, is not so ideal. The "best" fit HgCl(B) distribution from Cl₂ is shown in Figure 10 together with the distribution assigned by Dreiling and Setser. Although the distributions are similar, the former distribution has larger population in the higher v levels, which results in $\langle f_V \rangle = 0.61$ for the steady-state distribution compared to 0.55 for the present assignment. The situation for Br₂ and I₂ is similar with $\langle f_V \rangle$ being reduced from 0.49 to 0.44 and from 0.46 to 0.39, respectively; each comparison is for the steady-state distribution. The slight, but systematic, reduction in $\langle f_V \rangle$, is mainly a consequence of the altered transition dipole functions used in the present work.

V. Discussion

A. Polyatomic Reactants. Since the electron affinity (EA) values of the RX molecules generally are significant, ≥ 1 eV, the $V(Hg^+,RX^-)$ potentials play an important role in the quenching mechanism, which includes excitation transfer to dissociative RX* states, reactive quenching to give HgX(X), and intramultiplet relaxation by $E \rightarrow V$ transfer as competing channels to HgX(B) formation. For hydrogen-containing molecules, reactive quenching giving HgH(X) with an excergicity of $\sim 136 - D_0(H-R)$ kcal mol⁻¹ can be a competing channel.²⁵ Figure 11 shows sketches representative of two different Cl-R interactions of the exit channel potential for Hg+-Cl--R in collinear geometry. Since the entrance channel, $V(Hg^*-RCI)$, will be essentially flat up to \sim 4 Å, the entry position on the front face of the plots for different reagents can be identified by selecting the $\langle E \rangle$ and the equilibrium R(R-Cl) value. It should be remembered that the entrance channel potentials and, hence, the front faces of the sketches in Figure 11 are embedded in a quasi-continuum of Hg-RCl* states. From the nature of the exit channel potential, it is evident that low $\Gamma_{\text{HeX}*}$ arise mainly from competition with other couplings in the entrance channel, although for special cases, such as I2, the collision pair may reach the $V(Hg^+I_2^-)$ channel with subsequent



Figure 11. Schematic illustration of model diabatic potentials of the product exit channel, HgCl + R, as a function of $R(Hg^+-Cl^-)$ and $R(Cl^--R)$ for collinear geometry. The total potential energy is the sum of $V(Hg^+,Cl^-)$ and $V(Cl^-,R)$; the $V(Hg^+,Cl^-)$ was expressed as the Rittner potential, and $V(Cl^--R)$ as a Morse representation of the $Cl_2^{-(2}\Sigma_u^+)$ potential⁴³ for A and an adjusted Morse representation of the $Cl_2^{-(2}I_{Ig})$ potential for B. The potential surface in B was chosen to display a less abrupt release of repulsive energy between Cl^- and the neutral fragment. The location of entrance channel diabatic potentials for different reactions can be identified by selecting $\langle E \rangle$ from Table VI and choosing a value for $R_e(Cl-R)$; $R_e(Cl_2) = 1.99$ Å.

return to V(Hg,I₂*). Table VIII lists some adiabatic EA values and thermal electron attachment rate constants. The reactive vertical EA provides a measure of the curve crossing location between $V(Hg^+, RX^-)$ and $V(Hg^+, RX)$ and the dissociative thermal attachment rate constant provides a measure of the ease for dissociative capture of an electron from Hg* or other pseudometal atoms. A correlation exists between the magnitude of the dissociative electron-attachment rate constants and k_{HgX*} or k_{XeX^*} . Conversely, the large k_{HgX^*} values suggest large 300 K attachment rate constants for CF₃I, CBr₄, and the nitrogen halide compounds. The generally lower k_{HgX^*} , relative to k_{XeX^*} in Table VIII, probably is a consequence of the smaller ionic-covalent curve crossing position for Hg relative to Xe, which allows opportunity for competing product channels. Assuming flat entrance channel potentials for $Xe({}^{3}P_{2})$ and $Hg({}^{3}P_{2})$, the 1.15 eV larger ionization energy of Hg(${}^{3}P_{2}$) results in ~1.5 Å smaller crossing position for the Hg(${}^{3}P_{2}$)-RX system.

Another noteworthy general point is the inverse correlation between k_{Hg^*} and $k_{\text{Hg}X^*}$, which suggests that the presence of $V(\text{Hg}^+, \text{RX}^-)$ does not aid intramultiplet mixing, if RX^- can lead to $\text{Hg}X^* + \text{R}$. If RX^- is a strongly bound state, such as SF_6^- , perhaps quenching via intramultiplet mixing would be aided. There certainly are strongly attractive interactions between Hg^{*} and NH₃, which do aid intramultiplet quenching.²⁶ The reduction in k_M^* as Cl atoms are substituted for H in the chloromethane series suggests that the main quenching pathway involves interactions with the C-Cl bonds. The intriguing questions associated with the mechanism (potentials) responsible for the large E-V transfer^{25,26} (intramultiplet relaxation) rate constants in the Hg(6s,6p) manifold will not be discussed further.

Within the uncertainties of the simulation procedure, the $\langle f_V(\text{HgX}) \rangle$ values assigned in this work for polyatomic reagents

agree with the earlier results from Dreiling and Setser.^{1b} Thus, the discussion given previously for the reaction dynamics need not be repeated. The most general point was the somewhat lower $\langle f_{\rm V}({\rm HgX}) \rangle$ vs. $\langle f_{\rm V}({\rm XeX}) \rangle$ for the reactions with CCl₄, CCl₃F,³³ CBr_4 , CF_3I , and the sulfur halides. It was noted that if the polyatomic radical retained the same internal energy during traversal of the exit channel potential for both reactions, then a smaller fraction is available for partitioning between $E_V(HgX \text{ or }$ XeX) and $E_{\rm T}$ for Hg(³P₂) than for Xe(³P₂), because the excergicity is less for the $Hg(^{3}P_{2})$ atom reactions. The present work continues to support that point of view. This argument probably should be used only for cases with sizeable k_{HgX*} values, because generalizations should not be based on minor product channels. The apparently larger $\langle f_V(HgBr) \rangle$ for CF₂ClBr and CCl₃Br relative to CBr_4 (which closely resembles CCl_4 and CCl_3F) may mean that CF₂Cl and CCl₃ retain less internal energy than does CBr₃ from the CBr₄ reaction. The $\langle f_V \rangle$ is nearly the same for both Xe* and Hg* reactions with PCl₃, which implies that PCl₂ retains little vibrational energy. The rather similar range (0.4–0.6) in $\langle f_{\rm V}$ -(HgX)) in Table VI for all reactions probably reflects the dissociative nature of the RX⁻ intermediate, which is prerequisite for significant HgX(B) product formation.

The general reduction of $\langle f_V(YbX) \rangle^{34a}$ vs. $\langle f_V(BaX) \rangle$ for some common RX reactions also can be rationalized by the reduced exoergicity of the Yb reactions³⁴ and the retention of common amounts of internal energy by R. The exoergicities for the $Xe({}^{3}P_{2})$ and Ba reactions are about the same,² but $\langle f_V(BaX) \rangle$ is significantly higher than $\langle f_V(XeX) \rangle$ for CBr₄, CHBr₃, CH₂Br₂, CF₃Br, and CH₃I. On the other hand, the $\langle f_V \rangle$ are similar, although the Ba values are slightly higher, for CCl_4 , CF_3I , and CH_2I_2 .^{2,34b} As noted previously,² the low Γ_{XeX^*} could be an explanation for the lower $\langle f_V(XeX) \rangle$ vs. $\langle f_V(BaX) \rangle$; i.e., trajectories which are diverted from HgX* or XeX* formation correspond to events which yield high vibrational energy products. The reaction of $Kr({}^{3}P_{2})$ with Cl₂ seems to be such an example and the excitation-transfer channel (Cl₂* formation) receives trajectories that would normally give high $E_{\rm v}({\rm KrCl}^*)$. Martin and co-workers^{8c} explain Cl₂* formation with an interesting phase matching model that facilitates return of trajectories from $V(Kr^+, Cl_2^-)$ to $V(Kr, Cl_2^*)$. This corresponds to the stretching of $R(Kr^+-Cl_2^-)$ before the motion of $R(Cl^--Cl)$ removes the trajectories from the coupling region of the potential surface, see Figure 11. Although the trends in $\langle f_V(MX) \rangle$ for a given RX series are the same for Ba, Yb, Hg(³P₂), and $Xe({}^{3}P_{2})$, the different absolute $\langle f_{V} \rangle$ for individual metal atoms implies that significant differences exist in the $V(M^+, RX^-)$ potential surfaces. The $V(Xe^+,XR^-)$ and $V(Ba^+,XR^-)$ probably differ significantly from each other and from alkali metal atoms at short range because of the very different open shell structures of Xe⁺ and Ba⁺. If a better understanding of the dynamics for electron attachment by the various halogen containing molecules was available, effects associated with the different positive ions on the $V(M^+, RX^-)$ potential could be better considered. In this context the activation energies for Na reacting³⁵ with CFCl₃, CF₂Cl₂, and CF₃Cl, which increase as 1.5, 4.5, and 8.8 kcal mol⁻¹ in accordance with the trend in thermal attachment rate constants (or cross sections), is noteworthy. The dynamical interpretation of the bimodal BaBr vibrational distribution^{36a} found for Ba⁺ CF₃Br must be related to the $Hg(^{3}P_{2})$ reactions with caution, because only a small fraction of the $Hg(^{3}P_{2})$ quenching by CF₃Br gives HgX^{*} , i.e., if the competing "dark" channels did not exist would the HgX(B) distributions differ significantly from those observed?^{36b}

⁽³³⁾ Although $(f_V(XeCl))$ did decrease slightly for CCl₃F relative to CCl₄, the change is not large, ref 3.

^{(34) (}a) Dirscherl, R.; Lee, H. U. J. Chem. Phys. **1980**, 73, 831 and reference noted therein. (b) Holmes, B. E.; Setser, D. W. In *Physical Chemistry of Fast Reactions*; Smith, I. W. M., Ed.; Plenum: New York, 1980; Vol. 2. Caution must be used in comparing $\langle f_V(BaX) \rangle$ values because authors have used different $D_0(BaX)$ values in the computation of $\langle E \rangle$. (35) Husain, D.; Marshall, P. J. Chem. Soc., Faraday Trans. 2, **1985**, 81,

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In fact, the crucial question for understanding the quenching of Hg(6s,6p) atoms by polyatomic halide containing molecules is identification of the nonchemiluminescence product channels. The even smaller $\Gamma_{HgX^{\bullet}}$ from reactions of the lower energy spin-orbit Hg(6s,6p) states is probably a consequence of the smaller crossing position for $V(Hg^*, RX^-)$ and $V(Hg^*, RX)$, which enhances competing exit channels, although there may be some selectivity associated with the natural correlation from the different Ω potentials correlating to the ${}^{3}P_{2}$, ${}^{3}P_{1}$, and ${}^{3}P_{0}$ states.^{1b,10,37}

The limits for the bond energies of the N-Cl-containing compounds are in the 52-55 kcal mol⁻¹ range. The limit for CF₃N-Cl-Br is somewhat lower, ≤ 46 kcal mol⁻¹, as would be expected. To our knowledge there are no other measurements available for comparison. These values are similar to the upper limit of 57.3 kcal mol⁻¹ for $D(NCl_2-Cl)$ based upon observation³⁸ of chemical reaction between Cl atoms and NCl₃, but larger than $D_0(ON-Cl)$ and $D_0(O_2N-Cl)$, which are in the 35-40 kcal mol⁻¹ range. The HgCl(B) vibrational distributions from the four nitrogen chloride molecules are similar, but not identical. The limit set for D_0 -(BrCF₂CF₂-I) seems reasonable when compared to similar compounds.23b

Several polyatomic molecules were chosen to investigate the competition between two HgX(B) exit channels. In most cases only the heavier mercury halide product was observed. The ClF₂C-NClF and F₃C-NClBr molecules are particularly interesting because HgF(B), HgCl(B), and HgBr(B) are observed from the appropriate nitrogen halide precursor and the selectivity demonstrates the favoring of a specific channel in the competitive situation. The lowest unfilled molecular orbital for a RNClBr type molecule is an antibonding orbital situated mainly on the halogen atom with the smaller ionization potential, i.e., the heavier halogen, in spite of the slightly greater EA of Cl(3.651 eV) vs. that for Br(3.364) eV.³⁹ Putting the electron on the lighter halogen atom would correspond to an excited state of the radical anion. Thus, the product selectivity can be explained from the localization of the electron in an antibonding molecular orbital that mainly is on the heavier halogen atom together with the dissociation correlating to the heavier halogen ion; e.g., the Brchannel is lower in energy than the Cl⁻ channel because D_0 - $(RNCl-Br) < D_0(RNBr-Cl)$. The situation is similar for CCl_3Br , and the radical anion has the electron in a σ^* antibonding orbital localized mainly on the C-Br bond. The dynamics for the BrC- F_2CF_2I reaction probably is different; the EA of $I(3.061 \text{ eV})^{39}$ is lower than for Br and the thermochemistry for the two channels is rather similar, although I⁻ formation still is slightly more exoergic. Possibly the two channels are essentially isolated and resemble the CF₃Br and CF₃I reactions. If the effective vertical EA for formation of $Br-(CF_2CF_2I)$ is considerably smaller than for $(BrCF_2CF_2)-I^-$, the curve-crossing position in the HgBr(B) formation channel would be on the repulsive part of $V(Hg^*,RX)$ and this would explain the selectivity for HgI(B).

A high propensity for the CN product channel exists for metal atom and $Xe({}^{3}P_{2,1})$ atom reactions with the halogen cyanides, 10d,e which implies a mechanism in common with $Hg(^{3}P_{2})$ reactions. We favor the ionic-covalent curve-crossing, reactive-quenching mechanism for $Hg(^{3}P_{2})$ or $Xe(^{3}P_{2})$ with XCN followed by predissociation^{5a} of HgCN^{*} or XeCN^{*}, despite recent claims to the contrary for Ar^{*} with BrCN,⁴⁰ because of the very similar nature of the products from metal or pseudometal atom reactions with XCN and because the rate constants for dissociative attachment of thermal electrons by X-CN are large.³² Furthermore, the excitation transfer between Hg* and CN, which gives a broad CN(B) vibrational distribution, can be argued to proceed via the Hg⁺CN⁻ intermediate. The EA of CN is about 0.8 eV larger that I, which probably is the critical factor governing the product

branching from (Hg⁺,ICN⁻). Photodissociation⁴¹ of ICN is interpreted in terms of a bent upper state, arising from a $\pi \rightarrow \pi^*$ excitation. The excited state readily dissociates and the bond in I-CN* is greatly weakened. The alkali metal atom reactions⁴² with ICN give forward scattering, which implies that ICN⁻ is dissociative in nature, even though the extra electron is in a π^* orbital. Herschbach et al.42 also found forward scattering from reactions of alkali metal atoms with SCl_2 . Since SCl_2^- is expected to be nearly linear, the reaction dynamics associated with the change in the SCl₂ geometry may lead to rotational excitation of the products. Perhaps this partly explains why HgCl(B) and XeCl(B) tend not to be excited to the full thermochemical limit in the SCl₂ and S_2Cl_2 reactions.

B. Diatomic Halogen Reactants. Although the branching fractions decline, the HgX(B) distribution from Hg(${}^{3}P_{0}$) or Hg- $({}^{3}P_{1})$ reactions tend to be of the same form as those from Hg $({}^{3}P_{2})$ atom reactions. The trajectories that find the HgX(B) exit channel apparently do follow the same potential surface, even though they start on different spin-orbit entrance channel potentials. The spin-orbit dependence of the product branching fractions will not be considered further.^{1b} In the following discussion, attention is focused on the Hg(³P₂) reactions for which $\Gamma_{HeX*} \approx 1.0$.

We have extended the $Hg(^{3}P_{2})$ atom studies to include ICl and IBr, reinvestigated Cl_2 , Br_2 , and I_2 , and made new analyses for the energy disposal from the collision-free, HgX(B-X) chemiluminescence spectra. The new $\langle f_V \rangle$ assignments are slightly smaller than before, but still decline in the Cl_2 , Br_2 , and I_2 series. The HgX(B) vibrational distributions are shown in Figure 10. The $\langle f_{\rm V} \rangle$ values for the steady-state distributions are 0.55, 0.44, and 0.39 vs. 0.75, 3 0.4866, 50-0.56, 2 and 0.426a, 50-0.462 for Cl₂, Br₂, and I_2 with Hg(³P₂) and Xe(³P₂), respectively. The $\langle f_V \rangle$ values for the initial distributions are about 10% lower for XeX and about 5% lower for HgX (see Table VI). The $\langle f_V(HgCl) \rangle$ is less than for $\langle f_{\rm V}({\rm XeCl}) \rangle$; however, the $\langle f_{\rm V} \rangle$ values for the bromides and iodides are similar for the two systems. The product branching for ICl and IBr with $Hg({}^{3}P_{2})$ are similar to those for $Xe({}^{3}P_{2})^{4a}$ with the more excergic channel being favored by about a factor of 2, see Table II. The HgX(B) vibrational distributions from ICl and IBr are nearly the same as from the respective homonuclear reactants; i.e., the energy disposal seems to depend more upon the HgX(B) product than upon the starting halogen molecule. Although the spectra have not been as extensively analyzed, the same trend holds for the $Xe({}^{3}P_{2,1})$ reactions with the mixed halogens, as can be seen by examination of the XeX(B-X)spectra.3,4a,8d

With this new information about the X_2 and XY reactions, at least three broad questions can be addressed.

(i) What is responsible for the reduction in $\langle f_V(HgCl) \rangle$ relative to $\langle f_V(XeCl) \rangle$ and for the systematic decline in $\langle f_V(HgX) \rangle$ and $\langle f_{\rm V}({\rm XeX}) \rangle$ in the Cl₂, Br₂, I₂ series? A corollary is the explanation for why $\langle f_V(HgI) \rangle$ is less than $\langle f_V(HgCl) \rangle$ from the ICl reaction.

(ii) Is there evidence for formation of $X(^{2}P_{1/2})$, as well as $X(^{2}P_{3/2})$, in the Hg($^{3}P_{2}$) or Xe($^{3}P_{2}$) atom reactions? A corollary is the degree of involvement of the excited X_2^{-*} or XY^{-*} states.

(iii) Why are the $\langle f_{\rm V}({\rm HgX}) \rangle$ and $\langle f_{\rm V}({\rm XeX}) \rangle$ values from the Br_2 , IBr, and I_2 reactions so much lower than for the alkali and alkaline earth metal atom reactions?^{2,34b,43}

Recent molecular beam studies of $Xe({}^{3}P_{2})$ atom reactions have some bearing on these questions. The polarization of the XeX* chemiluminescence from the Cl₂, Br₂, and I₂ reaction increases with collision velocity and the degree of product alignment closely matches results from metal atom reactions,^{8a} which strengthens the analogy between Xe(6s) atom and metal atom reactions. However, in the thermal velocity regime the degree of XeX* alignment is actually quite low and is in the order $I_2 > Br_2 > Cl_2$. These results reflect the importance of short-range parts of the potential surfaces and show that these forces depend on the given

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halogen molecule. Martin and co-workers^{8d} have studied $Xe({}^{3}P_{2})$ with polarized IBr; the total reaction cross section was largest for approach of Xe* parallel to the plane of rotation of IBr and smallest for the perpendicular approach. This observation, as well as the XeI* formation channel, was discussed in terms of the IBr⁻⁽² Π) excited state, which correlates to XeI* + Br, as the intermediate ion state. Recent theoretical work by Gislason and co-workers⁴⁴ has emphasized that vibrational motion in X_2 can be as important as relative translational motion in coupling the covalent and ionic diabatic potentials. This idea may be important in explaining dynamical trends in the X_2 series, since $\omega_e(X_2)$ and the relative locations of the X_2 and X_2^- potentials change with halogen.43 This work44 also provides an explanation for why the "effective reactive" electron affinity for X_2 need not be the vertical electron affinity in harpooning-type reactions.

In our opinion the large difference in vibrational energy disposal for the Cl_2 and Br_2 or I_2 reactions and between the HgCl(B) and HgI(B) channels for ICl cannot be explained by the anticipated differences in the adiabatic potential surfaces constructed from the $X_2^{-}(2\Sigma_u^+)$ states.⁴³ We suggest that the reactions giving low vibrational energy must involve, in part, a potential surface incorporating the $X_2^{-(2\Pi_g)}$ state, which will have a rather different repulsive energy release compared to the potential surface based on the $X_2^{-(2\Sigma_u^+)}$ state (see Figure 11a). This is an especially attractive explanation for the ICl and IBr reactions because the XeCl* or HgCl* and XeBr* or HgBr* channels correlate mainly (but not exclusively) with the ${}^{2}\Sigma^{+}$ state of ICl⁻ and IBr⁻, whereas the XeI* and HgI* products correlate only with the $^{2}\Pi$ states of ICl⁻ and IBr⁻. From the trend in the $\langle f_V \rangle$ values, this argument suggests that the $Xe^* + Cl_2$ reaction mainly proceeds by the potential arising from $Cl_2^{-(2\Sigma_u^+)}$, whereas the Br₂ and I₂ reactions involve potentials based on both the ${}^{2}\Sigma_{u}^{+}$ and the ${}^{2}\Pi_{g}$ states. The Hg* + Cl₂ case is somewhat ambiguous, since $\langle \tilde{f}_V(HgCl) \rangle$ is intermediate. This line of reasoning is supported by the relative positions of the $X_2({}^{2}\Pi_{e})$ potentials recently recommended by Wentworth and Chen.⁴⁵ The vertical electron affinities in the Cl₂, Br₂, and I₂ series for the $X_2^{-}(^{2}\Pi_g)$ states are -2.5, -0.5, and -0.03 eV, respectively. Although the ${}^{2}\Pi_{g}$ potentials are above the neutral X₂ potential at $R_e(X_2)$, the ${}^2\Pi_g$ potential does become increasingly accessible in the series. The crossing positions are at $R > R_e$, and prestretching of X_2 by the approach of Hg^{*} or Xe* will make $X_2^{-}(^{2}\Pi_{\alpha})$ even more accessible. The positions of the ²II curves for ICl and IBr are not known, although the adiabatic electron affinities for the ${}^{2}\Sigma^{+}$ states are large, 2.5-2.4 eV.⁴⁶ In fact, the positions of the ${}^{2}\Pi_{g}$ curve for X₂ still are in dispute,^{45,47} depending upon the method used to study them. In summary, a variable degree of involvement of the $X_2^{-(2\Pi_g)}$ or $XY^{-(2\Pi)}$ potentials could explain the change in $\langle f_V(HgX) \rangle$ or $\langle f_V(XeX) \rangle$ in the X₂ series or between Xe* vs. Hg*. The symmetry constraints arising from the different types of outer electrons and different atomic ion cores for $Xe(5p^{5}6s, {}^{3}P_{2})$ and $Hg(6s6p, {}^{3}P_{2})$ could be factors affecting the relative importance of the two negative ion states.

The apparent large difference between the energy disposal of alkali metal atoms vs. Hg* or Xe* can be discussed using the same framework. In general, the alkali metal atom reactions^{34b,48} are thought to give $\langle f_V(MX) \rangle \gtrsim 0.8$ with no obvious dependence on M or X_2 . However, a study⁴⁸ of Ca, Sr, and Ba reactions with ICl found a large difference in recoil velocities for the two channels with MI being larger by a factor of ~ 3 . This means that the MI channel had less vibrational energy, which is exactly analogous to our results for Hg* and Xe* with ICl. There also was con-

siderable difference in the scattering pattern with MI being more broadly scattered. The general view^{48,49} is that the M + XYreactions proceed via the $XY^{-}(^{2}\Sigma^{+})$ and $XY^{-}(^{2}\Pi)$ surfaces mentioned above. Apparently, the alkali metal atom reactions with X₂ proceed mainly upon the lowest adiabatic potential surface derived from $X_2^{-(2\Sigma_u^+)}$, whereas the Hg* and Xe* cases involve two surfaces, especially for Br_2 and I_2 .

In our prior interpretation of the energy disposal for Hg* and Xe* atom reactions, we suggested that a variable degree of X- $({}^{2}\mathbf{P}_{1/2})$ product formation could explain the trends in $\langle f_{V} \rangle$ for Cl₂, Br₂, and I₂, since the $X(^{2}P_{1/2})$ spin-orbit energy increases in this series. There is no direct experimental evidence to support this suggestion and the tendency for the new XeX^{6a,b,50} and HgX distributions to have less obvious two-component character reduces our enthusiasm for this idea. Furthermore, the ICl experiments argue against such an interpretation. If $I({}^{2}P_{1/2})$ was a product, the $\langle f_V(HgCl) \rangle$ from ICl should have been much lower than from Cl_2 and the $\langle f_V(HgBr) \rangle$ from IBr lower than from Br_2 .⁵¹ In fact, these distributions are similar to the X2 reactions. Thus, we doubt that $X({}^{2}P_{1/2})$ formation is a significant factor for the change in $\langle f_{\rm V}({\rm HgX}) \rangle$ or $\langle f_{\rm V}({\rm XeX}) \rangle$ in the Cl₂, Br₂, and I₂ series. After this manuscript was complete, we received a preprint from Simons and co-workers 50 which also advocated the $X_2({}^2\Pi_g)$ potential, rather than Xe(^2P_{1/2}) formation, to explain the variable $\langle f_V(XeX)\rangle$ in the Cl_2 , Br_2 , I_2 series.

Martin and co-workers discussed the ways that Xe* trajectories can reach the potential surface corresponding to $IBr^{-}(^{2}\Pi)$. Two possibilities are inefficient coupling to the IBr⁻($^{2}\Sigma^{+}$) potential in the $V(Xe^*, IBr)$ entrance channel followed by transfer to $IBr^{-(2\Pi)}$ potential at a second crossing at a smaller $R(Xe^*-IBr)$ distance, or a mixing between the two $V(Xe^+, IBr^-)$ and $V(Xe^+, IBr^{-*})$ potential surfaces at short range. The location of the crossing with IBr(² Π) inferred from diabatic curves for Hg(³P₂) suggests that the second crossing may be inaccessible at thermal energies. On the other hand, if the trajectories only reach the IBr($^{2}\Pi$) based surface late in the exit channel, the $\langle f_V(\text{HgI}) \text{ or } \langle f_V(\text{XeI}) \rangle$ values probably would not be seriously affected. An effort to construct some realistic potentials, perhaps using the method of Gislason,⁴⁴ is needed to provide more insight into how trajectories can reach the surface corresponding to the $X_2^{-}(^2\Pi_g)$ or $XY(^2\Pi)$ states. In the absence of such information, we infer that trajectories for the cases with low $\langle f_V(\text{HgX}) \rangle$ do reach the $V(\text{Hg}^+, X_2^{-}(^2\Pi))$ potential early in the course of the reaction because of coupling between the two ion pair surfaces; this may be a consequence of prestretching which alters the "effective" vertical electron affinities, perhaps from electron migration⁵² during the reactive collision due to the position of Hg⁺ or Xe⁺, or from a change in favored approach geometry for the various halogen molecules.

Conclusions

The flowing-afterglow technique has been used to observe $HgX(B^{2}\Sigma^{+}\!-\!X^{2}\Sigma^{+})$ chemiluminescence from the reactions of $Hg({}^{3}P_{2})$ metastable atoms with several halogen (X = Cl, Br, I)-containing molecules. The chemiluminescence was used to assign rate constants for HgX(B) formation and nascent vibrational distributions. The latter were obtained via computer simulation of the spectra, which was based upon improved models for the potentials and transition dipole functions for HgCl, HgBr, and HgI. The $\langle f_{\rm V}({\rm HgX}) \rangle$ values range from 0.4 to 0.6 for reactions with significant $\Gamma_{\text{HgX}*}$ values. The energy disposal pattern is used to discuss the reaction dynamics of $Hg(^{3}P_{2})$ reacting with halogen-containing molecules in terms of the analogous harpooning

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⁽⁵¹⁾ Some caution should be maintained because the $X_2^{-(2\Pi_g)}$ states do correlate, in part, to $X^- + X({}^2P_{1/2})$ whereas the ICl(${}^2\Pi$) state does not. (52) Kuntz, P. J.; Mok, M. H.; Polanyi, J. C. J. Chem. Phys. **1969**, 50, 4623.



Figure 12. Plot of relative HgCl(B-X) intensity, the monitor for [Hg- $({}^{3}P_{2})$], vs. Hg concentration. The maximum intensity, I^{0} , is normalized for each carrier gas; however, $I^{0}(Ar) > I^{0}(Ne) > I^{0}(He)$.



Figure 13. Plot of $(Hg_2^* \rightarrow 2Hg + h\nu)$ emission intensity vs. the square of the mercury concentration. As would be expected, the three-body recombination rate constants giving Hg_2^* are in the order $k_{Ar} > k_{Ne} > k_{He}$.



Figure 14. Plot of the $Hg(^{3}P_{1}-^{1}S_{0})/NO(A-X)$ emission intensity ratio vs. Hg concentration. The decline in the ratio results from radiation trapping of the resonance 253.7-nm line by Hg atoms.

mechanism of metal atom reactions. Emphasis is placed upon the nature of the $V(\text{Hg}^+, X_2^-)$ or $V(\text{Hg}^+, XR^-)$ potentials in the exit channel. The higher $\langle f_V(\text{HgCl}) \rangle$ relative to $\langle f_V(\text{HgI}) \rangle$ from ICl and for the reaction of Cl₂ vs. I₂ is rationalized by suggesting the participation of a second potential surface consisting of the electronically excited I₂⁻⁽²Π_g) or ICl⁻⁽²Π) states for I₂ and ICl, respectively. The reaction of Hg(³P₂) with ICN gives CN(A) emission via excitation transfer in a secondary reaction. In general, there is a close analogy between the reactions of Hg(³P₂) and Xe(³P₂) with respect to the branching fractions for HgX* and XeX* formation and for vibrational energy disposal. The Hg-



Figure 15. Plot of HgCl(B-X) intensity (the monitor of $[Hg, {}^{3}P_{2}]$) vs. discharge voltage for various pressures of He, Ne, and Ar. The results of this plot can be combined with results of Figure 12 to obtain the overall best conditions for generating Hg(${}^{3}P_{2}$) in the flowing-afterglow reactor.

 $({}^{3}P_{0,2})$ flowing-afterglow reactor is described in the Appendix.

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Appendix. Characterization of the Flowing-Afterglow Source for $Hg(^{3}P_{2})$ and $Hg(^{3}P_{0})$ Atoms

Investigation of the $Hg({}^{3}P_{2})$ and $Hg({}^{3}P_{0})$ atom reactions required characterization of the flowing-afterglow reactor as a source of metastable Hg^{*} atoms. Therefore, several parameters affecting the [Hg^{*}], such as the mercury reservoir temperature and the nature and pressure of the carrier gas, were systematically studied. The [Hg, ${}^{3}P_{2}$] was monitored by observing the HgCl(B-X) emission intensity resulting from the reaction of Hg(${}^{3}P_{2}$) with Cl₂.

An important practical consideration for obtaining stable metastable atom concentration was a constant liquid N_2 level in the Dewars for the molecular sieve traps used to purify the carrier gas. As the liquid N2 was depleted, both the reactor pressure and mercury concentration gradually changed. The ground-state Hg concentration was found to be especially important with respect to the optimum [Hg*], as well as for radiation trapping of the $Hg({}^{3}P_{1}-{}^{1}S_{0})$ resonance line. The Hg concentration was adjusted by controlling the temperature of the refluxing column of Hg through which the prepurified carrier gas flow passed. The carrier gas, assumed to be saturated with mercury at the measured temperature and pressure at the top of the reflux column, was transported to the reaction zone through heated (75 °C) lines to prevent Hg vapor condensation. The mercury concentration in the reactor was given by the [Hg] at the top of the condenser multiplied by the ratio of the total pressure in the reactor to that at the top of the refluxing column.

The variation of the HgCl(B-X) emission intensity with [Hg] is shown graphically in Figure 12 for Ar, Ne, and He carrier gases. Clearly the [Hg(${}^{3}P_{2}$)] depends on both [Hg] and the nature of the carrier gas. Examination of Figure 12 shows that $I_{HgCl^{+}}$ increases linearly with rising [Hg] for a limited range of [Hg]. At higher [Hg] the HgCl(B-X) emission intensity, or [Hg, ${}^{3}P_{2}$], became approximately constant for a given carrier gas pressure. The curves for the different carrier gases are normalized and the

plateaus do not correspond to the same [Hg^{*}]. The plateau for $Hg(^{3}P_{2})$ formation results, in part, because of a loss process that depends on [Hg], i.e., the conversion of $Hg(^{3}P_{2})$ and $Hg(^{3}P_{0})$ to Hg_{2}^{*} by three-body recombination.

$$Hg^* + Hg + Ar \rightarrow Hg_2^* + Ar$$
 (A1)

$$Hg_2^* \rightarrow 2Hg + h\nu (335 \text{ nm})$$

The excited-state mercury dimer Hg_2^* can be detected by observation of the 335-nm emission. The dependence of this emission intensity upon [Hg] and Ar pressure is shown in Figure 13; the Hg_2^* formation is second order in Hg since in this concentration range [Hg^{*}] is proportional to [Hg]. In fact, this flowing-afterglow mercury metastable reactor should be a good way to study the three-body recombination of the $Hg(^{3}P_{2})$ and $Hg(^{3}P_{0})$ atoms in He, Ne, and Ar buffer gases; however, such work was not attempted for this study. This flowing-afterglow technique might also permit isolation and characterization of long-lived Hg_2^* states by doing experiments at longer times in the flow reactor.

The quenching of the $[Hg(^{3}P_{2})]$ can lead to formation of $Hg(^{3}P_{1})$. In order to accurately determine the $Hg(^{3}P_{1})$ formation rate, the radiation trapping of the $Hg(^{3}P_{1}-^{1}S_{0})$ transition at 253.7 nm was characterized as a function of [Hg]. This was accomplished by monitoring the $Hg(^{3}P_{1}-^{1}S_{0})$ and the NO(A-X) relative emission intensities from the reaction with NO

$$Hg({}^{3}P_{2}) + NO \rightarrow NO(A, v'=0) + Hg \qquad \Delta H^{\circ}_{0} = 0.5 \text{ kcal mol}^{-1} \text{ (A2)}$$
$$\rightarrow Hg({}^{3}P_{1}) + NO \qquad \Delta H^{\circ}_{0} = -13 \text{ kcal mol}^{-1}$$

 \rightarrow other channels

The observed $I(Hg(^{3}P_{1}))/I(NO,A)$ ratio, f, as a function of [Hg] is shown in Figure 14. The increase of the ratio with declining [Hg] is a consequence of diminished radiative imprisonment. For the intramultiplet relaxation studies reported in the main paper,

[Hg] was $(0.8-1.6) \times 10^{13}$ atom cm⁻³ and a correction to the observed $I(Hg, ^{3}P_{1})$ for the degree of radiation imprisonment was made according to the results shown in Figure 14.

The vibrational relaxation⁵³ of the HgX(B) formed in high vibrational levels by chemical reaction was a subject of interest. For that reason the operation of the metastable mercury atom flowing-afterglow was characterized for a broad range of He, Ne, and Ar pressure. The results are summarized in Figure 15. As the pressure is increased, the discharge voltage must be decreased for optimal Hg(${}^{3}P_{2}$) production. Experiments were done up to 25 Torr for the three carrier gases; even higher pressures could be used if a larger pump was utilized to reduce the flow time between the discharge and observation zone. As illustrated in Figure 12, higher [Hg] is required for Ne and He carrier gases than with Ar for optimum [Hg, ${}^{3}P_{2}$]. This is probably a consequence of faster diffusion of Hg(${}^{3}P_{2}$) to the walls followed by quenching in the lighter gases.

Registry No. ICl, 7790-99-0; IBr, 7789-33-5; CCl₄, 56-23-5; CCl₃F, 75-69-4; CHCl₃, 67-66-3; CH₂Cl₂, 75-09-2; CH₃Cl, 74-87-3; COCl₂, 75-44-5; CCl₃Br, 75-62-7; CBr₄, 558-13-4; CF₂ClBr, 353-59-3; CF₂Br₂, 75-61-6; CHBr₃, 75-25-2; ICF₂CF₂Br, 421-70-5; PCl₃, 7719-12-2; SCl₂, 10545-99-0; S₂Cl₂, 10025-67-9; PBr₃, 7789-60-8; F₂CNCl, 28245-33-2; F₃CNCl₂, 13880-73-4; CIF₂CNClF, 33757-11-8; CIF₂CNCl₂, 28245-34-3; F₃CNClBr, 88453-17-2; ICN, 506-78-5; BrCN, 506-68-3; CF₃CINCl₂, 28245-34-3; CF₂CINFCl, 33757-11-8; CIF₂CINCl₂, 28245-34-3; CF₂CINFCl, 33757-11-8; CF₂CINCl₂, 28245-34-3; CF₂CINFCl, 33757-11-8; CF₂NCl₂, 28245-34-3; CF₂CINFCl, 33757-11-8; CF₂NCl₂, 28245-33-2; K₂CINFCl, 33757-11-8; CF₂NCl₂, 28245-34-3; CF₂CINFCl, 33757-11-8; CF₂NCl₂, 28245-33-2; CI₂, 7782-50-5; Br₂, 7726-95-6; I₂, 7553-56-2; Hg, 7439-97-6.

Molecular Beam Photodissociation Study of Methyl Nitrite in the Near-Ultraviolet Region

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The photodissociation of methyl nitrite (CH₃ONO) at 350, 248, and 193 nm was studied by photofragment translational spectroscopy in a pulsed molecular beam. Translational energy distributions $P(E_t)$ in the center-of-mass (CM) frame were derived from the time-of-flight spectra of the neutral photofragments CH₃O and NO. Angular distributions of the photoproducts were determined by measuring the dissociation yield as a function of the laser polarization angle, providing anisotropy parameters $\beta(350 \text{ nm}) = -0.70 \pm 0.05$ and $\beta(248 \text{ nm}) = +1.4 \pm 0.1$. These strongly anisotropic distributions imply that the dissociation process occurs on a subpicosecond time scale. Photodissociation at 350 nm is discussed in conjunction with a LIF study of the NO internal state distributions. At 248 nm the transition moment is almost parallel to the fragment recoil direction and dissociation is thought to occur on a strongly repulsive upper-state potential energy surface. At 193 nm the average translational energy amounts to $43 \pm 1\%$ of the available energy. This fraction is significantly smaller than the $53 \pm 2\%$ found at 248 nm.

Introduction

The investigation of photodissociation processes of polyatomic molecules has become a profitable way to elucidate the microscopic dynamics of chemical reactions.^{1,2} Among the various experimental approaches, probing of the product states by laser-induced fluorescence (LIF) on the one hand and molecular beam photofragment translational spectroscopy on the other hand have been

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⁽⁵⁴⁾ In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)

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particularly fruitful. These two methods differ in their advantages and disadvantages and can be considered complementary. LIF spectroscopy in combination with Doppler spectroscopy, fully exploiting various polarization schemes, has in favorable cases been capable of yielding an almost complete microscopic characterization of dissociation processes.³⁻⁵ In contrast, photofragment spectroscopy with mass spectrometric product detection may not

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