

EXCIPLEX LASER KINETICS

Everett MA 02149

Avco Everett Research Laboratory, Inc.

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2385 Revere Beach Parkway

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REPORT SUMMARY

Efficient scaling of mercury monohalide lasers to high average power requires knowledge of the processes responsible for the formation and quenching of the upper laser level. From the formation kinetics one can determine the upper state production efficiency. The quenching kinetics enables one to choose the appropriate mix and determine the laser saturation flux. These processes together with the upper and lower level relaxation in XeF have been studied this year at AERL.

In this report we outline the investigation involved in determining the quenching of $\text{HgCl} \star (B^2 \Sigma_{1/2}^+)$ and $\text{HgBr} \star (B^2 \Sigma_{1/2}^+)$ which are the upper levels of these laser systems. Collisional quenching by the rare gases and various halogen donor candidates was measured using a Xe flashlamp to photolytically pump HgX_2 (X = Cl, Br) salts to produce $\text{HgX} \star B$ state.

Measurements were made of rates of quenching of HgCl* $(B^{2}\Sigma_{1/2}^{+})$ by He, Ne, Ar, Kr, Xe, N₂, Cl₂, HCl, and CCl₄ at pressures below 3000 torr and of HgBr* $(B^{2}\Sigma_{1/2}^{+})$ by He, Ar, Xe, N₂, Br₂, CF₃Br, CCl₃Br at pressures below 1000 torr.

Lasing and fluorescence measurements at AERL on the HgCl* system indicate that none of the measured rates is fast enough to explain the results. A possible candidate which we have identified that could rapidly quench HgCl* $(B^2\Sigma_{1/2}^+)$ is Hg. The rate of quenching of HgCl* $(B^2\Sigma_{1/2}^+)$ by Hg is an important rate which should be measured. $17812 \cdot 1031$

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I. INTRODUCTION

Efficient scaling of mercury monohalide lasers to high average power requires knowledge of the processes responsible for the formation and quenching of the upper laser level. From the formation kinetics one can determine the upper state production efficiency. The quenching kinetics enables one to choose the appropriate mix and determine the laser saturation flux.

An apparatus has been set up in which measurements of the formation processes viz.

 $Hg^{*} ({}^{3}P_{1}) + AX \rightarrow HgX^{*} + Ar$ (1) $Hg^{*} ({}^{3}P_{0})$

(where X = Cl, Br) are presently being made. A schematic diagram of the apparatus is shown in Figure 1.

Quenching measurements have been made in a second device. In this device HgCl* is photolytically produced by optically exciting $HgCl_2$. The same apparatus can be used to excite other metal and rare gas complexes. The device is small, allowing rapid screening using repetitive pulsing and signal averaging techniques. A detail description of the apparatus appears in Section II.

Measurements of the rates of collisional quenching of HgCl* $(B^2 \Sigma_{1/2}^+)$ by He, Ar, Xe, N₂, Cl₂, HCl and CCl₄ are described in



Figure 1 Schematic Diagram of Apparatus for HgX* Formation Experiments

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Section III. Steady state measurements are made of HgCl* fluorescence by photolyzing HgCl₂ using Xe^{*}₂ radiation. A background pressure of [Xe] \geq 100 torr ensures that the HgCl* is vibrationally relaxed. He, Ar and N₂ exhibited small quenching rates while Xe did exhibit a three body dependence for high pressure. These rates are derived by using an estimated HgCl* (B² $\Sigma^{+}_{1/2}$) lifetime of 29 nsec.

A significant number of measurements has been made of HgCl* and HgBr* quenching. Tables I and II summarize the results of these measurements.

TABLE I

HgCl* QUENCHING

(Assuming $\tau_{HgCl} \star = 29$ nsec)

Q	<u>kot</u>		kq	
Не	9×10^{-22}	cm ³	3.1×1^{-14}	cm ³ /sec
Ne	7.3 x 10^{-22}	cm ³	2.5×10^{-14}	cm ³ /sec
Ar	1.1×10^{-21}	cm ³	3.8×10^{-14}	cm ³ /awx
Kr	1.6×10^{-21}	cm ³	5.6 x 10^{-14}	cm ³ /sec
Xe	6.9×10^{-21}	cm^3	2.4 x 10^{-13}	cm ³ /sec (2 body)
Xe	2.7×10^{-40}	cm ⁶	9.2 x 10^{-33}	cm ⁶ /sec (3 body)
N 2	1.4×10^{-21}	cm ³	4.7×10^{-14}	cm ³ /sec
Ct 2	3.8×10^{-18}	cm ³	1.3×10^{-10}	cm ³ /sec
HCl	2.5×10^{-18}	cm ³	8.6×10^{-11}	cm ³ /sec
cce 4	3.5×10^{-18}	cm^3	1.2×10^{-10}	$\rm cm^3/sec$

TABLE 11

HgBr* QUENCHING FOR ^THgBr* = 23 nsec

	$\frac{k_{Q_3}}{(cm^3)}$	(cm ³ /sec)
Не	< 1.5 x 10^{-21}	
Ar	< 1.5 x 10^{-21}	
Xe	7.1 x 10^{-21}	3.1×10^{-13}
N ₂	< 1.5 x 10^{-21}	
Br ₂	6.9×10^{-18}	3×10^{-10}
HBr	3×10^{-18}	1.3×10^{-10}
CF ₃ Br	2.1×10^{-18}	9×10^{-11}
CCl Br	4.4×10^{-18}	1.9×10^{-10}

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II. DEVICE FOR QUENCHING STUDIES ON RARE GAS AND METAL HALIDE EXCITED COMPLEXES

A new class of molecular lasers has been developed over the past few years -- the exciplex lasers. These lasers include the rare gas halides of which KrF, ⁽¹⁾ XeF⁽²⁾ and ArF⁽³⁾ appear to be good candidates for high efficiency and high power and the mercury monohalide lasers of which HqCl ⁽⁴⁾ and HqBr ⁽⁵⁾ also appears to be good candidates. Although the spectra of these species have been excited in various ways they are not fully understood. Low pressure studies using either a flowing afterglow or e-beams generally exhibit broad spectra since the upper state is not vibrationally equilibrated. At high pressure using either e-beam or electric discharge excitation, the intense laser bands become significantly sharper and for cases where the lower state is bound the transitions to different vibrational levels of the ground state become resolved. These conditions are similar to those which result using high pressure laser mixtures. The e-beam or discharge approaches, however, have their limitations for certain kinetic studies. The main problem is the complexity added to the analysis due to the presence of large electron densities.

A new instrument is described here in which the upper levels of these laser systems may be populated by using photolytic pumping, at various pressures, in the absence of electrons.

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This compact device can be of use in spectral and kinetic studies at gas temperatures up to several hundred degrees centigrade. Measurements have been made, to date, on mercury chloride⁽⁶⁾ and mercury bromide.⁽⁷⁾ This paper will describe the experimental technique and its application to the measurement of mercury chloride kinetics. A more detailed analysis of these measurements will be presented elsewhere.

Excited mercury chloride is produced photolytically from mercuric chloride vapor

 $hv + HgCb \rightarrow HgCl * + Cl$.

Wieland has examined ⁽⁸⁾ the excitation of the mercuric halides in detail and has determined that absorption at $\lambda = 1810$ Å maximizes production of HgCl* (B² $\Sigma_{1/2}^+$), while for mercuric bromide $\lambda = 1950$ Å maximizes HgBr* (B² $\Sigma_{1/2}^+$). If on the other hand, one wished to produce HgBr* C or D state then one could pump at 1700 Å or 1600 Å, respectively. Thus, the spectra and excited state kinetics of the various mercury halides, other metal halides and even the rare gas halide systems, all of which are of current laser interest are accessible for study in an electron free environment.

A schematic diagram of the experimental apparatus is shown in Figure 2. The reaction cell containing HgCl_2 is heated in a dual oven arrangement. The reservoir portion of the cell is maintained at a temperature, T_1 , which is typically ~ 90°C providing a HgCl_2 vapor pressure of ~ 50 µm. The main body of the cell is at a higher temperature, $T_2 \sim 200°$ C, to ensure that no mercuric chloride condenses on the sapphire cell window.

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The Xe lamp is made of quartz with a sapphire output window similar in design to one described by Hoffman, Tanaka and Larrabee. ⁽⁹⁾ The lamp is drawn essentially to scale in Figure 2 in which the cooling jacket is 25 mm in diameter. Reliable operation is achieved using Al electrodes of 99.999% purity and evacuating the lamp and cell to the low 10^{-7} torr range. The lamp is run with pure Xe at pressures between 150 torr and 250 torr much in the same way as described by Gedanken, et al. ⁽¹⁰⁾ The emission from the lamp in the vacuum ultraviolet is from Xe₂* and peaked at 1750 Å, however, the lamp also emits throughout the ultraviolet and visible spectrum. Since the HgCl* fluorescence signal of interest is also in the visible, the lamp background at these wavelengths is reduced by the use of a filter peaked at 1810 Å. For measurements on mercury bromide a filter peaked at 1950 Å has been used.

The Xe lamp is pulsed with 20 kV at ~ 350 Hz with a pulsewidth ~ 1 µsec. A schematic diagram showing the pulsing circuit is shown in Figure 3. HgCl* fluorescence signals are detected either directly on a photomultiplier through an 80 nm bandpass filter to isolate the B + X emission bands or through a monochormator ($\Delta l = 6$ nm) as shown in Figure 2. The signals are averaged on a boxcar integrator (PAR Model 160) and displayed on an x-y recorder. Typical spectral data are shown in Figure 4. The top trace shows the observed HgCl* emission obtained with 50 µm pressure of HgCl₂. The time to sweep through such a spectrum is roughly 15 min. The bottom trace of Figure 4 shows a HgCl* emission spectrum taken under conditions similar to the top trace but with 200 torr of Xe buffer gas added.

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Figure 2 Schematic Diagram of Experimental Apparatus for HgX* Quenching Experiments

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Figure 4a Measured HgCl* Emission with $[HgCl_2] = 50 \ \mu m$

4b Measured HgCl* Emission with $[HgCl_2] = 50 \ \mu m$ and [Xe] = 200 Torr. The signal scale is the same as in Figure 4a.

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Planimeter measurements of Figures 4a and 4b show comparable areas (total energy emitted) for these two cases which indicates negligible HgCl* quenching at this Xe pressure. However, the dramatic change in the spectrum arises from the rapid relaxation of the HgCl* vibrational levels by Xe. The significant difference between the two traces occurs because in the upper trace the HgCl* $(B^{2}\Sigma_{1/2}^{+})$ vibrational manifold is not relaxed so that emission from v' = 0, 1, 2, 3 etc. is present and results in overlapping bands which broaden and diffuse the spectrum near 5600 Å. In addition a broad shoulder appears with significant contribution extending to roughly 3750 Å which is identified with transmitions from $B^2 \Sigma_{1/2}^+$ levels v' ~ 20-25 to $X^2 \Sigma_{1/2}^+$ levels v" ~ 0-5. When Xe is added at pressures above 100 torr the upper vibrational manifold of HgCl* $(B^2 \Sigma_{1/2}^+)$ is relaxed. Thus, in Figure 4b the various vibrational transitions (0,v") are clearly defined with the most intense peak at $v' = 0 \rightarrow v'' = 22$. This prepares the initial state of the system more precisely and makes studies of, for example, quenching kinetics of $B^2 \Sigma_{1/2}^+$ (v' = 0) straightforward.

In this optical pumping technique, the kinetics analysis can be complicated by the presence of quenching gas absorption at the pump wavelength. An absorption cell located between the lamp and reaction cell is used in additional experiments to measure the absorption cross sections of the various quenching gases at the excitation wavelength. In this experimental configuration the absorption at 1810 R is measured by filling the absorption cell

with the quenching gas and monitoring the resulting decrease in HqCC* fluorescence. Thus, we are able to make a measurement of a vacuum UV cross section, without the use of a vacuum UV monochromator, by observing a visible fluorescence signal. All the components between the lamp and the reaction cell are closely coupled to each other, minimizing intermediate air spaces and the resulting vacuum ultraviolet absorption by O_2 . The end of the absorption cell closest to the reaction cell is apertured to a diameter of ~ 6 mm by applying an Aquadag mask to reduce edge effects such as scattering.

A case in which the quenching molecule absorbs at the excitation wavelength (1810 Å) is the quenching of HgCl* by HCl. The quenching measurements were preceded by a determination of the HCl absorption cross section which was found to be $a_{\rm HCl} \approx 9 \times 10^{-19} \text{ cm}^2$. This cross section agrees with the work of Myer and Samson⁽¹¹⁾ within the experimental uncertainty and will be discussed in detail elsewhere.

III. TWO BODY COLLISIONAL QUENCHING KINETICS OF $HgCl * (B^2\Sigma)$

Laser action has been achieved on the mercury monohalides by pure e-beam pumping, $^{(4,5)}$ electric discharges, $^{(12,14)}$ and also photolytic pumping. $^{(15)}$ In order to optimize the efficiency of these laser systems, a detailed knowledge of the heavy-particle quenching kinetics is important. In this paper, we report measurements of the quenching rate of HgCl* by He, Ar, Xe, N₂, Cl₂, HCl, and CCl₄. These rates were obtained by analyzing the steadystate dependence of the HgCl* fluorescence intensity on the partial pressure of the quenching gas.

Mercury chloride is produced in the excited state, $B^2 \Sigma_{1/2}^+$, by optically pumping HgCl₂ vapor, ⁽¹⁶⁾ at $\lambda = 1810$ Å, which reduces the possibility of producing other excited HgCl species. Spontaneous emission from excited HgCl * molecule in the B+X bands is used to monitor the excited state density. The radiative lifetime of HgCl * has been recently calculated by Duzy and Hyman ⁽¹⁷⁾ as 20 nsec. Considering the uncertainties in this calculation, we have normalized their results to the measured HgBr* lifetime ⁽¹⁸⁾ of 23 nsec and estimate the radiative lifetime of HgCl * as t = 29 nsec.

A modified Stern-Volmer analysis has been applied to the variatiion of emission intensity with pressure of the additive gas to determine the quenching rate constants for various gases

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quenching HgCl*. This optical pumping technique avoids any ambiguities which might be introduced by the presence of electrons.

A schematic diagram of the experimental apparatus is shown in Figure 2. The reaction cell containing HgCl, is heated in a dual-oven arrangement. The reservoir portion of the cell is maintained at a temprature T_1 which is typically ~ 90°C providing a HgCl , vapor pressure of ~ 50 $\mu m.$ The main body of the cell is at a higher temperature, $T_2 \sim 200$ °C, to ensure that HgCl₂ does not deposit on the sapphire cell window. The Xe lamp is similar in design to one described by Hoffman, Tanaka, and Larrabee (9) but it is made of quartz and has a sapphire output window. This lamp pulsed at ~ 350 Hz with pure Xe at pressures between 150 and 250 torr similar to the lamp described by Gedanken et al. (10) Thus, the emission from the lamp in the vacuum ultraviolet is from Xe* and is peaked at 1750 \hat{A} ; however, the lamp also emits throughout the ultraviolet and visible spectrum. A 36 nm bandpass filter peaked at 1810 A selects the HqCl excitation wavelength and reduces the visible light background in the region of HgCl* fluoresence. An absorption cell located between the lamp and reaction cell is used in additional experiments to measure the absorption cross sections of the various quenching gases at the excitation wavelength. In this experimental configuration the absorption at 1810 \AA is measured by filling the absorption cell with quenching gas and monitoring the resulting decrease in HgCl* fluorescence.

The HgCl* fluorescence signals are detected either directly on a photomultiplier tube using a 80-nm bandpass filter to isolate the B+X emission bands or through a monochrometer as shown in Figure 2. The signals are averaged on a boxcar integrator (PAR Model 160) and displayed on an x-y recorder. The top trace [Figure 4a] shows the observed HqCC* emission obtained with 50 µm pressure of HgCl₂. Figure 4b shows an HgCl* spectrum taken under similar conditions but with 200 torr of Xe buffer gas added. Planimeter measurements show comparable areas (total energy emitted) for these two cases which indicates negligible HgCl* quenching. The dramatic change in the spectra arises from the rapid relaxation of the HgCl * vibrational levels by Xe. In the upper trace the HqCl* vibrational manifold is not relaxed so that emission from $v' \ge 0$ is present and results in overlapping bands which broaden and diffuse the spectrum near 5600 Å. This suggests that high vibrational levels of the B state are produced in the photodissociation of HgCl. In Figure 4b, the excited state vibrational levels are relaxed and vibrational transitions from v' = 0 are clearly observed with the most intense peak at v' = 0 + v'' = 22. Several spectra were taken at varying Xe pressures and indicated that $B^{2}\Sigma$ state is vibrationally relaxes at Xe pressures of roughly 100 torr. The fluorescence spectrum in Figure 4b is similar to that observed in HgCl * laser experiments⁽⁴⁾ which used a 3-amagat Ar/Xe laser gas mix. All the quenching data presented below were taken with at least 100 torr of Xe present to ensure that electronic quenching of the upper laser level, v" = 0, was being observed. The quenching by Xe will be shown to be negligible under these conditions.

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The rate equation governing the density of the excited mercury chloride, [HgCl*], yields the steady state HgCl* emission signal

$$S_{Q} = \frac{[\text{HgCl}^{\dagger}]_{Q}}{\tau} = \frac{\exp(-\alpha) \Lambda}{1 + k_{O}[Q]\tau + k^{\dagger}[\text{HgCl}_{2}]\tau}$$
(2)

Here $\alpha = [Q] \circ_Q^{\ell}$, where \circ_Q is the absorption coefficient of the quenching molecule, Q, at the excitation wavelength, and ℓ is the absorption path length. The numerator is proportional to Λ , the source term for production of HgCl* which depends linearly on pump intensity. This source term is thus reduced by the exponential for cases where the quenching molecule absorbs at the excitation wavelength. We now define the ratio of the flourescence signal without quenching to the signal S₀.

$$R = \exp \left(\alpha\right) \left\{ 1 + \frac{k_Q[Q]}{1/\tau + k' [HgC\ell_2]} \right\}$$
(3)

The density of HgCl₂ typically used in these experiments is 1.5 x 10¹⁵ cm⁻³ and even if we assume k' has a gas kinetic rate (k' = 2 x 10⁻¹⁰ cm³ sec⁻¹) we have $1/\tau \gg$ k' [HgCl₂] for $\tau =$ 29 nsec. Thus to a good approximation R exp (- α) = 1 + k_Q[Q] τ and we can use a modified Stern-Volmer analysis which plots R exp (- α) vs [Q] resulting in a strainght line with slope k_Q τ . Since the rare gases do not absorb light at the excitation wavelength, $\alpha = 0$, and the standard Stern-Volmer expression results.

The possibility of a relatively long-lived (1-10 nsec) intermediate excited state HgC(* which could be guenched prior to

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dissociation has been considered. Spectroscopic studies of the photodissociation of the mercury dihalides (19,20) as well as recent laser photolysis (15) of HgBr₂ do not exhibit evidence of such intermediate states. This is consistent with the possibility of numercous curve crossings in the excited states of these triatomics suggested by recent analysis (21) of the potential energy surfaces of HgI₂. Consequently, we will assume that the photodissociation is instantaneous in the analysis.

Measurements were made of the quenching of HgCl * by several of the rare gases and N_2 . He, Ar, and N_2 showed no measurable quenching of the electronic state of HgCl * over the pressure

dies (0-1000 torr). This leads to an upper bound for these uching rates of 5 x 10^{-14} cm³/sec when one takes into account the sensitivity of the experiment and the overall uncertainties of the measurement. The only measurement in the literature to which one might compare is the work of Tibilow⁽²²⁾ which reports no observed quenching of HgCl* by N₂. The only rare gas studied here in which quenching was observed was Xe for which we determined $k_{xe}^{T} = 6.9 \times 10^{-21} \text{ cm}^{-3}$. The observed pressure dependence of the data suggests that this is a two-body process and assuming $\tau = 29$ nsec, the two body quenching rate constant is $k_Q = 2.4 \times 10^{-13} \text{ cm}^3/\text{sec}$. A new high-pressure cell is being constructed in which three-body quenching and the effects of Hg on HgCl* can be examined.

A case in which the quenching molecule absorbs at the excitation wavelength 1810 $\stackrel{\circ}{A}$ is shown in Figure 5. The guenching measurments were preceded by a determination of the HCl absorption cross section which was found to be $\alpha_{\rm HCL} \simeq 9 \times 10^{-19} {\rm cm}^2$. This cross section agrees with the work of Myer and Samson⁽¹¹⁾ and will be discussed in detail elsewhere.⁽⁷⁾ The slope determined from the data of Figure 5 results in a value $k_{HC} t =$ 2.5 x 10^{-18} cm³ which corresponds to a quenching rate constant $k_0 = 8.6 \times 10^{-11} \text{ cm}^3/\text{sec}$ assuming $\tau = 29$ nsec. Quenching rate constants were also measured for CCl_4 and Cl_2 which were used as CL donors in previous e-beam-pumped and discharge-pumped lasing experiments. The measured values of the product k_{OT} for the various atoms and molecules are listed in Table III and we have also deduced the guenching rate constants assuming $\tau = 29$ nsec. The overall uncertainty in these measurements is ± 25%. Although the lifetime has not been accurately determined for HqCl*, it has been shown (23) that important laser parameters such as fluorescence efficiency and saturation flux depend only on the measured product of the quenching rate and upper state lifetime.

Using the quenching rates given above, an estimate of the saturation flux can be obtained for arbitrary mixtures of Ar/Hg/ Cl₂ and Ar/Xe/Hg/CCl₄ which have been used respectively in discharge pumping and e-beam pumping of the HgCl * laser. The measurement of Hg quenching of HgCl * is in progress and here we estimate this quenching rate constant to be $k_0 = 2 \times 10^{-11} \text{ cm}^3/\text{sec}$

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Figure 5 Measured Data for HCl Quenching HgCl*. The HCl was added as a 2% and 4% mix in Xe. At the higher HCl pressure the Xe pressure is up to 1000 Torr. The small effect of Xe quenching the HgCl has been accounted for.

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TABLE III

HgCl * QUENCHING

(Assuming $\tau_{HgCl} \star = 29$ nsec)

Q	$\frac{k_{O^{\frac{1}{3}}}}{(cm^{\frac{1}{3}})}$	k (HgCl*) (Cm ³ /sec)
Не	< 1.5 x 10^{-21}	
Ar	< 1.5×10^{-21}	
Xe	6.9×10^{-21}	2.4×10^{-13}
N ₂	< 1.5 x 10^{-21}	
c ₂	3.8×10^{-18}	1.3×10^{-10}
НС	2.5×10^{-18}	8.6×10^{-11}
CC 4	3.5×10^{-18}	1.2×10^{-10}

which is comparable to the rate constant of ArF* quenching by Ar⁽²⁴⁾ and XeF* quenching by Xe.⁽²⁵⁾ The saturation flux $\phi_{_{\rm S}}$ can be computed using the following expression.⁽²⁶⁾

$$\phi_{\mathbf{B}} = \frac{\hbar v}{\sigma_{\mathbf{B}} \tau} \left(1 + \kappa_{\mathbf{A}\mathbf{C}\mathbf{\hat{v}}} \tau \left[\mathbf{A}\mathbf{C}\mathbf{\hat{v}} \right] + \kappa_{\mathbf{A}\mathbf{F}} \tau \left[\mathbf{A}\mathbf{F} \right] \right)$$
(4)

+ $K_{Xe^{T}} [Xe] + K_{Hq^{T}} [Hq])$,

where $\sigma_{\rm g}$ is the stimulated cross section, hv is the photon energy 1 is the HgCC* radiative lifetime, and k_i the quenching rate constant for each gas component. It should be noted that the saturation flux defined above is applicable in the limit that the population of the lower laser is negligible. From the HgCC* spontaneous spectra⁽⁴⁾ we have estimated $hv/\sigma_{\rm g}r$ to be 0.035 MW/cm². For typical laser mixes containing 1% CC₄, 2% Hg, and 97% Ar at a total pressure of 2 amagats and 1% CCC₄, 2% Hg, 11% Xe, and 86% Ar at a similar total pressure, one obtains $\phi = 0.12$ MW/cm².

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