**INVESTIGATION OF Hg_2^* AS A DISCHARGE
PUMPED OPTICAL STORAGE MEDIUM**

Final Report

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SUMMARY

This report describes work performed in the period 1 October 1977 to 30 September 1978 on the extraction of energy from metastable Hg_2^* by optical techniques. The major accomplishments have included:

- (a) Assessment of optical extraction techniques for laser fusion applications.
- (b) Demonstration of 20X enhancements in the population of the UV-radiating level by optical pumping with mid-IR lasers.
- (c) Analysis of the IR optical pumping process through the induced emission spectrum.
- (d) Parametric studies of the excitation wavelength, temperature and pressure dependences of extraction by optical pumping.
- (e) Studies of the saturation of mid-IR optical pumping.
- (f) Modeling of large-scale extraction for laser fusion applications.
- (g) Studies of optical pumping of Hg_2 by high power ArF laser (193 nm) radiation.
- (h) Studies of Hg_2 excimer structure and collisional destruction rates.

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INVESTIGATION OF Hg_2^+ AS A DISCHARGE PUMPED OPTICAL STORAGE MEDIUM

I. INTRODUCTION

High-pressure mercury vapor is known to possess several characteristics which make it attractive as a medium for an efficient, high power laser in the near ultraviolet. One of the most important of these characteristics is the collisional and radiative metastability of the lower molecular excimer states. Theoretical predictions as well as several recent kinetic studies have shown that in thermal equilibrium at reasonable temperatures nearly all of the Hg_2 excimer population resides in the lowest lying 0_g^+ excited states. These are located several thousand wavenumbers below the upper state of the prospective laser transition [$1_u \rightarrow 0_g^+(X)$] and are not coupled to the ground state by a single-photon radiative transition. In the sections below, we will describe our progress on experiments designed to determine the feasibility of extracting the energy stored in the 0_g^+ levels by means of an intense infrared pulse.

There are two generic approaches to energy extraction from metastable states: collisional and optical. Because of the typically unfavorable ratio of collisional to spontaneous rates in visible systems, the former approach is not generally useful and will not be discussed here. In optical extraction from metastables, the transfer rate from the storage to the radiating state is a function of the external switching field and can therefore be adjusted to overwhelm the quenching rate of the radiating state. Several different approaches to extraction have been discussed by both Carman¹ and Harris *et al.*² in connection with atomic systems. They are summarized schematically in Fig. 1(a), (b), and (c). The parametric process c does not result in a net energy gain in the extraction process, but may be important as a competing process with higher optical gain. In an exciplex system, the dissociative lower state eliminates this possibility. In addition, we have included in Fig. 1(d), the technique of optical pumping. This is generally not a practical approach in atomic systems because it requires the existence of a high power switch laser which is exactly resonant with the 1-2 level spacing.

Many of the attractive aspects of exciplex lasers are present in an exciplex energy extraction scheme. If the storage level is the lowest excited state, the collisional formation channels can efficiently drive molecules into this state from higher lying atomic and molecular levels. The dissociative ground state is as important in creating an inversion and increasing extraction efficiency as it is in a standard exciplex laser. One important benefit of the extraction process is that choice of the extraction wavelength allows one to tune the laser output wavelength. In an exciplex system, this is particularly important because of the presence of absorption either in excited states of the laser molecule or in other species in the kinetic formation chain. Thus the selection of the proper extraction wavelength can allow shifting of the laser gain into a region of lower absorption.

In this report, we describe experiments in which significant enhancements (up to 20 X) have been observed in the Hg_2 1_u population under HF, DF, and HBr laser switching. The required switching and extraction fluxes are calculated for a large-scale system. Also included are two appendices detailing closely related strong pumping experiments in which an ArF laser was used for excitation.

II. MOLECULAR STRUCTURE AND KINETICS OF Hg_2 : BACKGROUND

Because of its importance in classical gaseous electronics, molecular mercury has been the subject of numerous experimental investigations, one of the earliest of which was the pioneering work by Lord Rayleigh on mercury band structure.³ Despite this long history, it was only recently that many of the essential details of the spectroscopy and kinetics of the lower Hg_2 electronic states were uncovered.^{4,5} This work utilized the temperature and pressure dependence of the excimer radiation from the first radiating level in Hg_2 , which is collisionally coupled to lower nonradiating levels, to provide details on the location and kinetics of the lower levels. These lower levels are of central concern in high pressure electronically excited Hg_2 because most of the excited state population resides in them.

In Fig. 2, we show the potential curve structure of Hg_2 . This was generated by Mies *et al.*⁶ by applying spin-orbit correction to an *ab initio* calculation of the lighter atom analog of Hg_2 , Mg_2 . Note that the absolute energy scale has not been scaled with existing spectroscopic data. Direct *ab initio* calculations are extremely difficult because relativistic corrections and multi-electron correlations must be taken into account.

Mercury is a heavy atom so that the most appropriate spectroscopic framework is that of Hund's case c coupling, and the notation used in Fig. 2 reflects that framework. For case c, the selection rules $g \leftrightarrow g$, and $++ -$ are valid; thus, a single photon transition from these levels to the ground state is forbidden. The first level having an allowed transition to the ground state is the 1_u level. The repulsive ground state has a weakly bound, Van der Waals well of 460 cm^{-1} depth at 6 Bohr (Ref. 4). In optically or discharge excited Hg_2 at moderate pressures, the $1 \rightarrow 0_g(X)$ transition appears as a smooth unstructured continuum centered at 335 nm. The width of the band increases with temperature as progressively higher vibrational levels are thermally accessed.

In our extraction scheme, to be discussed below, we will require optical transitions among the lower six states. These states are all derived from the excited atom (in the separated configuration) being in the triplet manifold. The best estimates of the positions and spacing of these states are summarized in Fig. 3(a) (Ref. 7). It is important to note, however, that since none of the lower four levels has been observed spectroscopically, there are significant uncertainties inherent in the Fig. 3(a). Included in the figure are estimates of the square of the transition moment at 5 Bohr. Two strong transitions, $0_g^+ \rightarrow 1_u$ and $1_g \rightarrow 1_u$ dominate the various possible infrared transitions.

Typically, formation of these molecular states proceeds via three-body recombination involving various atomic precursors. Notice that despite the fact that the molecular ionic curves are too high to contribute to the formation of these states, as is the case for the upper laser levels in the rare gas halide lasers, three-body formation from the triplet manifold is an extremely efficient production mechanism.⁵ More complex production channels are possible, however. For example, collisional predissociation of the $0_g^+(^1P_1, ^1S_0)$ state has been shown to provide an effective source of the atomic precursors.⁸ Thus, as in many systems, collisional processes involving a large variety of higher lying molecular states efficiently funnel energy into the stable lower states.

The rate constants for these collisional processes are extremely fast; for instance, for the coupling of the 1_u level with the four lower lying states, the rate constant is $\approx 5 \times 10^{-11} \text{ sec}^{-1} \text{ cm}^3$ (Ref. 5). As a result, at moderate pressures the relative population of these levels can be

described by a Boltzmann distribution at or slightly above the cell temperature. It is then possible to adjust the population in the 1_u level relative to that in the lower lying reservoir states by simply adjusting the cell temperature. Note, however, that except at extremely hot temperatures, $T_{\text{cell}} \sim 1500$ K, the percentage in the 1_u level is negligible.

Collisions can also lead to the destruction of the reservoir states. The dominant loss processes are biexcimer quenching,

and trimer formation

The former process is only important at high excimer densities, and, therefore, for a given storage time, it serves to limit the maximum excimer density. Its rate constant has been measured to be between 1 and $20 \times 10^{-11} \text{ sec}^{-1} \text{ cm}^3$ (Refs. 9 and 10). Thus, for an excited state density of $1 \times 10^{16} \text{ cm}^{-3}$ (5 J/l), the storage time is $\geq 1 \mu\text{sec}$.

While the rate of trimer formation has not been measured directly, it may be assumed to be approximately equal to the Hg_2 formation rate. Hence both species will be formed simultaneously. However, the trimer excited state, which radiates on a dissociative band centered at 500 nm, lies lower in energy than the Hg_2 0_g^+ states by approximately 3700 cm^{-1} . Thus, in equilibrium, the dimer population will be enhanced at high temperature and low pressure. In addition, it has been shown that under discharge conditions,¹¹ trimers are dissociated via electron impact, apparently as a result of their weaker bond strength. While these experiments have shown that superelastic electron collisions can be important in depopulating the dimer excimers as well, experiments with an e-beam sustained Hg discharge indicate that sizable populations of Hg_2 can exist.¹²

III. EXTRACTION PROCESS

The extraction process which we are investigating for Hg_2 is shown schematically in Fig. 3(b). We can use electron or optical excitation to store energy in the Hg_2 reservoir states. A pulsed HF or other middle IR laser can then be used to switch population out of these states and into the 1_u radiating level. An inversion between the 1_u and $0_g^+(X)$ state permits laser action at approximately 330 nm.

As stated earlier, optical energy extraction has been carefully examined for the case of atomic systems such as iodine. However, for a heavy excimer such as Hg_2 , the molecular structure is considerably more complex, and the suitability of various extraction techniques must be reexamined accordingly.

In general terms, the two features of the Hg_2 structure which differ most from the atomic case are the line density in the bound-bound switching step and the repulsive nature of the final state. Both of these features have the effect of increasing the line width and, hence, reducing the cross section for either single or two photon processes. As a result, and as has been shown by Kelley,¹³ the cross section for nonresonant Raman and two-photon stimulated emission is negligibly small. We will not consider these processes for the remainder of the paper. The remaining two extraction techniques are resonant Raman and optical pumping. Before discussing these in detail, it is necessary to consider the spectroscopy of the bound-bound transition.

Because the vibrational spacing for the reservoir and 1_u states is small compared to kT , the mean thermal energy, (i.e., ~ 120 vs 400 cm^{-1}), there will be many possible members in each absorption band sequence (constant Δv). Each will be slightly shifted by vibrational anharmonicity. Further, because Hg_2 is heavy, it will have an extremely dense rotational spacing (for the P branch). Finally, the 21 common isotopic species of Hg_2 will further increase the line density. Hence, the density within the $0_g^- \rightarrow 1_u(0_g^- \rightarrow 0_u^-)$ band system will be between $10^3 - 10^4$ absorption lines per cm^{-1} . The interline spacing is thus narrower than the HF laser line width and the Doppler (300 MHz) and pressure (>200 MHz at a density of $2 \times 10^{18} \text{ cm}^{-3}$) broadened width of the transition, and the absorpton will appear continuous.

As a result, it is reasonable that for each infrared extraction wavelength a combination of optical pumping and near resonant Raman scattering will be possible. In many ways, the situation is similar to argon laser light scattering in I_2 , which has been studied extensively in a series of papers by Rousseau, Williams, and coworkers.¹⁴ They determined that at high pressures, ≥ 25 Torr, collisional redistribution (or, in another viewpoint, pressure broadening) cause optical pumping and its subsequent fluorescence to dominate the scattered light. Note that in the case where one is comparing optical pumping and Raman for exact resonance, the use of the standard perturbation treatment for Raman scattering is inappropriate. On account of both of these facts, we will refer to our extraction technique as optical pumping throughout the remainder of the paper.

We can now calculate an effective cross section for stimulated emission. An exact calculation is extremely difficult because of the complexities in computing the Franck-Condon factors and because of uncertainties in the collisional model. The reader is referred to Ref. 13 for a more extensive discussion of these points. In the calculation that follows we have adopted a simplified treatment, but it is one which preserves the physics and allows estimation of the effective cross section to within a factor of two or three.

The gain on the $1_u \rightarrow 0_g^+(X)$ transition is given by

$$g(\nu_u) = \sum_v \sigma_{23}(\nu_u, v) N_2(v) \quad (1)$$

where the subscripts 1 (referred to later), 2, 3 denote the 0_g^- , 1_u , and $0_g^+(X)$ levels, respectively; $\sigma(\nu_u, v)$ is an optical cross section at a given UV frequency, ν_u , and for a given vibrational quantum number, v , in state 2; and $N_2(v)$ is the population in level v of state 2. If we average over the vibrational population of a nearly thermalized band (see next section for experimental justification of this assumption) and consider the gain, g_0 only at line center, 335 nm,

$$g_0 = \bar{\sigma}_{23} N_2 \quad (2)$$

In such a case it can be shown that

$$\sigma_{23} = \frac{\tilde{A} \lambda_u^2}{8\pi \Delta \nu_u} \quad (3)$$

where $\tilde{A}$ is the A coefficient of the average vibronic level, λ is the wavelength at the UV band center, and $\Delta \nu_u$ is the width (FWHM) in Hz of the thermalized band. The transition bandwidth, $\Delta \nu_u$, is a quantity which can be experimentally determined. Its use presupposes that the band shape is sufficiently well behaved that it can be approximated by a Gaussian band shape. For a

nearly thermalized vibrational distribution, the relatively small variation in the transition wavelength and the dipole moment allow use of the averaged values for $\tilde{A}$, λ_u , and $\Delta\nu_u$.

The total population in the 1_u state can be obtained by using the fact that the infrared laser linewidth spans many discrete transitions, and, as a result, the $0_g^- \rightarrow 1_u$ transition can be treated as a quasi-continuum with a bandwidth given by the difference in transition frequencies at the right and left hand turning points [Fig. 3(a)]. Then, for intensities less than saturation,

$$N_2 = \tilde{\alpha}_{12} I_R / (h\nu_R \Gamma N) \quad (4)$$

where $\tilde{\alpha}_{12}$ is the averaged absorption coefficient, I_R is the intensity of the infrared pulse, ν_R is the infrared frequency, and ΓN is the collisional deexcitation rate out of the 1_u level. Note that in obtaining (4), we have assumed that the collisional deexcitation rate is faster than the optically pumping rate. This condition will hold over most of the parameter space of interest for the Hg₂ extraction system. For reasons similar to those stated above,

$$\tilde{\alpha}_{12} = \tilde{\sigma}_{12} N_1 \quad (5)$$

where N_1 is now the Hg₂(0_g^-) density. Combining 2, 3, and 4 we obtain the total effective cross section.

$$\sigma = \frac{\sigma_{12} \sigma_{23} I_R}{\Gamma N h \nu} \quad (6)$$

As a representative case, we calculate the total cross section for a Hg density of $3 \times 10^{18} \text{ cm}^{-3}$ and an extraction flux of $2 \times 10^8 \text{ W/cm}^2$. Using the data given in Ref. 5 and 6, we then obtain $\sigma_{23} = 3.6 \times 10^{-19} \text{ cm}^2$ and $\Gamma N = 1.4 \times 10^8 \text{ sec}^{-1}$. In calculating σ_{12} , however, we assume that either by intramolecular perturbation or by collisional processes, the 1_u and 0_u^- levels are sufficiently coupled that two-thirds of the excited population resides in the 1_u state. In this case, the appropriate matrix element to use is that for the $0_g^- \rightarrow 0_u^-$ transition which is ten times greater than that for the $0_g^- \rightarrow 1_u$ transition. Then $\sigma_{12} = 5.2 \times 10^{-20} \text{ cm}^2$, and $\sigma = 4.4 \times 10^{-19} \text{ cm}^2$, which corresponds to a gain of $4.4 \times 10^{-3} \text{ cm}^{-1}$ for the assumed conditions and an excited state density of 10^{16} cm^{-3} .

In this simplified cross section calculation, we have ignored the fact that excimer line-shapes may possess considerable structure which can reduce or enhance the calculated cross section over that made with the average bandwidth, $\Delta\nu_u$. In thermalized spectra this structure is often reduced by the superposition of many excited vibronic states. While our induced spectra, which are described below, possess a considerable thermalized component, they also have a portion which is explainable on the basis of a structured lineshape; we will therefore outline the physical basis for this structure.

The lineshape for an excimer transition, which is the inverse of the bandwidth function $\Delta\nu_u(\nu)$, is determined by the Franck-Condon overlap of the upper vibronic state wavefunction with various continua wavefunctions of the repulsive lower state.¹⁵ In Fig. 4, we show that for each value of the internuclear coordinate, a particular transition frequency is appropriate (dotted line). The final continuum state of the transition is determined by the requirement for conservation of both internuclear position and momentum. In general, the lineshape from a single vibronic state has an oscillatory envelope which results from undulations in the upper state wavefunction and interferences between degenerate, component wavelengths of the emission spectrum. While there is not a simple expression for the lineshape which has general validity, analytic approximations are available for the cases of a steeply repulsive^{16,17} or an essentially

flat lower potential.¹⁵ The former case is termed the reflection approximation since it results in a lineshape which is the square of the upper state wavefunction distorted by the slope of (or "reflected" by) the lower state potential. Then the line shape $g(\nu)$ is given by

$$g(\nu) \propto \frac{|\psi_u(r)|^2}{|dU_g/dr|} \quad (7)$$

where ψ_u is the upper state wavefunction, U_g is the ground state potential, and r is the internuclear coordinate. For the flat lower potential, the lineshape is essentially the Fourier transform of the upper state wavefunction. Note that in this discussion we have ignored the effect of molecular rotation. This is justified since its dominant effect is to broaden somewhat the oscillatory structure.

In our case, the reflection approximation is more appropriate, particularly to the left of the equilibrium internuclear distance. The inset of Fig. 4 shows the oscillatory continuum for the $\text{Hg}_2 1_u(v=8) \rightarrow 0_g^+(X)$ transition in one isotopic species, which is obtained with a calculation using the reflection approximation. Inclusion of the other 20 isotopic species of Hg_2 would only blur the structure.

IV. EXPERIMENTAL APPARATUS

In the past, both mercury-discharge lamps and ultraviolet lasers have been used to excite the mercury excimer 1_u and reservoir levels. Although lamp excitation is effective, scattered light both in and out of the pump band complicates the analysis. We therefore used these lamps only for initial cell purity checks and for apparatus calibration. A more satisfactory technique is to excite the red wing of 3P_1 Hg resonance line with the 257.2 nm output from a doubled Ar ion laser. Three-body recombination then populates the molecular states of interest. In addition to spectral purity, use of this technique gives a better spatially defined excitation region than does lamp excitation.⁴ Therefore, it is used for the extraction measurements. In our apparatus (see Fig. 5) the 514.5 nm output of a 10-W argon ion laser was frequency doubled in a temperature phase-matched ADP crystal to produce a 5-mW beam at 257.2 nm. Note that the excimer density produced by this technique (10^{10} cm^{-3}) is insufficient for a gain measurement.

Three chemical lasers were used to provide the counter-propagating infrared pulse used in the optical extraction experiments. These lasers, which were HF, DF, and HBr, were excited in a high-pressure, transverse-discharge device which has been previously described in Ref. 18. The HF and DF lasers produced up to 0.5 J and the HBr laser up to 100 mJ in a multi-line output. Use of an intracavity grating in combination with an extended cavity path length allowed the laser to be operated on a single vibrational-rotational line for HF. By adjusting the laser gas pressure, HF pulse lengths ranging from 50 to 1000 ns were obtained.

Great care must be taken in the preparation of mercury cells for spectroscopic studies at high pressure. This is because of the chemical reactivity of mercury and the metastable nature of many of its most important atomic and molecular states. Our sample preparation generally followed the procedures described by Drullinger *et al.*⁴ Laboratory-grade mercury was first purified by two successive distillations into sealed ampoules. Cells of ultraviolet-grade fused silica were then baked at 1000°C under a vacuum of 10^{-7} Torr, and the mercury was distilled into them from the purified ampoules. As a final check for impurities, the decay times of the molecular 335 and 485 nm bands were measured after ArF laser excitation⁸ and compared with

the known decay times of these bands. During the experiments, the mercury cells were heated in a conventional two-temperature firebrick oven, allowing independent control of the mercury density and temperature. The cells themselves were constructed from rectangular quartz cells of 1 cm² cross-sectional area. A 100 mm length of 5 mm i.d. quartz tubing was fused directly to the cell to form a well-isolated reservoir for the liquid mercury.

Ultraviolet and visible spectra were measured with a 1/4 m monochromator equipped with an 1P28 photomultiplier. The induced pulse spectra were averaged with a combination mini-computer and transient digitizer with 100 ns temporal resolution. For experiments in which spectral resolution of the induced emission was unnecessary, a Corning 7-60 UV-pass filter was utilized alone with the photomultiplier to isolate the fluorescence. The infrared laser spectrum was monitored with a 2 m grating monochromator using cooled Au:Ge and InSb detectors.

V. EXPERIMENTAL RESULTS AND DISCUSSION

The work to be presented in this section will provide an experimental basis for the discussion of Section 3. Measurements and interpretation of the induced spectra for HF and DF excitation will be provided. The variation of the induced signal with excitation wavelength will also be discussed. Finally, measurements of the induced signal relative to the thermal background and the saturation of this signal with infrared intensity will be presented and compared with the value expected on the basis of the physics of Section 3. Throughout, we will stress the implications of our results with regard to practical optical energy extraction from Hg₂.

A. Induced Spectrum

The induced $1_u \rightarrow 0_g^+(X)$ emission spectrum for HF pumping is shown in Fig. 6. This was taken by averaging the emission at 5 nm intervals with a detector resolution of 2 nm. The thermal emission, as recorded on the same apparatus, is plotted below this spectrum. As will be shown below, the induced emission is both from unrelaxed high-lying states in the 1_u well (right and left features) which are near those directly excited by the infrared laser, and from thermalized vibrational levels within the same state (the central broad component at 335 nm).

Since the bottom of the 1_u well is inaccessible to direct pumping with infrared photon energies greater than the $1_u - 0_g^-$ potential minimum separation, 2600 cm⁻¹, the peak at 335 nm indicates that there is some relaxation within the 1_u state. In the nonthermal HF-induced spectra, the emission near 335 nm contains a significant contribution from the same states that radiate near the peak of the spectrum at 310 nm. This may be seen by considering the anticipated bound-free emission from the 1_u to the $0_g^+(X)$ potential curves. Because of this, the semiclassical treatment used by Smith *et al.*⁴ to treat the thermalized fluorescence may not be applied to the induced emission from near the band center. However, as will be discussed below, the distribution of states emitting in the wings of the spectrum becomes heavily weighted towards states of decreasing energy. In this region, the analysis of Smith *et al.*⁴ becomes applicable and the relative population in the 1_u levels is given by the expression

$$n(E_{1_u}) \propto \eta_\lambda \frac{\lambda^2 I_\lambda}{A_\lambda \phi_\lambda} \quad (8)$$

where E_{1_u} is the energy (in the 1_u state) of the levels fluorescing most strongly at λ , η_λ is the detection efficiency, I_λ is the induced fluorescence intensity at λ , A_λ is the Einstein A coefficient at λ , and ϕ_λ is the associated line shape factor (see Ref. 4). Using the $A_\lambda \phi_\lambda$ values in Ref. 4, we have generated the population distributions from the wings of the HF-induced spectra. This is shown in Fig. 7. Also plotted is the curve corresponding to a Boltzmann distribution at the cell temperature. At energies high up in the 1_u well, the slope of the induced distribution becomes very close to the slope of the thermal Boltzmann distribution. As stated above, this region of the spectrum arises from directly excited 1_u vibronic levels. As we move further to the blue from 310 nm and thus up the vibrational levels of the 1_u state, each level is in turn excited from levels higher in the excited 0_g^- vibrational manifold [Fig. 3(b)]. As a result, the 1_u vibrational population should reflect the thermal vibrational distribution in the 0_g^- state. The fact that the distribution of Fig. 7 is within experimental error at the cell temperature indicates that absorption cross section is independent of vibrational state. A similar result holds for the weak feature near 360 nm in the red wing of fluorescence spectrum.

Our interpretation of the origin of the three induced spectral components in Fig. 6 is further supported by calculations based on the estimated Hg_2 potential curves. For this calculation, we used the reflection approximation to obtain the Franck-Condon factors for the UV band. The details of the calculation are given in the Addendum. In Fig. 8(a), we show the computed spectrum which is obtained with only $v = 8$ through 14 excited in the 1_u state. In that case, there is a depression in the center of the spectrum because of the absence of the strong emitters in the vicinity of 335 nm, that is, molecules in the first eight vibronic levels of 1_u . If population is added in $v = 0$ through $v = 8$, with a somewhat elevated vibrational temperature, then the spectrum resembles the experimental value [Fig. 8(b)]. Notice, however, that both the blue and red wings of the spectrum are unchanged since this portion of emission is dominated by molecules in $v > 8$. A plot of the wave number versus I_λ in this region of the spectrum yields a slope at the vibrational temperature of the $v = 8 \rightarrow v = 14$ levels. Because Fig. 6 was obtained under conditions of multiline excitation, it is to be expected that some broadening of the induced spectrum will be present.

With improvements in the infrared laser beam quality, intracavity line selection, and tighter focusing, it has been possible to obtain sufficient single-line intensities so that induced ultraviolet spectra can be investigated using monochromatic excitation. Several of these are shown in Fig. 9. Much sharper features are observed than with multiline excitation. Making use of the previous analysis, a spacing between the minima of the 1_u and 0_g^- wells of $2620 \pm 50 \text{ cm}^{-1}$ can be consistently inferred from all such spectra. Figure 9 also shows that the peak of the ultraviolet emission can be "tuned" considerably by varying the infrared switching wavelength.

As the wavelength of the excitation source is lengthened, the minimum energy of the directly pumped states falls lower in the 1_u well. Thus the maximum in the induced spectra should appear closer to the thermalized maximum at 335 nm. Figure 10 shows the induced spectrum which is obtained with multiline DF excitation. The shift is that expected on the basis of the wavelength difference between HF and DF lasers.

The measurements presented in this section have two implications with regard to a practical energy extraction scheme. First, the fact that the blue wing of the induced fluorescence has a Boltzmann dependence indicates that many vibrational levels are pumped with a single infrared frequency. As a result, the requirements for vibrational cross relaxation necessary to switch

a large proportion of the population out of the 0_g^+ level are reduced. Second, by shifting the wavelength in the infrared switching pulse, we can alter the emission profile of the induced fluorescence. In an optical storage application, this provides a method of tuning the wavelength of maximum gain, and hence offers a method of avoiding the excited state absorption which may be a problem in metal vapor lasers.⁹

B. Magnitude and Temperature Dependence of the Induced Emission Using a Multiline HF Pump Laser

A quantity which is of direct practical interest in these studies is the ratio of the infrared induced i_u emission to the steady-state thermal value, the enhancement ratio, ϵ . Use of this quantity eliminates spurious variation in the steady state dimer density. The enhancement ratio was measured over a wide range of Hg density and cell temperatures using a multiline HF pump source of 12 MW/cm² intensity. The measured values varied from $\epsilon = 20$ at 3.3×10^{17} cm⁻³ and 320°C to $\epsilon = 2.5$ at 7.8×10^{18} cm⁻³ and 530°C as shown in Fig. 11. Using Eq. (4) and the value of the enhancement at the high density, we calculate the effective cross section to be 3.2×10^{-20} cm². This is in reasonable accord with the cross section which was estimated on the basis of collisionally or collisionlessly mixed i_u and 0_u^+ states.

We have measured the temperature dependence of the induced emission at 335 and 310 nm, corresponding to emission from the center and induced spike, respectively. The enhancement ratio at a particular wavelength may be written as

$$\epsilon_\lambda = \frac{N_\lambda}{N_\lambda^0} \quad (9)$$

where N_λ , N_λ^0 are the population of sublevels contributing to the emission at λ for the induced nonthermal and thermal conditions, respectively.

If we assume (see C below) that the laser-induced population in N_λ is a steady state value determined by the laser pump rate into that sublevel and a collisional rate out of it, then we may further use the fact that the lower-level population remains thermally equilibrated during laser pumping and the notation of Fig. 12 to find

$$\epsilon_\lambda = N_\lambda C \exp\{(E_g + E_\lambda)/kT\} \quad (10)$$

where C is a constant depending only weakly on T , the cell temperature. For the wing of the emission band, $N_\lambda \propto \exp[-E_g/kT]$, since we have shown the emitting vibronic levels are directly pumped from the 0_g^+ level. As a result,

$$\epsilon_\lambda \propto \exp[E_L/kT] \quad (\lambda \leq 310 \text{ nm}) \quad (11)$$

where we have used the fact that the laser photon energy, E_L , is equal to $E_g + E_\lambda - E_g$. For emission at the center of the band, $E_\lambda = 0$, and

$$\epsilon_{335} = N_{335} C \exp[E_g/kT] \quad (12)$$

The induced population at 335 nm is indirectly collisionally and directly optically fed from the sum of all lower level vibronic states. Thus, N_{335} is independent of temperature and

$$\epsilon_{335} \propto \exp[E_g/kT] \quad (13)$$

The measured slopes for the 335 and 310 nm emissions are E_g and E_L , respectively, as predicted by Eqs. (11) and (13).

Finally, at the Hg densities which were typical for our experiments, most of the Hg_2 1_u molecules were collisionally quenched before they radiated. This suggests that by applying a saturating ultraviolet pulse simultaneously with the infrared switch, both the extraction time and required infrared energy could be reduced. Application of the set of steady-state rate equations to this situation supports this conclusion.¹⁹ Similarly, if the enhancement is not limited by collisional infedding rates (as shown by the induced spectrum), the same improvement in extraction efficiency may be possible by simply operating at lower atomic densities.

C. Time Dependence of the Induced Emission

For the purposes of modeling the extraction process, it is necessary to know the effective cross section for the collisional relaxation of the radiating (1_u) state. This quantity has been previously determined by Stock *et al.* from an analysis of the decay times of the 1_u fluorescence following pulsed excitation at 257 nm. However, in their analysis it was necessary to assume a condition of quasi-equilibrium in the radiating states. As is indicated by the fluorescence spectrum, this is probably inappropriate for the fast pulse infrared extraction conditions. To make a direct measurement of this quantity under infrared pumping, an attempt has been made to resolve the 1_u decay. Since the averaging electronics did not have an adequate bandwidth, it was necessary to do this on a single pulse basis and, because of the weak signals involved, this limited the measurement to atomic densities in excess of $4 \times 10^{18} \text{ cm}^{-3}$. By adjusting the laser gas pressures, it was possible to reduce the infrared pulse length to 75 ns. However, at the lowest density the fluorescence decay was still not resolved. This indicates a decay time faster than 20 ns at $4 \times 10^{18} \text{ cm}^{-3}$, and therefore a relaxation rate constant in excess of $1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

D. Induced Emission as a Function of Excitation Wavelength

The excitation wavelength was varied by using individual vibrational-rotational lines from the HF and DF lasers and by using the multiwavelength output from an HBr laser. The HF and DF laser lines were selected with greater than 95% purity by means of a grating and spatial filter external to the laser cavity. The induced ultraviolet fluorescence was then detected broadband through the Corning 7-60 filter. Typically, for the stronger lines, the peak laser flux was $\sim 500 \text{ kW/cm}^2$. Since constant fluorescence quantum yield may be assumed, the absorption spectrum may be obtained from the excitation spectrum which is plotted in Fig. 13. As may be seen, there is remarkably little structure within the HF and DF bands. This shows that the absorption is nearly continuous in the ranges sampled. In addition, it is surprising that the absorption is flat over such a large range, from 2.7 - 4.2 μm , i.e., that the breadth of the absorption band envelope is so large. This is due to the fact that the potential curves for the two relevant states have a significant shift in the position of their potential-energy minima. As a result, the Franck-Condon factors are spread over a large range in transition wavelength. In addition, the relatively large thermal excitation in the 0_g^- molecules means that wavelengths $> 4 \mu\text{m}$, which are present in the HBr output, can still excite out of the 0_g^- well.

In measuring the excitation spectrum shown in Fig. 13, care was taken not to saturate the absorption. This can be seen in the insert to Fig. 13 where the induced emission is shown to be a linear function of multiline energy density. Note that the energy density per laser line is

comparable with the single-line intensities used in obtaining Fig. 13, since line selection in this experiment was made external to the cavity.

E. Modeling of the Extraction Process

Most of the work on this project was focused on understanding the basic kinetics of the extraction process, and on measurements of the critical parameters such as cross sections, etc. However, some attention was given to the development of simple but meaningful models of the entire extraction process.

The essential aspects of extraction in an optically thin sample of laser medium (Hg_2 with a background of Hg) can be determined with the following rate equations for the storage level population, N_1 , and the 1_u level population, N_2 :

$$N_2 = B_{R1} I_R N_1 - (\beta_{L1} I_L + \alpha_1 N + \beta_{R1} I_R) N_2 \quad (14)$$

$$N_1 = -\beta_{R1} I_R N_1 + (\beta_{L1} I_L + \alpha_1 N) N_2 \quad (15)$$

where $\beta_{R,L}$ and $I_{R,L}$ are the optical cross section and photon flux for the infrared (R) and ultraviolet (L) portion of the extraction process, respectively, and α_1 is the rate constant for the relaxation of the 1_u level (see Fig. 14). Since the extraction process will occur on time scale short compared with the Hg electronic excitation time, the total level population is considered as a fixed initial condition. We have solved these equations for the case of a 10-ns infrared pulse. After the pulse, we then computed the reduction in the total excited state population, $(N_2 + N_1)|_{t=0} - (N_2 + N_1)|_{t=10 \text{ ns}}$. The percentage reduction gives the percentage of total stored energy which is extracted.

Figure 15 shows a typical set of results. Notice that for an infrared flux of 4.4 J/cm^2 and an ultraviolet flux of 11 J/cm^2 , 90% of the stored optical energy can be extracted during the assumed 10-ns optical pulse. Losses due to relaxation of the upper state are thus negligible during the extraction process.

VI. CONCLUSIONS AND POTENTIAL EXTENSIONS OF THIS WORK

A. Storage in the 1_u State

We have shown the feasibility of using a metastable excimer system for an optical energy storage laser. A review of the Hg_2 kinetic and spectroscopic data suggests that energy densities of 5 J/l may be stored on a $1\text{-}\mu\text{s}$ time scale. The gain cross section for optical extraction with a multiline HF laser is estimated to be $4.4 \times 10^{-19} \text{ cm}^2$. Our experiments have confirmed the estimated cross section for the infrared portion of the extraction process, and elucidated the details of the 1_u excited state distribution and $1_u \rightarrow 0_g^+(X)$ induced emission.

Optical pumping with middle infrared laser has shown:

- (1) Enhancements of 20X in the UV emission intensity can be obtained even in a pressure regime for which the lifetime of the 1_u state is dominated by collisional quenching.
- (2) Integrated band enhancements are nearly independent of infrared bandwidth or wavelength in the $4.2\text{-}2.6\text{-}\mu\text{m}$ range.

- (3) The Franck-Condon factors for infrared absorption from the Hg_2 reservoir states are nearly independent of the initial vibrational state - allowing many storage levels to be pumped with a single infrared wavelength.
- (4) The peak of the UV emission, and therefore, the maximum stimulated-emission cross section can be tuned over a range exceeding 30 nm by varying the infrared pumping wavelength within the HF/DF bands.

Because of signal-to-noise limitations with the present apparatus, experiments have been restricted to atomic densities $> 5 \times 10^{17} \text{ cm}^{-3}$. In this regime,

$$N\alpha_1 \gg (1/\tau_{1_u})$$

where N is the Hg density, α_1 is again the rate constant for collisional (bimolecular) relaxation of the 1_u manifold of states, and τ_{1_u} is the radiative lifetime of the same states. In this highly quenched regime, most of 1_u manifold of states excited by the infrared field are relaxed by collisions before they can spontaneously radiate. For efficient extraction of the Hg excimers in a 1 to 10 ns pulse, it is therefore necessary to accomplish the following:

- (1) Apply a saturating ultraviolet field at the driver wavelength simultaneously with the infrared extraction pulse.
- (2) Apply the infrared field over the same time interval (1-10 ns) that amplifications is needed.

A possible alternative is to make use of the long radiative lifetime of the 1_u state by operating at lower Hg densities. This approach would allow the infrared field to be applied as a long pulse (50-500 ns). To match the 1_u storage time to the pulse length of efficient HF lasers (~ 50 ns), the Hg density should be kept below $\sim 10^{18} \text{ cm}^{-3}$. At these densities, the 1_u excimer population is unquenched during the application of the relatively long infrared pulse. This population could then be extracted with a short ultraviolet pulse applied at the end of the infrared pumping cycle. It is of interest to investigate using inert gas buffers as a means of increasing the 1_u vibrational relaxation without substantially affecting its quenching time.

B. Excited State Absorption

Previous measurements in the metal excimers have revealed both positive²⁰ and negative^{9,21} gain at fixed probe frequencies. The first complete, tunable probe scans of the discharge-pumped Hg_2 (Ref. 12) and HgCd (Ref. 23) gain/excited-state absorption spectra have been reported. In this connection, it is important to identify accurately the relevant spectral regions where absorption does exist since sizable alterations of the excimer population distribution are possible with infrared pumping or with variation of the discharge conditions (as is evident from the vastly different observed discharge spectra^{11,22,24}). It may also be possible to make use of an intense infrared field to bleach a local hole in the excited-state absorption spectrum.

C. Optical Pumping

Our experiments with ArF laser pumping of Hg cells have shown that strong photoassociative absorption occurs in Hg at 193 nm (Refs. 8 and 17). The reaction is

Although the O_u^+ radiates to the ground state rapidly, it is also prone to collisional predissociation

When M is an Hg atom, the bimolecular rate constant for this reaction is $5.6 \times 10^{-10} \text{ cm}^3/\text{s}$, (Ref. 8) leading to efficient production of $Hg(6^3P)$ atoms at mercury pressures exceeding $5 \times 10^{18} \text{ cm}^{-3}$. The $Hg(6^3P)$ atoms formed in this way then produce the lowest lying excimer levels according to the kinetic chain studied by Smith *et al.*⁴

Since the sequence of reactions (16)-(18) can lead to conversion of the ArF laser photons into the low-lying Hg excimers with near-unit quantum efficiency, Hg vapor (or Hg/Cd vapor mixes) are potentially interesting storage media for frequency down shifting and pulse shortening of an ArF driver. Also, it has been recently found that the blue wing of the 253.7 nm Hg line can be extended to produce absorption at KrF laser wavelengths with He buffering.²⁵ This would permit similar down shifting and pulse shortening for a KrF driver in He/Hg mixes.

The absorption characterized by (16) occurs with a bimolecular coefficient of $5 \times 10^{-38} \text{ cm}^{-6}$. This implies that, for absorption lengths on the order of 1 m, atomic Hg densities on the order of $5 \times 10^{17} \text{ cm}^{-3}$ are required. Even at such low pressures (without buffering), the photoassociative absorption will saturate at high 193 nm fluxes because the mercury free-atom pair distribution function readjusts collisionlessly on a time scale of less than 10^{-15} sec . To take full advantage of this potential for low Hg pressure, low-temperature (<230°C) operation, gases other than Hg must be found to serve the function of M in reactions 17 and 18.

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ADDENDUM BOUND-FREE SPECTRA OF Hg₂

For a heavy molecule, in a high vibrational level, the WKBKJ approximation can be used to obtain the following compact expression for the Franck-Condon integral of the transition,

$$\langle \psi_u | \psi_g \rangle \approx \frac{C'}{(kV')^{1/2}} \cos[\phi_u(r) - \phi_g(r)] \Big|_{r=r^*} \quad (19)$$

where C' is a constant; $k \equiv k_g(r)$ is the local wave number of the molecule; $\phi_j(r)$ is the WKBKJ phase of the molecule in state j ; and V' is the derivative of the difference between the potential energy for the upper, $U_u(r)$, and lower, $U_g(r)$, states, and r^* is defined below. The wavenumber of the molecule in state j is related to the potential energy curves by $k_j^2(r) = 2\mu [E_j - U_j(r)/h^2]$ where μ is the molecular reduced mass, E_j is the maximum value of the potential energy in state j , h is Planck's constant, and r is the internuclear distance relative to the minimum of the potential well. In the WKBKJ approximation, the phase $\phi_j(r)$ is given by $\phi_j(r) = \int_{r_j}^r k_j(r) dr - \pi/4$ where r_j is the left hand turning point (in Fig. 2, for example) for state j . The symbol r^* denotes the internuclear distance at which $k_u(r) = k_g(r)$; and thus the Franck-Condon requirement for preservation of momentum and internuclear distance during the transition is fulfilled. This requirement provides a mapping of the fluorescence wavelength with the internuclear coordinate of the upper state:

$$\lambda(r^*) = hc^2 / (U_u(r^*) - U_g(r^*)) \quad (20)$$

If $U_g(r)$ is strongly repulsive over the range in r for the upper state, then $\phi_u(r^*) \gg \phi_g(r^*)$ and (19) may be approximated by

$$\langle \psi_u | \psi_g \rangle \approx \frac{C'}{(kV')^{1/2}} \cos[\phi_u(r^*)] \quad (21)$$

But by using the expression for the WKBKJ wavefunction, (21) is found to be

$$\langle \psi_u | \psi_g \rangle \approx \frac{C'}{(V')^{1/2}} \psi_u(r^*) \quad (22)$$

We can now obtain a closed-form expression for the variation of the Franck-Condon integral with r^* by fitting the upper and lower state potentials with quadratic and exponential potentials, respectively, viz,

$$U_u(r) = E_u + 1/2 Kr^2 \quad (23)$$

$$U_g(r) = E_g e^{-\alpha r} \quad (24)$$

where E_u and E_g are the potential energies at $r = 0$, K is the spring constant for the quadratic well, and α is the repulsive exponential factor. In this case, the wavefunction for the upper state will be that for an harmonic oscillator

$$\psi_u = \left(\frac{\beta/\pi}{2^{\nu} \nu!} \right)^{1/2} \exp(-1/2 \beta r^2) H_{\nu}(\beta^{1/2} r) \quad (25)$$

where ν is the vibrational quantum number, $\beta = (\mu K/h^2)^{1/2}$, and $H_\nu(\beta^{1/2}r)$ an Hermite polynomial. Then the square of the Franck-Condon integral is given by

$$|\langle \psi_u | \psi_g \rangle|^2 \sim \exp(-\alpha r^* - \beta r^{*2}) \left[\frac{H_\nu^2(\beta^{1/2}r^*)}{2^\nu (\nu!)} \right] \quad (26)$$

where we have retained only the dependencies on r and ν .

The spontaneous emission intensity at a given frequency, $A(\nu)$, is proportional to $|\langle \psi_u | \psi_g \rangle|^2 \nu^3$. Thus, using (20) and (26),

$$A(\nu) \sim \left[E_u + \frac{\beta^2 \hbar^2 r^2}{2\mu} - E_g \exp(-\alpha r) \right]^3 \times \exp(-\alpha r^* - \beta r^{*2}) \left[\frac{H_\nu^2(\beta^{1/2}r^*)}{2^\nu (\nu!)} \right] \quad (27)$$

This expression based on the reflection approximation (21) was used to obtain Fig. 3 and 3(a) and (b).

Finally, the assumption used to simplify the phase which appears in Eq. (21) breaks down at approximately $r > 0$. As a result, the quantitative aspects of the left side of the above cited figures are not valid. For example, the left-hand maximum should be much sharper. However, the qualitative features are valid, and thus we have used the approximation for our application.

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Fig. 1. Schematic summary of various techniques for optical energy extraction from metastable species: (a) and (b) near resonant stimulated Raman and two-photon amplification, (c) parametric amplification, and (d) optical pumping.

Fig. 2. Hg₂ energy level structure from Ref. 6. No correction on the absolute energy scale has been made.

Fig. 3. (a) Detailed diagram of first five excited states of Hg_2 . The energy scale is from Ref. 5 and the squares of the transition moment in e.s.u. (digits in arrows) are from Ref. 6. (b) Summary of extraction process in Hg_2 .

Fig. 4. Expected band profile for emission from $v = 8$ in the 1_u state to $0_g^-(X)$ state, using a calculation based on the reflection approximation. In the inset, the difference between the solid line in the 1_u state and the dotted line in the $0_g^-(X)$ state gives the variation in transition wavenumber as a function of internuclear distance.

Fig. 5. Apparatus used in experiments to investigate energy extraction in Hg_2 .

Fig. 6. Spontaneous emission profile of Hg_2 330-nm band using a multiline HF laser pump (Hg density $7 \times 10^{18} \text{ cm}^{-3}$, 660 K).

Fig. 7. Population distribution of emitters in HF pumped 1_u state (cell temperature 660 K).

Fig. 8. (a) Calculated spontaneous emission profile of Hg_2 molecules in $v = 8$ through $v = 14$ vibrational states of 1_0 electronic level. A relative population given by a Boltzmann distribution at the cell temperature is assumed. (b) Same as (a) except that a thermal population commencing at $v = 0$ is added. The temperature of this new distribution was taken to be 1.2 times greater than the cell temperature. There are approximately 2 times more thermalized molecules than directly pumped molecules.

Fig. 9. Spontaneous emission in Hg_2 induced by single line [P(7), $v = 2 \rightarrow 1$] HF laser (Hg density and temperature same as Fig. 6).

Fig. 10. Spontaneous emission in Hg_2 induced by multiline DF laser (Hg density and temperature same as Fig. 6).

Fig. 11. Infrared-induced ultraviolet (band integrated) emission intensities normalized to emission intensities at thermal equilibrium (at the same density and temperature and with HF pumping).

Fig. 12. Graphical definition of quantities used in Section 5C.

Fig. 13. Induced emission for various pump wavelengths. The inset shows the induced emission as a function of laser energy for a HF multiline source.

Fig. 14. Graphical definition of quantities used in Section 5E.

Fig. 15. Energy extracted as a function of infrared and ultraviolet fluxes.

APPENDIX I
CONDON INTERNAL DIFFRACTION IN THE $O_u^+ \rightarrow O_g^+$ FLUORESCENCE
OF PHOTOASSOCIATED Hg_2

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APPENDIX II
COLLISION INDUCED PREDISSOCIATION IN PHOTOASSOCIATED Hg_2

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