FAR INFRARED CHEMICAL LASERS

Progress Report

for Period December 1, 1974 - July 31, 1975

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Abstract of Progress Report

Flash photolysis of selected mixtures of (A) $O_3/H_2O/O_2$ and (B) O_3/H_2 in a laser cavity results in far infrared stimulated emission principally at (A) 357 cm^{-1} and (B) 286 cm^{-1} . Experimental and computational studies of these systems have established the pumping mechanisms to be (A),

and (B),

This work has shown the selectivity of both (A) an energy transfer pumping mechanism and (B) an energy of reaction pumping mechanism in which in both cases energy matches govern narrowly the upper state in which the inversion builds.

Concurrently, the design and fabrication of a laser cavity of twice the length and 25 times the mode volume has proceeded. The goal of this one will be chemical pumping of the HCN laser at 30 cm^{-1} . This device has been carried to within, perhaps, three months of becoming operational.

Progress Report

Period: December 1, 1974 - July 31, 1975

The H₂O Lasers

In the initial proposal leading to the award of this contract, questions were discussed concerning the emitters and the pumping mechanisms of two far infrared chemical lasers recently discovered in this laboratory. Both were one-shot pulse affairs that were initiated by UV flash photolytic decomposition of O₃ into O(¹D) and O₂(¹Δ_g). Mixtures of O₃/O₂/H₂O emitted at 357 cm⁻¹ while mixtures of O₃/H₂ showed laser oscillation at 285 cm⁻¹. At the beginning of this period it was known that H₂O carried the 357 cm⁻¹ line, as it is one of the strongest emissions from the pulsed-discharge H₂O laser. The carrier of the 285 cm⁻¹ line was unknown; it is not a strong line (although present) in the H₂O discharge laser, and its possible assignments in the latter could not be applicable to the chemically pumped analogue.

During the eight months of this contract all of the basic questions of both of these lasers have been answered and several other interesting results have emerged. Two papers describing these have been written and preprints are enclosed. These will be submitted in substantially the present form to the Journal of Chemical Physics. In the case of the O₃/O₂/H₂O system, the main question was the pumping mechanism. There seems no doubt that it is the energy transfer reaction, reaction (3)

This is an unusual case of electronic-vibrational energy exchange. The mechanism has been established by experimental studies of rates of onset of laser oscillation and computer simulation of output pulse shape.

The case of the 285 cm^{-1} , O_3/H_2 , laser has yielded a number of surprises. Careful searching through recently published excited state energy levels of Flaud and Camy-Peyret¹ (the work which vitiated the Benedict² assignment described in the original proposal) was rewarded by the finding of two states of H_2O involving a necessary bend-stretch interaction. Careful searching of the output spectrum of the laser yielded other oscillating transitions associated with the same interacting levels. This is convincing evidence for the emitter being water and specific levels being $(100)14_{2,3} - (010)13_{11,2}$. Thus in this case a population inversion is created in levels different from those in the case of the $\text{O}_2(^1\Sigma) \rightarrow \text{H}_2\text{O}$ transfer laser. Excitation energy does not migrate through the various rovibrational modes until it fills a level more favorable for giving birth to an inversion (a notion which might have been expected from energy-transfer pumping experiments in the CO_2 laser). The package of energy pumped into the molecule in this case must be fairly well concentrated over a narrow group of levels near 5940 cm^{-1} [$(100)14_{2,13}$] and undergoes stimulated emission rather than filtering down to $(001)6_{33}$ at 4408 cm^{-1} , the upper state of the intrinsically stronger 357 cm^{-1} line. This package of pumping energy in this case has been shown to be the energy of the exothermic reaction

its rather remarkable specificity may be dictated by the molecular dynamics of the step (4) as well as the energy of reaction. This step may feed the symmetric stretch (100) in preference to the asymmetric stretch (001), but the observed inversion can also be influenced by the reaction's feeding of certain of the lower states of allowed transitions from or to the interacting states. The complete mechanism,

has been used to plot the computer-simulated profiles of the output pulse and has been substantiated by their agreement with experiment.

It is significant that in the calculation the threshold for stimulated emission cannot be attained unless the OH has at least one quantum of vibrational energy which can be used as a step to surmount the activation energy barrier. This condition is, of course, consonant with the observation of OH lasing from $v \leq 3$ in the near infrared. The study of the relation between near and far infrared lasing has not as yet been made, but experimental and computational work has proceeded on the temporal behavior of the OH rovibrational output pulse near 3600 cm^{-1} . Its behavior is consistent with the first two steps, (5) and (6) of the above mechanism. The computer and oscilloscope outputs have been found to be in excellent agreement with this.

Figure (1) shows two views of the apparatus constructed for this work.

The state of the research as of June 1975 was reported at the Ohio State Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 18, 1975.

To complement the energy transfer water laser work, it was decided to take a quick look to see if CO_2 could be pumped with $\text{O}_2(^1\Sigma_g^+)$. If so, would the output frequencies show any specificity, or would oscillations be observed from all metastable levels as in the CO_2 discharge? The reason for the expectation of success with this system was a report by Orgrzylo and Thrush³ in which they describe CO_2 chemiluminescent emission from (101) and (02¹1) to (000) when CO_2 is mixed with $\text{O}_2(^1\Sigma_g^+)$. The CO_2 excitation was accompanied by relaxation of the $\text{O}_2(^1\Sigma_g^+)$ to $\text{O}_2(^1\Delta_g)$. The laser experiment suggested was accomplished by replacement of the H_2O in the $\text{O}_3/\text{O}_2/\text{H}_2\text{O}$ system by CO_2 (ratio 60/15/1). The resulting laser output, shown in Fig. (5) was measured to be in the familiar 10.5μ band of CO_2 . Furthermore, the flash energy dependence of the intensity of the output pulse is first order, consistent with an energy transfer pumping mechanism. The laser emission is in the (001) — (100) band which is different from the chemiluminescence result. It would require some vibrational relaxation before emission. This is quite different from the observations with H_2O , but consistent with the fact that the upper state of the CO_2 laser is metastable and this property is necessary for the build-up of an inversion. This is not the case with H_2O . Of course, the details of this system have not yet been examined and will be mentioned in the accompanying Renewal Proposal.

The HCN Lasers

The design and construction of apparatus for chemical pumping of the

HCN ($\sim 30 \text{ cm}^{-1}$) laser has proceeded at a satisfactory rate. Because of the long wavelength and necessity for large diameter optics, the whole device is much larger than that shown in Fig. (1). The length of the cavity was made as long as practicable, to maximize the mode volume, within the constraints of manageable flash-tube length. Progress to date can be assessed by a look at some photographs. Fig. (2) shows the outer plexiglass vacuum tube 23 cm in diameter and 4 m long. Inside of this is a cylindrical internally-aluminized reflector, on hand but not installed, and a circle of six xenon flash tubes. The flash tubes are powered by the 2 μf , 50 kv capacitor through the spark gap evident in Fig. (3). The laser cavity proper is enclosed by a translatable 18 cm diameter spherical mirror of radius 8 m and a flat with a 1 cm diameter hole. These are all shown in Fig. (4). The detector has been constructed from a chip of epitaxially-grown sulfur-doped gallium-arsenide on a GaAs substrate. This has not as yet been tested and may have to be replaced by less durable but more abundant indium antimonide if it is not a satisfactory material. (It has been extremely difficult to obtain photoconductive materials for this long wavelength region.) A spectrometer is in place for analyzing the output radiation. The electronic components will at first be borrowed from the H_2O laser.

For the remainder of this contract period, September through November, loose ends of the H_2O laser work will be tied; better figures will be prepared for publication of the enclosed papers, and the experimental work on the CO_2 and CO Transfer lasers will be accomplished. It is expected that the large new photolysis cavity will be tested and become operational in about this period of time. It appears now as if there will be no funds remaining at our disposal at the end of the first contract year.

The principal investigator has devoted approximately 90% of his time and effort to this work since the beginning of the contract. He expects to be able to devote 65% of his time to it through the termination date of this period, November 30, 1975.

Two preprints are enclosed:

1. G. D. Downey and D. W. Robinson, "Chemical Pumping of the Water Vapor Laser I, to be submitted.
2. G. D. Downey and D. W. Robinson, "Chemical Pumping of the Water Vapor Laser II, to be submitted.

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Figure 1 unavailable. To be sent under separate cover.

FIG. 2

FIG. 3

FIG. 4

Chemical Pumping Of The Water
Vapor Laser I*

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Abstract: Flash photolysis of mixtures of $O_2/H_2O/O_3$ leads to lasing at 357.53 cm^{-1} . Emission at this wavenumber coincides with that of the strongest line observed from both the pulsed and CW water vapor discharge lasers, and accordingly is assigned to the $(001)6_{33} - (020)5_{50}$ transition in water. The pumping scheme

where H_2O^+ subsequently lases, is consistent with all the experimental observations. Computer modeling of this sequence of reactions reproduces both the observed pulse's profile and its onset delay after flash initiation.

Introduction

The analysis and understanding of chemically pumped HF, DF, CO, CO_2 and N_2O lasers has produced a wealth of information on the fate of the energy released by the pumping reaction, most often an energy transfer from a vibrationally excited diatomic molecule. To this date, H_2O has not been studied in this manner. As the lasing species, it is a particularly favorable candidate as over one-hundred lines in the far-infrared are observed to lase in pulsed discharges through water vapor.¹ Since the perturbations, which give rise to the observed lasing, exist between both of the stretching fundamentals and $2\nu_2$, and any vibrational excitation produced selectively in H_2O either by an exoergic reaction or an energy transfer can lead to specific level inversions.

In the water vapor discharge laser itself, very little is known about the role of chemical reactions. In general, their contribution is considered to be small in comparison to that of direct electron impact excitation.^{2,3} Thus, to assess accurately their roles, conditions must be found where they constitute the only possible pumping mechanism.

We report here the first case of chemical pumping of the strongest and most-studied line of the water vapor laser. This line at 357.51 cm^{-1} in the pulsed discharge laser has a τ_{delay} of 1.6 μsec , a τ_{duration} of 5.4 μsec , and a peak power output of 1.2 watts.⁴ In the work presented here, where the pumping mechanism can only be due to chemical reactions, these parameters are decidedly different. Studies are presented of

this line as a function of total pressure, gas mixture ratios, reactant substituents, and foreign gas additives.

Experimental

A. Apparatus

The laser tube is a 1.75 m long, 17 cm diameter glass tube enclosing a cylindrical reflector which optically couples the 3 cm diameter laser cavity to the 1 cm diameter colinear flash tube located 3 cm above its optic axis. The internal, near-hemispherical resonator consists of one plane mirror and a 4.8 m radius spherical mirror with a 3 mm hole. This is followed by a 100 μ m thick polyethylene window. The quartz flash tube is filled with Xe ($5 \leq P_{\text{Xe}} \leq 10$ torr) and is energized by discharge of a 14.5 μ f, 20 kv capacitor. The flash profile is monitored at 250 nm using a quartz monochromator and an EMI 9783B photomultiplier. Typical flash energies are 1600 joules with a rise time of 10 μ sec. The laser emission is dispersed with a 1 m grating Ebert spectrometer⁵ and detected with a liquid helium-immersed Ga:Ge photoconductor, the output of which is displayed on a Tektronix 565 dual beam oscilloscope. Calibration was accomplished with atmospheric water.

B. Gases

Pure gases were used directly from the cylinders without further purification. O_3 was prepared by passing O_2 through a Welsbach ozonator, and adsorbed on silica gel. It was purified by purging at this temperature with He gas, cooling with liquid N_2 , and pumping the He gas off the silica gel. Mixtures were prepared in a 5 l glass bulb, blackened on the outside to exclude room light. All pressures were

measured with a Texas Instruments Precision Bourdon Gauge.

Observations and Discussion

Preliminary calculations based on an $O_2(^1\Sigma_g^+)$ to H_2O energy transfer mechanism, which at one time was thought to be involved in a different H_2O laser (II)⁶, dictated the choice of initial trial conditions which led to discovery of the laser reported here. Optimally, flash photolysis of 3.6 torr of a 9/2/1 = $O_2/H_2O/O_3$ mixture leads to lasing at 357.53 cm^{-1} with a peak power of 50 mw, an oscilloscope trace of which is shown in Figure 1. The identification of the observed line with the 357.51 cm^{-1} line (assigned $(001)6_{33} - (020)5_{50}$)¹ of the water vapor discharge laser is virtually certain. Not only is the wavenumber agreement within experimental error, but no known transitions in the other species present in the reacting mixture are close enough for serious consideration.

With a constant 2/1 = H_2O/O_3 ratio, lasing can be obtained over a wide range of O_2/O_3 ratios from as low as 6/1 to as large as 20/1 and total pressures ranging from 1.5 torr up to 9 torr. Substitution of N_2 , Ar, or He for O_2 does not yield detectable emission. Thus excitation of H_2O either by recombination of OH or by vibrational energy transfer from $OH(v \leq 2)$,⁷ which is a product of the $O(^1D) + H_2O$ reaction, or by electronic quenching of $O(^1D)$ produced by the flash cannot be responsible for this emission. Photolysis of a wide range of mixture ratios containing only H_2O and O_3 yields lasing on at least one of either the second, the third, or the fourth flashes, but never on the first. Thus these mixtures must be photolyzed at least once to produce the initially absent O_2 , so that lasing is

observed on some subsequent flash. Omission of H_2O entirely from the $\text{O}_2/\text{H}_2\text{O}/\text{O}_3$ mixtures results in no far-infrared emission. Both H_2O and O_2 are necessary reactants in the chemical pumping scheme initiated by O_3 photolysis.

Only one rapid reaction⁸ of $\text{O}_2(^3\Sigma_g^-)$ with the products of the near ultraviolet photolysis of O_3 is known, namely, the reaction

Furthermore, several workers have reported rapid quenching of $\text{O}_2(^1\Sigma_g^+)$ by H_2O ,^{9,10} although until recently nothing was known about the details of this energy transfer. In 1974 Ogryzlo and Thrush¹¹ observed infrared emission near 3700 cm^{-1} when H_2O was added to discharged O_2 containing only $\text{O}_2(^1\Delta_g)$ and $\text{O}_2(^3\Sigma_g^+)$ as excited species. In their experiments the sole reaction producing $\text{O}_2(^1\Sigma_g^+)$ was

Due to the second order dependence of the 3700 cm^{-1} emission intensity on the $\text{O}_2(^1\Delta_g)$ concentration, they showed that quenching of $\text{O}_2(^1\Sigma_g^+)$, not $\text{O}_2(^1\Delta_g)$, was responsible for the observed chemiluminescence. The emission was assigned to ν_3 of H_2O , however, with their low resolving power, a contribution from ν_1 could not be ruled out.

Consistent with their observations and our experimental data, a pumping scheme for emission at 357.53 cm^{-1} from flash photolysis of $\text{O}_2/\text{H}_2\text{O}/\text{O}_3$ mixtures is:

In the above scheme only one species produced by the flash leads to excitation of the H_2O ; a plot of laser peak power as a function of flash energy should thus be linear. Figure 2 shows that over the accessible flash energy range (lower limit set by breakdown of the triggering spark gap; upper limit by the capacitor's peak voltage rating), the laser peak power output is a linear function of flash energy.

Confirmation of this pumping scheme was sought by computer modeling as described by Molina and Pimentel.¹² The prediction of the laser output from 3.6 torr of a 9/2/1 = $O_2/H_2O/O_3$ mixture for the proposed energy transfer mechanism is shown in Figure 3. The experimentally found 5 μsec pulse onset delay (4.95 μsec calc.), peak power maximum at 15 μsec (15.0 μsec calc.), and slow decay are all reproduced by the calculations. The initial spikes are not observed experimentally; this may be due to the limiting bandwidth of the pulse amplifier.¹³

Due to the fact that lasing is complete in the first 100 μsec ; only those reactions which involve major species and for which $k \geq 10^{-15} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1}$ were included in the calculations.¹⁴

Figure 4(a) schematically depicts the pumping scheme; Figure 4(b) lists the rate constants of the reactions used in the scheme to describe the pumping and competing processes in this system. Fifty percent¹⁵ of the O_3 initially present was assumed to be decomposed by the flash. A rotational lifetime of 10^{-6} sec was assumed for the upper and lower laser levels of H_2O ; this represents a lower limit, as for the pulsed water vapor's 357.51 cm^{-1} line, rotational lifetimes $\geq 10^{-6}$ sec have been reported.² The rate constant for the excitation of H_2O was assumed to be that of the known quenching rate of $O_2(^1\Sigma_g^+)$ by H_2O .^{9,10} If this rate constant is taken to be half of that, the laser pulse is calculated to have the same profile but a somewhat longer initial onset delay of 8.15 μsec , whereas 5 μsec is observed.

The large O_2/O_3 ratios necessary for laser emission are consistent with the proposed mechanism, as both H_2O and O_3 compete strongly with O_2 for the flash-produced $O(^1D)$.¹⁶ The computer model does reflect the observed changes in the laser emission as the O_2/O_3 ratio is increased. Figure 5(a) shows the oscilloscope trace of the laser pulse from 3.6 torr of a 18/2/1 = $O_2/H_2O/O_3$ mixture and Figure 5(b) the computer calculated laser output profile for these initial conditions.

Experimentally, the addition of H_2 , He, Ar, or N_2 to the 9:2:1 mixture suppresses emission. Large additions (up to torr) of He only can be made without significant quenching of the laser output. Since He is a poor quencher of both $O(^1D)$ ¹⁷ and $O_2(^1\Sigma_g^+)$,^{9,10} the

observed effect is expected. Rapid quenching with smaller additions of Ar, N₂, and H₂ is observed and would be expected, as the rate constants for quenching of O(¹D) by Ar¹⁸ and N₂¹⁶ and for the reaction of O(¹D) with H₂¹⁷ ≥ to that for the O(¹D) with O₂(³Σ_g⁻)¹⁶ reaction.

Given that the O₂(¹Σ_g⁺) → O₂(¹Δ_g) quenching reaction is operative in inverting the level population of H₂O, some comments may be made concerning the vibrational state of O₂(¹Δ_g). If O₂(¹Σ_g⁺) v = 0 produced by Reaction (2)⁹ is quenched to O₂(¹Δ_g) v = 1, the energy transfer Reaction (3) is resonant (3755 cm⁻¹ available) for excitation of H₂O (000 J = 5,6) to the 001, J = 6 state. If v = 0 were the final state of the O₂(¹Δ_g), 5238.5 cm⁻¹ would be available, which is enough to excite the 011 state of H₂O. No laser transitions from 011 are possible due to the lack of the necessary perturbations for low J levels in this state.¹ Thus one would be unable directly to detect population of 011 by laser emission. Ogryzlo and Thrush¹¹ did not observe any chemiluminescence from 011, in their experiments, however, they could not attribute this to selective quenching of O₂(¹Σ_g⁺) to v = 1 of O₂(¹Δ_g), as on their time scale relaxation of v₂ in H₂O by collision with O₂ (1 in 1000 collisions is effective) was too rapid to permit detection of any v₂ excitation. Furthermore, in this chemical laser, excitation of H₂O to the 011 state, collisional relaxation of this to 001 (effective in 1 out of 40 collisions for H₂O as the partner),¹⁹ and subsequent lasing is also not possible. The calculations show that this could not under any circumstances reproduce the 5 μsec delay observed. To account for this short delay, the major

proportion of the quenching must excite 001 directly. Thus, as in the case of CO_2 ,¹¹ quenching of $v = 0 \text{ O}_2(^1\Sigma_g^+)$ to $v = 1 \text{ O}_2(^1\Delta_g)$ must be the predominant process. A good energy match for the energy transfer reaction is required by this mechanism. If D_2O were the quencher of $\text{O}_2(^1\Sigma_g^+)$, the energy match would be defective by 1000 cm^{-1} ; accordingly lasing from $\text{O}_2/\text{D}_2\text{O}/\text{O}_3$ mixtures has not been observed.

In H_2^{16}O only one 001-020 resonance is known; for this vibrational pair only the 357.51 cm^{-1} transition oscillates strongly in the discharge. All other primary and secondary transitions (11 possible, 9 observed;¹ associated with this single 001-020 perturbation are at least two orders of magnitude weaker. The lack of lasing here on any of these other transitions associated with this resonance in the chemically-pumped laser is reasonable in light of the sensitivity limits of the detector.

Although Orgyzlo and Thrush in their experiments could not distinguish between specific excitation of v_1 and v_3 , it is possible to do so here. A strong line is observed in the water discharge laser that is assigned to a $v_1 - 2v_2$ transition at 303.51 cm^{-1} .¹ Excitation of this line's initial level $(100)4_{33}$ from $J = 1, 2$ of the ground state is also resonant for 3755 cm^{-1} . Thus, since oscillation in the chemical laser at 303.53 cm^{-1} is not observed, excitation of v_1 from quenching of $\text{O}_2(^1\Sigma_g^+)$ by water is unlikely. Experiments with H_2^{18}O further substantiate this. In H_2^{18}O no $v_3 - 2v_2$ resonances are known. Of the several $v_1 - 2v_2$ perturbations possible, the $(100)6_{43} - (020)6_{61}$ pair does lead to intense stimulated emission at 353.42 cm^{-1} (assigned

$(100)6_{43} - (020)5_{50}^1$) in the H_2^{18}O discharge laser. The upper state of this H_2^{18}O laser line differs only by 28 cm^{-1} from that of $(001)6_{33}$, the upper state of the H_2^{16}O laser line pumped here by the energy transfer from $\text{O}_2(^1\Sigma_g^+)$. Thus, if excitation of ν_1 by this reaction occurred, certainly the $(100)6_{43}$ level in H_2^{18}O should be populated and lasing at 353.42 cm^{-1} would occur. No emission was observed from flash photolysis of $\text{O}_2/\text{H}_2^{18}\text{O}/\text{O}_3$ mixtures. We conclude that energy transfer from $\text{O}_2(^1\Sigma_g^+)$ to H_2O selectively excites ν_3 !

Conclusion

From the evidence presented it can be stated that the 357.53 cm^{-1} "single-line" laser is the result of an electronic to vibrational energy transfer. Pumping of a molecular gas laser by this type of an exchange, has not been reported for any other diatomic or polyatomic molecule. It has further been shown that quenching of $\text{O}_2(^1\Sigma_g^+)$ $v = 0$ by H_2O to $\text{O}_2(^1\Delta_g)$ $v = 1$, predominates and that it selectively excites ν_3 of H_2O . From this study, one could project the possibility of CW pumping of this line in a fast flow injection system by addition of H_2^{16}O to either a discharged O_2 or premixed $\text{O}(^1\text{D})$ and O_2 stream.

In a comparison of these investigations with those of the pulsed water vapor discharge laser, the results dictate that the type of mechanism established for the former (pulse width $> 30\text{ }\mu\text{sec}$) cannot be important in the latter (pulse width of $5.4\text{ }\mu\text{sec}$). Even under these favorable circumstances pumping by vibrationally excited OH does not occur. No new lines have been found, which might have been expected here, where selective vibrational state pumping occurs.

Flash photolysis of gas mixtures with an O_2/O_3 ratio greater than 6/1 appears to be a useful means of rapidly producing $O_2(^1\Sigma_g^+)$ for studies of the fate of its electronic excitation in quenching reactions. Investigations where infrared lasing by the product species is used to probe the specificity of these reactions are in progress in this laboratory.

Acknowledgement

We express our sincere thanks to Professor S. Kimmel and B. Silver of the Technion-Israel Institute for a gift of the $H_2^{18}O$, and to Dr. I. Poehler for the Ga doped Ge element used as a detector. We further acknowledge financial support of this research by the Energy Research and Development Administration, and contributions from the Dunning Fund of The Johns Hopkins Chemistry Department at an early, critical stage.

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- 15. This is consistent with the observations that the second photolysis flash of the same mixture produces lasing at one-third the peak power of the first, while the third photolysis flash results in no laser emission.
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- Fig. 1. Laser emission at 357.53 cm^{-1} observed from flash photolysis of 3.6 torr of a 9/2/1 = $\text{O}_2/\text{H}_2\text{O}/\text{O}_3$ mixture (upper trace - 5 $\mu\text{sec}/\text{div}$; lower trace shows flash profile - 10 $\mu\text{sec}/\text{div}$).
- Fig. 2. Plot of laser peak power as a function of flash energy for photolysis of 3.6 torr of a 9/2/1 = $\text{O}_2/\text{H}_2\text{O}/\text{O}_3$ mixture. Not Available.
- Fig. 3. Calculated H_2O laser emission from flash photolysis of 3.6 torr of a 9/2/1 = $\text{O}_2/\text{H}_2\text{O}/\text{O}_3$ mixture (Experimental shown in Figure 1).
- Fig. 4. (a). Schematic representation of the proposed mechanism for 357.51 cm^{-1} emission from $\text{O}_2/\text{H}_2\text{O}/\text{O}_3$ photolyzed mixtures showing both the pumping reaction chain and competing processes.
(b). Reactions and their rate constants used in the computer calculations.
- Fig. 5. (a). Laser emission at 357.53 cm^{-1} observed from flash photolysis of 3.6 torr of an 18/2/1 = $\text{O}_2/\text{H}_2\text{O}/\text{O}_3$ mixture (upper trace - 5 $\mu\text{sec}/\text{div}$; lower trace shows flash profile - 10 $\mu\text{sec}/\text{div}$). Not available.
(b). Calculated H_2O laser emission for these initial conditions.

Fig. 1

(a).

PROPOSED PUMPING MECHANISM

(b).

Reactions Included In Model

$k(\text{cm}^3 \cdot \text{molecule}^{-2} \cdot \text{sec}^{-1})$

Ref.

$$7.0 \times 10^{-11}$$

(16)

$$3.0 \times 10^{-10}$$

(16)

$$2.7 \times 10^{-10}$$

(16)

$$4.0 \times 10^{-12}$$

(9,10)

$$2.5 \times 10^{-11}$$

(8)

$$1.0 \times 10^{-15}$$

(9,10)

$$2.6 \times 10^{-12}$$

(20)

Chemical Pumping Of The Water
Vapor Laser II*

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Abstract: Laser emission at 273.03 cm^{-1} , 262.33 cm^{-1} , and 590.24 cm^{-1} has been observed from flash photolysis of H_2 and O_3 mixtures, in addition to that at 285.55 cm^{-1} , which has been previously reported. All four lines are assigned to laser transitions connected with the $(100)13_{1,12} - (010)13_{11,2}$ resonance in H_2O . This lasing has been shown to be pumped by the reaction sequence

where $\text{H}_2\text{O}^\dagger$ subsequently emits. The vibrational excitation of $\text{OH}^\dagger$ is effective in overcoming the activation energy barrier of reaction (4b).

Introduction

Laser oscillation at 285.55 cm^{-1} from flash photolysis of 3.4 torr of a $3/1 = \text{H}_2/\text{O}_3$ mixture has been previously reported.¹ Emission at this wavenumber is also observed in the water vapor discharge laser for which two alternative assignments have been proposed: either $(100)7_{34} - (100)6_{23}$ or $(020)13_{3,10} - (020)11_{2,9}$.² Since the first possibility requires a primary laser transition (148.88 cm^{-1}) to depopulate its lower level, and lasing at 148.88 cm^{-1} was not observed in this system, the latter assignment was favored in the previous communication. Recently published high J energy levels for the 100, 020, and 001 states of H_2O ,³ now place this transition at 288.27 cm^{-1} , well outside the experimental error limits, invalidating this previous identification.

Since the first report¹ the experimental apparatus has been refined and the laser emission spectrum has been reinvestigated over a wider range of total pressures, mixture ratios, and flash energies. Emission at several other wavenumbers has been observed; these lines oscillate simultaneously with that at 285.55 cm^{-1} and have identical profiles and pulse onset delays. Based on these results and recalculation of predicted laser transitions associated with known H_2O perturbations using Flaud and Camy-Payret's energy levels,³ all four laser lines can be unambiguously assigned.

In the original report¹ a mechanism was proposed involving energy transfer from $\text{O}_2(^1\Sigma_g^+)$ to H_2O , the $\text{O}_2(^1\Sigma_g^+)$ being produced by the photolysis. Recent evidence indicates that the major photolysis product is $\text{O}_2(^1\Delta_g)$,^{4,5} not $\text{O}_2(^1\Sigma_g^+)$. This mechanism also requires that the laser peak power be second order in flash energy and the present report shows that the flash

energy dependence of all the laser lines is first order. Thus $O_2(^1\Sigma_g^+)$ cannot be pumping the 285.55 cm^{-1} line in this system.⁶

Experimental

The apparatus and method for preparing O_3 has been previously described.⁷ In addition a Block Associates KH51 InSb detector was used to monitor near IR emission. For these experiments the outcoupling hole was reduced to 1 mm and the polyethylene window was replaced by a 5 mm thick KCl flat. After more than two hours storage time in the mixing bulb, the far-infrared laser's output from photolyzed $H_2 + O_3$ mixtures decreased significantly as a function of time. Therefore, small batches ($P < 100$ torr) were prepared and used rapidly to avoid variations in laser peak power output caused by decomposition.

Observations

Flash photolysis of H_2 and O_3 mixtures ($10 \geq H_2/O_3 \geq 2$) at total pressures of less than 5 torr produces laser emission at 285.55 cm^{-1} , 273.03 cm^{-1} , 590.24 cm^{-1} , 262.33 cm^{-1} , and 357.53 cm^{-1} . Maximum peak power at both 285.55 cm^{-1} and 273.03 cm^{-1} is obtained from flash photolysis of 3.3 torr of a mixture where $H_2/O_3 = 7/1$. For these conditions Figure 1 shows oscilloscope traces of the observed lines. Emission at all wavenumbers is rapidly quenched by addition of Ar, O_2 , N_2 , $H_2^{16}O$, $H_2^{18}O$ and H_2O_2 and by increasing the total pressure above 4 torr. Addition (up to 3 torr) of He can be made without effecting the observed output, while larger additions gradually suppress emission. Over the entire ratio range of mixtures which produce lasing, each of these lines has an onset delay of 15 μsec and a minimum pulse half-width of 10 μsec . Near-

infrared lasing is also observed from these mixtures (Figure 2). Its total emission has a 4 μ sec onset delay and pulse half-width of 4 μ sec. D_2 substitution for H_2 produces neither far-infrared nor near-infrared lasing.

Discussion

The observed laser lines can be assigned to H_2O on the basis of the following considerations. The D_2 experiments show that the emitter is a hydride. Of the hydrogen-containing species present, these being H_2O , HO_2 , OH , H_2 and H , H_2O is the only one with known transitions falling near the observed lines. Emission at these wavenumbers is also observed in pulsed water vapor discharge lasers.

The 357.53 cm^{-1} line observed here is within experimental error ($\pm .10\text{ cm}^{-1}$) of that of the strongest line (357.51 cm^{-1}) of the water vapor discharge laser. It is thus assigned to the $(001)6_{33} - (020)5_{50}$ transition² in H_2O . Of the other eleven predicted laser transitions for the $(001)6_{33} - (020)6_{51}$ resonance, none is within 10 cm^{-1} of the other lines observed here. These others then must be assigned to transitions arising from some other bend-stretch pair(s).

In their review of the water vapor discharge laser, Benedict, et. al.² assigned the 590.60 cm^{-1} and the 273.18 cm^{-1} lines to two H_2O transitions with a common upper level ($(010)13_{11,2} - (010)12_{10,3}$ and $(010)13_{11,2} - (010)13_{10,3}$ respectively)). Both of these transitions are associated with the $(010)13_{11,2} - (100)13_{1,12}$ resonance. Figure 3 is an energy level diagram showing this resonance and predicted laser transitions from it. The 262.56 cm^{-1} transition (not previously assigned) is within the uncertainty limits of the

(010)13_{10,3} - (010)13_{9,4} laser transition. It also shares a common level with the assigned 273.18 cm⁻¹ line. Use of Flaud and Camy-Peyret's (100) energy levels³ now places the (100)14_{2,13} - (010)13_{11,2} transition at 285.77 cm⁻¹, well within experimental error and level uncertainty limits of the observed line at 285.55 cm⁻¹. On the basis of good wave-number agreement, the 285.55 cm⁻¹, 273.03 cm⁻¹, 590.24 cm⁻¹, and 262.33 cm⁻¹ lines from this chemical laser are assigned to transitions (Table I), all of which are connected to these two interacting levels. Since the H₂O discharge laser spectrum is so rich, and assignment is based mostly on energy matches between the observed wavenumbers and those of calculated transitions, an unambiguous assignment is not always possible. Here under chemical pumping specific inversions are created and this difficulty is not encountered. Indeed, it is probable that the assignments found here for the 285.55 cm⁻¹ and 262.33 cm⁻¹ lines also apply under discharge pumping conditions.

As to the nature of the pumping reaction in this laser, the evidence clearly points to some exoergic reaction producing H₂O⁺. If it were an energy transfer to H₂O from some excited species, then both reactants would be products resulting from the flash photolysis, since H₂O is not initially present. The peak laser power would then be second order in flash energy. However, experimentally for all the observed lines, this dependence is first order (Figure 4). For a pumping reaction to fit the observed flash energy dependence, either O₃ or H₂ must be an initial reactant. The only reaction in this system which produces H₂O and meets this requirement is

This is exoergic by 5250 cm^{-1} , somewhat less than the 5940 cm^{-1} energy of the upper level of the 285.55 cm^{-1} line; however, contributions from rovibrational excitation of OH could make this difference insignificant.

The role of both vibrationally and rotationally non-thermalized OH cannot be minimized in this system. OH is rapidly produced by Reactions (2) and (3). Reaction (2) can populate $v \leq 4$ levels⁸ while Reaction (3) has been shown to produce $v = 7, 8, 9$ excitation almost exclusively.⁹ Furthermore, near-infrared lasing has been reported from flash photolysis of H_2 and O_3 mixtures.¹⁰ Here weak laser emission near 3200 cm^{-1} is observed at the pressures optimized for far-infrared lasing; pressures three times larger produce very intense near-infrared lasing. The $v = 2 \rightarrow 1$ assigned lines are the strongest (Figure 2). The others are weaker by at least a factor of 10. Calculations¹¹ with Reaction (2) pumping the near infrared lasing reproduce the observed pulse's onset delay. These calculations also indicate that though Reaction (3) produces OH as rapidly as Reaction (2) in this system, V - V relaxation of the initially produced $v > 6$ vibrational distribution is too slow to reproduce the pulse's 4 μsec onset delay after flash initiation. As lasing is most intense on the $v = 2 \rightarrow 1$ transitions, more than 50% of the exothermicity of reaction (2) is converted into OH vibrational excitation. This is analogous to the reaction between F and $\text{H}_2(\text{D}_2)$ where 66% of the reaction's exothermicity is channeled into HF (DF) vibration.¹²

Although Reaction (3) seems not to be pumping the observed near-infrared emission here, it is an important source of highly excited OH in this system. A pumping mechanism for the far infrared lasing incorporating these arguments

is

Reaction (4a) cannot produce $\text{H}_2\text{O}^\dagger$, since even if all OH sources produced OH exclusively in $v = 0$, calculations show that k_{4a} ($6.97 \times 10^{-15} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1}$)¹³ is too slow to overcome losses and pump the observed lasing. Reaction (4) has an activation energy of 4.6 kcal/mole.¹⁴ One OH vibrational energy quantum, if it were completely effective in overcoming this barrier, could enhance k_{4b} over k_{4a} by at least a factor of 1000.

The laser emission computed¹¹ for this pumping mechanism is shown in Figure 5. The reactions and rate constants employed are listed in Table II. The values of k_{4b} taken and the resulting laser pulse's characteristics are listed in Table III. An enhancement of k_{4b} over k_{4a} by at least a factor of 50 is necessary to produce lasing; a factor of 100 is required to account for the observed pulse's onset delay after flash initiation.

Though the rate constant of Reaction (4a) is well known, specific higher vibrational state rate constants have not been reported. On the other hand specific vibrational state rate constants have been measured for the reaction

Coltharp, Worley, and Potter reported that $k_{v=2} = 2.0 \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1}$.¹⁵ This represents an enhancement by a factor of 36 over the $k_{v=0}$ value ($5.5 \times 10^{-14} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1}$) that several workers have reported.^{16,17} Thus at least for this reaction the vibrational energy of OH is very effective in overcoming the activation energy barrier (1.0 kcal/mole).¹⁶ Measurement of specific vibrational state rate constants for Reaction (4) would permit more detailed modeling of the lasing observed here.

The fact, that under all conditions the 285.55 cm^{-1} line is the strongest, and under some conditions the only line that lases, indicates that the reaction primarily inverts 100 and 010. The other laser lines are then weaker, as they are pure rotational transitions in v_2 , which form a cascade from the lower level of the 285.55 cm^{-1} line. Since the resonator parameters are optimized for 300 cm^{-1} lasing, the 273.03 cm^{-1} cascade path predominates over the 590.24 cm^{-1} one. Though many $v_1 - 2v_2$ resonances are known, to which discharge laser lines are assigned, an intensive spectral search revealed no emission at these wavenumbers. Thus the pumping reaction does not invert v_1 and $2v_2$, though a slight $v_3 - 2v_2$ inversion is indicated by the weak 357.53 cm^{-1} line. This could be interpreted to indicate that the reaction populates all rotational levels of v_1 , $2v_2$, and v_3 whose energies are close to the exoergicity of Reaction (4) but not high J levels of v_2 . The latter case would require most of the reaction's exoergicity to be converted into rotational excitation of H_2O for which there is no precedent. The only inversions possible then are between v_1 and v_2 or v_3 and v_2 . Only one perturbation exists between

either of these pairs of levels, namely $(100)13_{1,12} \sim (010)13_{2,11}$. The strongest laser transitions observed here are assigned to this bend-stretch pair.

Conclusion

For a polyatomic molecule, this is one of the first examples of chemical pumping by an exoergic reaction rather than by an energy transfer process. The only other known cases are those of CO_2 ¹⁸ and HCN .¹⁹ The lines observed in this chemical laser are seen only weakly in the H_2O discharge laser, but probably are due to the same transitions. Their previously tentative discharge laser assignments have thus been clarified.

The near infrared laser resulting from photolysis of H_2 and O_3 mixtures is found to be pumped by the $\text{O}(^1\text{D}) + \text{H}_2 \longrightarrow \text{OH}^\dagger + \text{H}$ reaction. The far-infrared emission is pumped by the reaction $\text{OH}^\dagger + \text{H}_2 \longrightarrow \text{H}_2\text{O}^\dagger + \text{H}$ where the vibrational energy of $\text{OH}^\dagger$ is at least 30% effective in overcoming the activation energy barrier of this reaction.

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TABLE I. Laser lines assigned to the $(100)13_{1,12} - (010)13_{11,2}$ H_2O resonance. ((010) levels from Ref. 26, (100) levels from Ref. 3)).

TABLE II. Reactions and their rate constants used in the computations.

TABLE III. Values of k_{4b} tried in the calculations and the resulting characteristics of the 285.55 cm^{-1} laser pulse. (Experimentally $\tau_{\text{delay}} = 15\text{ }\mu\text{sec}$, $\tau_{\text{maximum peak power}} = 19\text{ }\mu\text{sec}$; see Figure 1a).

TABLE I

<u>Observed Line</u> <u>(cm⁻¹)</u>	<u>Assignment</u>	<u>Calculated</u> <u>(cm⁻¹)</u>
285.55	(100)14 _{2,13} - (010)13 _{11,2}	285.77
273.03	(010)13 _{11,2} - (010)13 _{10,3}	273.37
590.24	(010)13 _{11,2} - (010)12 _{10,3}	590.73
262.37	(010)13 _{10,3} - (010)13 _{9,4}	262.17

TABLE 11

	Reaction	$k(\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1})$	Ref.
(2a)	$\text{O}(^1\text{D}) + \text{H}_2 \longrightarrow \text{OH} + \text{H}$	7.5×10^{-11}	(20)
(2b)	$\text{O}(^1\text{D}) + \text{H}_2 \longrightarrow \text{OH}^\dagger + \text{H}$	2.3×10^{-10}	(20)
(3)	$\text{H} + \text{O}_3 \longrightarrow \text{OH}^\dagger + \text{H}$	2.6×10^{-11}	(22)
(4a)	$\text{OH} + \text{H}_2 \longrightarrow \text{H}_2\text{O} + \text{H}$	7.0×10^{-15}	(13) (14)
(4b)	$\text{OH}^\dagger + \text{H}_2 \longrightarrow \text{H}_2\text{O}^\dagger + \text{H}$	(see Table 111)	
(6a)	$\text{OH} + \text{O}_3 \longrightarrow \text{HO}_2 + \text{O}_2$	5.5×10^{-14}	(16) (17)
(6b)	$\text{OH}^\dagger + \text{O}_3 \longrightarrow \text{HO}_2 + \text{O}_2$	2.0×10^{-12}	(15)
(7)	$\text{O}(^1\text{D}) + \text{O}_3 \longrightarrow 2\text{O} + \text{O}_2$	2.7×10^{-10}	(23)
(8)	$\text{O}(^1\text{D}) + \text{H}_2\text{O} \longrightarrow \text{OH} + \text{OH}$	3.0×10^{-10}	(23)
(9)	$\text{O}(^1\text{D}) + \text{HO}_2 \longrightarrow \text{OH} + \text{O}_2$	6.0×10^{-11}	(22)
(10)	$\text{OH} + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{O}$	2.6×10^{-12}	(22)
(11)	$\text{HO}_2 + \text{O}_3 \longrightarrow \text{OH} + 2\text{O}_2$	1.1×10^{-15}	(24)
(12)	$\text{HO}_2 + \text{HO}_2 \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2$	3.0×10^{-12}	(25)
(13)	$\text{OH} + \text{HO}_2 \longrightarrow \text{H}_2\text{O} + \text{O}$	1.6×10^{-10}	(24)
(14)	$\text{OH} + \text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{HO}_2$	1.3×10^{-13}	(22)

TABLE III

k_{4b} ($\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{sec}^{-1}$)	τ_{onset} (μsec)	$\tau_{\text{maximum peak power}}$ (μsec)
6.97×10^{-15}	*	*
6.97×10^{-14}	*	*
3.49×10^{-13}	23	26
6.97×10^{-13}	14	21
6.97×10^{-12}	6	10

* No lasing

FIG. 1. Far-infrared laser emission observed from flash photolysis of 3.3 torr of a 7/1 = H_2/O_3 mixture (a) 285.55 cm^{-1} line, (b) 273.03 cm^{-1} line, (c) 590.24 cm^{-1} line, (d) 357.53 cm^{-1} line, (e) 262.37 cm^{-1} line (upper trace - $5 \text{ } \mu\text{sec/div}$; lower trace shows flash profile - $10 \text{ } \mu\text{sec/div}$).

FIG. 2. Near-infrared laser emission observed from 10.8 torr of a 7/1 = H_2/O_3 mixture (upper trace - $2 \text{ } \mu\text{sec/div}$; lower trace shows flash profile - $2 \text{ } \mu\text{sec/div}$).

FIG. 3. Energy level diagram of the $(100)13_{1,12} - (010)13_{11,2}$ resonance in H_2O and some of the laser transitions connected to these levels. The observed transitions are underlined.

FIG. 4. Plot of laser peak power as a function of flash energy from photolysis of 3.3 torr of a 7/1 = H_2/O_3 mixture.

FIG. 5. Calculated 285.55 cm^{-1} line laser emission from flash photolysis of 3.3 torr of a 7/1 = H_2/O_3 mixture ($k_{4b} = 6.97 \times 10^{-13}$; see Table III).

285.55 cm⁻¹

Fig. 1(a).

273.03cm⁻¹

Fig. 1 (b),

590.24 cm^{-1}

357.53 cm^{-1}

Fig. 1(d),

NEAR IR EMISSION FROM 10.8 Torr OF A 7:1 MIXTURE OF H_2O_3 .

OBSERVED TRANSITIONS

τ DELAY

$P_1 K_4$	$v = 1 - 0$	5 μsec
$P_1 K_5$	$v = 1 - 0$	6 μsec
$P_1 K_4$	$v = 2 - 1$	3 μsec
$P_1 K_5$	$v = 2 - 1$	4 μsec
$P_1 K_6$	$v = 2 - 1$	5 μsec
$P_1 K_4$	$v = 3 - 2$	6 μsec
$P_1 K_5$	$v = 3 - 2$	7 μsec

INTENSITY (MILLIVOLTS)

650
600
550
500
450
400
350
300
250

1000

1100

1200

1300

1400

1500

1600

FLASH ENERGY (JOULES)

○ - 285.55 cm^{-1}

△ - 273.03 cm^{-1}

○

○

○

○

○

○

○

△

△

△

△

△

△

Fig. 5