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Chemical Lasers Produced from $O(^3P)$ Atom Reactions. I. Observation of CO and HF Laser Emissions from Several O Atom Reactions

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We have recently reported several new chemical laser reactions involving $O(^1D)$ atoms [1–5]. The $O(^1D)$ atom was generated by the ultraviolet (UV) flash photolysis of O_3.

In the O_3 systems, however, the importance of many exothermic reactions involving the deactivated, ground-state $O(^3P)$ atoms cannot be closely examined on account of complication due to side reactions. In our previous study of the $O(^1D)$ + CN reaction [5], for example, we found that the addition of rare gas such as Ar or Xe, particularly the latter, to the lasing mixture quenches CO laser emission pronouncedly. This can be readily accounted for by the fact that rare gases are very efficient in deactivating $O(^1D)$ to $O(^3P)$ [6]. Since the reaction of the $O(^3P)$ atom with CN yielding CO + N (^4S or ^2D), although very exothermic, does not compete efficiently with other CN removal reactions such as CN + O_3 and CN + O_2 ($^1\Delta_g$ or $^3\Sigma_g^-$),[1] the importance of the $O(^3P)$ + CN reaction as a laser pumping process cannot be studied in the O_3–XCN systems.

We have set up a new vacuum UV ($\lambda \geq 165$ nm) flash apparatus to investigate various $O(^3P)$ atom reaction that produce stimulated emissions. The schematic diagram of the present setup is shown in Figure 1. A Suprasil laser tube (2.2-cm I.D., 1.0-m length), fitted with NaCl windows at the Brewster angle, was positioned in an optical cavity formed by two 2.5-cm diameter, 3-m radius gold-coated mirrors at a separation of about 1.2 m; one of the mirrors contained a 1-mm coupling hole at its center. Two quartz flash lamps, each 40 cm long and 3.4 cm in I.D., were concentrically sealed, at about 2 cm apart, to the Suprasil laser tube. The space between the two flash lamps was used as a sample inlet, directly connected to the all-glass, greaseless vacuum system which could be readily pumped down to 10^{-5} torr. This arrangement was made to avoid sampling the flashed mixture for gas analysis through the large dead-space at both ends of the laser tube. The laser tube was housed in parallel with another 85-cm-long, 2.2-cm-I.D. quartz flash lamp in an aluminum foil reflector. The quartz flash lamp was used for the photolysis above 200 nm; 10 torr 1% Xe in Ar was used as the light source.

The vacuum UV flash output had a rise time, to its maximum, of about 15 μsec and a half-width of about 45 μsec. In the present work, the flash energy varied from 0.7 to 2.0 KJ. Laser emissions were analyzed by passing the beams through a 25-cm Perkins-Elmer grating monochromator and were observed by an Au:Ge detector, maintained at 77°K, in conjunction with an oscilloscope.

In this communication, we report briefly the preliminary results obtained from several

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[1] $k_{O_2+CN} = 4k_{O+CN}$ at 300°K, where O_2 is in its ground electronic $^3\Sigma_g$ state; accordingly, $k_{O_2(^1\Delta)+CN}$ and k_{O_3+CN} should be orders of magnitude greater than k_{O+CN}. The original references for O_2 + CN and O + CN can be found in Brus and Lin [5].

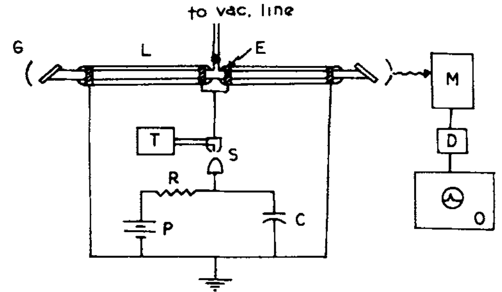

Figure 1. Schematic diagram of the vacuum UV flash apparatus: L = laser tube; E = stainless steel ring electrode; G = gold-coated mirror; M = monochromator; D = Au:Ge detector; S = spark gap; T = 30 KV trigger module, R = 400 kΩ charging resistor; C = 14 μf capacitor; O = oscilloscope; P = 25 KV d.c. power supply. The dimensions and other details of the laser tube can be found in the text.

$O(^3P)$ atom reactions that generate stimulated emissions. The $O(^3P)$ atom was produced by the vacuum UV flash photodissociation of SO_2:

$$SO_2 + h\nu\ (\lambda \geq 165\ \text{nm}) \rightarrow O(^3P) + SO(^3\Sigma^-)$$

The primary processes yielding $O(^1D)$ atoms, which may complicate our kinetic and mechanistic interpretations, are energetically unattainable above 165 nm. Nevertheless, we have tested the possibility of their formation by flashing the mixture of SO_2, CHF_3, and SF_6 under the same conditions as employed in the present studies. No HF laser emission was detected. The $O(^1D) + CHF_3$ reaction has been shown to generate HF laser emission [2]. The higher stabilities of SO_2 and SO in the present systems also help retard the occurrence of many undesirable side reactions such as those mentioned before.

We have investigated seven $O(^3P)$ atom reactions; they are summarized in Table I. In most cases, the pertinent reactant or the radical source was flashed in the presence of SO_6 and SF_6. The latter was present in large excess to minimize the rise of rotational-translational temperature of the system to enhance the laser output. Occasionally, He or Ar was used instead of SF_6; but they were found to be less efficient than SF_6 in enhancing the laser output. All laser mixtures were prepared according to the composition SO_2:compound:SF_6 = 1:1:20 in these preliminary experiments. SO_2 was found to be indispensable to laser oscillations for all cases studied, except the C_2N_2 system from which the 5-μm CN laser emission was detected when SO_2 was absent.[2]

Typical laser emission traces obtained from these systems are shown in Figure 2. The laser emissions were subjected to preliminary frequency analysis by using both the appropriate band-pass filters and the Perkin-Elmer monochromater, fitted with a 6-μm grating (first order for CO and second order for HF), with slits wide open. The lasing species thus identified are given in Table I, together with the proposed pumping mechanisms.

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[2] The 5-μm laser was originally reported by M. A. Pollack [7] in the UV flash photolysis of C_2N_2. But the CN laser oscillation is distinctively different from the CO emission when SO_2 is present. No laser emission was detected when ClCN and BrCN were flashed with UV or vacuum UV in the absence of SO_2.

TABLE I. Summary of CO and HF laser systems investigated in this work.

Reaction mixture	Lasing species	I^a	Initiation processes	Chemical pumping reaction	$-\Delta H°$, kcal/mole
(1) SO_2-XCN	CO	M	$SO_2 + h\nu \rightarrow SO + O$	$O + CN \xrightarrow{1a} CO† + N(^2D)$	18.8
(X = Cl, Br, CN)			$XCN + h\nu \rightarrow X + CN$	$O + CN \xrightarrow{1b} CO† + N(^4S)$	73.8
(2) SO_2-C_2H_2	CO	W	$SO_2 + h\nu \rightarrow SO + O$	$O + C_2H_2 \xrightarrow{2} CO† + CH_2$	47
				$O + CH_2 \xrightarrow{3} CO† + 2H$	75
(3) SO_2-CH_2Br_2	CO	M	$SO_2 + h\nu \rightarrow SO + O$	reaction (3)	
			$CH_2Br_2 + h\nu \rightarrow CH_2 + 2Br$		
(4) SO_2-$CHBr_3$	CO	VS	$SO_2 + h\nu \rightarrow SO + O$	$O + CH \xrightarrow{4} CO† + H$	176
			$CHBr_3 + h\nu \rightarrow CH + 3Br$		
(5) SO_2-$CHFCl_2$	HF	S	$SO_2 + h\nu \rightarrow SO + O$	$O + CHF \xrightarrow{5a} HFCO†$	180^b
			$CHFCl_2 + h\nu \rightarrow CHF +$ 2Cl (or Cl_2)	$\xrightarrow{5b} HF† + CO$	181^b
(6) SO_2-CHF_2Cl	HF	W	$SO_2 + h\nu \rightarrow SO + O$	$O + CHF_2 \xrightarrow{a} HF_2CO\cdot†$	90^c
			$CHF_2Cl + h\nu \rightarrow CHF_2 + Cl$	$\xrightarrow{6b} HF† + FCO$	103^d
(7) SO_2-CH_2FCl	HF	M	$SO_2 + h\nu \rightarrow SO + O$	$O + CH_2F \xrightarrow{7a} H_2FCO\cdot†$	90_c
			$CH_2FC + h\nu \rightarrow CH_2F + Cl$	$\xrightarrow{7b} HF† + HCO$	114^d

[a] Relative peak intensity of laser emission; VS = very strong, S = strong, M = medium, and W = weak.

[b] Estimated by taking $D(CHF{=}O) \simeq D(CH_2{=}O) = 180$ kcal/mole. On the basis of this value and the heat of formation of HFCO, $\Delta H_f°(HFCO) \simeq -90$ kcal/mole, one can readily obtain the overall exothermicity.

[c] Assuming $D(R{-}O\cdot) \simeq D(CH_3{-}O\cdot) = 90$ kcal/mole, where R = CH_2F and CHF_2.

[d] These overall exothermicities were estimated by assuming $D(CH_2F{-}H) \simeq D(CH_3{-}H) = 104$ kcal/mole.

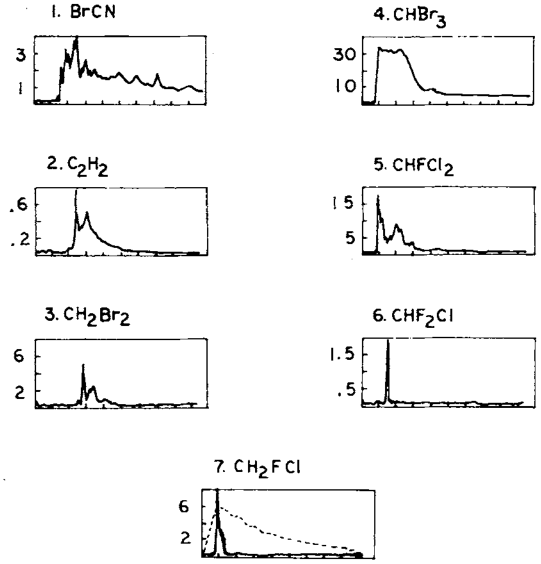

Figure 2. Typical laser emissions traces. In all cases, SO_2:compound:SF_6 = 1:1:20; P_t = 20 torr; flash energy = 1.6 KJ. Ordinate = Laser emission intensity (volt/div.), abscissa = time (10 μsec/div.); dotted curve = flash output.

The exothermicities of these pumping processes, given in Table I, were calculated on the basis of heats of formation of various species compiled by Benson [8]. In cases where the heats of formation are not available, they were estimated by assigning plausible values for the dissociation energies of the new bonds formed as described in the footnote of the table.

More detailed parametric as well as mechanistic studies of these new laser systems are in progress. The complete results of this series of reactions will be reported in full detail in the near future.

Bibliography

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