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John H. Smith and Dean W. Robinson

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Chemical pumping of pure rotational HF lasers[a)]

John H. Smith and Dean W. Robinson

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

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Pure rotational laser oscillation has been observed in HF following flash photolysis of various mixtures of trifluoromethyl halide, acetylenic compound, and argon in the ration of 1:1:100. Specifically, mixtures of $CF_3I + C_2H_2$, $CF_3I + CH_3C_2H$, and $CF_3Br + C_2H_2$ exhibit different patterns of laser intensity, and, further, are markedly different from patterns generated by the known photoelimination system CH_2CF_2. The above systems show laser intensity at lower rotational levels than could be explained by simple $V \rightarrow R$ collision induced mechanisms (as in the case of CH_2CF_2). Further, the intensities in these anomalously low rotational levels appear to be a function of the identity of the electronically excited halide (I^* or Br^*) produced photolytically. A computer simulation model has been constructed which relaxes nascent HF through $V \rightarrow R$ transfer (formed vibrationally and rotationally excited by elimination) but incorporates an additional pumping mechanism, that of quenching of I^* or Br^* by these relaxing HF molecules. Most of the experimentally observed laser intensities are explained on the basis of this new pumping mechanism.

I. INTRODUCTION

Previous reports from this laboratory on diatomic pure rotational lasers, pumped by vibration to rotation energy transfer, have described results with the molecules OH[1] and NH.[2] These were prepared in vibrational disequilibrium by the reactions

$$O(^1D) + H_2 \rightarrow OH^\dagger + H$$

and

$$HN_3 \xrightarrow{h\nu} NH^\dagger + N_2 \ .$$

The nascent vibrational distribution depends, of course, on the thermodynamics and perhaps the dynamics of the preparatory process. The vibrationally excited molecules, on collision with atoms, relax through multiple rotational inversions on their way to equilibrium. The time evolution of these rotational inversions is followed by observing laser oscillation between the rotational levels. The flow of population among the vibrational states has been computed using an elementary model, and agreement with experiment allows one to enjoy some confidence in the interpretation.

When the vibrationally and rotationally excited reaction products are formed, the observed laser action naturally depends upon this initial distribution. Producing the same molecule in different initial distributions should be interesting as a further test of the interpretation. The molecule HF can be prepared in a large number of ways; it is a diatomic hydride like OH and NH and vibrational HF laser studies have shown that substantial vibrational excitation is the general rule in many reactions. In this paper are reported some results in which the $HF^\dagger$ was prepared by photolysis of the three mixtures $CF_3I + C_2H_2$, $CF_3I + H_3CCH$, and $CF_3Br + C_2H_2$ as well as the simpler system CH_2F_2 for purposes of comparisons, all with a large excess of rare gas to induce the vibration to rotation transfer.

II. EXPERIMENTAL

The experimental apparatus used for these studies is the same has been described previously.[1,2] Mixtures of trifluoromethyl halide, acetylenic partner, and argon, in the ratio 1 : 1 : 100, or CH_2CF_2 and argon in a ratio 1 : 100, at a total pressure of 14 Torr were introduced into the laser cavity (1.75 m long, semiconfocal) and flash photolyzed with a Suprasil flash lamp parallel to the cavity. Laser emission (or superfluorescence) was coupled out through a 5% hole and dispersed with a grating spectrometer. A gallium-doped germanium crystal at 4 K was used as a photoconductive detector.

Because the short wavelength cutoff of Suprasil is 165 nm, and fluorine atoms might be expected from F_3CI photolysis, experiments were conducted seeking a fluorine abstraction origin of HF. Hydrogen fluoride pure rotational stimulated emission was not observed from flashed mixtures of F_3CI plus CH_4, C_2H_6, C_2H_4, C_6H_6, and others. These are known[3] to give HF vibrational lasing. As no attempt was made to keep the lamps clean, it is doubtful that the limit of 165 nm was even approached.

III. OBSERVATIONS

Pure rotational emission (laser or superfluorescence) has been observed from HF following the flash photolysis of mixtures of $CF_3I + C_2H_2$, $CF_3I + H_3CC_2H$, $CF_3Br + C_2H_2$, and H_2CCF_2 all in a large excess of argon, Compared to the system OH,[1] NH,[2] and the known photoelimination[4] of HF from H_2CCF_2, the HF from the trifluoromethyl reactions emitted from anomalously low values of J. The frequencies and assignments of these emission lines for the trifluoromethyl halide–acetylenic mixtures are listed in Table I. Figure 1 depicts the inversions as reflected in the intensities, which are proportional to the "heights" of the curves at points midway between the upper and lower J level of the transitions.

The appearance with time of a few selected examples of the far infrared pulse emissions is shown in Fig. 2. In two of the oscilloscope pictures can be seen the in-

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TABLE I. Emission lines of trifluoromethyl halide–acetylene mixtures.

	Assignment	Measured (cm^{-1})	Calculated[a] (cm^{-1})
$CF_3I+HC\equiv CH$			
$v=0$	$R(9)$	401.3	402.8
	$R(10)$	441.4	441.2
	$R(11)$	478.8	479.0
$v=1$	$R(9)$	386.4	387.6
	$R(10)$	423.9	424.5
	$R(11)$	460.5	460.8
$CF_3Br+HC\equiv CH$			
$v=0$	$R(9)$	398.0	402.8
	$R(10)$	441.9	441.2
	$R(11)$	478.5	479.0
$v=1$	$R(10)$	421.5	424.5
	$R(11)$	459.2	460.8
$CF_3I+CH_3-C\equiv C-H$			
$v=0$	$R(8)$	359.5	363.9
	$R(9)$	402.5	402.8
	$R(10)$	441.0	441.2
	$R(11)$	478.0	479.0
	$R(12)$	514.2	516.3
$v=1$	$R(9)$	386.8	387.6
	$R(10)$	423.5	424.5
	$R(11)$	460.4	460.8

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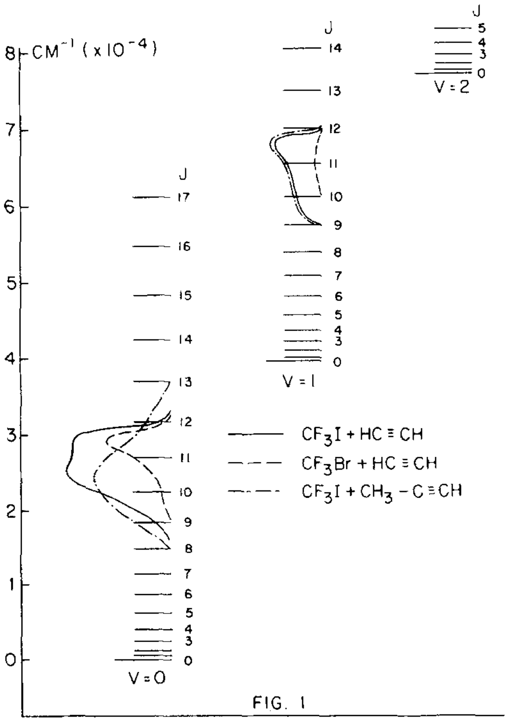

FIG. 1. Relative intensities of far-infrared laser emission following flash photolysis of mixtures of trifluoroalkylhalides and acetylenic compounds in a large excess of argon. The intensities are measured relatively from right to left from the center of a pure-rotational transition which exhibits laser emission.

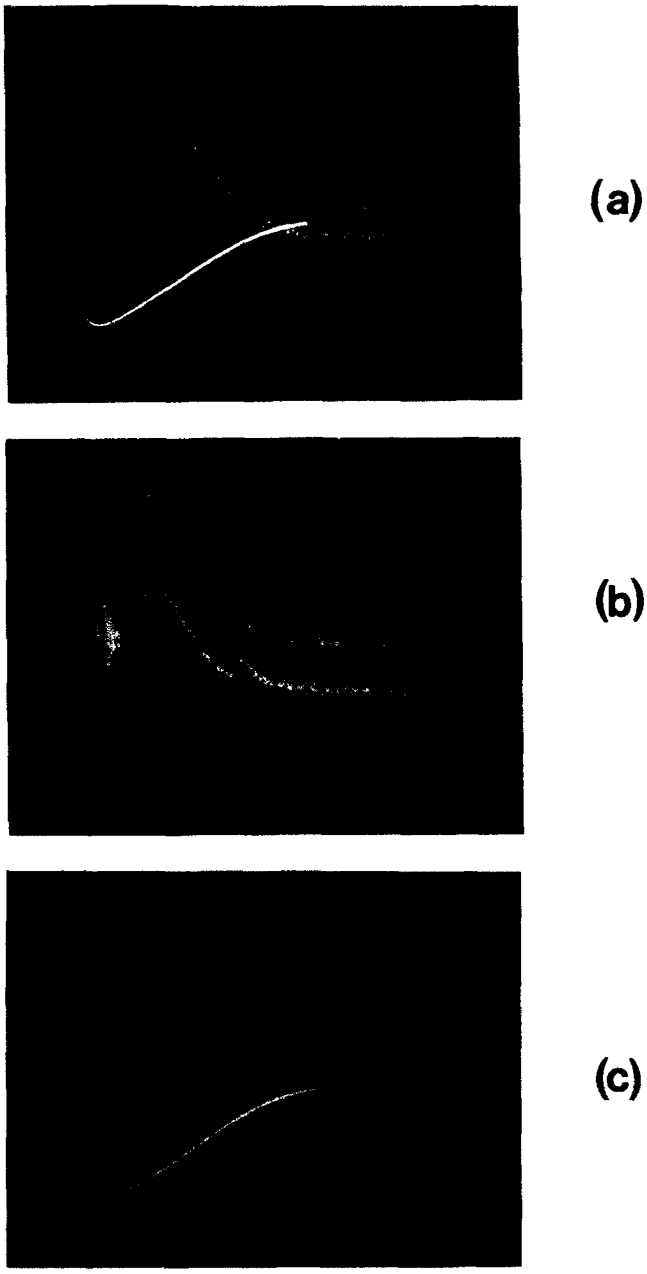

FIG. 2. Far-infrared laser emission from photolysis of 14 Torr of 1:1:100 trifluoroalkyl halide: acetylenic compound: argon mixture. In (b) and (c) the upper trace gives the laser emission and the lower the flash profile (1 div. = 10 μs): (a) $R(10)$, $v=0$ $CF_3I+C_2H_2$; (b) (upper) $R(11)$, $v=0$ $CF_3I+C_2H_2$; (lower) $R(9)$, $v=0$ $CF_3I+C_2H_2$; (c) $R(10)$, $v=0$ $CF_3I+C_3H_4$.

verted profile of the ultraviolet end of the flashlamp's spectral output. In Fig. 3 the analogous laser intensity distribution is shown for HF generated by photoelimination from H_2CCF_2. This will be compared to Fig. 1. The observed intensities of all HF emissions were in the same range as for the OH^1 and NH^2 systems previously observed. There was no question that stimulated emission was involved.

IV. DISCUSSION

In the trifluoromethyl halide–acetylenic mixtures, both partners are susceptible to photolysis. CF_3I^5 and

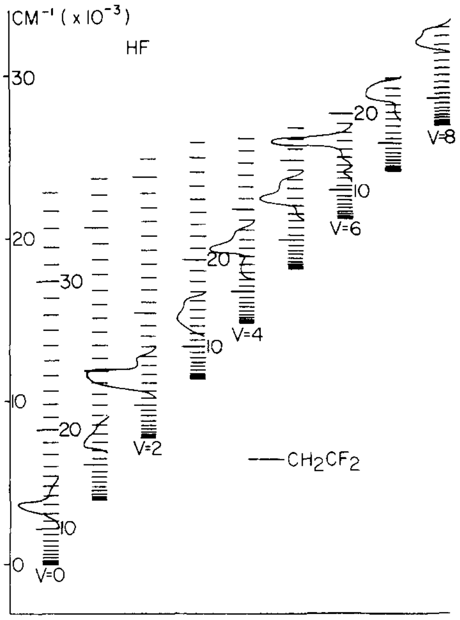

FIG. 3. Relative intensities of far-infrared emission following flash photolysis of mixtures of 1 : 100 CH_2CF_2: argon. The relative intensities are measured as in Fig. 1.

CF_3Br[6] yield CF_3 radicals and excited halogen atoms in the $^2P_{1/2}$ state. An electronic population inversion with respect to the ground state $^2P_{3/2}$ is generated which leads to stimulated emission at 7603 and 3685 cm^{-1} for I^* and Br^*, respectively. Furthermore, photolysis of the acetylene is known to produce electronically excited $C_2H_2^*$ and $C_3H_4^*$ or the radicals $\cdot C_2H$ and $HC\equiv\dot{C}-CH_2$.[7–10]

Little can be stated concerning the details of the mechanism that starts with an attack by the CF_3 on the ground state or excited hydrocarbon and ends with a vibrationally excited HF. There is probably a CF_3-acetylene adduct that α, β eliminates HF. One observation is that the vibrational excitation of the HF produced depends upon both the halide of the original trifluoromethyl halide and the acetylenic victim of the CF_3 attack. Another is that HF is an efficient quencher of the $^2P_{1/2}$ state of the halogen atoms, the electronic energy going largely into extra vibrational quanta of the diatomic molecule. In both cases of I^* and Br^* the $E-V$ match of excited halogen to vibrational quanta of HF is quite good: two quanta for the I^* and one of the Br^*.

The postulate of HF elimination from an adduct is supported by the observation that $CF_3I + HCN$ mixtures do not exhibit HF laser action. HCN is isoelectronic with H_2C_2, and dissociates (or predissociates) in an analogous manner into a hydrogen atom and a CN radical. This negative evidence is damaging to a hydrogen abstraction mechanism. It is most reasonable, then, that an α, β elimination is involved and that the HF vibrational excitation might be expected, by the Franck–Condon principle, to be similar to the case of $H_2C=CF_2 + h\nu$.

The involvement of the excited halogen atoms in the vibrational distribution of HF was tested by noting that substitution of H_3CI for F_3CI with acetylene and argon leads to very intense $I(^2P_{1/2}) \rightarrow I(^2P_{3/2})$ laser oscillation. This cannot be found in the F_3CI case, so the important quencher of $I(^2P_{1/2})$ is either CF_3I or HF or both. It is known[11] that HF is a rapid $E \rightarrow V$ de-exciter of this state, being resonantly transferred to $v=2$. The absolute rate is not needed in this model since the time scale is left arbitrary to the very end. Rather, as with all of the other energy transfer processes $V \rightarrow R$ and $R \rightarrow R$, the rates are taken to be proportional to the inverse exponential of a constant c times the energy gap.[12] We emphasize the simplicity of the concept: Collisional energy transfer depends not on the "kind" of energy lost or gained but only on the inelasticity of the collision—the amount which must pass into or out of the translational pool. Clearly, the constant c is only an arbitrary time-scaling parameter. The HF formation must be fast, producing the remarkably efficient quencher HF before the $I^* \rightarrow I$ photons build up to threshold.[13]

As can be seen on comparison of Fig. 3 with Fig. 1, the rotational laser intensity patterns on excitation from a simple photoelimination from $H_2C=CF_2$ are quite different from the more complicated examples. In fact, the distribution of inversions is very similar to the previously reported[14] examples of OH and OD prepared from the reactants $O(^1D) + H_2(D_2)$. One similarity is that the inversions occur at high J levels of v that match in energy the low J (Boltzmann) levels of $v+1$. $R \rightarrow R, T$ transfer continually tends to maximize population in low J levels of all vibrational states; the $V \rightarrow R$ transfer shifts this population to the next lower v with the least energy defect possible. Another similarity is that the most intense rotational emissions in each vibrational state have a tendency towards higher values of J as v increases.

The patterns in Fig. 1 for the $F_3CX + HC\equiv CR$ mixtures are quite different. Aside from the differences in vibrational energy available to the molecule, it is apparent that pure rotational oscillation occurs between J levels anomalously low compared to the matching $J=2$ levels of the next higher v. This appears inconsistent with the standard feeding mechanism, and it cannot be reproduced with the same computer simulation previously employed. It can, however, be understood and computer modeled when account is taken of the electronically excited halogen atoms.

It was assumed that after the HF molecules were produced in some nascent vibrational distribution, dependent upon the exothermicity of the elimination step, they were subject to a certain probability of energy increase depending on the amount of electronic energy of the colliding halide (7603 cm^{-1} for I^* or 3685 cm^{-1} in the case of Br^*). The probability of this $E \rightarrow V$ transfer was taken to be the same as for the $R \rightarrow R$ and $V \rightarrow R$ exchanges depending only on the inverse exponential of the energy gap. Each population in every rotational level of $v=0$ and $v=1$ was depleted by the amount $n_{J,v}e^{-\Delta E\cdot c}$ during each increment in (arbitrary) time during the relaxation process. In this expression $n_{J,v}$ is the population in the level J, v during any particular time interval, c is an arbitrary constant determining the time scale, and ΔE is the energy defect between the electronic energy of the halogen and the the energy interval be-

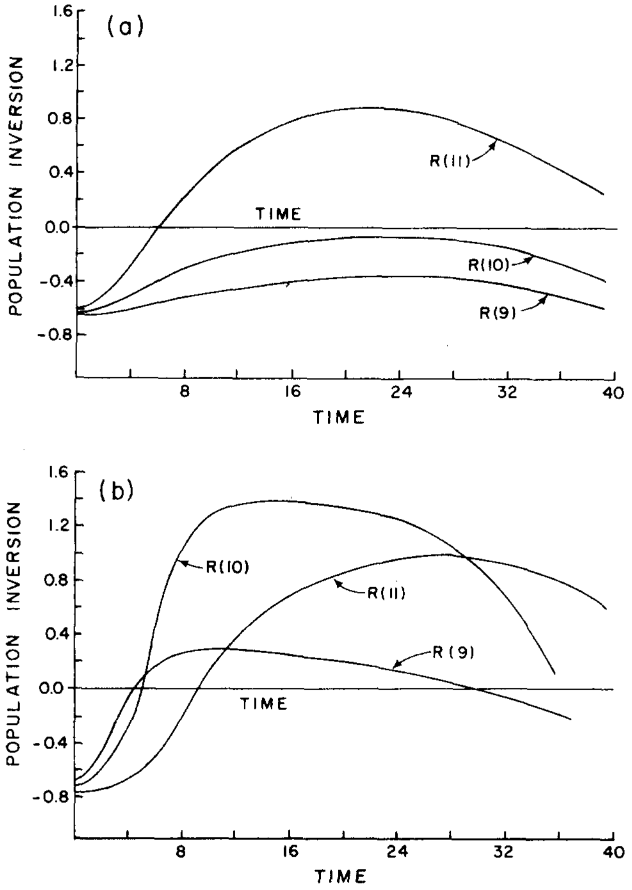

FIG. 4. Computer simulation of $v=0$ population inversions which are generated following flash photolysis of trifluoroalkyl halides and acetylenic compounds (transitions not shown did not exhibit inversions). (a) Nascent HF (excited vibrationally and rotationally from photoelimination) quenching Br* following photolysis of $CF_3Br + HC{\equiv}CH$. The inversion generated at $R(11)$ but not $R(9)$ and $R(10)$ (all in $v=0$) may be compared to the experimentally observed intensities in Fig. 1. (b) Nascent HF quenching I* following photolysis of $CF_3I + HC{\equiv}CH$. The inversions generated at $R(9)$, $R(10)$, and $R(11)$ (all in $v=0$) may be compared to the relative intensities of these transitions observed experimentally in Fig. 1. Both axes are in arbitrary units.

tween the appropriate rovibrational levels of HF. The selection rule on J of $\Delta J = 0, \pm 1$ was maintained largely for simplicity. This is in harmony with the restriction of $J = \pm 1$ for $R \rightarrow R$ transfers.[12] Thus, for instance, I* was quenched by HF ($v=0$) according to

$$\Delta E = [7603 - (E^{v=2}_{J,J\pm1} - E^{v=0}_{J})] \ .$$

This I* quenching enhances HF ($v=2$) and depletes HF ($v=0$) at J values which give the best energy match. The best matches are found to occur for HF ($v=0$, J'') + I* → HF ($v=2$, J') + I at $J''=8$, 9, 10, and for HF ($v=0$, J'') + Br* → HF ($v=1$, J') + Br at $J''=5$, 6, 7. These rotational levels of $v=0$ will therefore be most efficiently depleted by the $E-V$ transfer.

In the CF_3I plus acetylenic compound this removal of population from $J=8$, 9, 10 enhances the inversion at anomalously low J, illustrated in Fig. 1. This is not the case with CF_3Br because, although the same transfers are operating, the levels $J=5$, 6, 7 are so low that the rate of rotational relaxation is competitive with the time to the threshold of stimulated emission. The $R(11)$ emission in both CF_3I and CF_3Br mixtures is probably due to the normal mechanism of intramolecular $V \rightarrow R$ conversion.

The above physical description of the dynamic system has been corroborated by computer simulation. This is shown in Fig. 4. The model used is similar to the one employed[1,2] to treat the results with OH, OD, and NH; it differs only in the necessary addition of the effects on the HF levels of the halogen $E \rightarrow V$ transfer. The model incorporates $V \rightarrow R$ and $R \rightarrow R$, T transfer, which are functions of vibration, rotation, and mass of the collision partners (always HF–Ar) with further accommodation of possible $V \rightarrow T$ energy loss on impact. The few parameters employed were taken to be the same as those for NH,[2] an analogous system in that it lased only in $v=0$, 1.

It is seen in Fig. 1 that $v=1$ emission for the reactant F_3CBr is much less intense than that for F_3CI, in harmony with the contention that halogen atom quenching is a significant contributor to pumping. The I* increases the vibrational excitation from $v=0$ to $v=2$ which pumps pure rotational $v=1$ inversions, while the Br* can only raise the molecule from $v=0$ to $v=1$.

Referring again to Figs. 1 and 2, it will be seen that photolysis of CF_3I, $CH_3C{\equiv}CH$ mixtures gives a different pattern of emission intensity and pulse shape from the CF_3I, $HC{\equiv}CH$ mixtures. The pulse from the former occurs at lower values of J and is spread over more rotational levels. The peak is at a later time with a somewhat longer emission tail. These observations may be attributed to the intermediate from which the HF is eliminated. In the methyl acetylene case the vibrational mode bath is larger and better able to store the energy that finally arrives in the HF, causing its elimination.

Finally, it may be seen in Fig. 2 that some of the laser output pulses [F_3CI, C_2H_2 mixtures, $R(9)$ and $R(10)\,v=0$] have abrupt spikes of intensity superimposed on the normal oscillograph pattern. These may be due to the feeding of the $v=0$ levels $J=10$, 11 by cascading laser oscillation in the near infrared ($v=0$, $J=10+\text{I}^* \rightarrow v=2$, $J=9 \xrightarrow[\text{near IR}]{\text{lase}} v=1$, $J=10 \xrightarrow[\text{near IR}]{\text{lase}} v=0$, $J=11$, for example) after pumping up with I*.

V. CONCLUSIONS

It can be concluded from this work that HF, like OH, OD, and NH, can be made to oscillate on pure rotational levels through chemical pumping. Whereas a few years ago it was generally held that collisional relaxation would be too rapid for threshold ever to be reached, it is clear now that intramolecular collisional $V-R$ transfer is a pumping process that is applicable to many diatomic hydrides. Furthermore, the specifics of the intensity distribution and its behavior with time can quite easily be used to follow the flow of population with time and ultimately test nascent vibrational population distributions before collisions have altered them.

This preliminary work on HF used different reactions, whose mechanisms are only vaguely known, to produce HF†, and this HF† was further pumped by I* and Br* by $E \rightarrow V$ transfer. The different chemical reactions between F_3CI and F_3Br and $HC\equiv CH$ and $CH_3C\equiv CH$ yielded HF in distributions that varied with the halogen and the alkyne. Vibrational excitation remained much lower ($v \leq 3$) than that observed for photoelimination from $F_2C=CH_2$ ($v \leq 8$).

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