AIP | The Journal of Chemical Physics

Hydrogen Fluoride Elimination Chemical Laser

Michael J. Berry and George C. Pimentel

Citation: The Journal of Chemical Physics **49**, 5190 (1968); doi: 10.1063/1.1670020
View online: http://dx.doi.org/10.1063/1.1670020
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/49/11?ver=pdfcov
Published by the AIP Publishing

distribution is broader for Cl+DI than for $H+X_2$, and apparently for Cl+HI than for Cl+DI. This is likely to be connected with the tendency for a *light* central atom to "clout" the departing halogen atom; a tendency which would be even more marked for Cl+HI than Cl+DI.[9] (4) There is increasing evidence that the LEPS equation with spectroscopic values for β gives an interaction which operates over too short a range. In the present work, and also in trajectory calculations on the reactions of "hot" T,[10] it proved necessary to increase the range of interaction between the reagents. The failure of our trajectory calculations to account for the vibrators in low v levels for Cl+HI could be due to the fact that the range of interaction between the products was not increased, and hence there were too few secondary encounters.

---

* This work was supported by the National Research Council of Canada, the U.S. Air Force Cambridge Research Laboratories, and the Petroleum Research Fund administered by the American Chemical Society. We are indebted to the Institute of Computer Science, University of Toronto, for the use of their facilities. Three of us (K. G. A., W. H. W., and K. B. W.) thank the National Research Council for scholarships.

[1] (a) J. C. Polanyi and S. D. Rosner, J. Chem. Phys. **38**, 1028, (1963) (Part I); (b) P. J. Kuntz, E. M. Nemeth, J. C. Polanyi, S. D. Rosner, and C. E. Young, *ibid.* **44**, 1168 (1966) (Part II).

[2] For details of the 3D coordinates see P. J. Kuntz, M. H. Mok, and J. C. Polanyi, J. Chem. Phys. (Part V, to be published).

[3] For details of this calculation see J. C. Polanyi and W. H. Wong, J. Chem. Phys. (to be published).

[4] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N.J., 1950), p. 101.

[5] K. G. Anlauf, P. J. Kuntz, D. H. Maylotte, P. D. Pacey, and J. C. Polanyi, Discussions Faraday Soc. **44**, 183 (1967). There is a mistake in this paper. The experimental results for $H+Cl_2$, it is correctly stated, require $\mathcal{R}_\perp \simeq 70\%-80\%$. For $H+Br_2$ the results require $\mathcal{R}_\perp \simeq 60\%-70\%$. Finding (ii) in the theoretical section is, however, incorrect: the LEPS equation for $H+Br_2$ with $(a=b=c=)S=0$ *does* predict a lowered E_c and decreased $\mathcal{R}_\perp$ as compared with that for $H+Cl_2$. The values are $E_c=1.8$ kcal mole^{-1}, $\mathcal{R}_\perp=59\%$. It is unnecessary to introduce $S=0.1$ as we did (due to a numerical error).

[6] D. H. Maylotte and J. C. Polanyi (unpublished); D. H. Maylotte, Ph.D. thesis, University of Toronto, Canada, 1968.

[7] (a) J. C. Polanyi, J. Appl. Optics **2**, 109 (1965); (b) Ref. 5 discusses this in terms of a change from repulsive to "mixed" energy release; (c) J. C. Polanyi, Discussions Faraday Soc. **44**, 227 (1967).

[8] J. C. Polanyi, J. Quant. Spectry. Radiative Transfer **3**, 471 (1963).

[9] The effect of secondary "clouting" encounters in removing incipient vibration is demonstrated in Part V.[2] The increased tendency for such encounters in $\mathcal{H}+\mathcal{L}\mathcal{H}$ is exemplified in P. J. Kuntz, E. M. Nemeth, and J. C. Polanyi, J. Chem. Phys. (Part IV, to be published).

[10] P. J. Kuntz, E. M. Nemeth, J. C. Polanyi, and W. H. Wong, J. Chem. Phys. (to be published).

Hydrogen Fluoride Elimination Chemical Laser

Michael J. Berry and George C. Pimentel
Chemistry Department, University of California, Berkeley, California 94720

(Received 13 September 1968)

Vibrationally excited 1,1,1-trifluoroethane can be produced by radical combination.[1] Subsequent elimination of HF distributes 60–80 kcal of energy between the products. We have found that this sequence of reactions produces hydrogen fluoride laser emission:

$$CF_3+CH_3 \rightarrow CF_3CH_3\dagger \rightarrow CF_2CH_2+HF\dagger.$$

Emission has been observed from both HF and DF in $v=1\rightarrow 0$ and $v=2\rightarrow 1$ transitions, but no $3\rightarrow 2$ emission was detected. Table I lists the observed frequencies, threshold times, and identifications.

Typically a mixture of $CH_3I(CD_3I)$ and CF_3I(60 mole%, optimum) was photolyzed with a 2000J xenon flash (half-peak duration, 20 μsec.) in a 50-cm quartz laser tube (10-mm i.d.; sapphire Brewster angle windows). The tube occupied an optical cavity formed by two 1.2-m radius gold-surfaced mirrors placed 1 m apart. Light reflected out of the cavity from the sapphire windows was directed onto two PEM InSb detectors; one of the beams was first passed through a Jarrell–Ash 1-m grating monochromator. Atomic iodine laser emission[2] at 1.315 μ, which always occurred, was removed with an LP 177 infrared filter (IR Industries). Detector responses were recorded with a dual trace oscilloscope and the traces were simultaneously triggered by the flash with an EGG #SGD-100 photodiode.

Hydrogen fluoride laser emission was observed at total gas pressures from 0.5 mm up to 40 mm (DF) or 50 mm (HF) with optimum intensity at 7 mm (DF) or 10 mm (HF). Identification of individual vibration–rotation lines was based upon correspondence between

Table I. HF and DF laser transitions,[a] frequencies, and threshold times.[b]

Transition	HF ν(cm^{-1})	HF Δt(μsec)	DF ν(cm^{-1})	DF Δt(μsec)
		$v=1\rightarrow 0$		
$P_1(4)$	3788.0[c]	6		
$P_1(6)$	3693.8	7.5	2768	7.5
$P_1(7)$	3644.3	7.5–8	2743	8.5
$P_1(8)$	3593.9[d]	10	2718	8.5
$P_1(9)$	3542.2[c]	10.5	2691	9
$P_1(10)$	3489.5	11.5–12	2665	9.5
$P_1(11)$	3436.0	12	2638	10.5
$P_1(12)$	3381.3	15	2611	12
$P_1(13)$	3327[d]	17	2583	13.5
$P_1(14)$	3271[d]	17.5	2555	15.5
$P_1(15)$			2527	17
$P_1(16)$			2498	18
		$v=2\rightarrow 1$		
$P_2(6)$	3531.3	7.5	2680	7.5
$P_2(7)$	3483.7	9	2656	8
$P_2(8)$	3434.9	10	2631	8.5
$P_2(9)$	3385.0	10.5	2606	10.5
$P_2(10)$	3334.3	10.5	2580	11.5
$P_2(11)$	3283[d]	13	2554	10.5
$P_2(12)$			2527	12
$P_2(13)$			2500	13–14
$P_2(14)$			2473	16–17

[a] Conditions: $CF_3I/CH_3I(CD_3I)=1.5$; total pressure = 10 mm (HF), 7 mm (DF); 2000J flash; 1-cm^{-1} slit unless otherwise noted.

[b] Threshold time Δt is the time lapse between the flash trigger and the transition threshold.

[c] Calibration lines measured with an 0.2-cm^{-1} slit.

[d] Slit about 10 cm^{-1}.

measured and calculated frequencies using HF constants given by Mann *et al.*[3] and DF constants given by Spanbauer *et al.*[4] The monochromator calibration was verified to ±0.2 cm^{-1} with relatively isolated, hence readily identified, lines in HF [$P_1(4)$ and $P_1(9)$]. The search for other lines was based upon calculated frequencies; 1-cm^{-1} spectral slitwidths were used for HF and about 10-cm^{-1} slitwidths for DF. Additional confirmation of the assignments was provided by coincidence measurements between several of the assigned lines and their known counterparts in the $UF_6/H_2(D_2)$ laser.[5] Table I shows that for HF, $P_1(4)$ is the first line to reach threshold, but thereafter, each $P_2(J)$ transition reaches threshold just before the $P_1(J+1)$ transition that it pumps. DF shows the same pattern of $P_2(J)$ vs $P_1(J+1)$ lines, but it is difficult to say whether $P_1(6)$ or $P_2(6)$ is the first line to reach threshold. Total laser duration is about 10–15 μsec and each line has an approximate duration (pressure-dependent) between 0.5–5 μsec. Preliminary gain measurements indicate that HF and DF have roughly the same gain (if scaled to the same pressure): HF, $>5db/m$ at 4.6-mm sample pressure; DF, $>2db/m$ at 1.4 mm. Power levels are about 30–40% of those of the $UF_6/H_2(D_2)$ lasers.

Added argon quenches the higher $P(J)$ lines until, with argon in 100:1 excess, $P_2(6)$, $P_2(7)$, $P_1(4)$, $P_1(6)$, and $P_1(7)$ make up the total emission from HF. However, for a moderate excess of argon (~10:1), the total emission intensity is approximately doubled. Hexafluoroethane (C_2F_6) also raises the total intensity, but it produces an additional quenching effect. A 20:1 excess of C_2F_6 preferentially quenches 2→1 HF emission while 1→0 lines out to $P_1(7)$ still emit. With either inert gas present, a single laser tube filling would reach laser threshold in several successive flashes, whereas without inert gas, emission occurred only on the first flash.

We believe that both Ar and C_2F_6 act to moderate temperature rise and guarantee rotational equilibration. In addition, C_2F_6 is probably quite effective in deactivating the vibrationally excited trifluoroethane. Assuming HF deactivation is negligible (as suggested in earlier work[5]) and that rotational temperature is 300°K, the observation that $P_1(4)$ reaches threshold first in HF implies[5] that N_1/N_0 (the population ratio for $v=1$ and $v=0$) is in the range 0.58–0.90. A corresponding calculation for DF, assuming $P_1(6)$ and $P_2(6)$ emit simultaneously, yields ratios of $N_1/N_0=0.63$–0.76 and $N_2/N_1=0.64$–0.78.

The hydrogen fluoride elimination laser is a new type of chemical laser, the first in which a unimolecular chemical reaction provides the pumping mechanism. Other elimination lasers are being sought, and we expect them to be numerous. It seems certain that systematic study of the laser emission dependence upon vibrational deactivation will elucidate the role of vibrational excitation in unimolecular decomposition.

We wish to acknowledge research support from the U. S. Air Force Office of Scientific Research. Also, we gratefully thank Dr. Eric Whittle for focussing our attention on the potentiality of radical–radical reactions as possible chemical laser sources.

[1] R. D. Giles and E. Whittle, Trans. Faraday Soc. **61**, 1425 (1965).

[2] J. V. V. Kasper and G. C. Pimentel, Appl. Phys. Letters **5**, 231 (1964).

[3] D. E. Mann, B. A. Thrush, D. R. Lide, Jr., J. J. Ball, and N. Acquista, J. Chem. Phys. **34**, 420 (1961).

[4] R. N. Spanbauer, K. N. Rao, and L. H. Jones, J. Mol. Spectry. **16**, 100 (1965).

[5] K. L. Kompa, J. H. Parker, and G. C. Pimentel, J. Chem. Phys. 49, 4257 (1968).

Photodetachment of $[OH(H_2O)]^-$*

STEPHEN GOLUB† AND BRUCE STEINER
National Bureau of Standards, Washington, D. C. 20234

(Received 13 September 1968)

We have recently come across and begun to study the ion $[OH(H_2O)]^-$,[1] whose characteristics indicate that it may play a role in atmospheric physics.[2] In examining the negative ions formed in a hot cathode arc discharge through an ammonia–water vapor mixture at a pressure approximately 7 N/m^2 (0.05 torr), we observed (in addition to beams of mass 1, 16, and 17) a 0.1–1-nA ion beam at mass 35; at the same time a much weaker beam of mass 37 ions is observed.

The ions formed in this arc are analyzed in a second-order, double-focusing mass analyzer (focusing in velocity spread as well as aperture in the deflection plane).[3,4] Figure 1 shows a mass scan of the region between mass 35 and mass 37. The smaller member of the doublet at mass 35 is seen to be 3 times the main peak at mass 37 as required by the well-known isotopic abundances of ^{35}Cl and ^{37}Cl. The mass 35 splitting, 0.039±0.006 amu, is equivalent to the ^{35}Cl–H_3O_2 mass difference, 0.044 amu, and is twice that of either the ^{35}Cl–OF or the OF–H_3O_2 mass differences.

The $H_3{}^{16}O^{18}O^-$ peak is observed with increased amplification along with the ^{37}Cl as a second doublet with

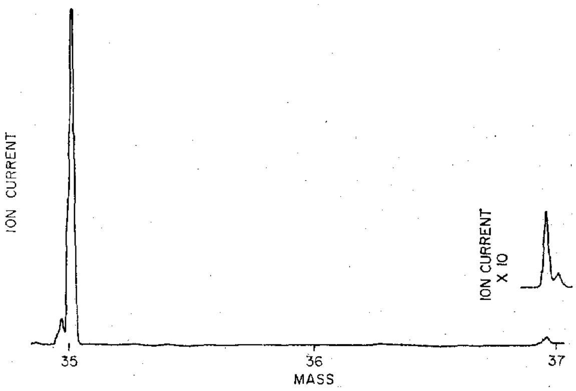

FIG. 1. Mass spectrum of the region containing $^{35}Cl^-$, $H_3{}^{16}O_2{}^-$, $^{37}Cl^-$, and $H_3{}^{16}O{}^{18}O^-$. The insert at mass 37 represents an additional amplification by a factor of 10.