AIP | The Journal of Chemical Physics

Relaxation of vibrationally excited HF in levels v=1 and v=2. II. By CH4, C2H6, C3H8, C2H2, and C2H4

K. G. Anlauf, P. H. Dawson, and J. A. Herman

Citation: The Journal of Chemical Physics **58**, 5354 (1973); doi: 10.1063/1.1679151
View online: http://dx.doi.org/10.1063/1.1679151
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/58/12?ver=pdfcov
Published by the AIP Publishing

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 58, NUMBER 12 15 JUNE 1973

Relaxation of vibrationally excited HF in levels $v=1$ and $v=2$. II. By CH_4, C_2H_6, C_3H_8, C_2H_2, and C_2H_4

K. G. Anlauf, P. H. Dawson, and J. A. Herman

Centre de Recherches sur les Atomes et les Molécules, Faculté des Sciences, Université Laval, Québec 10e, Canada

(Received 7 November 1972)

The rate constants for the vibrational deactivation of HF($v=1,2$) by CH_4, C_2H_6, C_3H_8, and C_2H_2 were measured by monitoring the decay of $HF^†$ rotation-vibration emission in a fast flow system. For these hydrocarbons the energy transfer processes are very efficient. In the case of C_2H_4 the rate constant could only be estimated.

INTRODUCTION

There have been a number of recent measurements near room temperature of deactivation of vibrationally excited HF by HF,[1–5] H_2,[1,6] and CO_2.[1–3] The principal techniques have been the observation of chemiluminescence in "steady-state reactor" systems,[2] and of laser induced fluorescence.[3–5] Flow tube techniques are also being used[6,7] and we have described in detail elsewhere the use of a medium pressure flow tube system and its application to measurements of relaxation of $HF^†$ by H_2 and CO_2. The results are in reasonable accord with other measurements for H_2 but differ for the case of CO_2.

In this work, we have found unusually high rates of relaxation of HF ($v=2$) by hydrocarbons. These rates have not previously been measured. This process could be of great significance in limiting the performance of high pressure pulsed discharge (TEA) chemical lasers.[8,9]

EXPERIMENTAL AND ANALYSIS

The apparatus was a Teflon-coated flow tube of rectangular cross section (6.5×3 cm) with calcium fluoride windows down the sides of the tube. A special gas injector system, designed for rapid mixing, was used to produce vibrationally excited HF by the very fast reaction of fluorine atoms with hydrocarbons:

$$F+RH \rightarrow HF^†(v)+R,$$

where $v \leq 3$ for the case of $RH \equiv C_2H_4$, CH_4, C_2H_6, and C_3H_8, and $v \leq 2$ for $RH \equiv C_2H_2$.

F atoms were produced by passing CF_4 in excess helium through a microwave discharge. The CF_4 flow was generally very low ($\leq 0.5\times10^{-3}$ torr partial pressure). For the case of C_2H_2 and C_2H_4, a higher flow ($\leq 4\times10^{-3}$ torr) was needed in order to achieve a workable HF emission intensity. There was no evidence that the CF_4 or helium present contributed significantly to gas phase deactivation. The total pressure in the flow tube was maintained close to 2.5 torr, except for wall effect measurements.

The chemiluminescence was observed at different times after the gas mixing, by means of a moveable 0.5 m Jarrell-Ash grating spectrometer. The radiation (chopped at 43 cps) was detected by a PbS cell (−80°C) which was coupled to a phase-sensitive lock-in amplifier and chart recorder. A black body radiation source was used to calibrate the detector for wavelength sensitivity. Since the $HF^†$ was in rotational equilibrium (320°K) it was sufficient to monitor only the $1P3$ and $2P3$ rotation–vibration lines. These intensities could then be converted to $v=1$ and $v=2$ populations when necessary.

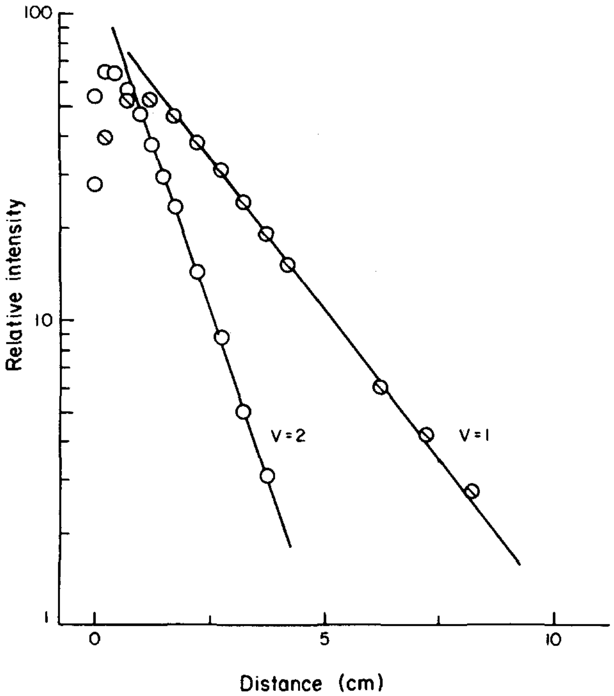

FIG. 1. Decay of HF $2P3$ and $1P3$ rotation–vibration emission as a function of distance in the flow tube. Total pressure=2.48 torr. Inflows: 4.3 atm·cm^3 min^{-1} of CH_4, 1.6 atm·cm^3 min^{-1} of CF_4, and 5110 atm·cm^3 min^{-1} of helium.

The entrance slits to the spectrometer were such that the spatial resolution was 0.2 cm, corresponding to a time resolution along the axis of the flow tube of 0.16×10^{-3} sec. The factor for converting the distance along the tube's axis to time was determined by measuring the volumetric flow rate of the system (using a Hast-

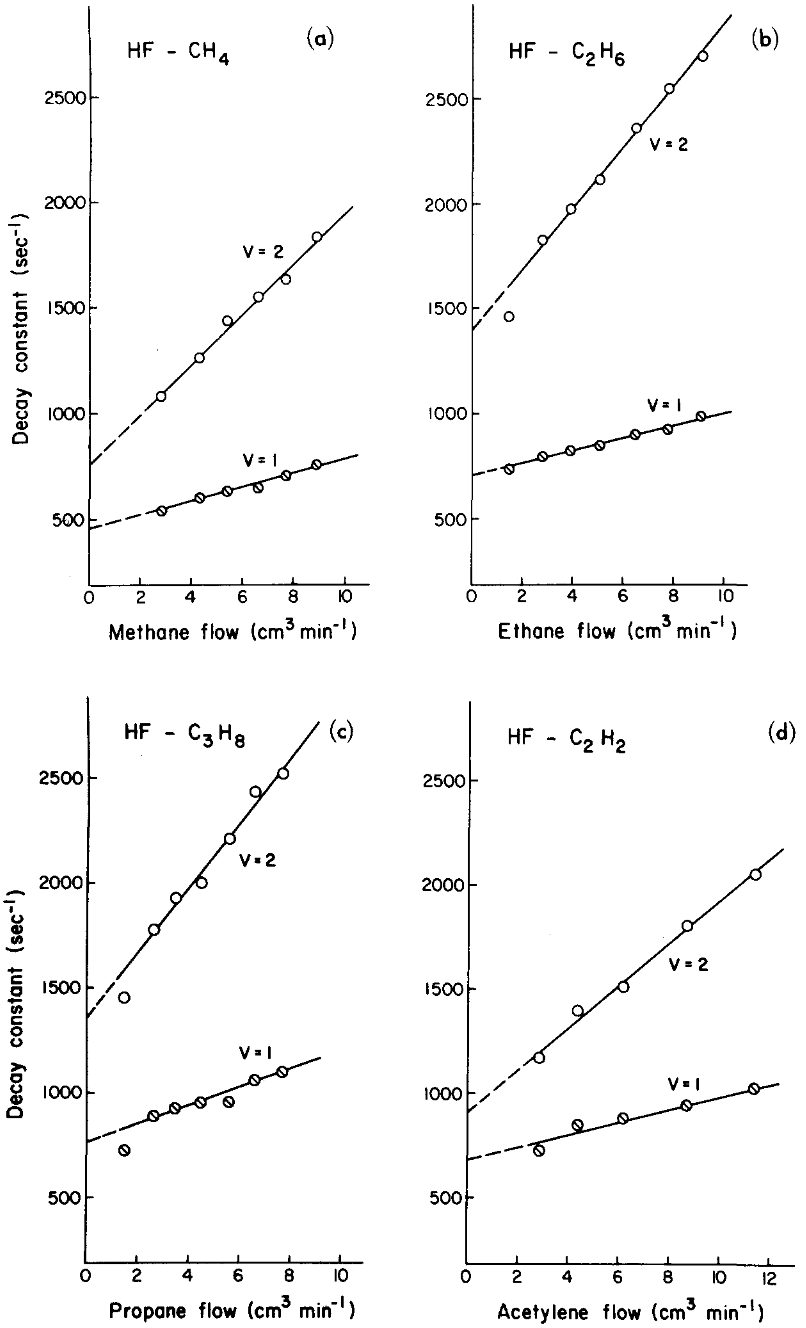

FIG. 2. Effect of hydrocarbon inflows on the decay constants using helium as diluent.Total pressure$\simeq$2.5 torr, helium inflow 5150 atm·cm^3 min^{-1}, CF_4 inflow$\simeq$ 1.5 atm·cm^3 min^{-1} for a, b, and c and $\simeq$8.5 atm·cm^3 min^{-1} for d. Note that 1 atm·cm^3 min^{-1}M0.48$\times 10^{-3}$ torr.

ings–Raydist electronic flowmeter LF-5K and a Wallace–Tiernan absolute pressure gauge). For helium, this was 26.1$\times 10^3$ atm·cm^{3}sec^{-1}. On dividing this by the area of the tube (21.4 cm^2) one obtains the linear flow rate: 1223 cm sec^{-1} or 1 cm$\equiv$0.82 msec.

More complete details on the apparatus and the analysis of the data may be found in Paper I of this series.[7] An important modification to this earlier arrangement was the introduction of a side arm on the main flow tube. Condensible reaction products were collected in a liquid nitrogen cooled trap by auxiliary pumping through this side arm (10–20 min collection time). The products were subsequently analyzed mass-spectrometrically using a Varian/MAT CH7.

RESULTS

The emission from levels $v=1$ and $v=2$ decayed exponentially down the flow tube for all the measured hydrocarbon flow rates (except for level $v=1$ in the case of added C_2H_4); these flows were generally 1–12 cm^3 min^{-1} which represented a partial pressure of 0.5–6$\times$ 10^{-3} torr.

A typical intensity decay plot for the 1*P*3 and 2*P*3

TABLE I. HF vibrational deactivation rate constants.[a]

Deactivating gas	$HF_{v=1}$	$HF_{v=2}$
CH_4	6.4×10^4 (1.2×10^{12})	2.3×10^5 (4.2×10^{12})
C_2H_6	5.6×10^4 (1.0×10^{12})	2.8×10^5 (5.1×10^{12})
C_3H_8	8.3×10^4 (1.5×10^{12})	3.0×10^5 (5.4×10^{12})
C_2H_2	5.9×10^4 (1.1×10^{12})	2.0×10^5 (3.6×10^{12})
C_2H_4	$\sim5\times10^4$ (9×10^{11})	$\sim2.2\times10^5$ (4.0×10^{12})
H_2[b]	2.4×10^4 (4.3×10^{11})	4.3×10^4 (7.8×10^{11})

[a] Units are $sec^{-1}\cdot torr^{-1}$ for values without parentheses; values in parentheses are in $cm^3\ mole^{-1}\cdot sec^{-1}$.

[b] Reference 7.

lines is seen in Fig. 1. Slopes derived from such semilogarithmic plots give, for levels $v=1$ and $v=2$, decay constants which represent the sum of spontaneous emission, wall deactivation and deactivation by the added gases. On plotting these decay constants versus the concentration of the deactivating hydrocarbon one should obtain a straight line of slope equal to the vibrational deactivation rate constant. This simple and direct analysis on levels $v=1$, 2 was possible for two reasons. Firstly, the amount of HF ($v=3$) observed in these experiments was too small to significantly influence the interpretation of measurements on HF ($v=2$) after the short distance where the initial reaction occurred. Secondly, a computer simulation of levels $v=1$, 2 confirmed their measured decay characteristics and showed that the level $v=2$ decayed so rapidly that its relative contribution to $v=1$ became unimportant at the later times down the tube where the $v=1$ decay slopes were measured.

After allowing for the consumption of hydrocarbon by the F atoms one can determine the intercepts on the plots of decay constants versus concentration. These intercepts should equal the sum of the radiational, wall and remnant gas phase deactivation rates. The wall deactivation rate may be independently determined by plotting the decay constant vs the inverse total pressure in the vessel.

Figures 2(a)–2(d) show the decay constants as a function of the hydrocarbon concentrations. All the data can be fitted very satisfactorily by straight lines. Their slopes are equal to the vibrational deactivation rate constants which are summarized in Table I; for comparison, the value for H_2 has been included.

Intercepts were determined from Figs. 2(a)–2(d). These values were in accord with those calculated from the radiational and the measured wall deactivation rates. The small differences that did appear could be attributed to either experimental error or remnant gas phase deactivation (by hydrocarbon radicals formed in the reaction or HF–HF interactions).

One significant difference between the saturated and unsaturated hydrocarbons was found in the initial $(v=2):(v=1)$ population ratios. The reactions of F atoms with acetylene and ethylene produced appreciably less HF ($v=2$) relative to HF ($v=1$). For acetylene this is expected since the exoergicity of the reaction is only sufficient to populate $v=2$ ($J=0$, 1). Unfortunately, the pumping speed of our apparatus is not sufficiently fast to allow the quantitative determination of the initial population distributions of these reactions.

In Paper I[7] we had observed and discussed the effect of feedback of vibrational energy to HF from H_2 ($v=1$), the latter having been excited in previous collisions with the $HF^{\dagger}$. This process had the effect of producing a "tail" in the HF ($v=1$) intensity decay. For the hydrocarbons, only ethylene exhibited this behavior. Figure 3 shows $v=1$, 2 intensity decay curves for a relatively high C_2H_4 inflow. It is seen that the $v=1$

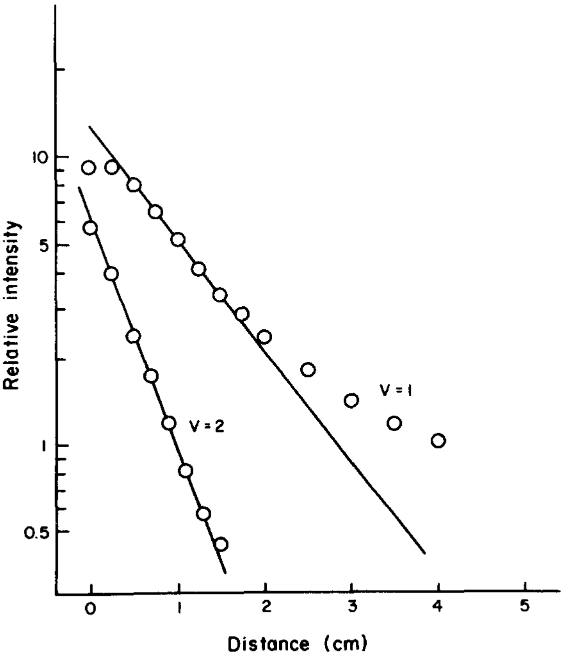

FIG. 3. Decay of HF 2*P*3 and 1*P*3 rotation–vibration emission as a function of distance in the flow tube. Note the curvature in the $v=1$ decay. Total pressure = 2.6 torr. Inflows: 11.2 $atm\cdot cm^3\ min^{-1}$ of C_2H_4, 8.4 $atm\cdot cm^3\ min^{-1}$ of CF_4, and 5360 $atm\cdot cm^3\ min^{-1}$ of helium.

decay was appreciably modified at longer times down the tube. This anomaly, in addition to the large *F* atom inflow, indicated the necessity for a mass-spectrometric analysis of the products. It was found as expected that the reactions with CH_4, C_2H_6, C_3H_8, and C_2H_2 were straightforward and that fluorination of the parent hydrocarbon molecule was negligibly small. That is to say, less than 2% relative to the H atom abstraction reaction (1). However, we found that the C_2H_4 was almost entirely consumed to form C_2H_3F, C_2H_2, and some $C_2H_2F_2$, and only a small proportion of the F atoms went to form HF. We had obtained an apparent rate constant of 3.3×10^5 $torr^{-1}\cdot sec^{-1}$ for HF ($v=2$) in this mixture of products. Subsequently we used $F+H_2$ as the primary reaction and added C_2H_4 to this mixture. Under these conditions, the H_2 consumed a large fraction of the F atoms to form HF and the C_2H_4 was only about 20% fluorinated. Hence the deactivation rate constants as determined from these decay curves yielded upper limits; these were $k_{v=2}\gtrsim2.2\times10^5$ $torr^{-1}\cdot sec^{-1}$ and $k_{v=1}\gtrsim5\times10^4$ $torr^{-1}\cdot sec^{-1}$. Using CH_4 in place of H_2 as the primary reactant yielded the same values. Hence, owing to the complication in the reaction mechanism for C_2H_4, the "tail" in the $v=1$ decay curve of Fig. 3 cannot unambiguously be identified with either feedback from an excited species or formation of excited HF down the tube.

For all these hydrocarbon reactions a faint orange chemiluminescence of unknown origin was observed.

DISCUSSION

From Table I it becomes evident that the deactivation of $HF^{\dagger}$ by these hydrocarbons is very fast (~250 collisions per deactivation for $HF_{v=1}$) and is significantly larger than that for H_2 (~1000 collisions for $HF_{v=1}$). This difference cannot be accounted for by a change in the gas kinetic collision cross-section. Since the process for $HF^{\dagger}$–H_2 energy transfer is already close to resonance, the higher efficiency for the hydrocarbons can only be attributed to a stronger interaction with the HF during the collisional transfer.

The variations in the deactivation rate constants among the various hydrocarbons are not large enough to allow a correlation of these variations with particular hydrocarbon properties. Changes in gas kinetic collision cross-section would account for some of the observed variations. The $v=2$ deactivation rate constant values were between 3.3 to 5.0 times those for $v=1$. The $v=2$ deactivation probability would be favored on account of the higher vibrational quantum number and the energy transfer could be closer to resonance. The many possible combinations of vibrational modes in the hydrocarbons make it difficult to assign the levels involved in the energy transfer process.

ACKNOWLEDGMENT

We would like to express gratitude to the Canadian Defence Research Board, Valcartier, for support of this work.

---

[1] J. K. Hancock and W. H. Green, J. Chem. Phys. **56**, 2474 (1972); J. Chem. Phys. **57**, 4515 (1972).

[2] J. R. Airey and I. W. M. Smith, J. Chem. Phys. **57**, 1669 (1972).

[3] R. R. Stephens and T. A. Cool, J. Chem. Phys. **56**, 5863 (1972).

[4] J. R. Airey and S. F. Fried, Chem. Phys. Lett. **8**, 23 (1971).

[5] J. F. Bott, J. Chem. Phys. **57**, 96 (1972).

[6] M. A. Kwok, Conference on Chemical and Molecular Lasers, St. Louis, May 1972.

[7] K. G. Anlauf, P. H. Dawson, and J. A. Herman (unpublished).

[8] T. V. Jacobson and G. H. Kimbell, J. Appl. Phys. **42**, 3042 (1971).

[9] W. H. Green and M. C. Lin, J. Chem. Phys. **54**, 3222 (1971).