AN INVESTIGATION OF VIBRATIONAL ENERGY TRANSFER FROM HF *AND* DF *MOLECULES TO* CO_2 *MOLECULES*

G. K. VASIL'EV, E. F. MAKAROV, V. G. PAPIN, and V. L. TAL'ROZE

Institute of Chemical Physics, U.S.S.R. Academy of Sciences

Submitted February 4, 1971

Zh. Eksp. Teor. Fiz. **61**, 97—100 (July, 1971)

Vibrational energy transfer from HF and DF molecules to CO_2 molecules was studied by the chemiluminescent flow technique. Assuming slow v − v exchange between the molecule pairs HF − H_2 and DF − D_2, the respective rate constants at 400° K were found to be (in cm^3/sec-molecule): $k_{HF_1CO_2} = 1.8 \times 10^{-14}$ and $k_{DF, CO_2} = 3.3 \times 10^{-12}$; assuming rapid v − v exchange: $k_{HF, CO_2} \approx 1.1 \times 10^{-12}$ and $k_{DF, CO_2} = 50(3.3 \times 10^{-13} - k_{D_2, CO_2})$.

VIBRATIONAL exchange between a number of different molecules and CO_2 molecules, which was investigated in recently published work,[1-4] has an important role in combustion processes and in molecular gas lasers.[2,5-11] In[6-11] laser action was achieved using CO_2 molecules excited by the transfer of vibrational energy from HCl, HF, DF, and HBr molecules that were formed in chemical reactions.

In the present work a previously described chemiluminescent flow technique[12] is used to investigate the transfer of vibrational energy from HF and DF molecules to CO_2 molecules.

The experimental arrangement is shown in Fig. 1. Molecular hydrogen (or deuterium) entered the discharge tube 4; CO_2 gas and fluorine entered the reaction vessel 1 directly through calibrated apertures of ~100-μ diameter. Partial dissociation of the H_2 (D_2) took place in the discharge tube; HF (DF) molecules in a vibrationally excited state were formed mainly in the reaction $H(D) + F_2 \rightarrow HF(DF) + F$. The experiment consisted essentially in maintaining constant flow rates of $H_2(D_2)$ and F_2 while varying the flow rate of CO_2, and in observing the varying intensity of radiation from vibrationally excited v = 1 HF (DF) molecules as a function of the CO_2 concentration in the reaction vessel. The gas flow rates, which were determined from the decrease of pressures in tanks of known volumes, were in the following ranges (measured in μM/sec): H_2: 170—270; D_2: 105—210; F_2: 0.7—1.4; CO_2: 0—70. The respective partial pressures were 0.5—0.8: 0.3—0.7; (2—4) × 10^{-3}; and 0—0.2 Torr. The molecules remained an average time of 9×10^{-3} sec in the optical cell before their radiation was registered. The temperature in the reaction vessel was about 400° K.

The following conditions prevailed in our experiments: a) The concentration of H(D) atoms in the stream greatly exceeded the concentration of F_2 molecules, whose dissociation rate was much lower than the flow rate resulting from the reaction; b) the transfer rate of vibrational energy from excited HF (DF) molecules to CO_2 and $H_2(D_2)$ molecules greatly exceeded the rate of the inverse processes.

Because of the existing uncertainty regarding the deactivation rate constants of vibrationally excited HF (DF) molecules, the following two sets of assumptions governed the treatment of our experimental data:

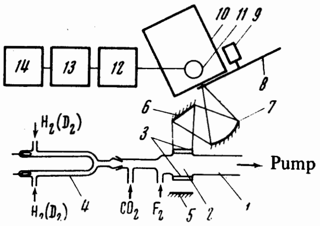

FIG. 1. Experimental arrangement. 1—Reaction vessel, 2—optical cell, 3—exit windows, 4—discharge tube, 5—plane mirror, 6 and 7—focusing mirrors, 8—modulator disk, 9—electric motor, 10—IKM-1 monochromator, 11—Au-Ge detector of radiation, 12—amplifier, 13—signal detection circuit, 14—automatic recorder.

1) The probabilities of intermolecular v − v exchange in the HF − HF and DF − DF cases are large, but in the HF − H_2 and DF − D_2 cases are small. Also, the characteristic formation time of excited HF (DF) molecules in the given reaction is much shorter than their deactivation time due to all processes. These assumptions are supported by the data of Kompa et al.[13] and by the (Russian) data of Chaĭkin and Arutyunov.

2) The characteristic times of intermolecular v − v exchange in the HF − H_2 and DF − D_2 cases are shorter than in the HF − CO_2 and DF − CO_2 cases, and are comparable with or shorter than the formation time of HF (DF) molecules in our reactor. These assumptions are supported by recent data in[14].

The assumptions 1) lead to

$$I_{\mathrm{HF},\, v=1} \sim \exp[-k_{\mathrm{HF},\, \mathrm{CO_2}}(\mathrm{CO_2})t], \tag{1}$$

and the assumptions 2) lead to

$$I_{\mathrm{HF},\, v=1} \sim \exp\left\{-\left[\frac{k_{\mathrm{H_2},\, \mathrm{HF}}}{k_{\mathrm{HF},\, \mathrm{H_2}}}\frac{(\mathrm{HF})}{(\mathrm{H_2})}k_{\mathrm{HF},\, \mathrm{CO_2}} + k_{\mathrm{H_2},\, \mathrm{CO_2}}\right](\mathrm{CO_2})\, t\right\}. \tag{2}$$

Here $I_{HF, v=1}$ is our measurement of the radiation intensity from HF molecules, k is the rate constant of vibrational energy transfer (cm^3/sec-molecule); (CO_2) is the concentration of CO_2 molecules in the reactor. (In analogous expressions for $I_{DF, v=1}$ all HF labels are to be replaced by DF, and H_2 by D_2.)

1. The transfer of vibrational energy from HF mole-

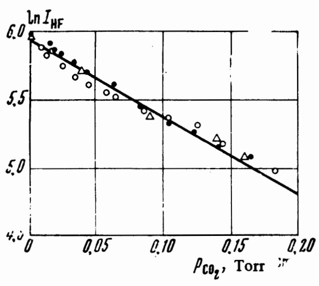

FIG. 2

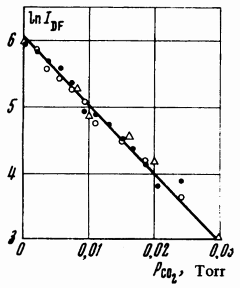

FIG. 3

FIG. 2. Intensity of radiation from HF molecules versus CO_2 pressure. Flow rates: ●–H_2 –270, F_2 –1.24; ○–H_2 –200, F_2–0.62; Δ–H_2 –170, F_2 –0.72 μM/sec.

FIG. 3. Intensity of radiation from DF molecules versus CO_2 pressure. Flow rates: ●–D_2 –210, F_2 –1.34; ○–D_2 –105, F_2 –1.24; Δ–D_2 –1.85, F_2 –0.97 μM/sec.

cules to CO_2 molecules occurs, as stated in[9], in the processes

$$HF_{v=1} + CO_2(00^00) \begin{array}{l} \nearrow HF_{v=0} + CO_2(10^01) + 242\,\text{cm}^{-1} \\ \searrow HF_{v=0} + CO_2(02^01) + 349\,\text{cm}^{-1} \end{array}, \quad (3)$$

where the upper laser level of CO_2 (00° 1) is populated in the processes

$$\begin{array}{l} CO_2(10^01) + CO_2(00^00) \rightarrow CO_2(00^01) + CO_2(10^00), \\ CO_2(02^01) + CO_2(00^00) \rightarrow CO_2(00^01) + CO_2(02^00). \end{array} \quad (4)$$

Figure 2 shows how the logarithm of the radiation intensity from HF molecules depends on the CO_2 concentration in the data from three different experiments. A single relative intensity scale was used on the basis of the signals in the absence of CO_2 molecules. The experimental points are well fitted by a straight line whose slope indicates that under conditions 1) we have $k_{HF,CO_2} = 1.8 \times 10^{-14}$ cm³/sec-molecule, and under conditions 2) we have $k_{HF,CO_2} = 60(1.8 \times 10^{-14} - k_{H_2CO_2})$ cm³/sec-molecule.

2. The transfer of vibrational energy from DF molecules to CO_2 molecules occurs in the process

$$DF_{v=1} + CO_2(00^00) \rightarrow DF_{v=0} + CO_2(00^01) + 557\,\text{cm}^{-1}. \quad (5)$$

Figure 3 illustrates how the logarithm of radiation intensity from $DF_{v=1}$ molecules depends on the CO_2 concentration in the reaction vessel. The slope of this graph shows that under conditions 1) we have $k_{DF,CO_2} = 3.3 \times 10^{-13}$ cm³/sec-molecule, and under conditions 2) we have $k_{DF,CO_2} = 50(3.3 \times 10^{-13} - k_{D_2,CO_2})$ cm³/sec-molecule.

Our experimental determination of k_{H_2,CO_2}, which appears as the subtrahend in the foregoing numerical expression for k_{HF,CO_2} under conditions 2), showed that $k_{H_2,CO_2} \ll 1.8 \times 10^{-14}$, i.e., $k_{HF,CO_2} \approx 1.1 \times 10^{-12}$ cm³/sec-molecule. We still have no data for k_{D_2,CO_2}. If it should be found that $k_{D_2,CO_2} \ll 3.3 \times 10^{-13}$, then under both conditions 1) and conditions 2) we would obtain the ratio $k_{DF,CO_2}/k_{HF,CO_2} \approx 20$.

The achievement of continuous laser action in the systems $D_2 + F_2 + CO_2$ and $H_2 + F_2 + CO_2$ has been reported in[9]. The power levels relative to identical flow rates of the reagents also differ by a factor of about 20. This indicates that the effects on the power output which are due to other factors (the "inutile" deactivation of HF and DF, the magnitudes of the average vibrational quanta, and the chemical reaction rates) are compensated randomly in both systems.

---

[1] R. L. Taylor, M. Camac, and R. M. Feinberg, Eleventh International Symposium on Combustion, The Combustion Institute, Pittsburgh, Pa., 1967, p. 49; R. L. Taylor and S. Bitterman, J. Chem. Phys. **50**, 1720 (1969).

[2] C. B. Moore, R. E. Wood, B.-L. Hu, and J. T. Yardley, J. Chem. Phys. **46**, 4222 (1967); W. A. Rosser, A. D. Wood, and E. T. Gerry, J. Chem. Phys. **50**, 4996 (1969).

[3] J. C. Stephenson, R. E. Wood, and C. B. Moore, J. Chem. Phys. **48**, 4790 (1968); J. C. Stephenson and C. B. Moore, J. Chem. Phys. **52**, 2333 (1970).

[4] H. J. Bauer and R. Schotter, J. Chem. Phys. **51**, 3261 (1969).

[5] C. K. N. Patel, Appl. Phys. Lett. **6**, 12 (1965).

[6] H. L. Chen, J. C. Stephenson, and C. B. Moore, Chem. Phys. Lett. **2**, 593 (1968).

[7] R. W. F. Gross, J. Chem. Phys. **50**, 1889 (1969).

[8] T. A. Cool, R. R. Stephens, and T. J. Falk, Int. J. Chem. Kinetics **1**, 495 (1969).

[9] T. A. Cool, T. J. Falk, and R. R. Stephens, Appl. Phys. Lett. **15**, 318 (1969).

[10] T. A. Cool and R. R. Stephens, J. Chem. Phys. **52**, 3304 (1970).

[11] N. G. Basov, V. T. Galochkin, L. V. Kulakov, E. P. Markin, A. I. Nikitin, and A. N. Oraevskiĭ, Collection, Kratkie soobshcheniya po fizike (Brief Communications in Physics), FIAN USSR, No. 8, 10 (1970).

[12] G. K. Vasil'ev, E. F. Makarov, V. G. Papin, and V. L. Tal'roze, in Mezhdunarodnyĭ simpozium po khimicheskim kvantovym generatoram (International Symposium on Chemical Lasers), Moscow, 1969; Dokl. Akad. Nauk SSSR **191**, 1077 (1970).

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

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

Translated by I. Emin
9