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20. Abstract

Preparatory experiments and construction of apparatus leading up to attempts to obtain the initial vibrational and rotational energy distribution of deuterium fluoride produced in the gas phase reaction

$$D + F_2 \xrightarrow{YIELDS} DF + F$$

are described. Discrepancies between results obtained with the present apparatus and that of other workers are discussed and resolved.

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EXPERIMENTAL DETERMINATION OF INITIAL VIBRATIONAL AND ROTATIONAL

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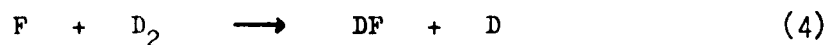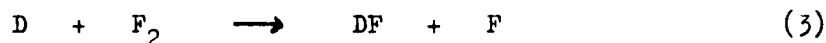
EXPERIMENTAL DETERMINATION OF INITIAL VIBRATIONAL AND ROTATIONAL ENERGY DISTRIBUTIONS FROM THE REACTION OF ATOMIC DEUTERIUM WITH MOLECULAR FLUORINE.

A great deal of effort at both the experimental and theoretical levels, has been put into attempting to understand the simple atom-molecule reactions. In the past two decades experimental studies have derived considerable impetus from the development of both molecular beam techniques and infrared chemiluminescence studies. Theoretical methods, especially the classical trajectory approach, have also benefited from the general availability of high speed computers.

Much of the present interest in the simple atom-molecule reactions is centred around those which produce either hydrogen fluoride or deuterium fluoride in vibrationally excited states. The reason for this interest lies in the powerful chemical lasers which have been developed out of such processes, especially from the H_2/F_2 and D_2/F_2 systems. These chemical lasers are based on the two competing reactions:

$$H + F_2 \longrightarrow HF + F \qquad (1)$$

$$F + H_2 \longrightarrow HF + H \qquad (2)$$
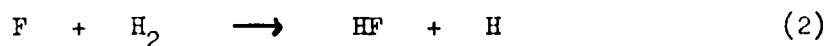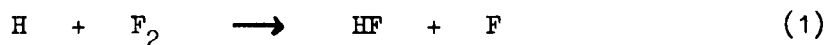
or the deuterium analogues:

$$D + F_2 \longrightarrow DF + F \qquad (3)$$

$$F + D_2 \longrightarrow DF + D \qquad (4)$$

of these four systems, whereas all four have been studied systemically

both by the classical trajectory method using semi-empirical potential energy surfaces, experimentally only 1, 2 and 4 have been studied. The experimental studies have been made by infrared chemiluminescence (1 - 3) and reaction (2) has also been studied by a crossed molecular beam technique (4). Reaction (4) has also been studied by the crossed molecular beam method (5).

In spite of the obvious importance of reaction (3) in the context of chemical laser applications, no experimental studies had been made of the vibrational and rotational energy distributions in the product deuterium fluoride at the time when this proposal was submitted. Since that time we have completed a study of the initial vibrational energy distribution using the measured relaxation infrared chemilumines-cence method (6). Although not completely unambiguous, that study strongly suggested that the most populated vibrational level of deuterium fluoride was $v' = 10$. It also determined relative primary rate constants for formation of deuterium fluoride in vibrational levels $v' = 2$ to $v' = 12$. The results indicated that 62 per cent of the available energy initially entered vibration.

There has often been some conflict between experimental results obtained by the measured relaxation infrared chemiluminescence method and those obtained by the lower pressure arrested relaxation method. This was one of the reasons that a study by the latter method was proposed. Additionally, the measured relaxation method gives no indication of the initial rotational energy distribution, which is a valuable additional quality so far as chemical laser applications are concerned.

Experimental

The apparatus used for arrested relaxation studies is shown in figure 1. The design of the reaction cell is critically important. In view of the desirability of operating at the minimum possible pressure it must possess an efficient light collecting system, contain an effective means of arresting the product state relaxation processes, and provide optimum pumping conditions. It is in the last respect that the present design differs most significantly from those of other workers. Pumping of the cell is effected by means of an Edwards 24 inch F2404 oil diffusion pump backed by an ISC 3000 Edwards rotary pump. The unthrottled throughput for hydrogen is 10 - 1200 dm^3 at a pressure of 10^{-4} torr. Perhaps most important, the entire bottom area of the reaction cell is exposed to the vacuum pump via a liquid nitrogen cooled chevron baffle. The remaining sides and top of the reaction cell are covered by an "inverted trough" of copper plate cooled by continuous passage of liquid nitrogen through copper coils silver soldered to its outer surface. The light collection system is a standard Welsh cell consisting of four semi-circular gold plated mirrors of 150 mm diameter, radius of curvature 530 mm, independently mounted in pairs and capable of individual adjustment from outside the cell.

Deuterium (Air Products Ltd. 99.999 per cent), fluorine (B.O.C. Ltd. 98.0 per cent) and argon (B.O.C. Ltd. 99.999 per cent) were used without further purification. Deuterium atoms were produced by a 100 W, 2450 MHz microwave discharge in deuterium. Fluorine atoms were produced by a similar discharge technique using carbon tetrafluoride as the precursor.

Due to the extreme toxicity and corrosive nature of fluorine, a number of modifications to the usual gas inlet and outlet systems

were necessitated. The molecular fluorine was introduced to the fluorine glass line through $\frac{1}{4}$ inch copper pipe. This line had previously been evacuated thoroughly to minimize adsorbed water. The flow rate was controlled by a stainless steel needle valve and measured using a calibrated capillary flow meter filled with a full fluorinated oil. Voltalef 90 grease was used on all glass stopcocks and glass to metal connections were made with teflon tubing. Excess fluorine was discharged into a trap containing a mixture of potassium hydroxide pellets and glass beads. The beads prevented trap blockage due to the formation of a solid crust of potassium fluoride.

The fundamental emission from DF spans a region (3.46 μm to 4.60 μm) in which the sensitivity of a conventional lead sulphide detector is low. It was therefore necessary to record the DF spectra in the first overtone region (1.75 μm to 2.96 μm) which lies near the peak of the detector's response.

The infrared spectrum of DF does not lend itself to simple analysis in the same way as hydrogen fluoride. The larger reduced mass and consequent smaller vibrational and rotational spacings result in many near coincidences of vibration–rotation lines within overlapped bands. Consequently a computer simulation technique is essential in order to analyse the spectra. In order to calculate the vibration–rotation line positions with sufficient accuracy it was found necessary to use a Dunham expression with 16 coefficients. This expression used the Dunham coefficients for HF (7) corrected for DF by means of the isotope relations (8)

$$\frac{Y_{1J}^{\ i}}{Y_{1J}} = \left(\frac{\mu}{\mu^i} \right) (1 + 2J)/2. \tag{5}$$

The trial vibrational and rotational population distributions ($N^{v'J'}$) input to the simulation program were converted to intensities by

$$I_{vJ}^{v'J'} = \frac{N^{v'J'}hc(\omega_{vJ}^{v'J'})^4 F_{vJ}^{v'J'} S_J A_v^{v'}}{(2J' + 1)(\omega_v^{v'})^3} , \qquad (6)$$

where $I_{vJ}^{v'J'}$ is the intensity and $\omega_{vJ}^{v'J'}$ is the frequency of transition from a state $(v'J')$ to state (v,J). $A_v^{v'}$ is the Einstein coefficient and $\omega_v^{v'}$ is the frequency of the pure vibrational transition $(v' \rightarrow v)$. S_J is the line strength and $F_{vJ}^{v'J'}$ is the rotation-vibration interaction factor, calculated using the full expression of Herman et al. (9). The Einstein coefficients used were those of Sileo and Cool (10).

As stated above, the emission intensity $(I_{vJ}^{v'J'})$ of any particular vibration-rotation line may be related to the population $(N^{v'J'})$ of that state by expression (6). In previous work an approximate expression was used to calculate the rotational contribution to the transition probability. To improve the accuracy of this study, a program was developed to calculate the contribution using the full expression of reference 9.

Results and analysis

Analysis of the DF spectra is further complicated by the non-Boltzmann nature of the rotational distributions to be found within any particular vibrational level. A considerable effort has therefore had to be put into developing computer programs capable of simulating these experimental distributions. This stage of the work has been completed, and we are confident that the computer simulation technique

is capable of giving a unique and unambiguous solution for both vibrational and rotational distributions in each of the significantly populated levels.

However, a totally unexpected and highly disturbing complication has led to a severe set-back in the progress of study of the atomic deuterium/molecular fluorine reaction. Doubts as to the reliability of the arrested relaxation method have been cast by two glaringly contradictory experimental studies of the reaction

$$F \quad + \quad HBr \quad \longrightarrow \quad HF^+_{v \leqslant 4} + Br \qquad (7)$$
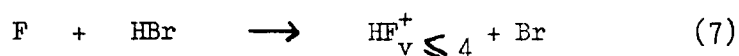
by this method.

The first published result by us (11) showed a typical vibrational distribution for hydrogen fluoride formed in an exo‾ergic reaction such as (7) i.e. the maximum vibrational population was to be found in the highest or next to highest available level on an energy basis. In this case maximum population was determined as being in $v' = 4$ for HF, indicative of a highly inverted distribution. However, a later study by Polanyi and co-workers (12) found that there was no population inversion and deduced that maximum population was in fact to be expected in the $v' = 0$ level. Since these workers used an interferometric system for obtaining their spectra, they were able to work at lower pressures than in our work and in theory should obtain more reliable data.

We therefore felt it imperative that we should make very thorough and detailed checks on our experimental method involving reaction (7) before proceeding any further with the main study of the D/F_2 system.

Systematic and detailed experiments have been carried out along a number of lines. Since the vibrational excitation in our work compared with the lower pressure studies of Polanyi et al is explained by those workers as due to the near match between low vibrational levels of HF and the $^2P_{\frac{1}{2}} \longleftrightarrow {}^2P_{3/2}$ transition of atomic bromine, it follows that the addition of atomic bromine to vibrationally excited hydrogen fluoride should lead to selective depopulation of the lower vibrational levels of HF. We have therefore tested the theory by observing the initial vibrational energy level distribution of HF formed in the reactions of atomic fluorine with hydrogen, methane and methyl iodide respectively. In each case we have observed vibrational populations which are identical within experimental error with those which have been published previously. It is well-known that the very fast reaction of atomic fluorine with molecular bromine according the equation

$$F + Br_2 \longrightarrow FBr + F \tag{8}$$
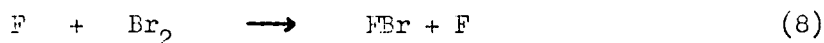
produces atomic bromine primarily in its ground $(^2P_{\frac{3}{2}})$ electronic state. Independent studies by photoelectron spectroscopy in these laboratories (13) has failed to detect the presence of excited bromine atoms. Hence, in each of the three reactions referred to above, molecular bromine was added. A decrease in overall emission was observed because of the competitive effect of reaction (8). However, in none of the cases was there any evidence for selective depopulation of any vibrational level of hydrogen fluoride. Hence, although we believe that from other studies (13) there is evidence for efficient energy transfer between vibrationally excited HF and atomic bromine, there is no evidence to support the belief that this process is more efficient when involving

$HF_{(v=1)}$ and $HF_{(v=2)}$ than with the next immediately higher levels.

Since the period covered by this report we have obtained further and, we believe, conclusive evidence in support of our original results concerning reaction (7). We have studied the initial vibrational and rotational energy level distributions of deuterium fluoride formed in the reaction

$$F + DBr \longrightarrow DF_{v \leqslant 6} + Br \qquad (9)$$
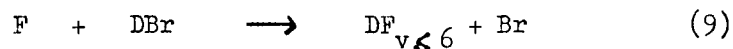
In this case the vibrational energy distribution mirrors our results on reaction (7). This is to be expected if the data are correct for (7), but if they were wrong because of energy transfer processes there would be significant differences, since the near resonances of reaction (7) would not be present in reaction (9). A full report of this work will appear in the scientific literature in due course. It is of interest to note that the analysis of the data from reaction (9) has given us an ideal opportunity to test our computer simulation procedures for deducing initial vibrational and rotational energy distributions of deuterium fluoride. Our earlier belief that a unique solution can be deduced has been substantiated.

It is hoped that the work on the atomic deuterium/molecular fluorine system can now be completed with the knowledge that the energy distributions obtained from the arrested relaxation method are indeed reliable.
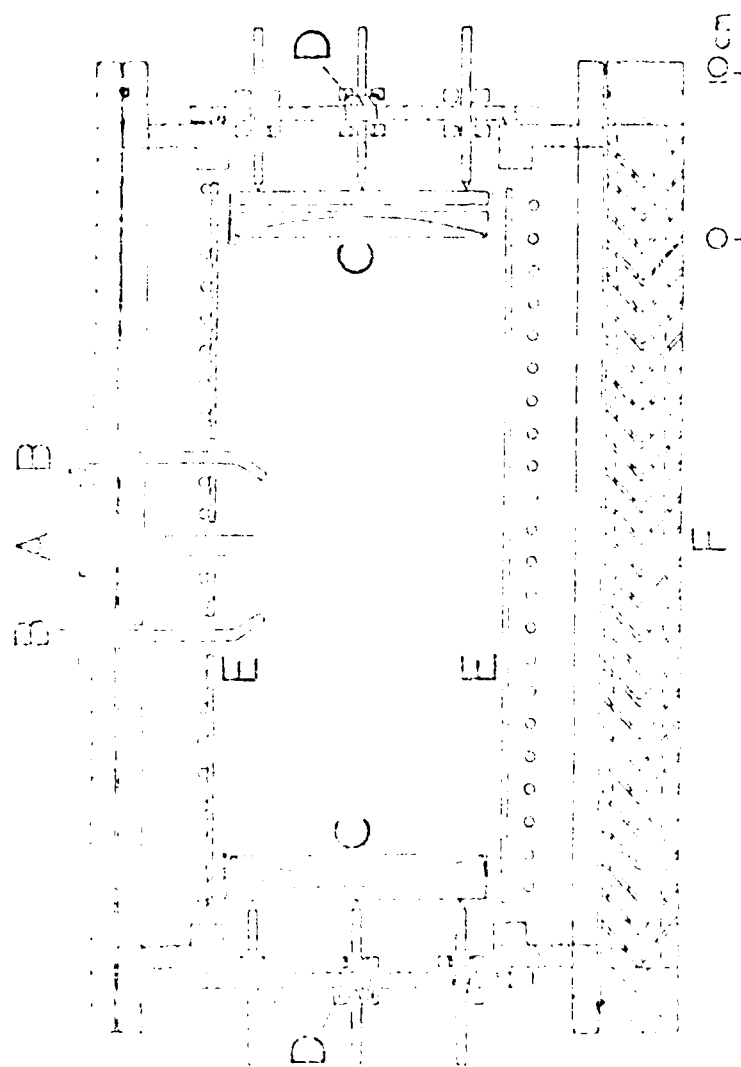
Fig. 1. Diagram of the reaction chamber. Key: A, B, inlet jets; C, Welch cell mirrors; D, lithium fluoride windows; E, cold wall; F, Chevron baffle, under which the diffusion pump is mounted.

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