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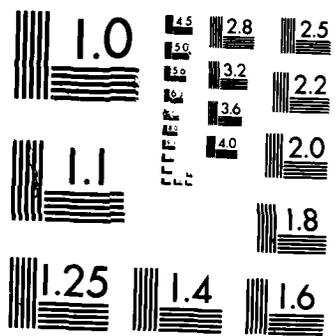
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STUDIES OF ENERGY TRANSFER AND SELECTIVE CHEMICAL REACTION  
USING TUNABLE IR RADIATION

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20. Abstract Tunable infrared lasers have been used to excite selected vibrational levels of molecules for kinetic studies. It was demonstrated that stimulated electronic Raman scattering (SERS) in Cs vapour provides a useful tunable source between 2.7 and 3.3 $\mu\text{m}$ . Later this source was supplanted by an optical parametric oscillator (OPO) supplying high energy pulses (1-5 mJ) over a wider range (1.5- 3.6 $\mu\text{m}$ ). Both sources have been used in detailed studies of the relaxation of HCN. When finished these experiments will yield the most complete picture of relaxation rates and pathways in any simple polyatomic molecule. In addition, new direct methods have yielded rates of relaxation of (a) high vibrational levels in HF, and (b) NO and OH in collision with other free radicals. Finally, some preliminary work on selective laser-induced chemistry both in the gas-phase and in low temperature matrices has been carried out.		

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## 1. INTRODUCTION

This project had two principal objectives. The first was to develop sources of tunable, coherent, infrared radiation. Two such sources have been employed in our research. Initially, we built a system which utilised stimulated electronic Raman scattering (SERS) in cesium vapour to down shift the frequencies of a dye laser, thereby producing pulses of radiation tunable between 3700 and 3000  $\text{cm}^{-1}$  (2.7 - 3.3 $\mu\text{m}$ ). Fairly soon, however, we were able to purchase an optical parametric oscillator (OPO) which provides higher pulse energies over a wider range of wavelengths (1.5 - 3.6 $\mu\text{m}$ ) and this took over from the SERS source. Both these sources are described briefly and evaluated in Section 2. Fuller descriptions can be found in some of the reprints appended to this Report. More recently, like several other laboratories we have begun to utilise stimulated vibrational Raman scattering (SVRS) in high pressure hydrogen to downshift dye laser frequencies. The properties of this source are also mentioned briefly in Section 2.

The second and main objective of our research has been to utilise pulsed, tunable, infrared lasers to excite specific molecular states for kinetic studies of their relaxation; for example, by observing their time-resolved infrared fluorescence. We soon came to the decision to study one prototype polyatomic molecule in detail and chose HCN. The results of this work are described in Section 3(a) and in three reprints and a preprint which are included with this report.

Along with our work on HCN, two other series of successful experiments on vibrational relaxation have been carried out. In the first of these, the Nd:YAG laser which normally pumps the OPO photolysed  $\text{F}_2$ , and hence initiated reactions of F atoms which generate HF in high vibrational levels ( $v \leq 6$ ). By observing time-resolved vibrational chemiluminescence, rates were obtained for relaxation of HF ( $v=3,4,6$ ) and for some F atom reactions. Secondly, somewhat different laser techniques have been used to study the vibrational relaxation of the free radicals NO and OH by other radicals. The rates are fast, indicating facile energy transfer when a strongly bound

collision complex is involved.

The results of our experiments on the vibrational relaxation of specific states of HCN, HF, OH and NO are reported in Section 3. Work on nearly all these species continues and this current research is mentioned briefly. We have made less progress in studies of chemical reaction, as distinct from relaxation, induced by tunable infrared radiation. Preliminary experiments on the selective rotational isomerisation of 2-fluoroethanol have been performed and are reported in Section 3(iv). Finally, recent attempts to establish the rate constants for the reactions of HF( $v=3,4,5$ ) with H atoms are described briefly.

## 2. TUNABLE INFRARED LASERS

### (i) Stimulated Electronic Raman Scattering (SERS) in Cesium Vapor.

Infrared frequency generation via SERS was first observed in 1973.<sup>1</sup> Subsequently, SERS in alkali metal vapors was investigated at Southampton University by Hanna and his coworkers.<sup>2</sup> The most useful medium for exploiting the SERS effect was shown to be cesium vapor and this was used in our experiments.

The SERS source that was constructed in Cambridge was described in detail in an earlier (1 May, 1979) Scientific Report prepared for USAFOSR<sup>3</sup> and by Petersen and Smith in a paper<sup>4</sup> (J. Chem. Phys., 71, 3346; 1979) of which a copy is included in the Appendix. Here, I shall simply recapitulate on the main features of this source and its potential for future applications.

SERS is a non-linear optical process in which incident radiation of frequency  $\omega_p$  generates a Raman shifted wave of frequency  $\omega_s$  which obeys the relationship

$$\omega_s = \omega_p - \Omega \quad (1)$$

In Cs vapor, the Raman shift  $\Omega$  leads to promotion of atoms from the  $6^2S$  ground state to  $7^2S$ . When the pump wave is

Table 1. Characteristics of the Dye Laser and of SERS Source.

Dye Laser

Wavelength	=	450 - 465 nm
Linewidth	=	$\sim 0.5 \text{ cm}^{-1}$
Output Energy	=	1.0 mJ/pulse
Repetition Rate	=	20 Hz

SERS Source

Frequency	=	3000 - 3700 $\text{cm}^{-1}$
Linewidth	=	$\sim 0.5 \text{ cm}^{-1}$
Output Energy	=	25 $\mu\text{J/pulse}$

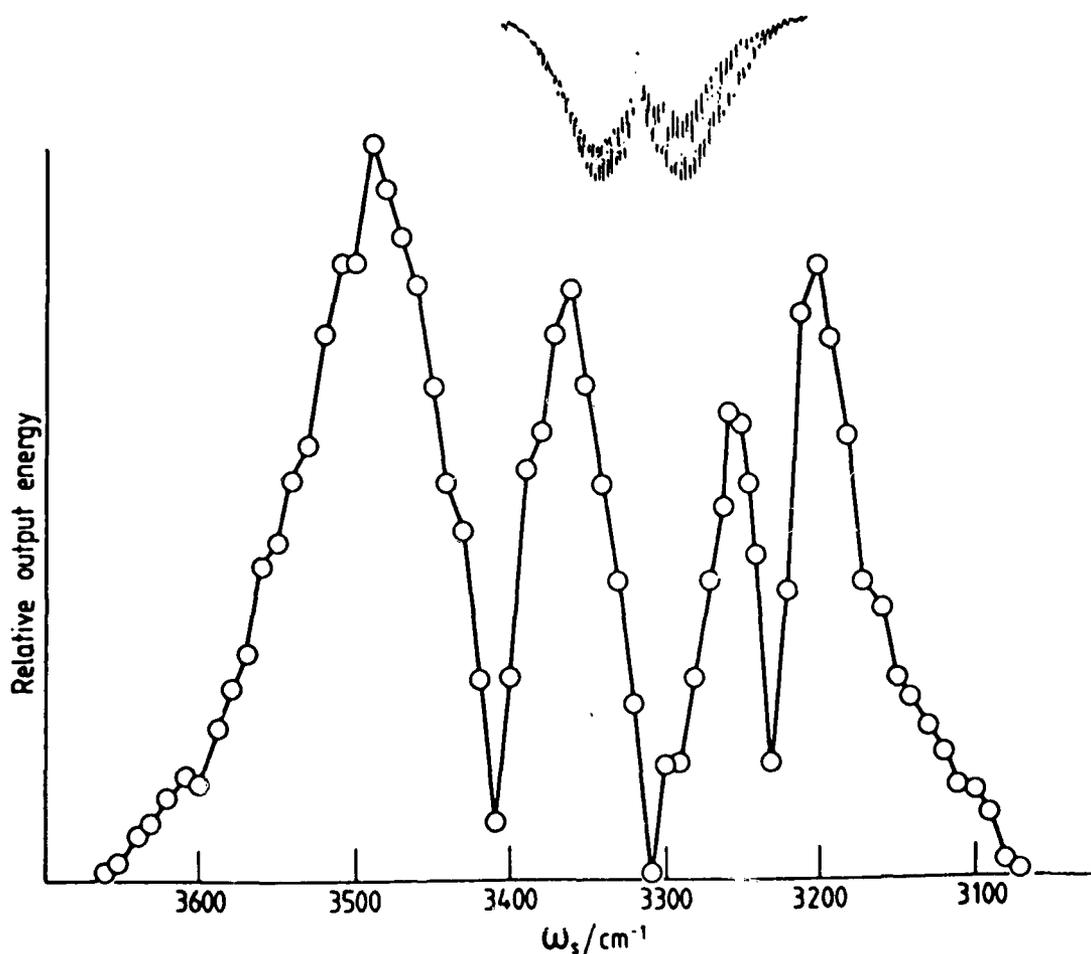


FIGURE 1. Variation of the output energy of the SERS source with frequency. The insert shows the  $\nu_3$  fundamental absorption of HCN

nearly resonant with the  $6^2P_{3/2,1/2} - 6^2S$  transitions, the scattering is enhanced. If  $\omega_p$  is sufficiently intense, stimulated Raman scattering occurs, and conversion of  $\omega_p$  to  $\omega_s$  can become the dominant optical process. With a dye laser tunable around  $\omega_p = 21,000 \text{ cm}^{-1}$ , then  $\omega_s$  is tunable near  $3,300 \text{ cm}^{-1}$ .

The characteristics and tuning range of the SERS source which we constructed are shown in Table 1 and Figure 1. The dye laser which we used was a simple, single oscillator, home-built device. It produced only 1 mJ per pulse, generating 25  $\mu\text{J}$  at the most favorable Raman-shifted frequency  $\omega_s$ . Current commercially available dye lasers pumped by the third harmonic of a Nd-YAG laser or by an excimer laser produce at least 10 mJ in the range of 450-465 nm. Coupled with an SERS source these should generate several hundred  $\mu\text{J}$  per pulse in the infrared around 3  $\mu\text{m}$ .

The prime advantage of an SERS source of tunable infrared radiation is its great practical simplicity and reliability. Moreover, if a dye laser is already available, the conversion is straightforward, reversible, and inexpensive. On the other hand, even with more powerful dye lasers it remains a low power source and, at least with a single SERS medium, it covers a rather narrow range of wavelengths.

#### ii) The Optical Parametric Oscillator

The optical parametric oscillator (OPO) used in our experiments was constructed by JK Lasers in consultation with R.C. Smith and his coworkers<sup>5,6</sup> at Southampton University. Briefly, a 1 cm x 5 cm, temperature stabilised,  $\text{LiNbO}_3$  rod is pumped by 1.06  $\mu\text{m}$  radiation from a Nd:YAG oscillator-amplifier laser system. The pump laser is operated at  $\text{TEM}_{00}$  and normally with an intracavity etalon to produce approximately 10 ns pulses of about 100 mJ energy.

The signal and idler frequencies,  $\omega_s$  and  $\omega_i$  ( $\omega_p = \omega_s + \omega_i$ ), from the OPO are selected by adjusting the grating, which with an output coupler forms the optical cavity, the angle of the  $\text{LiNbO}_3$  crystal, and finally the setting of an intracavity

etalon. Figure 2 shows the pulse energy of the OPO over its tuning range, compared with the energy level diagram of HCN. More details of the performance can be found in the papers by Arnold et al<sup>7</sup> which are included in the Appendix.

The OPO has proved reliable - if never easy - to use. Each new experimenter has required some period of practice before being able to obtain optimum performance. No more than routine failures, such as the need periodically to repolish and recoat optical components, have occurred. As a source for gas-phase studies, the OPO's chief disadvantage is its fairly wide linewidth. We usually operate at 0.1-0.2  $\text{cm}^{-1}$ ; many workers use broader output. In future work we may try to achieve further narrowing by inserting a prism beam expander into the cavity of the OPO.

### iii) Stimulated Vibrational Raman Scattering (SVRS) in High Pressure H<sub>2</sub>

Since the start of this project a new and powerful technique for generating tunable laser radiation has been reported.<sup>8</sup> It is based on stimulated vibrational Raman scattering in high pressure gases, H<sub>2</sub> and D<sub>2</sub> being the most useful as they produce the largest frequency shifts. As in our work on SERS, if the incident frequency is provided by a dye laser, it (and therefore the stimulated Raman frequencies) is tunable. Both Stokes and anti-Stokes frequencies are generated up to high order. It appears that the Stokes - shifted frequencies will be especially useful in providing pulsed tunable radiation in the range (0.75-1.5  $\mu\text{m}$ ) between those covered by dye lasers and by OPOs. Our own preliminary efforts to utilise such a source are described in Section 3(v).

## 3. KINETICS OF VIBRATIONALLY EXCITED SPECIES

### i) Relaxation of HCN

There are several reasons why a thorough study of the relaxation of HCN should be rewarding. First, there are the similarities and differences between HCN and the thoroughly

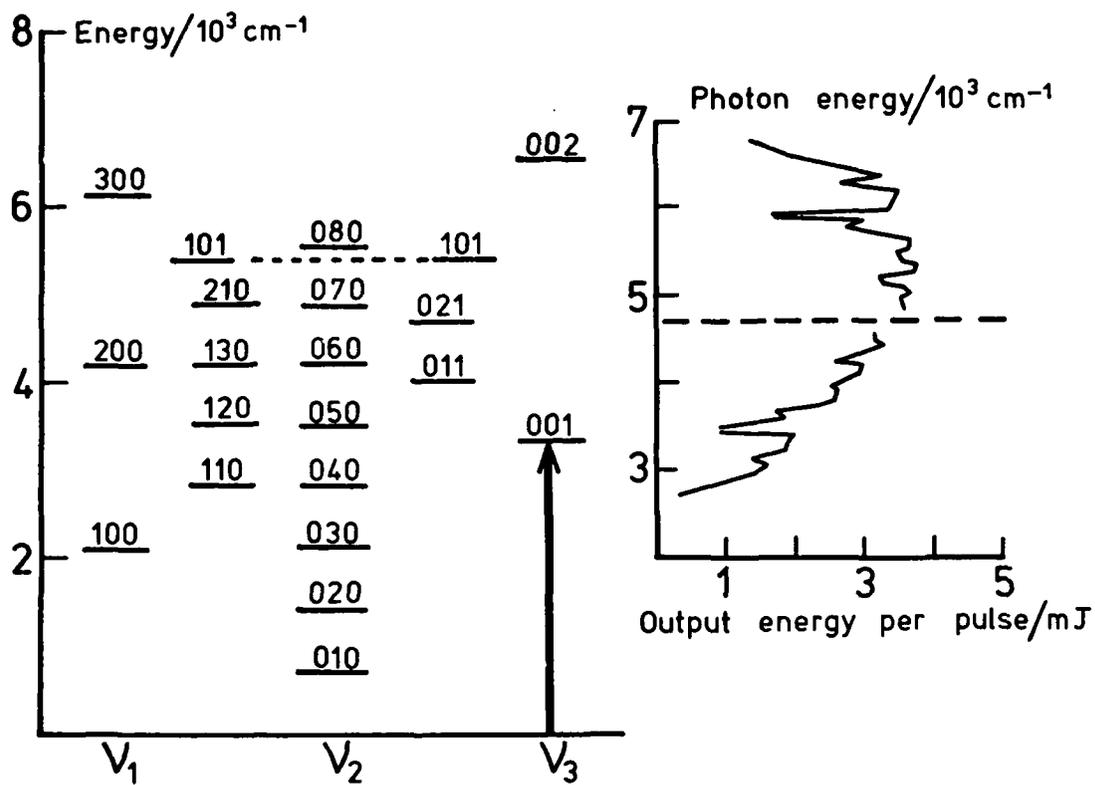


FIGURE 2. Comparison of the output energy from the optical parametric oscillator at different frequencies with the vibrational energy level diagram of HCN.

studied hydrogen halides. HCN is similar to the hydrogen halides in its ability to form strong hydrogen bonds and because its  $\nu_3$  mode is highly localised with the H atom vibrating against the CN group. On the other hand, intramolecular or intermode V-V energy transfer is possible in HCN although its greater moment of inertia makes V-R (vibration-rotation) transfer less likely. In addition, there exists extensive and accurate spectroscopic data on HCN, and its electronic and structural simplicity means that ab initio calculations of its internal potential and molecular eigenfunctions should be possible.

The vibrational energy level diagram of HCN is shown in Figure 2. In principle, a large number of excited states might be populated by absorption of a resonant OPO frequency. In practice, this number is reduced by the weakness of some transitions: for example, the high overtones of the  $\nu_2$  bending mode. Nevertheless, several HCN bands are strong enough for successful infrared fluorescence experiments.

In our work so far, accurate rate constants have been measured for the relaxation of HCN(001)<sup>4,6</sup> and HCN(002)<sup>9</sup> with a range of collision partners. These results are reported fully in papers appended to this report. This research constitutes the first real comparison of relaxation data for levels of a simple polyatomic molecule which differ only in the extent of excitation in the same mode.

Self-relaxation of both the (001) and (002) states is rapid and probably hydrogen-bonding attractive forces are at least partly responsible. However, our most interesting results are probably those for relaxation by the noble gas atoms. As the rate constants in Table 2 show, the rare gases all relax HCN(001) more rapidly than HCN(002). It seems very probable that relaxation of these states occurs by transfer to  $(12^00)$  and  $(12^01)$  respectively. Due to anharmonicity, the energy discrepancy between initial and final states is larger for  $\nu_3=2$  ( $\Delta E = 247 \text{ cm}^{-1}$ ) than for  $\nu_3=1$  ( $\Delta E = 191 \text{ cm}^{-1}$ ). The 'breathing sphere' theory of Stretton<sup>10</sup> is able to reproduce

Table 2. Comparison of rate constants ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for relaxation of HCN(002) and HCN(001) by noble gases.

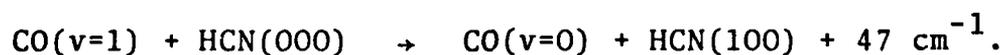
M	Experiment		'Breathing Sphere' Theory <sup>a</sup>	
	$k_{002}$	$k_{001}$	$k_{002}/k_{001}$	$k_{002}/k_{001}$
He	$5.6 \times 10^{-15}$	$6.4 \times 10^{-15}$	$0.87 \pm 0.06$	0.94
Ne	$3.8 \times 10^{-15}$	$6.3 \times 10^{-15}$	$0.61 \pm 0.06$	0.65
Ar	$3.0 \times 10^{-15}$	$6.5 \times 10^{-15}$	$0.46 \pm 0.07$	0.54
Kr	$3.2_5 \times 10^{-15}$	$7.1 \times 10^{-15}$	$0.46 \pm 0.05$	0.49

<sup>a</sup> based on the theory described in ref. 10 with the assumption that relaxation of HCN(00v<sub>3</sub>) is to HCN(12(v<sub>3</sub>-1)) and that the mixing between these initial and final states in the isolated molecules is inversely proportional to their energy separation.

the changes in relaxation rate for all the rare gases remarkably well (see last column of Table 2) if one assumes a change in the extent of mixing of final and initial states as  $\Delta E$  increases.

The absolute values of the rate constants in Table 2 show clearly that the  $\nu_3$  mode is not easily coupled to the other two in HCN. Preliminary experiments, in which emission at  $14\mu\text{m}$  was observed following excitation of the (001) state indicates that relaxation of the  $\nu_2$  mode is much more rapid. More accurate measurements are now under way on the relaxation of HCN(010) and of HCN(011). These should explore how much, if any, the relaxation rate of excitation in  $\nu_2$  is dependent on excitation in the much higher frequency vibration,  $\nu_3$ .

The CN-stretching mode,  $\nu_1$ , is almost infrared inactive and it is therefore impossible to obtain information about its relaxation directly. We intend to examine the relaxation of HCN(101), which should occur by loss of the  $\nu_1$  excitation. In addition, we hope to explore relaxation of HCN(100) by observing emission from CO( $v=1$ ) which may act as a 'marker' for the  $\nu_1$  fundamental of HCN because of the near-resonant process



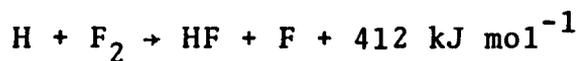
ii) Relaxation of HF( $v=3, 4$  and  $6$ )

Despite the development of the high power HF chemical laser and extensive studies of the vibrational relaxation of HF, our understanding of certain important processes remains imperfect. Thus, the exact role of near-resonant V-R energy transfer is still not clear,<sup>11</sup> and until recently there were virtually no direct measurements of the vibrational relaxation of HF in levels above  $v=1$ .

Over ten years ago we devised a method for deriving rate constants for relaxation of high vibrational levels from an analysis of the infrared chemiluminescence emitted by the products (CO, HF, DF) of exothermic reactions proceeding under steady-state conditions.<sup>12,13</sup> Within the last three years, we have developed a related but much more certain and direct method of obtaining the same kind of data from time-resolved experiments.

The fourth harmonic ( $\lambda=266$  nm) of the Nd:YAG laser, which also served as the primary pump for the OPO, was used to flash photolyse  $F_2$ . The F atoms then react with HX(X=Cl, Br or I) to produce HF in vibrational levels up to some maximum value ( $v_{\max} = 3, 4$  and  $6$  for Cl, Br and I). Emission is observed only from the highest level. Analysis of the time-resolved trace of the emission yields rate constants for (a) the reaction  $F + HX$ , and (b) for relaxation of  $HF(v_{\max})$ . This work is described fully in the papers by Smith and Wrigley<sup>14</sup> in Appendix 1. In the few cases where comparisons can be made (see Section 4.3 of Wrigley and Smith's paper), the agreement with data deduced from direct high overtone optical pumping<sup>15,16</sup> is excellent.

These experiments can be usefully extended in three ways. First, by using other reactions HF can be prepared in still higher vibrational levels. We are just starting experiments in which an ArF excimer laser ( $\lambda = 193$  nm) photolyzes HBr to produce H atoms. These will react with  $F_2$ :



and allows us to study relaxation of  $HF(v=7, 8$  and possibly  $9)$ .

In addition, it should be possible to investigate relaxation by a wider range of collision partners. Those with which HF can form strong H-bonds should prove interesting. Moreover, we hope to explore how the relaxation rate by He and Ar changes as the level of HF excitation increases.

Finally, we note that it should be possible to adapt the technique to examine the relaxation of other molecules. In view of our work on the lower levels of HCN, it would be especially rewarding to determine relaxation times for highly excited HCN, formed, for example, in the reactions of CN radicals with hydrogen halides.

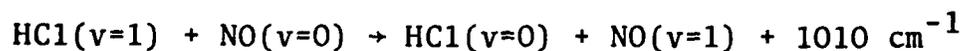
### iii) Relaxation of $NO(v=1)$ and $OH(v=1)$ by other radicals

For many years, the influence of 'chemical affinity' has been invoked whenever measured relaxation times have been shorter than expected. One clear case is where the

colliding species are both free radicals which are known to combine to form a 'stable' molecule. In such a case, if energy randomisation is complete in the collision complex, the rate of complex formation will usually be very close to the relaxation rate. To test these suppositions, we have made several measurements in the last 3 or 4 years of vibrational energy transfer in radical-radical collisions.

To excite OH(v=1) we chose to pump OH, formed in a steady-state concentration in a discharge-flow system, to  $A^2\Sigma^+(v=1)$  using a flashlamp pumped dye laser.<sup>17</sup> From that level re-emission takes place almost entirely to the  $X^2\Pi(v=0)$ , 61%, and  $v=1$ , 38%, levels. The subsequent decay of OH  $X^2\Pi(v=1)$  was monitored by observing its infrared fluorescence. Relaxation rates were measured with respect to NO and NO<sub>2</sub>; upper limits were established for the rate constants for relaxation by O<sub>2</sub> and Ar. Very recently, we have shown that it is possible to detect OH(v=1) by dye laser-induced fluorescence following flash photolysis of HNO<sub>3</sub>. We intend to make this method the basis for further studies of the kinetics of OH(v=1).

With NO, yet another technique was used to prepare vibrationally excited molecules. HCl was included in the gas mixture in the fluorescence cell and a fraction of it was excited by a pulse of radiation from an HCl chemical laser.<sup>18</sup> Part of this energy is transferred in a V-V transfer process :



The NO fluorescence was observed through a filter and analysis of these emission traces yielded rate constants for relaxation of NO(v=1) by radicals (O, Cl, Br, NO<sub>2</sub>, O<sub>2</sub>) included in the gas mixture.

Table 3 summarises the results of our experiments on relaxation in radical-radical collisions. The rate constants are compared with estimates based on the approximate theory of Quack and Troe<sup>19</sup>, and, where possible with rate constants for the corresponding radical association reaction in the limit of high pressure.<sup>20</sup> The agreement is fairly good and

Table 3. Comparison of rate constants ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for relaxation of one radical by another with (a) the rate constant ( $k^\infty$ ) for recombination of the same pair of radicals in the limit of high pressure, and (b) estimates of the relaxation rate by Quack and Troe's model.<sup>19</sup>

	$k_{\text{relax}}$	$k^\infty$	$k_{\text{relax,est.}}$
OH(v=1) + NO	$1.5 \times 10^{-11}$	$\sim 2 \times 10^{-11}$	-
OH(v=1) + NO <sub>2</sub>	$1.3 \times 10^{-11}$	$\sim 3 \times 10^{-11}$	$2.0 \times 10^{-11}$
NO(v=1) + O	$6.5 \times 10^{-11}$	$2.8 \times 10^{-11}$	$5.0 \times 10^{-11}$
NO(v=1) + Cl	$3.5 \times 10^{-11}$	$5.8 \times 10^{-11}$	$6.9 \times 10^{-11}$
NO(v=1) + Br	$2.0 \times 10^{-11}$	$3.3 \times 10^{-11}$	$5.4 \times 10^{-11}$
NO(v=1) + NO <sub>2</sub>	$1.8_5 \times 10^{-11}$	-	$7.4 \times 10^{-12}$

this - and the extreme rapidity of relaxation in the cases where a strong bond exists - appears to affirm that relaxation occurs as a result of the formation of a complex in which all the internal energy is rapidly randomised.

iv) IR laser-induced changes in low temperature matrices

Performing infrared laser-induced chemistry in low temperature matrices has several advantages. Primary among these is the dramatic reduction in thermal reaction rates. Reactions with even small potential barriers are extremely slow and may be dramatically accelerated by the energy supplied by single infrared photons. On the practical side, the lack of free rotation means that infrared bands collapse into single features with a linewidth comparable to that of the OPO.

We have participated in some preliminary studies of low temperature laser-induced chemistry in collaboration with Dr. M. Poliakoff (University of Nottingham) and Dr. L. Abouaf-Marguin (Universite de Paris-Sud). In these experiments we look for the induced rotational isomerisation of 2-fluoroethanol.<sup>21</sup>

2-fluoroethanol,  $\text{CH}_2\text{FCH}_2\text{OH}$ , has 5 different isomers, corresponding to trans- and gauche-configurations about the C-C and C-O bonds. In matrices, the  $G_g$  isomer, stabilised by an internal hydrogen bond predominates. Irradiation of 2-fluoroethanol with unfiltered radiation from a Nernst glower and with a cw HF laser which emits a frequency corresponding to that of the OH-fundamental, lead to  $G_g \rightarrow T_t$  isomerisation. With the OPO tuned to some absorption we were able to induce the same rotamerisation. No effect was observed when the matrix was irradiated at the frequency of the CH stretching mode.

Unfortunately, our results were not easily reproducible because a mismatch between the area irradiated and that observed by the IR spectrometer which is used to detect changes. Dr. Poliakoff has recently purchased a more suitable Fourier transform IR spectrometer and will make a further visit with it and his mobile Displex unit in the next few months. Meanwhile, we note that similar results to ours have been obtained by Shirk<sup>22</sup> using an F-center laser.

v) Single-photon vibrational photochemistry in the gas-phase.

In order to study the influence on the rates of elementary bimolecular reactions of specific vibrational excitation in one or other of the reagents, a number of formidable difficulties have to be overcome. We are attempting to investigate the reactions of atomic radicals (H, Cl, Br, O) with HF and HCN in different vibrational states. The H-F and H-CN bonds are unusually strong single bonds, so all of these reactions are endothermic. This means that they are very slow at room temperature and are likely to be efficiently enhanced by vibrational excitation. Moreover, the high frequencies of the HF and HCN( $\nu_3$ ) vibrations means that each quantum of vibrational excitation corresponds to a relatively large energy. On the other hand, both HF and HCN undergo very rapid self-relaxation.

In our current experiments, a high power pulsed dye laser excites HF directly to  $v=5$ . Emission in the (5,1) band is observed using a red-sensitive photomultiplier. In latter experiments, we plan to excite HF( $v=4$ ), HF( $v=3$ ) and overtones of the HCN( $\nu_3$ ) mode either using other dyes or the SVRS technique described in Section 3(iii). At present, our chief difficulties with this experiment arise from two sources. First, there is a high scattered light signal even after the usual subtraction procedure. Secondly, impurities in the H<sub>2</sub>/Ar mixture passed through the microwave discharge create an afterglow emission. Both these sources interfere with our very weak signals. The apparatus and technique are being improved to eliminate these problems.

## REFERENCES

- <sup>1</sup>P.P.Sorokin and J.R.Lankard, IEEE J.Quant. Electron., QE-9, 227 (1973)
- <sup>2</sup>D.Cotter, D.C.Hanna, P.A.Karkkainen and R.Wyatt, Optics Comm., 15, 143 (1975); D.Cotter, D.C.Hanna and R.Wyatt, Optics Comm., 16, 256 (1976); (c) D.Cotter and D.C.Hanna, J.Phys. B, 9, 2165 (1976); (d) D.Cotter and D.C.Hanna, Opt. and Quantum Electron., 9, 509 (1977).
- <sup>3</sup>I.W.M.Smith, Relaxation of HCN(001) using stimulated electronic Raman scattering in cesium vapour as a tunable infrared excitation source, Interim Scientific Report for USAFOSR, 1 May, 1979.
- <sup>4</sup>A.B.Petersen and I.W.M.Smith, J. Chem. Phys., 71, 3346 (1979).
- <sup>5</sup>R.Wyatt, A.J.Turner and R.C.Smith, in Lasers in Chemistry, ed. M.A.West (Elsevier, Amsterdam, 1977) p.206.
- <sup>6</sup>see also R.L. Herbst, R.N.Fleming and R.L.Byer, Appl. Phys. Lett., 25, 520 (1974).
- <sup>7</sup>(a)G.S.Arnold, R.P.Fernando and I.W.M.Smith, J. Chem. Phys., 73, 2773 (1980); (b) G.S.Arnold and I.W.M.Smith, J.C.S. Faraday 2, 77, 861 (1981).
- <sup>8</sup>(a)V.Wilke and W.Schmidt, Appl. Phys., 18, 177 (1979); (b) W.Hartig and W.Schmidt, Appl. Phys., 18, 235 (1979).
- <sup>9</sup>P.W.Hastings, M.K.Osborn, C.M.Sadowski and I.W.M.Smith, J.Chem.Phys., submitted August 1982.
- <sup>10</sup>J.L.Stretton, Trans. Faraday Soc., 61, 1053 (1965)
- <sup>11</sup>E.R.Sirkin and G.C.Pimentel, J.Chem. Phys., 77, 1315 (1982).
- <sup>12</sup>G.Hancock and I.W.M.Smith, Appl. Opt., 10, 1827 (1971).

- <sup>13</sup>(a) J.R. Airey and I.W.M. Smith, J.Chem.Phys., 57, 1669 (1972);  
(b) P.R. Poole and I.W.M. Smith, J.C.S. Faraday 2, 73, 1434  
and 1447 (1977).
- <sup>14</sup>(a) I.W.M. Smith and D.J. Wrigley, Chem.Phys.Lett., 70, 481  
(1980); (b) Chem. Phys., 63, 321 (1981).
- <sup>15</sup>(a) D.J. Douglas and C.B. Moore, Chem. Phys. Lett., 57, 485  
(1978); (b) J.Chem.Phys., 70, 1769 (1979)
- <sup>16</sup>(a) J.K. Lampert, G.M. Jurisch and F.F. Crim, Chem.Phys. Lett.,  
71, 258 (1980); (b) G.M. Jurisch and F.F. Crim, J.Chem.Phys.,  
74, 4455 (1981).
- <sup>17</sup>D.H. Jaffer and I.W.M. Smith, Faraday Discuss. Chem.Soc.,  
67, 212 (1979).
- <sup>18</sup>(a) R.P. Fernando and I.W.M. Smith, Chem.Phys. Lett., 66, 218  
(1979); (b) J.C.S. Faraday 2, 77, 459 (1981).
- <sup>19</sup>M. Quack and J. Troe, Ber. Bunsenges. Phys. Chem., 79, 170  
(1975) and 81, 160 (1977).
- <sup>20</sup>M.J. Howard and I.W.M. Smith, Kinetics of Radical-Radical  
Processes in the Gas-Phase, to be published in Prog. Reac.  
Kinetics.
- <sup>21</sup>J. Pourcin, G. Davidovics, L. Abouaf-Marguin, P.W. Hastings,  
I.W.M. Smith, N.J. Bristow and M. Poliakoff, paper at 3rd  
Int. Meeting on Matrix Isolation (Nottingham, England,  
July 1981).
- <sup>22</sup>report in Chem. Eng. News, 21 June, 1982 p.24.

APPENDIX: List of publications during the period of the grant. Copies of those papers marked by an asterisk are supplied.

LIST OF PUBLICATIONS 1977 - 1982

- I.W.M. Smith, Reactive and Inelastic Collisions involving Molecules in Selected Vibrational States, Specialist Periodical Reports of the Chemical Society, Reaction Kinetics, vol. 2, ed. R.J. Donovan, chap. 1 (1977)
- I.W.M. Smith, Reaction and Relaxation of Vibrationally Excited Molecules: A Classical Trajectory Study of Br + HCl ( $v'$ ) and Br + DCl ( $v'$ ) Collisions, Chem. Phys., 20, 431 (1977).
- I.W.M. Smith, Vibrational Relaxation in Atom-Exchange Reactions: Classical Trajectory Calculations on  $H_2(v) + H$  and  $D_2(v) + D$  Collisions on a Realistic Potential, Chem. Phys. Letters, 47, 219 (1977).
- K. Erler, D. Field, R. Zellner and I.W.M. Smith, The Recombination Reaction between Hydroxyl Radicals and Nitrogen Dioxide. OH + NO<sub>2</sub> + M (= He, CO<sub>2</sub>) in the Temperature Range 215 - 300 K. Ber. Bunsen. Gesell. Phys. Chem., 81, 22 (1977).
- I.W.M. Smith, The Dynamics of Collisions between Vibrationally Excited Diatomic Molecules and Potentially Reactive Atoms Ber. Bunsen. Gesell. Phys. Chem., 81, 126 (1977).

- C. Anastasi, P.P. Bemand and I.W.M. Smith, Rate Constants for:  
 $\text{OH} + \text{NO}_2 (+ \text{N}_2) \rightarrow \text{HNO}_3 (+ \text{N}_2)$  between 220 and 358<sup>o</sup>K, Chem.  
Phys. Letters, 37, 370 (1975).
- R.D.H. Brown, I.W.M. Smith and S.W.J. van der Merwe, Relaxation  
of HCl (v = 1) and DCl (v = 1) by Bromine Atoms, Chem. Phys.,  
15, 143 (1976).
- C. Anastasi and I.W.M. Smith, Rate Measurements of OH by Resonance  
Absorption. Part 5. Rate constants for the reaction  
 $\text{OH} + \text{NO}_2 (+ \text{M}) \rightarrow \text{HNO}_3 (+ \text{M})$  over a wide range of temperature  
and pressure, J.C.S. Faraday II, 72, 1459 (1976).
- I.W.M. Smith, Reactive and Inelastic Collisions involving Molecules  
in Selected Vibrational States, Specialist Periodical Reports  
of the Chemical Society, Reaction Kinetics, vol. 2, ed.  
R.J. Donovan, chap. 1 (1977)
- I.W.M. Smith, Reaction and Relaxation of Vibrationally Excited  
Molecules: A Classical Trajectory Study of Br + HCl (v') and  
Br + DCl (v') Collisions, Chem. Phys., 20, 431 (1977).
- I.W.M. Smith, Vibrational Relaxation in Atom-Exchange Reactions:  
Classical Trajectory Calculations on  $\text{H}_2(\text{v}) + \text{H}$  and  $\text{D}_2(\text{v}) + \text{D}$   
Collisions on a Realistic Potential, Chem. Phys. Letters,  
47, 219 (1977).
- K. Erler, D. Field, R. Zellner and I.W.M. Smith, The Recombination  
Reaction between Hydroxyl Radicals and Nitrogen Dioxide.  
 $\text{OH} + \text{NO}_2 + \text{M} (= \text{He}, \text{CO}_2)$  in the Temperature Range 213 - 300 K.  
Ber. Bunsen. Gesell. Phys. Chem., 81, 22 (1977).
- I.W.M. Smith, The Dynamics of Collisions between Vibrationally  
Excited Diatomic Molecules and Potentially Reactive Atoms  
Ber. Bunsen. Gesell. Phys. Chem., 81, 126 (1977).

I.W.M. Smith, The Mechanism of the OH + CO Reaction and the Stability of the HOCO Radical, Chem. Phys. Letters, 49, 112 (1977).

P.R. Poole and I.W.M. Smith, Quenching of Infrared Chemiluminescence. Part 6 - Rates of Energy Transfer from HF( $2 \leq v \leq 7$ ) to HF ( $v = 0$ ), H<sub>2</sub>, D<sub>2</sub> and HD, and from DF( $3 \leq v \leq 5$ ) to HF( $v = 0$ ). J.C.S. Faraday II, 73, 1434 (1977)

P.R. Poole and I.W.M. Smith, Quenching of Infrared Chemiluminescence. Part 7 - Rates of Energy Transfer from HF( $2 \leq v \leq 7$ ) and DF( $3 \leq v \leq 5$ ) to a Wide Range of Collision Partners. J.C.S. Faraday II, 73, 1437 (1977).

A.B. Petersen and I.W.M. Smith, Wavelength Dependence of the Branching Ratio for the Production of Br\*( $4^2P_{1/2}$ ) and Br( $4^2P_{3/2}$ ) in the Photolysis of Br<sub>2</sub>, in Lasers in Chemistry (Elsevier, Amsterdam, 1977) 112.

R.D.H. Brown and I.W.M. Smith, Absolute Rate Constants for the Reactions of O( $^3P$ ) Atoms with DCl and DBr, Int. J. Chem. Kinetics, 10, 1 (1978).

C. Anastasi and I.W.M. Smith, Rate Measurements of OH by Resonance Absorption. Part 6 - Rate Constants for OH + NO (+ M)  $\rightarrow$  HNO<sub>2</sub> (+ M) over a Wide Range of Temperature and Pressure, J.C.S. Faraday II, 74, 1056 (1978).

C. Anastasi, I.W.M. Smith and D.A. Parkes, Flash Photolysis Study of the Spectra of CH<sub>3</sub>O<sub>2</sub> and C(CH<sub>3</sub>)<sub>3</sub>O<sub>2</sub> Radicals and the Kinetics of their Mutual Reactions and with NO, J.C.S. Faraday I, 74, 1693 (1978).

A.B. Petersen and I.W.M. Smith, Vibrational Energy Transfer Studies using SERS as a Tunable IR Excitation Source, Proc. Xth International Quantum Electronics Conference, Atlanta, May 1978; J. Opt. Soc. Amer, 68 655 (1978).

- A.B. Peterson and I.W.M. Smith, Yields of  $\text{Br}^* (4^2\text{P}_{1/2})$  as a function of Wavelength in the Photodissociation of  $\text{Br}_2$  and  $\text{IBr}$ , *Chem. Phys.*, 30, 407 (1978).
- I.W.M. Smith, Laser Studies of the Relaxation and Reaction of Species in Defined Quantum States, in *Laser-Induced Processes in Molecules*, eds. K.L. Kompa and S.D. Smith (Springer-Verlag, Berlin, 1979).
- R.P. Fernando and I.W.M. Smith, Relaxation of  $\text{HBr}(v=1)$ ,  $\text{DBr}(v=1)$  and  $\text{HCl}(v=1)$  by Bromine atoms, *J.C.S. Faraday II*, 75, 1064, (1979).
- D.H. Jaffer and I.W.M. Smith, Time-resolved Measurements on the Relaxation of  $\text{OH}(v=1)$  by  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{O}_2$ , *Faraday Discussion Chem. Soc.*, 67, 212 (1979).
- C.B. Moore and I.W.M. Smith, Chemical Reactions of Vibrationally Excited Molecules, *Faraday Discussion Chem. Soc.*, 67, 146 (1979).
- A.B. Peterson and I.W.M. Smith, Relaxation of  $\text{HCN}(001)$  using Stimulated Electronic Raman Scattering in Cs Vapor as a Tunable Infrared Source, *J. Chem. Phys.*, 71, 3346 (1979).
- I.W.M. Smith, *Kinetics and Dynamics of Elementary Gas Reactions* (Butterworths, London and Boston, 1980).
- I.W.M. Smith, *Chemical Reactions of Selectively Energised Species in Physical Chemistry of Fast Reactions*, vol. 2: Reaction Dynamics, ed. I.W.M. Smith (Plenum, New York and London, 1980).
- R.P. Fernando and I.W.M. Smith, Vibrational Relaxation of  $\text{NO}$  by Atomic Oxygen, *Chem. Phys. Letters*, 66, 218 (1979).
- I.W.M. Smith, *Chemical Lasers, Optics and Laser Technology*, 12, 77 (1980).

M.J.Howard and I.W.M.Smith, Direct Rate Measurements on the Reactions:  
 $N + OH \rightarrow NO + H$  and  $O + OH \rightarrow O_2 + H$ , Chem. Phys. Letters, 69,  
40 (1980).

J.S.Robertshaw and I.W.M.Smith, Vibrational Energy Transfer from  
 $CO(v=1)$ ,  $N_2(v=1)$ ,  $CO_2(001)$ ,  $N_2O(001)$  and  $OCS(001)$  to  $O_3$ , J.C.S.  
Faraday II, 76, 1354 (1980).

I.W.M.Smith and D.J.Wrigley, Time-Resolved Vibrational Chemilumi-  
nescence : Rate Constants for the Reaction,  $F + HCl \rightarrow HF + Cl$ ,  
and for the Relaxation of  $HF(v=3)$  by  $HCl$ ,  $CO_2$ ,  $N_2O$ ,  $N_2$  and  $O_2$ ,  
Chem. Phys. Letters, 70, 481 (1980).

J.S.Robertshaw and I.W.M.Smith, Rate Data for :  $O + OCS \rightarrow SO + CO$   
and  $SO + O_3 \rightarrow SO_2 + O_2$  by a New Time-Resolved Technique. Int. J.  
Chem. Kinetics, 12, 729 (1980).

G.S.Arnold, R.P.Fernando and I.W.M.Smith, Vibrational Energy Transfer  
between  $HCN$  and  $DCN$  and Hydrogen and Dueterium Halides, J. Chem.  
Phys., 73, 2773 (1980).

R.P.Fernando and I.W.M.Smith, Vibrational Relaxation of  $NO(v=1)$  by  
Radical Species, J.C.S. Faraday II, 77, 459 (1981).

I.W.M.Smith, Combining Transition State Theory with Quasiclassical  
Trajectory Calculations. I : Collinear Collisions, J.C.S. Faraday II,  
77, 747 (1981).

G.S.Arnold and I.W.M.Smith, Vibrational Relaxation of  $HCN(001)$  by  
the Noble Gases,  $O_2$ ,  $N_2$  and  $CO$ , J.C.S. Faraday II, 77, 861 (1981).

M.J.Howard and I.W.M.Smith, Direct Rate Measurements on the Reactions :  
 $N + OH \rightarrow NO + H$  and  $O + OH \rightarrow O_2 + H$  from 250 K to 515 K, J.C.S.  
Faraday II, 77, 997 (1981).

I.W.M.Smith, Integrated Intensities for some Infrared Absorption  
Bands of  $HCN$ , J.C.S. Faraday II, 77, 2357 (1981).

- I.W.M.Smith and D.J.Wrigley, Time-Resolved Vibrational Chemiluminescence : Rate Constants for the Reactions :  $F + HBr, HI \rightarrow HF + Br$ , I and for the Relaxation of  $HF(v=4)$  and  $HF(v=6)$  by  $HBr, HI, CO_2, N_2O, CO, N_2$  and  $O_2$ , Chem. Phys., 63, 321 (1981).
- G.Hancock and I.W.M.Smith, Citation Classic : 'Quenching of Infrared Chemiluminescence. I. The Rates of Deexcitation of  $CO(4 \leq v \leq 13)$  by He, CO, NO,  $N_2, O_2, OCS, N_2O$  and  $CO_2$ ', Current Contents, 21, no. 30, 22 (1981).
- I.W.M.Smith, A New Collision Theory for Bimolecular Reactions, J. Chem. Education, 59, 9 (1982).
- J.S. Robertshaw and I.W.M.Smith, Kinetics of the  $OH + NO_2 + M$  Reaction at High Total Pressures, J.Phys. Chem., 86, 785 (1982).
- I.W.M.Smith, Vibrational Photochemistry using Lasers in Proceedings of 5th National Quantum Electronics Conference (Wiley, New York, 1982) in press.
- I.W.M.Smith, Lasers in the Study of Elementary Processes, Ber. Bunsenges. Phys. Chem., 86, 395 (1982).
- M.J.Howard and I.W.M.Smith, Direct Rate Measurements on the Reaction :  $D + OH \rightarrow OD + H$  from 300 K to 515 K, J.C.S. Faraday II, 78, 1403 (1982).
- M.J.Howard and I.W.M.Smith, The Kinetics of Radical-Radical Processes in the Gas-Phase, Prog. Reac. Kinetics, to be published (1982).
- P.W.Hastings, M.K.Osborn, C.M.Sadowski and I.W.M.Smith, Vibrational Relaxation of  $HCN(002)$ , J. Chem. Phys., submitted (1982).
- I.W.M.Smith, Lasers and Vibrational Relaxation in Small Molecules, to be published in Lasers as Reactants and Probes in Chemistry (Plenum, New York, 1982).

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