AD-A193 687 LASER STUDIES OF GAS PHASE RADICAL REACTIONS(U) OXFORD 1/1
UNIV (ENGLAND) PHYSICAL CHEMISTRY LAB G HANCOCK
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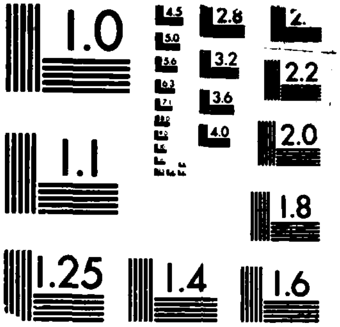
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Laser Studies of Gas Phase Radical Reactions

(2)

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5th Periodic Report

1 April - 29 Sept 1987

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Report

1) CF Chemistry

Pulsed discharges have been used to prepare CF_2 and CF radicals in the presence of O atoms, and the decay rates of both species have been measured simultaneously following the pulse. This has resulted in relative rates of the CF_2 and CF radical removal being obtained, and as the rate constant for the O + CF_2 reaction is known, this has enabled an estimate for the rate constant k for O + CF to be made. Our preliminary result is $k = 8.7 \times 10^{-11}$ cm^3 molecule^{-1}s^{-1}, ie close to the gas kinetic value. More detailed studies as a function of temperature are in progress.

2) O + CF and O + CF_2 reactions

Figures 1 and 2 show the first time resolved interferograms and their Fourier transforms obtained with the infrared emission spectrometer. The emission source was a pulsed black body: the time resolved spectra were taken in the near ir region with a photodiode and thus show a long wavelength cutoff which is not representative of the true emission. They serve to illustrate that the spectrometer and data acquisition systems are now working, and they have outlined the improvements needed to be made. By the next grant report we should have wavelength and time resolved emission and signals from the above named reactions.

3) H_2O photolysis

Professor J.B. Halpern's work on H_2O has come to a very satisfactory conclusion. In addition to the work mentioned in the last report he has now finished rotationally resolved polarisation measurements on OH $A^2\Sigma^4$ and OD $A^2\Sigma^4$ fragments from the two photon dissociation of H_2O, D_2O and has also studied teh 2+1 REMPI of H_2O, D_2O and HDO using a time of flight mass spectrometer to measure the identities of the ions formed (which in these cases are predominantly the parent ions). All of the H_2O work is presently being written up for publication.

Two other pieces of work have been carried out by Professor Halpern. One of these has been on a system described in the 3rd periodic report, that of measurements of initial rotational state distribution in the CO product of the reaction:

$$O + CS \rightarrow CO + S$$

The apparatus for this low pressure study has been completed during Professor Halpern's stay and a new student has started a full investigation of it.

The second study, completed by Professor Halpern, has involved the photolysis in the liquid phase of an azirine ring containing compound to produce a carbene radical on a species bound to an enzyme. Rapid reaction of the carbene with the enzyme to give degradation products then takes place, and the identification of these products is now providing information on the active site of the enzyme (isopenicillin N synthetase). This work has been carried out by Professor Halpern in conjunction with the Organic Chemistry Department, has introduced them to laser photolysis and a publication from this work is being prepared.

4) FCO

Repeated laser induced fluorescence experiments designed to observe the FCO radical have failed. We have no idea whether or not this is due to a vanishingly low quantum yield for fluorescence from the radical, to our assumption regarding the absorption spectrum in the gas phase (which are extrapolated from matrix isolation spectra) are wrong, or whether our background fluorescence in the reaction vessel is obscuring the data. More experiments to test these possibilities are in progress.

The research plans for the remainder of the contract are substantially as in the proposal and in the development of it as given in the periodic reports.

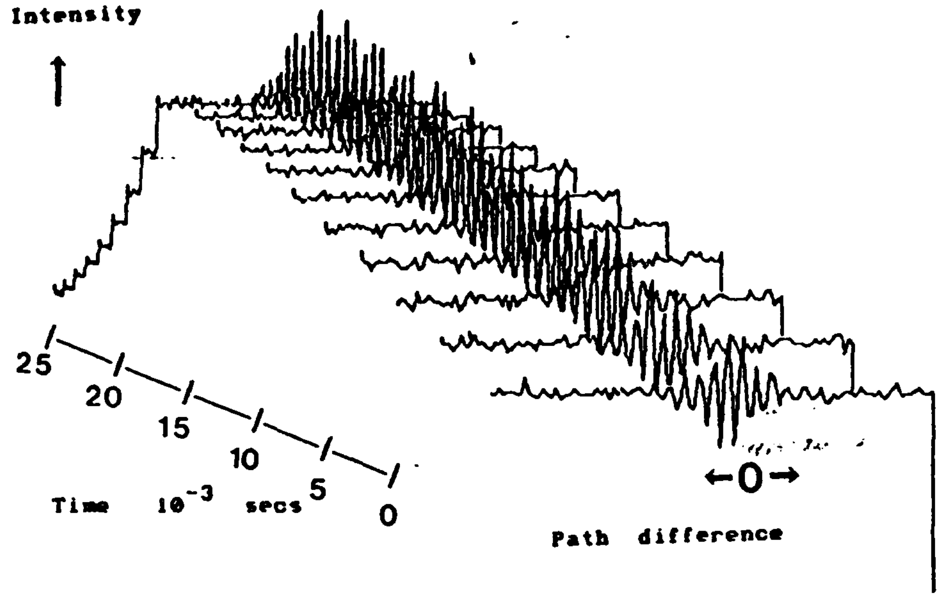
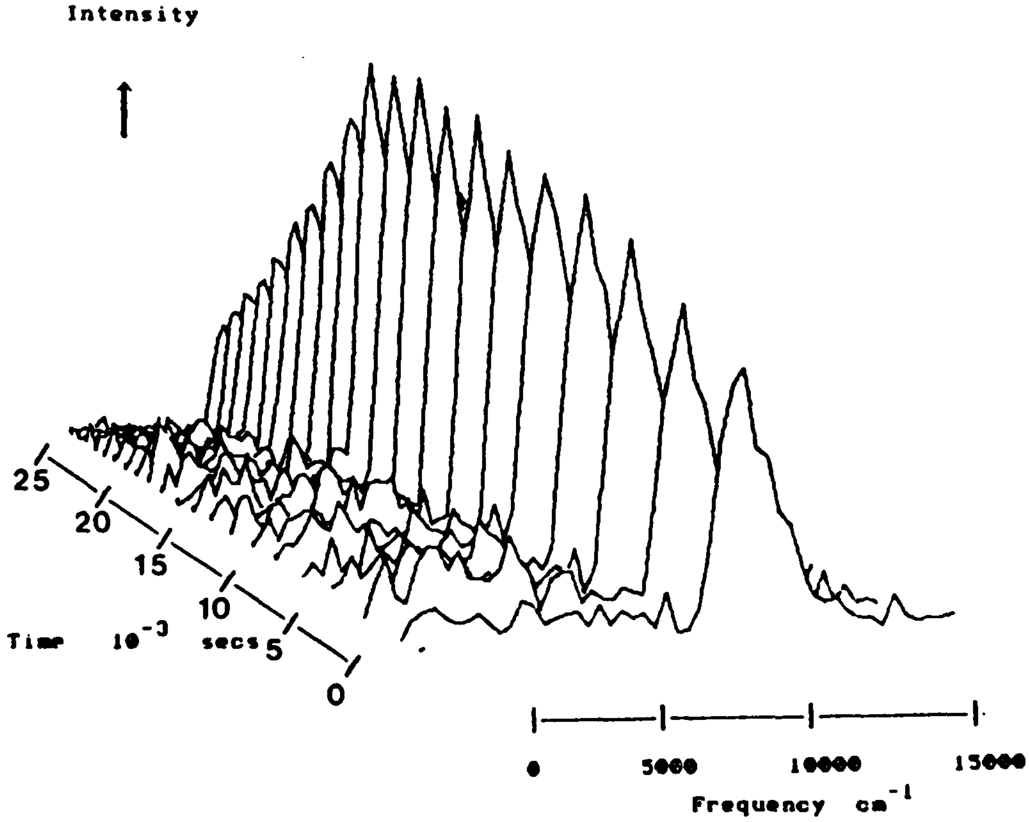


Fig 2 Fourier Transform giving time resolved spectra



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