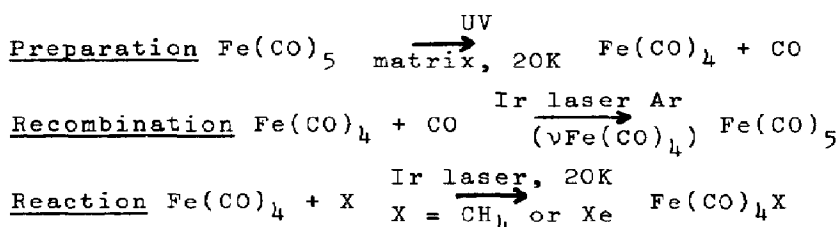


LOW TEMPERATURE IR PHOTOCHEMISTRY AND SPECTROSCOPY USING A TUNABLE SPIN FLIP
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Our experiments involve a combination of matrix isolation and i.r. laser induced photochemistry. Matrix isolation is a well established technique for stabilizing otherwise highly reactive molecules by trapping them in an inert solid, e.g. argon, at low temperatures, ~20K. In our studies, reactive fragments are prepared by u.v. photolysis of stable molecules, already isolated in the matrix. I.r. lasers are then used to excite these fragments and to promote either recombination or reaction with the matrix material itself^{2a,3}. For example



These reactions do not occur thermally at 20K but have activation barriers which can be overcome by absorption of only a single i.r. photon by an individual $\text{Fe}(\text{CO})_4$ molecule. The reaction rate is linearly dependent on the intensity of the i.r. laser.

The i.r. laser induced reactions are highly selective. They not only display isotopic³, stereochemical³ and orientational^{2b} selectivity but also selectivity between molecules isolated in different substitutional sites in the matrix^{2b}. Here we report the use of a c.w. Spin Flip Raman Laser (SFRL) for investigating matrix site effects in one C-O stretching mode of $\text{Fe}(\text{CO})_4$ isolated in an argon matrix.

The c.w. SFRL converts fixed frequency radiation, from a c.w. CO laser, into continuously tunable radiation by means of stimulated Raman scattering in a crystal of InSb, cooled to 4K and placed in a strong magnetic field. The laser is tuned by varying this magnetic field. The tuning range is limited at one end, $\sim 1900 \text{ cm}^{-1}$, by absorption by the InSb, and at the other end, $\sim 1800 \text{ cm}^{-1}$, by the increasing power threshold of the spin-flip process. The Edinburgh Instruments SFRL at Newcastle has been described in detail elsewhere⁴. In these experiments the SFRL produced output with a linewidth of 0.01 cm^{-1} , and up to 5 mW power. The SFRL was used at maximum power for photochemistry and at substantially lower powers for high resolution spectroscopy.

Samples of $\text{Fe}(\text{CO})_5$, enriched with $^{13}\text{C}^{18}\text{O}$, were isolated in Ar matrices at 20K, and $\text{Fe}(\text{CO})_4$ was generated by u.v. photolysis⁵. Isotopic enrichment was necessary to shift the C-O stretching frequencies of $\text{Fe}(\text{CO})_4$ into the tuning range of the SFRL. We studied the group of i.r. absorption bands, centred at 1880 cm^{-1} which was the basis of our previous laser photochemistry experiments^{2b}. Under the best resolution (ca. 0.6 cm^{-1}) obtainable with our conventional i.r. spectrometer, the group appears to consist of three bands separated by about 2 cm^{-1} with the central band, showing signs of doublet structure. The bands are all assigned to the same C-O stretching mode* of $\text{Fe}(\text{CO})_4$, and the multiplicity is attributed to "site-splitting". There are several different types of site which the molecules can occupy in the lattice, and each of these sites has a different characteristic effect on the vibrational frequencies of the trapped molecule. Using the SFRL to promote the reaction $\text{Fe}(\text{CO})_4 + \text{CO} \rightarrow \text{Fe}(\text{CO})_5$, we have confirmed that none of these bands are due to the same molecules. If laser irradiation at the frequency of one band reduces the intensity of that band, while leaving the other bands unaffected, then that band cannot be due to the same matrix isolated species as the other.

* $\text{Fe}(\text{CO})_4$ has a C_{2v} structure⁵, substantially distorted from tetrahedral, with bond angles of 145° and 120° .

The high resolution (0.01 cm^{-1}) SFRL spectrum, shows that the bands are much narrower and the splitting more complicated than appears from the conventional i.r. spectrum. There are no less than six bands with widths as narrow as 0.2 cm^{-1} . We have used the SFRL to promote completely selective reactions of molecules with absorptions separated by only 0.72 cm^{-1} . Our results show that in matrix, single photon reactions proceed rapidly even with relatively low laser powers. Good overlap between laser emission and matrix absorption appears to be more important than high laser power. It is encouraging that other workers are now reporting⁶ single photon i.r. laser induced reactions in matrices.

References

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