Infrared Laser-induced Photochemistry at Low Temperatures: Dramatic Isotope and Stereochemical Selectivity

By Allister McNeish, Martyn Poliakoff,* Kenneth P. Smith, and James J. Turner
(*Department of Inorganic Chemistry, The University, Newcastle upon Tyne* NE1 7RU)

Summary A combination of matrix isolation and i.r. laser photochemistry has allowed the selective reaction of molecules of ^{13}CO enriched $[Fe(CO)_4]$ which differ only in the stereochemical distribution of isotopic CO groups.

Infrared lasers are becoming increasingly important for promoting chemical reactions and separating isotopes. For example, irradiation of SF_6 (natural abundance $^{32}S = 95\%$; $^{34}S = 4{\cdot}2\%$) with a high power ($> 10^8$ W/cm^2) pulsed CO_2 laser, in the $10{\cdot}6\,\mu m$ region, destroys $^{32}SF_6$ but not $^{34}SF_6$.[1] This reaction involves multiphoton absorption by single molecules of $^{32}SF_6$ and is a case of non-linear photochemistry. A problem with such reactions, especially those induced by continuous wave (c.w.) lasers, is to avoid energy transfer between the excited molecules and other isotopic species, which results in an overall heating of the reaction mixture. This so-called Bunsen burner effect reduces or even destroys the isotopic selectivity of the reaction. We report how low temperature matrices can be used to minimize the effects of such energy transfer and describe an i.r.-induced reaction of $[Fe(CO)_4]$ which shows a remarkably high degree of selectivity.

The unsaturated complex $[Fe(CO)_4]$ was produced[2,3] in a CH_4 matrix at 20 K by u.v. irradiation of $[Fe(CO)_5]$, which can be regenerated by warming the matrix to 35 K [equation (1)]. Irradiation with the unfiltered light from the

$$[Fe(CO)_5] \underset{\text{Heat}}{\overset{h\nu}{\rightleftharpoons}} [Fe(CO)_4] + CO \qquad (1)$$

Nernst glower of an i.r. spectrometer results in the rapid formation of a rather unusual methane complex, $[Fe(CO)_4CH_4]$. Unlike $[Fe(CO)_5]$, $[Fe(CO)_4CH_4]$ cannot be formed from $[Fe(CO)_4]$ by annealing the matrix, presumably because the activation energy for the reaction is too high [equation (2)].†

$$[Fe(CO)_4] + CH_4 \underset{\text{Heat}}{\overset{\text{Nernst}}{\underset{\times}{\rightleftharpoons}}} [Fe(CO)_4CH_4] \qquad (2)$$

The laser irradiation experiment was performed using an Edinburgh Instruments c.w. CO laser‡ and ^{13}CO-enriched $[Fe(CO)_4]$. The results are illustrated in the Figure.

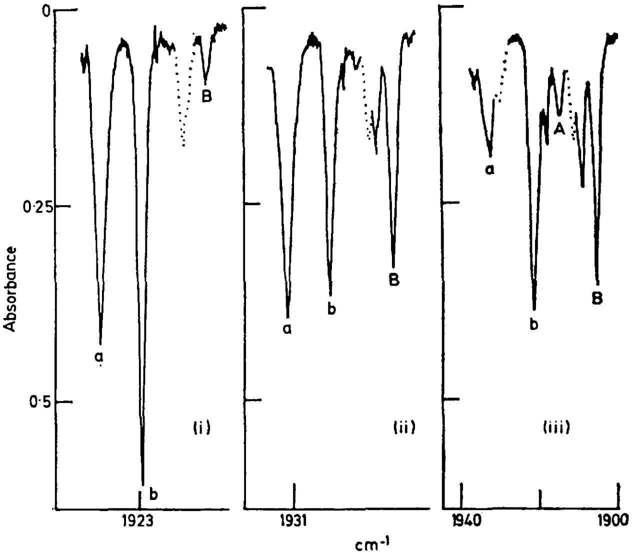
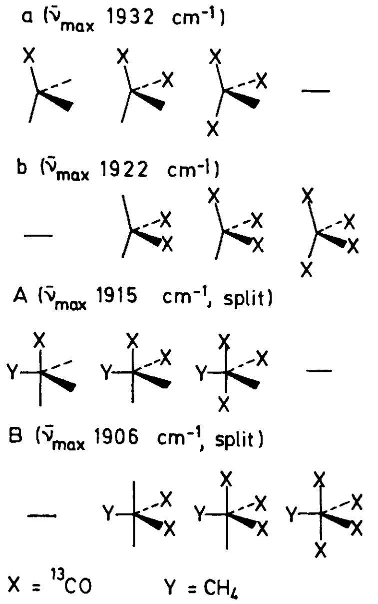


Figure. Part of the i.r. spectrum of a CH_4 matrix originally containing $[Fe(CO)_5]$ with *ca.* 66% ^{13}CO enrichment. $[Fe(CO)_5] : CH_4 = 1:4000$. (i) After u.v. irradiation; a and b are due to $[Fe(CO)_4]$, A and B $[Fe(CO)_4CH_4]$, ···· $[Fe(CO)_3]$. (ii) After 30 min irradiation with the c.w. CO laser at 1923 cm^{-1}, co-incident with band b. (iii) After 30 min irradiation at 1931 cm^{-1}, co-incident with band a. All spectra were recorded with a Ge filter[2,3] in the spectrometer beam.

Bands a, b, A, and B are assigned[3] respectively to the co-incident bands of groups of differently ^{13}CO substituted $[Fe(CO)_4]$ and $[Fe(CO)_4CH_4]$ molecules.

† I.r. spectra of ^{13}CO enriched samples indicate C_{2v} structures for both species, with bond angles of *ca.* 145 and 120° for $[Fe(CO)_4]$, and *ca.* 174 and 125° for $[Fe(CO)_4CH_4]$.

‡ The design of this laser has been described elsewhere (M. J. Colles, R. B. Dennis, J. W. Smith, J. S. Webb, and R. L. Allwood, *Optics and Laser Technology*, 1975, 7, 73). It can be tuned to produce output with a linewidth less than 10^{-4} cm^{-1} at one of a series of fixed frequencies separated by *ca.* 4 cm^{-1}. The laser beam was partially focussed to a 1 cm diameter spot. Laser powers at the front window of the low temperature apparatus were 400 mW (1923 cm^{-1}) and 650 mW (1931 cm^{-1}). At these power densities there was no change in the temperature of the matrix nor any sign of matrix evaporation during irradiation.



Whatever the mechanism of the reaction, we can conclude from the results that: (i) There was a dramatic decrease in intensity of the irradiated $[Fe(CO)_4]$ band, a or b, while the other band was substantially unaffected. There was a corresponding growth in the bands of $[Fe(CO)_4CH_4]$, A or B.§ Thus the following changes occur:

$$a(\tilde{\nu}_{max}\ 1932\ cm^{-1}) \xrightarrow{h\nu\ (1931\ cm^{-1})} A$$

$$b(\tilde{\nu}_{max}\ 1922\ cm^{-1}) \xrightarrow{h\nu\ (1923\ cm^{-1})} B$$

(ii) Laser irradiation promoted the reaction

$$[Fe(CO)_4] + CH_4 \xrightarrow{\text{i.r. laser } \nu_{CO}} [Fe(CO)_4CH_4]$$

which is not achieved by warming the matrix.

(iii) The selectivity is in complete contrast to the unselective reaction caused by broad-band radiation from the Nernst glower.[2,3]

(iv) The isotopic selectivity shows that there is not an efficient energy transfer from one isotopic species to another. Thus, the reaction is localised in the matrix cage.

(v) The laser has differentiated not only between molecules with different degrees of isotopic substitution but also between molecules with identical degrees of substitution but different stereochemical arrangements of the ^{13}CO groups.

(vi) Such selectivity could only have been achieved with an i.r. laser since these molecules have very broad u.v. and visible absorption bands which are insensitive to isotopic substitution.

Certain preliminary conclusions can also be drawn about the mechanism of the photochemical reaction. At the power densities used ($\leqslant$ 1 W/cm^2), the lifetime of the vibrationally excited states of $[Fe(CO)_4]$ would have to be extremely long for multiphoton absorption to be significant. Thus it seems probable that the reaction is a single photon process, although the overall quantum yield is low, $< 0{\cdot}01$.¶ The reaction is only the second example of linear i.r. photochemistry in matrices. Hall and Pimentel have previously shown[4] that the *cis* $\rightleftharpoons$ *trans* isomerization of HONO was promoted by broad-band black-body radiation in the region 3650—3200 cm^{-1}. However, laser radiation has much greater power in a narrow linewidth than conventional black bodies. Thus it is possible to excite a specific vibrational mode in a sufficient number of molecules to produce observable matrix photochemistry. It is clear that the combination of matrix isolation and i.r. laser photochemistry greatly extends the types of reactions which can be studied at low temperatures.

We thank the S.R.C. for support and Dr. J. K. Burdett and Mr. P. G. Buckley for their help.

(*Received*, 18*th August* 1976; *Com.* 957.)

---

§ These conclusions are supported by growth and decrease of the other C–O stretching bands (ref. 3) of a, b, A, and B which are not illustrated. During both laser irradiations there was some increase in the bands due to $[Fe(CO)_5]$.

¶ At the very low temperature employed ($RT = 0{\cdot}17$ kJ mol^{-1}) the energy of such a photon must be equal to or greater than the energy barrier for the reaction. This puts an upper limit of 1923 cm^{-1} (23 kJ mol^{-1}) on the barrier.

[1] *E.g.* J. L. Lyman, R. J. Jensen, J. Rink, C. P. Robinson, and S. D. Rockwood, *Appl. Phys. Letters*, **1975**, **27**, 87.
[2] M. Poliakoff and J. J. Turner, *J.C.S. Dalton*, 1973, 1351.
[3] M. Poliakoff and J. J. Turner, *J.C.S. Dalton*, 1974, 2276.
[4] R. T. Hall and G. C. Pimentel, *J. Chem. Phys.*, 1963, **38**, 1889.