MULTIPLE PHOTON I.R. LASER INDUCED ISOTOPIC ENRICHMENT OF SF_6 IN THE SOLID STATE. A SPECTROSCOPIC ARTEFACT

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A recent report of i.r. laser dissociation of SF_6 in low temperature matrices has posed interesting theoretical problems and opened up many exciting possibilities for further work[1]. Unfortunately, our attempts to repeat these experiments in Newcastle[2] have led us to believe that the results may be due to a spectroscopic artefact rather than isotopic enrichment.

The original experiment involved the matrix isolation of SF_6 in solid CO or Ar at 12K. I.r. spectra of the ν_3 S-F stretching mode of SF_6 show bands of $^{32}SF_6$ and $^{34}SF_6$ with the correct relative intensities ~22:1 for the natural abundance of ^{32}S and ^{34}S. The matrix was then irradiated with a series of pulses from a pulsed TEA CO_2 laser at 940.5 cm^{-1} (P (24), 0.5J cm^{-2}, 90 ns) co-incident with the $^{32}SF_6$ absorption. Although the bands of both $^{32}SF_6$ and $^{34}SF_6$ were reduced in intensity by the laser irradiation, the $^{32}SF_6$ band decreased substantially faster than the $^{34}SF_6$. This suggested isotopically selective dissociation of SF_6. No product bands were observed.

The experiment was repeated at Newcastle with slightly different laser parameters (P(26), 0.6Jcm^{-2}, 250 ns). However similar changes were seen in the relative intensities of the ^{32}S and ^{34}S bands. The CO matrix also displays absorption bands in the region of 2100 cm^{-1} due to natural abundance $^{13}C^{16}O$, $^{12}C^{17}O$ and $^{12}C^{18}O$. Although the relative intensities of these CO bands shouldhave remained unchanged during the experiment, the intensities were substantially altered by laser irradiation of the $^{32}SF_6$. Apparently enrichment of CO isotopes had also taken place! Clearly an alternative explanation is needed for the changes in the spectra.

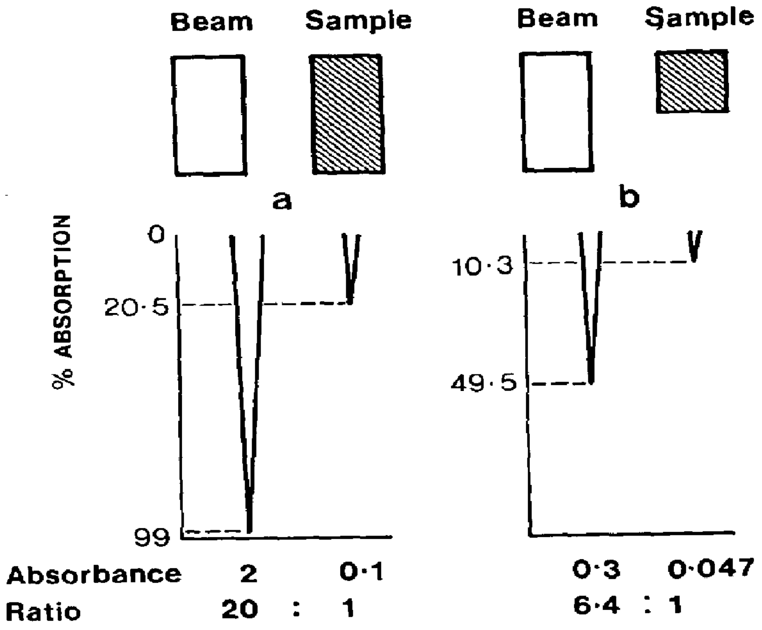

Figure 1 Simulated spectra to illustrate the spectroscopic artefact. (a) Sample completely filling the IR spectrometer beam (b) Sample having half the area of the beam.

The focussed CO_2 laser pulse does not irradiate the matrix surface with a uniform intensity. This results in patchy ablation of the matrix and causes an apparent breakdown of Beer's Law due to inhomegeneity of the sample. The Figures illustrate how this leads to an apparent change in the relative intensities of absorption bands. Figure a shows a simulated two band absorption spectrum, similar to SF_6, taken under normal spectroscopic conditions, with the sample totally filling the area of the spectrometer beam. The two bands absorb 99% and 20.5% of the light (absorbance 2.0 and 0.1 respectively). If the same sample filled only half the area of the spectrometer beam, Figure b, then the bands would absorb 99/2% and 20.5/2% i.e. 49.5% and 10.3% (absorbance 0.3 and 0.047). If these bands were due to isotopes of SF_6 then the second spectrum would appear to show an isotopic enrichment factor, $\beta = 3.1$ (0.3/0.047 / 2.0/0.1).

We have confirmed this explanation by achieving "laser enrichment" without the use of a laser! Patchy ablation was simulated by raising the matrix in spectrometer beam so that part of the beam passed underneath. The spectra were almost identical to those produced by laser irradiation.

In our experiments at least, isotopic selective dissociation of SF_6 is entirely an artefact. The results do not mean that multiple photon i.r. photochemistry in matrices is impossible, although rapid vibrational relaxation by the matrix and the absence of free rotation may make it difficult. It is clear, however, that the major question is how to prevent an intense laser pulse from destroying the matrix.

References

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