CARBON AND SULFUR ISOTOPE SEPARATION BY ArF LASER IRRADIATION OF CS_2[†]

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Summary

Single-photon isotope separation of carbon and sulfur isotopes has been carried out by irradiating a predissociative band of CS_2 with an ArF laser. Good selectivity for carbon isotopes was obtained with both broad-band and narrowed tuned laser outputs. Sulfur isotopic selectivity was found only upon irradiation with a tuned laser. The inherent simplicity of the technique suggests it should be useful for laboratory preparation of carbon-13 samples.

The irradiation of CS_2 with an ArF laser provides the basis for an exceptionally simple single-photon isotope separation process. Not only does the CS_2 molecule have a strong predissociative absorption with large isotopic shifts within the tuning range of the ArF laser [1], but the dissociation products form solid and polymeric deposits on the walls of the photolysis vessel [2, 3], obviating the need for chemical scavenging or product separation. Simply stated, isotopically selective excitation leads to a single gas phase product: enriched CS_2. With no requirement beyond tuning the ArF laser, selectivity for both carbon and sulfur isotopes has been demonstrated.

The free-running ArF laser emits a broad lasing line (4 Å wide) centered at 1934 Å [4]. With a simple dispersive prism chain in the cavity, this line may be narrowed to less than 0.5 Å and tuned from 1922 to 1944 Å, or almost the full width of the fluorescent output [5]. Figure 1 shows two CS_2 isotopic absorption curves taken with ArF fluorescence as the light source. The light transmitted through a 10 cm sample cell was dispersed by a 0.5 m spectrograph and detected by a scintillator-enhanced silicon-intensified-target vidicon array. The top curve is the fluorescence alone; the middle plot

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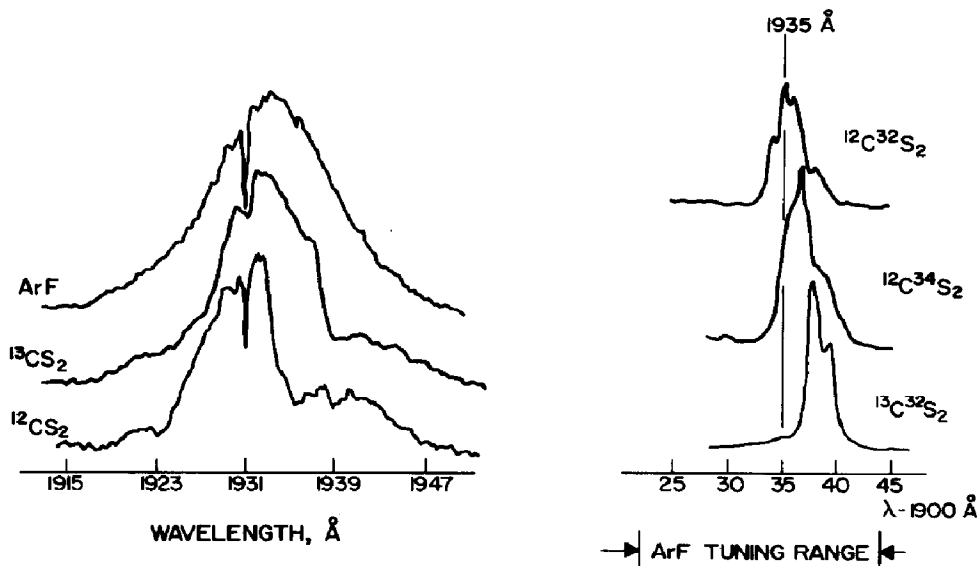
Fig. 1. Absorption of ArF fluorescence (ArF) by natural CS_2 ($^{12}CS_2$) and by 70% ^{13}C-enriched CS_2 ($^{13}CS_2$).

Fig. 2. Densitometer traces of CS_2 absorption peaks in a 3 m vacuum UV spectrograph. The wavelengths were calibrated against Schumann–Runge O_2 absorption lines.

shows the absorption feature resulting from a 0.015 Torr sample of 70% $^{13}CS_2$–30% $^{12}CS_2$; the bottom curve was taken with natural CS_2 (98.9% $^{12}CS_2$) in the sample cell. This preliminary result shows the large carbon isotope shifts that obtain in this wavelength region.

More detailed spectra were taken with a 3 m vacuum spectrograph and UV-sensitive plates, resulting in the densitometer traces of Fig. 2. In addition to the previous isotopic compositions, a sample with 90% $^{12}C^{34}S_2$ was examined. Although the ^{34}S species of interest in a natural sample is actually $^{12}C^{32}S^{34}S$, which would have a shift of about half of that shown it is clear that with the narrow linewidth and wavelength accuracy (±0.2 Å) of the tuned ArF laser, it should be possible to establish some degree of selectivity for the preferential reaction of any isotopic species. The present study concentrated on the ^{12}C–^{13}C problem, but a modest degree of sulfur selectivity is plainly evident from the data.

Figure 3 shows a schematic diagram of the apparatus used in the separation experiments. The wavelength of the tuned laser was set (with mirror M_2 removed) by comparison with the Schumann–Runge absorption bands of molecular oxygen [6]. These lines are easily seen in ArF fluorescence propagated through atmospheric oxygen. Once the wavelength was set, M_2 was replaced and the 10 cm photolysis cell was irradiated. The energy per shot varied from 1 to 10 mJ as a function of wavelength, but the pulse length of 25 ns and the 1 Hz repetition rate were constant. In all studies reported here the cell was filled with 70% $^{13}CS_2$–30%$^{12}CS_2$ in order more nearly to equalize the mass peaks of interest. All fills were at a pressure of 1.0 Torr. A fluores-
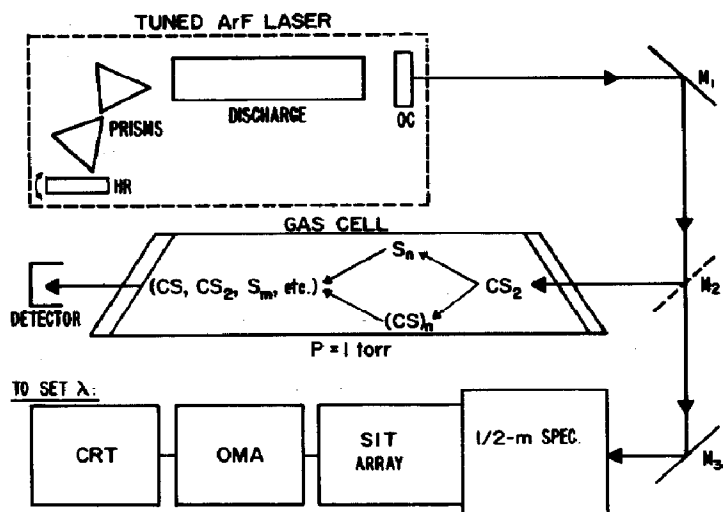
Fig. 3. A schematic diagram of the experimental apparatus, indicating both the procedure for setting the laser wavelength and for detecting the first transmission of laser light through the CS_2 sample.

cent card was used to detect the first signs of laser light emerging from the cell, at which point the irradiation was halted. This degree of exposure resulted in the fractions reacted ranging from 30 to 70%, depending upon the wavelength being used. The total laser energy deposited in the sample was always between 5 and 10 J, as measured with a pyroelectric detector.

After irradiation, the contents of the sample cell were analyzed by a quadrupole mass spectrometer. The pressure of the remaining gas was also measured to determine the fraction reacted. The mass analysis was complicated by the fact that CS_2 adheres tenaciously to almost all surfaces. Only after a ClF_3 purging procedure was adopted was it possible to remove all detectable residues of previous samples of CS_2. Since the starting composition of the samples was predominantly $^{13}C^{32}S_2$, all isotopic ratios were normalized to the amplitude of the mass 77 peak.

The ArF photon is absorbed into the $A(^1B_2)$ state [7, 8], leading to the dissociation of the molecule into CS and S. Both of these products eventually condense on the walls of the sample cell as solid sulfur or a $(CS)_n$ polymer [2, 3]. The polymerization seems to be aided by the presence of previous deposits; dirty sample cells usually gave improved separation factors. For the sake of reproducibility, all data reported here were obtained with initially clean cells. These results thus represent conservative estimates of the attainable selectivities.

A comparison of the total energy absorbed in the gas with the amount of energy required to decompose the molecules in the fraction reacted resulted in an estimate of the apparent quantum yield; this photochemical yield was only 10%. This result suggests non-dissociative energy disposal channels and/or back reactions after the initial decomposition. Since the $A(^1B_2)$ state is so strongly predissociated that the rotational lines are diffuse

[1], the former seems unlikely. It is also true that previous studies [9 - 12] of the post-photolysis kinetics of CS_2 showed no evidence of any major recombination reactions, since S atoms disappeared much more rapidly than did CS radicals. This study apparently is the first, albeit approximate, quantum yield measurement. At this time there is no ready explanation for the low photochemical quantum yield.

The analytic normalization to mass 77 resulted in relative isotopic selectivities (reaction probabilities for mass m relative to the reaction probability for mass 77) which are the normally calculated quantities [13]. An absolute selectivity factor, the reaction probability for mass m relative to the total reaction probability for the CS_2 sample, seemed more to the point. To derive this factor we started with the definition of absolute selectivity:

$$\alpha_t^m = \frac{\ln(N_1^m/N_0^m)}{\ln(\Sigma N_1^m/\Sigma N_0^m)}$$

where the Ns are the numbers of molecules of mass m before (subscript 0) and after (subscript 1) irradiation. The enrichment factor is defined as [13]

$$\beta^m = X_1^m/X_0^m$$

where X^m is the mass peak height (normalized to $X^{77} = 1$). An average enrichment factor is then

$$\bar{\beta} = (\Sigma N_0^m \beta^m)/(\Sigma N_0^m) = \Sigma X_1^m/\Sigma X_0^m$$

and the surviving fraction is

$$f = N_1/N_0 = P_1/P_0 \qquad \text{(pressure ratio)}$$

Then it is true that

$$N_1^{77}/N_0^{77} = f/\bar{\beta}$$

and one may derive the desired relation

$$\alpha_t^m = \frac{\ln(\beta^m f) - \ln\bar{\beta}}{\ln f}$$

in which the first term on the right-hand side is the mass 77 normalized selectivity factor α^m and the second term is a correction for the reactivity of the dominant mass 77 species.

The data which resulted from the tuned irradiation of CS_2 are presented in Fig. 4 in terms of the absolute selectivity factors. The data points are shown in individual plots for masses 76, 77 and 79, and the solid lines are compared in the bottom part of the figure. The results for mass 78 are omitted because of the low concentration of that isotopic species. The comparison of the mass 77 and 79 curves shows the sulfur isotope effect, which is seen as a delayed crossing of the $\alpha = 1.0$ line for mass 79. In Fig. 5 we show the positions of the mass curves relative to the $^{12}CS_2$ and $^{13}CS_2$ absorption peaks shown in Fig. 2.
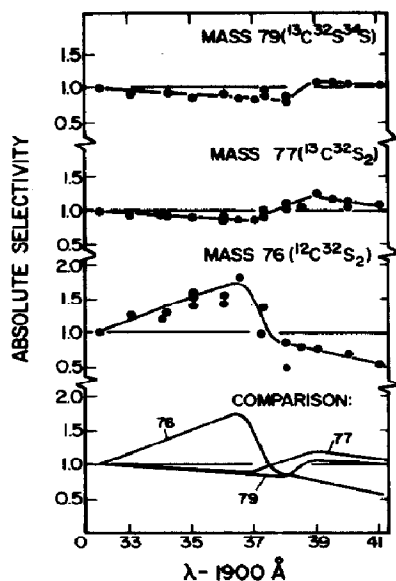
Fig. 4. Absolute selectivity factors for masses 76, 77 and 79. The individual data are shown in the top three plots and the smooth line results are compared in the lowest plot. An α_t of 1.0 indicates no selectivity; note that the mass 79 line crosses 1.0 at a longer wavelength than the mass 77 line, indicating a detectable difference from the ^{34}S in the mass 79 molecule.
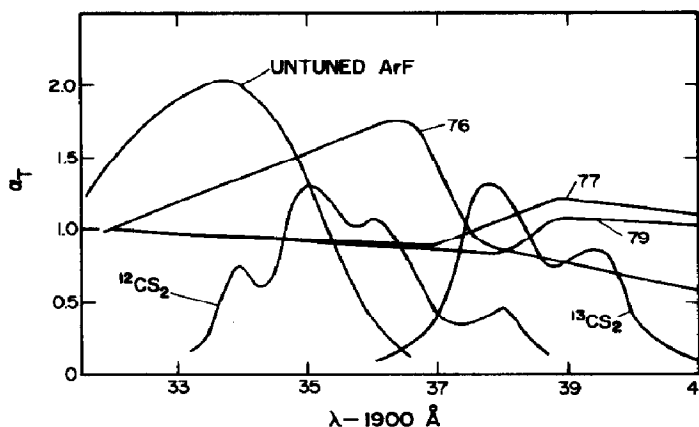
Fig. 5. A comparison of the CS_2 selectivity factor plot with the absorption peaks of Fig. 2 and the output of an untuned ArF laser.

Also shown in Fig. 5 is the lasing output typical of an untuned ArF laser. Clearly, this spectral output should preferentially dissociate the $^{12}CS_2$ in the mix. Irradiation of a 1.0 Torr 70% $^{13}CS_2$ sample with the untuned laser gave the results

$$\alpha_t^{76} = 1.41$$

$$\alpha_t^{77} = 0.95$$

demonstrating that reasonably effective separations can be obtained even with the untuned laser.

One obvious feature of the results is that the observed separation factors are substantially lower than the spectroscopic excitation selectivies. Previous kinetic studies showed that sulfur atoms rapidly react to form S_2, which condenses on the cell walls [9 - 12]. CS radicals, however, have a gas phase lifetime of many minutes [9]. Since sulfur atom exchange between CS and CS_2 is also a carbon isotope scrambling reaction, a suitable chemical scavenger for CS might improve the attained separation. The spectroscopic selectivity itself could also be improved by cooling the gas, which should considerably sharpen the absorption bands.

We conclude that even without these improvements, the technique used in these studies should have applications in the small-scale laboratory

preparation of enriched $^{13}CS_2$ samples. There have been a number of reports on laser separation of carbon isotopes [14 - 19]. The method reported here is superior primarily in its inherent simplicity. It is distinctly inferior to previous work [14, 18, 19] in the separation factors which have been obtained to date. However, the results of this preliminary investigation suggest that the major factors limiting the performance of this process might be eliminated once the details of the CS_2 photochemistry and photolysis are more thoroughly understood. Since ArF lasers are relatively simple high efficiency devices, the continued development of this process could lead to an economically viable means of producing separated carbon isotopes.

Acknowledgments

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