

Research Council of Canada for support in the form of operating grants (T.C. and W.G.L.) and to the Province of Alberta for a scholarship (J.B.). Particular thanks are extended to Dr. Jan Troup, Molecular Structure Corp., Texas, for the X-ray structure determination and to Dr. T. Ziegler for helpful discussions and the use of his computer programs.

Supplementary Material Available: A listing of structure factor amplitudes and a table of intermolecular contacts up to 4 Å (5 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) (a) J. Bojes and T. Chivers, *J. Chem. Soc., Chem. Commun.*, 453 (1977); (b) *Inorg. Chem.*, **17**, 318 (1978).
- (2) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **5**, 1767 (1966).
- (3) R. Steudel, F. Rose, R. Reinhardt, and H. Bradaczek, *Z. Naturforsch. B*, **32**, 488 (1977).
- (4) A. J. Banister and H. G. Clarke, *J. Chem. Soc., Dalton Trans.*, 2661 (1972).
- (5) A. J. Banister, *Nature (London) Phys. Sci.*, **237**, 92 (1972).
- (6) D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, in preparation.
- (7) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
- (8) See paragraph at end of paper regarding supplementary material.
- (9) J. C. Slater, *Adv. Quantum Chem.*, **6**, 1 (1972).
- (10) E. J. Baerends, D. E. Ellis, and P. Ros, *Chem. Phys.*, **2**, 41 (1973).
- (11) D. E. Ellis, *Int. J. Quantum Chem.*, **2**, 43 (1968).
- (12) (a) T. Ziegler, A. Rauk, and E. J. Baerends, *Chem. Phys.*, **16**, 209 (1976); (b) *Theor. Chim. Acta*, **43**, 261 (1977); (c) T. Ziegler and A. Rauk, *ibid.*, **46**, 1 (1977); (d) M. Trsic and W. G. Laidlaw, *Can. J. Chem.*, **56**, 1582 (1978); (e) W. G. Laidlaw and M. Trsic, *Chem. Phys.*, in press.
- (13) E. J. Baerends and P. Ros, *Int. J. Quantum Chem.*, in press.
- (14) E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 177 (1974).
- (15) (a) F. P. Boer and W. N. Lipscomb, *J. Chem. Phys.*, **50**, 989 (1969); (b) B. Roos and P. Siegbahn, *Theor. Chim. Acta*, **17**, 199 (1970); (c) F. J. Marsh and M. S. Gordon, *Chem. Phys. Lett.*, **45**, 255 (1977).
- (16) A. J. Banister and J. A. Durrant, *J. Chem. Res. (M)*, 1912 (1978).
- (17) T. Ziegler, private communication.
- (18) R. R. Adkins and A. G. Turner, *J. Am. Chem. Soc.*, **100**, 1383 (1978).
- (19) J. Bojes and T. Chivers, *Inorg. Chem.*, in press.
- (20) J. S. Anderson and J. S. Ogden, *J. Chem. Phys.*, **51**, 4189 (1969).
- (21) R. M. Atkins and P. L. Timms, *Spectrochim. Acta, Part A*, **33**, 853 (1977).
- (22) G. E. Coxon and D. B. Sowerby, *Inorg. Chim. Acta*, **1**, 381 (1967).
- (23) J. Emsley, *J. Chem. Soc. A*, 109 (1970).
- (24) P. O. Offenhartz, "Atomic and Molecular Orbital Theory", McGraw-Hill, New York, 1970. See eq 10.97 for the formula for calculating orbital overlap population, eq 10.98 for overlap population, and eq 10.102 for gross electron charge.
- (25) T. Chivers, L. Fielding, W. G. Laidlaw, and M. Trsic, to be published.
- (26) A. G. Turner and F. S. Mortimer, *Inorg. Chem.*, **5**, 906 (1966).
- (27) The atomic charge is the nuclear charge minus its gross atomic charge; see, for example, ref 24.
- (28) M. S. Gopinathan and M. A. Whitehead, *Can. J. Chem.*, **53**, 1343 (1975).
- (29) D. R. Salahub and R. P. Messmer, *J. Chem. Phys.*, **64**, 2039 (1976).
- (30) K. Tanaka, T. Yamabe, A. Tachiban, H. Kato, and K. Fukui, *J. Phys. Chem.*, **82**, 2121 (1978).
- (31) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
- (32) R. L. Patton and W. L. Jolly, *Inorg. Chem.*, **8**, 1392 (1969).
- (33) M. Goehring, H. Herb, and H. Missemeyer, *Z. Anorg. Allg. Chem.*, **267**, 238 (1952).
- (34) A. W. Cordes, R. F. Kruh, and E. K. Gordon, *Inorg. Chem.*, **4**, 681 (1965).
- (35) T. Chivers and L. Fielding, *J. Chem. Soc., Chem. Commun.*, 212 (1978).
- (36) L. Zborilova, J. Touzin, D. Navratilova, and J. Mrksova, *Z. Chem.*, **12**, 27 (1972).
- (37) T. Chivers and L. Fielding, unpublished observations.
- (38) R. J. Gillespie, P. R. Ireland, and J. E. Vekris, *Can. J. Chem.*, **53**, 3147 (1975).
- (39) T. N. Guru Row and P. Coppens, *Inorg. Chem.*, **17**, 1670 (1978), and references cited therein.
- (40) H. W. Roesky, W. Grosse-Bowing, I. Rayment, and H. M. M. Shearer, *J. Chem. Soc., Chem. Commun.*, 735 (1975).
- (41) A. J. Banister, J. A. Durrant, I. Rayment, and H. M. M. Shearer, *J. Chem. Soc., Dalton Trans.*, 928 (1976).
- (42) A weak band at ca. 950 cm^{-1} , previously reported for the infrared and Raman spectra of $\text{Cs}^+\text{S}_3\text{N}_3^-$,^{1b} has not been observed in the spectra of samples that have been prepared subsequently.

Photolytic Separation of Carbon Isotopes in Cryogenic Solutions of Carbon Disulfide

Samuel M. Freund, William B. Maier II, Redus F. Holland, and Willard H. Beattie*

Contribution from the University of California, Los Alamos Scientific Laboratory, P.O. Box 1663, Los Alamos, New Mexico 87545. Received October 16, 1978

Abstract: We report the separation of carbon isotopes by photolysis of CS_2 in cryogenic solutions of nitrogen, krypton, and argon with 206-nm light from an iodine resonance lamp. The spectral distribution of the ultraviolet absorption depends on solvent. Thus, in liquid nitrogen the photolytic rate of $^{13}\text{CS}_2$ is greater than that of $^{12}\text{CS}_2$, whereas in liquid krypton and liquid argon the reverse is true.

Introduction

Recent success in the separation of D from H in cryogenic solutions of formaldehyde in our laboratory¹ has stimulated interest in extending the technique to the separation of isotopes of other light elements.² The concurrent vapor-phase isotope separation of carbon isotopes from the low-pressure photolysis of CS_2 with light from an ArF laser,³ the existence of predissociative states which give rise to well-defined vibronic structure in the region 185–215 nm,^{4–8} and the availability of a convenient and powerful resonance lamp photolysis source^{6,9} suggested that CS_2 might be a suitable candidate for a liquid-phase separation.

In this paper we report the photolytic separation of carbon isotopes in cryogenic solutions of CS_2 in nitrogen, krypton, and argon with 206-nm light from an iodine resonance lamp.

The ultraviolet absorption spectrum of carbon disulfide is

different in different solvents, so that the photodestruction rates of $^{12}\text{CS}_2$ relative to $^{13}\text{CS}_2$ can easily be varied.¹⁰

Experimental Section

The apparatus used for both the spectroscopy and the photochemistry experiments have been described in detail in ref 1. Ultraviolet absorption spectra were obtained with a Cary Model 17 spectrophotometer. Photolyses were performed in copper two-way cells. Corning 7940 UV filter material (4 mm thick) was used to pass UV light, and CaF_2 windows allowed simultaneous monitoring of the disappearance of CS_2 with a Perkin-Elmer 180 infrared spectrophotometer. No attempt was made to monitor products.

The $^{12}\text{CS}_2$ concentration was monitored through a 2.6-cm path length at 1531.1 cm^{-1} ($\sigma_{\text{ir}} = 1.63 \times 10^{-16} \text{ cm}^2$) and the $^{13}\text{CS}_2$ at 1481.0 cm^{-1} ($\sigma_{\text{ir}} = 1.31 \times 10^{-16} \text{ cm}^2$). These wavenumbers correspond to the collapsed and shifted ν_3 rotation-vibration band in liquid argon (LAr) at -170°C .¹¹ Here the σ 's are the measured peak ab-

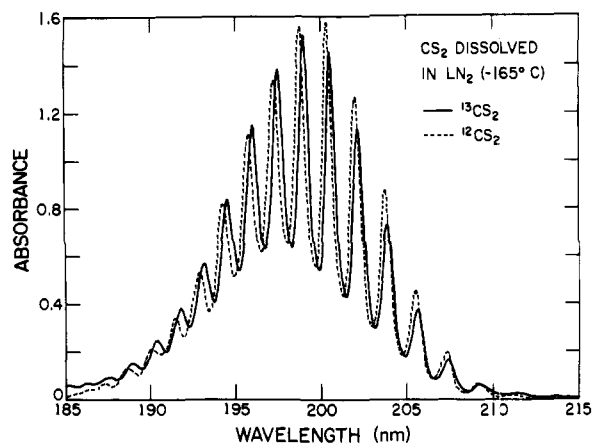


Figure 1. Ultraviolet spectra of ¹²CS₂ and ¹³CS₂ dissolved in liquid nitrogen at -165°C . The areas of the two curves are normalized to compensate for differences in quantity of material in solution. Approximately 5×10^{15} molecules/cm³ are present in solution. $\sigma_{\text{peak}} \sim 2.5 \times 10^{-16}$ cm², which is very close to our measured gas-phase value for this quantity (cf. ref 4). The optical path length is 2.6 cm, and the spectral resolution is about 3 Å. The absorbance is defined to be $\log(I_0/I)$, where I_0 and I are the incident and transmitted light intensity, respectively.

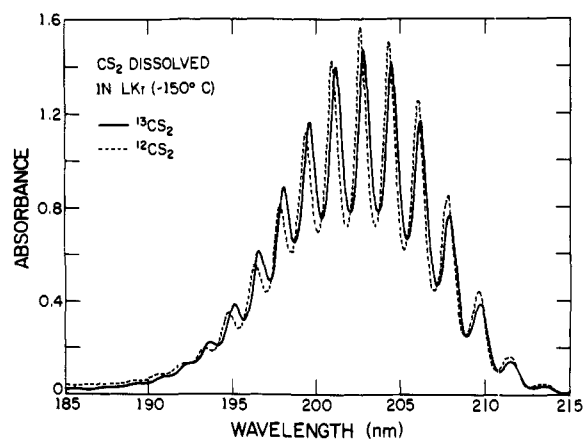


Figure 2. Ultraviolet spectra of ¹²CS₂ and ¹³CS₂ dissolved in liquid krypton at -150°C . The areas of the two curves are normalized to compensate for differences in quantity of material in solution. Approximately 5×10^{15} molecules/cm³ are present in solution. $\sigma_{\text{peak}} \sim 2.5 \times 10^{-16}$ cm², which is very close to our measured gas-phase value for this quantity (cf. ref 4). The optical path length is 2.6 cm, and the spectral resolution is about 3 Å. The absorbance is defined to be $\log(I_0/I)$ where I_0 and I are the incident and transmitted light intensity, respectively.

sorption cross sections at the wavenumbers quoted. All spectra were taken with a 1.5-s time constant at a scan speed of $0.15 \text{ cm}^{-1} \text{ s}^{-1}$ with an instrumental resolution of 1.0 cm^{-1} . The full width at half-maximum absorbance of the absorption features is about 1.5 cm^{-1} . Corresponding bands were used in LKr and LN₂.

The ¹²CS₂ (Matheson Coleman and Bell) and ¹³CS₂ (Merck Sharp and Dohme) samples were cooled to liquid nitrogen temperature, pumped on, and warmed several times for purification. Commercial, high-purity Ar, Kr, and N₂ were used without further purification.

Solutions were prepared by sweeping measured quantities of gaseous CS₂ into partially filled cells of liquefied solvent with the gaseous solvent.^{1,2} The cell is completely filled by liquefying additional solvent gas while vigorously stirring the solution by means of a Teflon-coated magnetic stirrer. In order to have sufficient solubility of the CS₂ in LN₂, the cell was held at a temperature of -165°C and a pressure of $>12\,400$ Torr.

The iodine resonance lamp was constructed from a section of 0.6 cm diameter \times 0.1 cm wall quartz tubing which was evacuated and flamed with a torch to remove adsorbed gases. The tube was vented, several iodine crystals were added, the tube was reevacuated to 10^{-4} Torr, and the I₂ was distilled under vacuum several times between hot and cold sections of the tube to remove water and other impurities;

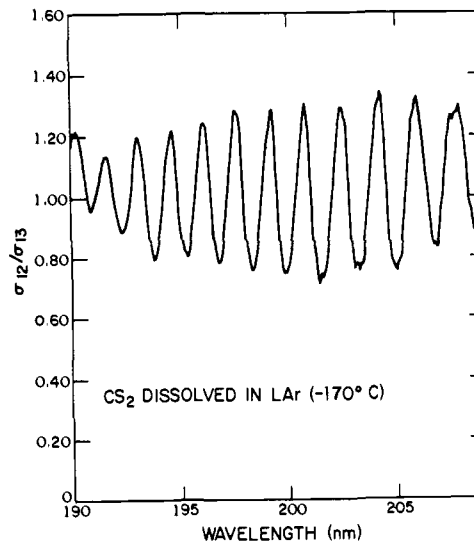


Figure 3. Spectroscopic contrast ratio, σ_{12}/σ_{13} , for ¹²CS₂ and ¹³CS₂ in liquid argon at -170°C as a function of wavelength.

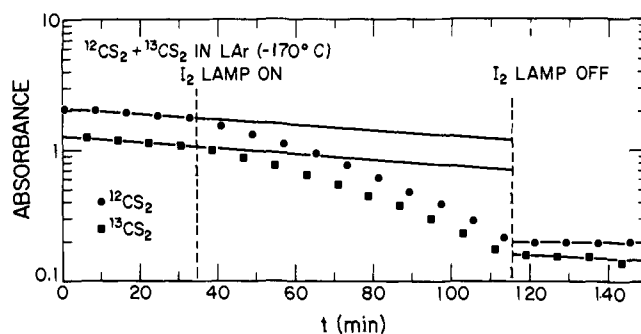


Figure 4. Infrared absorbance $[\ln(I_0/I)]$ vs. time during photolysis for a mixture of ¹²CS₂ and ¹³CS₂ in liquid argon at -170°C . Peak absorbances of the 1531.1- and 1481.0-cm⁻¹ bands of ¹²CS₂ and ¹³CS₂, respectively, are represented by ● and ■. The vertical dashed lines indicate times at which light from the iodine resonance lamp was admitted or excluded from the cell. The solid curves are extrapolations of the slow decreases in CS₂ concentration that occur where there is no photolyzing radiation.

the tube was then sealed. A Kiva Instrument Corp. microwave generator operated at 95 W of output power was coupled to an Evenston-type cavity. The iodine resonance lamp provided approximately 30 mW of power at 206 nm. Other lines of longer wavelength were present but could not contribute to the photolysis. Therefore, the spectral output of the lamp was utilized without dispersion. The lamp ran continuously for hours with little attention, but the power output was found to vary with time. Photolyses were, therefore, performed with mixtures of ¹²CS₂ and ¹³CS₂ to ensure that identical light fluxes reached both types of molecules.

Results and Discussion

Figures 1 and 2 show the UV absorption spectra of ¹²CS₂ and ¹³CS₂ in LN₂ and LKr at -165 and -150°C , respectively. These spectral absorptions, which are reported to arise from the $\tilde{A}^1B_2 \leftarrow \tilde{X}^1\Sigma_g^+$ transition,^{4,5} appear at longer wavelengths in LKr than they do in LN₂.¹⁰ Smaller shifts occur as a result of temperature changes.¹⁰ The isotopic shifts are apparent in both figures as well.

Figure 3 shows the spectroscopic contrast ratio (σ_{12}/σ_{13}) for CS₂ in LAr at -170°C as a function of wavelength. Here the σ 's are the measured absorption cross sections. Either ¹³CS₂ or ¹²CS₂ may be preferentially excited by choosing the appropriate wavelength for the photolyzing radiation.

The infrared absorbances of ¹²CS₂ are proportional to their concentrations and are plotted as functions of time in Figure 4. As the CS₂ is photolyzed, the number of ultraviolet photons

Table I. Spectroscopic Contrast Ratios^a at 206 nm and Observed Ratios of Rates of Photolysis

solvent ^b	temp, °C	k_{12}/k_{13}	σ_{12}/σ_{13}	Δ , % ^c	% photolyzed		photolysis ^d time, s
					¹² CS ₂	¹³ CS ₂	
LAr	-170	1.22	1.32	8	83	77	4846
LKr	-150	1.10	1.18	7	52	49	3915
LN ₂	-165	0.94	0.85	10 ^e	70	72	678

^aContrast ratio is defined as the ratio of cross sections, σ_{12}/σ_{13} , at a single wavelength. ^bApproximately 5×10^{16} molecules/cm³ of each of ¹²CS₂ and ¹³CS₂ were dissolved in LAr and LKr and 1×10^{16} molecules/cm³ in LN₂. ^c Δ is the percentage difference between σ_{12}/σ_{13} and k_{12}/k_{13} . $\Delta = 100 (\sigma_{12}/\sigma_{13} - k_{12}/k_{13})/(\sigma_{12}/\sigma_{13})$. ^dPhotolysis times varied dramatically depending on the condition of the resonance lamp. New lamps gave short irradiation times because of increased light flux. ^eHere Δ is the percentage difference between σ_{13}/σ_{12} and k_{13}/k_{12} .

absorbed changes, and so the plot of absorbance vs. time in Figure 4 is curved when the lamp is on. This curvature is found to be consistent with the assumption that the photolysis can be described by

$$dn_i/dt = -k_i \phi n_i \quad (i = 12, 13) \quad (1)$$

where n_i is the number density of each ⁱCS₂ species, k_i is a constant, and ϕ is the photolyzing light flux at any point in space. The distribution of CS₂ should be uniform within the cell, and so, if eq 1 is integrated over the cell's volume, V , one finds $dN_i/dt = -K_i N_i$ where $N_i = n_i V$ and $K_i = k_i \int \phi dV$. Thus, $dN_{12}/dN_{13} = K_{12}N_{12}/K_{13}N_{13}$, and

$$\frac{K_{12}}{K_{13}} = \frac{\ln(N_{12}/N_{12}^0)}{\ln(N_{13}/N_{13}^0)} = \frac{\ln(n_{12}/n_{12}^0)}{\ln(n_{13}/n_{13}^0)} = \frac{k_{12}}{k_{13}} \quad (2)$$

If n_i^0 and n_i are now taken to be the number densities of ⁱCS₂ before and after photolysis, k_{12}/k_{13} may be obtained accurately despite the curvature in the plots of n_i vs. time. If isotopic scrambling reactions are unimportant and if the decomposition is unimolecular, then $k_i \propto \sigma_i$, where σ_i is the ultraviolet absorption cross section of ⁱCS₂.

Table I gives the values of k_{12}/k_{13} and of σ_{12}/σ_{13} at 206 nm. The values of k_{12}/k_{13} have been approximately corrected for the background disappearance of CS₂ without photolysis. The extended straight lines in Figure 4 show this background decrease for one case. The background decrease is attributed to wall effects and is different for different runs, but it is equal for the two isotopic species. The estimated maximum uncertainty in k_{12}/k_{13} is $\pm 3\%$, so the results in Table I clearly indicate that photolytic enrichment of isotopically labeled CS₂ has occurred.

In Table I, σ_{12}/σ_{13} is seen to be 7–10% different than k_{12}/k_{13} . Since we estimate that σ_{12}/σ_{13} is known within $\pm 5\%$, the measured values of k_{12}/k_{13} are not quite within experimental error of σ_{12}/σ_{13} . The differences could be caused by isotopic scrambling reactions, by unrecognized systematic error in σ_{12}/σ_{13} , by differences in quantum efficiency for ¹³CS₂ and ¹²CS₂, or by nonselective, photolyzing continuum radiation from the iodine lamp. (If such continuum radiation had totaled >5% of the 206-nm radiation, we would have detected it, however.)

The efficiency, ϵ , with which absorbed photons are utilized in this photolysis is roughly 10^{-3} . This number is equal to the number of molecules photolyzed divided by the total number of photons incident on the cell. Since not all of the incident photons were absorbed by the CS₂, the number is somewhat lower than the true quantum efficiency of the process, but

nevertheless the quantum efficiency in these solutions is considerably lower than that found in the photolysis of CS₂ vapor.³

Conclusions

We have demonstrated that photolysis of dissolved CS₂ can significantly alter carbon isotope ratios in cryogenic solutions. Of special interest is the fact that, depending upon which cryogenic solvent is used, either ¹²CS₂ or ¹³CS₂ can be made to photolyze more rapidly for a given wavelength of photolyzing radiation. This occurs because the UV absorption spectrum of the CS₂ shifts in wavelength with solvent, thereby changing the spectroscopic contrast ratio.

The slight curvature of the logarithm of the absorbance as a function of time can be explained by the changing optical density of the solution as the photolysis proceeds. The ratios of the measured photolysis rates are reasonably similar to the spectroscopic contrast ratios.

The poor photon utilization efficiency, ϵ , does not augur well for an economical isotope enrichment process, unless a suitable scavenger and/or solvent can be found which will significantly increase ϵ .

Acknowledgments. The authors are grateful to J. P. Aldridge for the support given this work and to Bruce Stewart and Ruth Sherman for their technical assistance. Andrew Kozubal helped with the computer analysis of the data. This work was performed under the auspices of the U.S. Department of Energy.

References and Notes

- W. B. Maier II, S. M. Freund, R. F. Holland, and W. H. Beattie, *J. Chem. Phys.*, **69**, 1961 (1978); S. M. Freund, W. B. Maier II, R. F. Holland, and W. H. Beattie, *Anal. Chem.*, **50**, 1260 (1978).
- See also G. L. DePoorter and C. K. Rofer-DePoorter, *Inorg. Nucl. Chem. Lett.*, **13**, 459 (1977); C. K. Rofer-DePoorter and G. L. DePoorter, *J. Inorg. Nucl. Chem.*, in press; C. K. Rofer-DePoorter and G. L. DePoorter, *Chem. Phys. Lett.*, in press.
- T. R. Loree, J. H. Clark, B. Butterfield, J. L. Lyman, and R. Engleman, *Chem. Phys. Lett.*, submitted for publication.
- J. W. Rabalais, J. M. McDonald, V. Scherr, and S. P. McGlynn, *Chem. Rev.*, **71**, 73 (1971).
- G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand-Reinhold, Princeton, N.J., 1966.
- R. Engleman, Jr., LASL Office Memorandum, GMX-2, 1971.
- N. Basco and A. E. Pearson, *Trans. Faraday Soc.*, **63**, 2684 (1967).
- W. P. Wood and J. Heicklen, *J. Photochem.*, **2**, 173 (1973).
- P. Harteck, R. R. Reeves, Jr., and B. A. Thompson, *Z. Naturforsch. A*, **19**, 2 (1964).
- S. M. Freund and W. H. Beattie, to be submitted.
- T. Shimanouchi, "Tables of Molecular Vibrational Frequencies", Consolidated Vol. 1, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 39** (1972).