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LETTERS

Large Mass Independent Sulfur Isotope Fractionations during the Photopolymerization of $^{12}CS_2$ and $^{13}CS_2$

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Broad band solar irradiation of gas- and liquid-phase $^{13}CS_2$ produces polymers that are mass independently and mass dependently fractionated, respectively. The observed sulfur isotopic results differ significantly from those for $^{12}CS_2$. Gas-phase photolysis of $^{12}CS_2$ produces $[^{12}CS_2]_x$ that is fractionated in sulfur isotopes with $\delta^{34}S = 45.85‰$, $\delta^{33}S = 28.31‰$, and $\delta^{36}S = 37.6‰$, while liquid-phase photolysis yields $[^{12}CS]_x$ fractionated in sulfur isotopes with $\delta^{34}S = 32.48‰$, $\delta^{33}S = 16.98‰$, and $\delta^{36}S = 56.7‰$. Gas-phase photolysis of $^{13}CS_2$ produces $[^{13}CS_2]_x$ that is fractionated in sulfur isotopes with $\delta^{34}S = 114.65‰$, $\delta^{33}S = 80.84‰$, and $\delta^{36}S = 168.7‰$, while liquid-phase photolysis yields $[^{13}CS]_x$ fractionated in sulfur isotopes with $\delta^{34}S = 10.43‰$, $\delta^{33}S = 7.75‰$, and $\delta^{36}S = 22.4‰$. The large effect that ^{13}C enrichment has on the sulfur isotope distribution excludes a symmetry-dependent process as the origin for the mass-independent effect. Franck−Condon and vibronic coupling effects on nonradiative decay and intersystem crossing rates for the lowest excited states are suggested as the source of the mass-independent process. The absence of anomalous isotope effects for the materials prepared by liquid-phase photolysis support this proposal.

Carbon disulfide is an important component of gaseous nebulae, which includes the presolar nebula and primitive planetary atmospheres.[1−3] It is also a trace atmospheric component with biogenic and anthropogenic sources.[4−20] At higher concentrations (>10 ppm) carbon disulfide photopolymerizes to yield $[CS_2]_x$ when irradiated at 313 nm.[21,22] Irradiation at shorter wavelengths (λ < 240 nm) causes C−S bond dissociation and yields a complex product mixture.[23] The $[CS_2]_x$ produced by 313 nm irradiation shows anomalous mass-independent ^{33}S, ^{34}S, and ^{36}S isotopic fractionations that are also observed in sulfur compounds of some meteorites.[23−27] Photopolymerization of carbon disulfide may thus be an important primary reaction for carbon speciation in the presolar nebula and possibly serve as an agent in trapping planetary gases. We now report that photopolymerization of $^{13}CS_2$ yields $[^{13}CS_2]_x$ with a distinct and much larger mass-independent fractionation of sulfur isotopes than that of $^{12}CS_2$. In addition, the solution-phase photopolymerization of $^{12}CS_2$ and $^{13}CS_2$ yields flexible polymers with the approximate stoichiometries $[^{12}CS]_x$ and $[^{13}CS]_x$. These liquid-phase products exhibit normal mass-dependent sulfur isotope fractionations. The unusual enrichments obtained during gas-phase photolysis suggest that photophysical effects provide a mechanism for mass-independent heavy atom isotope enrichment. This is potentially significant to the interpretation of environmental isotope ratios as well as the design of isotope enrichment schemes.

The photopolymers $[^{12}CS_2]_x$ and $[^{13}CS_2]_x$ were prepared by solar irradiation of a mixture of high purity nitrogen and gas-phase $^{12}CS_2$ or $^{13}CS_2$ (98% carbon-13 Cambridge Isotope Labs), respectively.[28] The photopolymers $[^{12}CS]_x$ and $[^{13}CS]_x$ were

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synthesized by solar irradiation of corresponding liquid CS_2 samples.[29] After exposure to sunlight, for a total of about 60 h, the contiguous flexible film that lined the flask was collected and washed with fresh carbon disulfide to remove elemental sulfur byproduct.

A technique for the extraction of meteoritic sulfur was modified to perform the high-resolution sulfur isotopic analyses.[25,30] Photoproduct was dissolved in 90% fuming nitric acid pretreated with $BaCl_2$ to remove SO_4^{2-} contaminant and converted to SF_6 for isotopic analysis,[31,32] which was finally purified by gas chromatography.[33,34] Isotope analyses were performed on a Finnigan MAT252 triple collector isotopic ratio mass spectrometer. Two measurements provided ratios of 34/32, 33/32, 36/32. Errors associated with these measurements are ±0.03‰ for δ^{34}S and δ^{33}S, and ±0.4‰ for δ^{36}S.[35]

Three isotope plots (δ^{33}S vs δ^{34}S and δ^{36}S vs δ^{34}S) for the $[^{12}CS_2]_x$ and $[^{13}CS_2]_x$ produced by solar irradiation of vapor-phase carbon disulfide are shown in Figure 1. The fractionation data for $[^{12}CS]_x$ and $[^{13}CS]_x$ produced by solar irradiation of liquid-phase carbon disulfide are also shown. Mass-dependent fractionation lines are included in each plot, and the data are normalized to a starting CS_2 isotopic composition of $\delta^{33}S = \delta^{34}S = \delta^{36}S = 0$. There are several remarkable features of these plots. First, the heavy isotope enrichments observed for the photoproducts from gas-phase photolyses are far greater than those due to normal chemical processes. For example, the δ^{34}S range found in sedimentary rock spans a range of −40 to +50‰, while the δ^{34}S compositions observed in $[^{13}CS_2]_x$ approach +130‰, and for δ^{36}S ∼+165‰.[35] Second, the fractionations are mass independent and lie far from the mass-dependent lines ($\delta^{33}S = 0.5\ \delta^{34}S$; $\delta^{36}S = 2\delta^{34}S$) that define conventional isotope effects.[36] Third, the various $[CS_2]_x$ samples show small variations between them, and all the data appear to lie on a common line (dashed) with a nonzero intercept. A nonzero intercept implies intervention of at least two fractionation processes, one (or both) of which is mass dependent. By contrast, the photopolymer obtained from liquid-phase photolysis exhibits normal mass-dependent fractionation regardless of whether $^{12}CS_2$ or $^{13}CS_2$ is used.

The conventional explanation for the mass-independent oxygen isotope fractionations during ozone production invokes a symmetry-dependent process.[37,38] However, an alternative theory based on the nature of the collision process has been proposed.[39] A symmetry-dependent process cannot explain the fractionation observed during gas-phase photopolymerization of carbon disulfide. Isotopic substitution at carbon does not alter the point group symmetry, yet large changes occur in sulfur isotope enrichments. Furthermore, a symmetry-dependent process requires equal enrichments in all three minor sulfur isotopes. Nuclear spin effects do not appear to be important, since ^{33}S and ^{13}C possess nuclear spins, but anomalous enrichments occur for all combinations of sulfur and carbon isotopes. Spin effects are also estimated to be too small to appreciably alter equilibrium and kinetic isotope effects for heavy atoms.[40] A new mechanism is required to explain the mass-independent fractionations observed during the gas-phase photolysis of CS_2. One possibility is that the process is of photophysical origin.

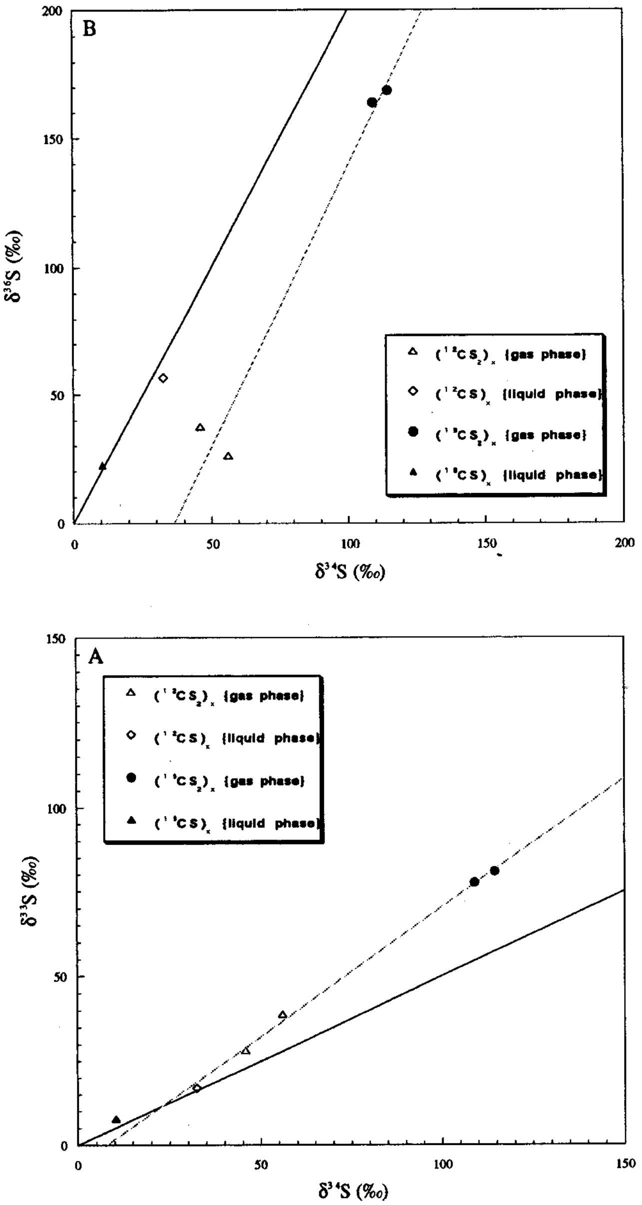
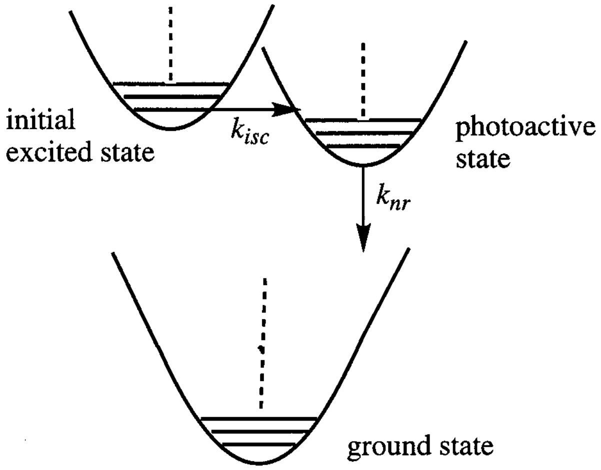


Figure 1. Three-isotope plots for $[^{12}CS_2]_x$ (△), $[^{12}CS]_x$ (◇), $[^{13}CS_2]_x$ (●), and $[^{13}CS]_x$ (▲) produced by solar photolysis. The $^{12}CS_2$ data was taken from the literature.[22] The ideal mass fractionation lines are shown as solid lines in each plot. Dashed lines are linear least-squares fits of the fractionations observed in the gas-phase samples. Data are normalized to a starting CS_2 isotopic composition of $\delta^{34}S = \delta^{33}S = \delta^{36}S = 0$. (A) δ^{33}S versus δ^{34}S. (B) δ^{36}S versus δ^{34}S. The slope of the solid line in (A) is 1/2. The slope of the solid line in (B) is 2.

Gas-phase photochemical studies have shown that carbon disulfide photopolymerization occurs even under conditions where fluorescence from the lowest excited singlet states is collisionally quenched by a buffer gas, such as N_2.[21,41] This implies that photopolymerization is occurring from a long-lived excited state, which is probably of triplet character. Although the lowest excited states of carbon disulfide have not been definitively assigned,[42] it is thought that the absorption system between 290 and 340 nm consists of excited states derived from the $(\pi_g)^3(\pi_u)^1$ electronic configuration.[43] Both the singlet and triplet states derived from Renner−Teller splitting of the $^1\Delta_u$ and $^3\Delta_u$ electronic states are thought to lie in this region and the molecule adopts a bent geometry in these states.[44,45] Detailed assignments of the rovibronic levels in the electronic absorption spectrum have been hindered by the strong vibronic and spin−orbit couplings between overlapping electronic states, which have been termed "remarkable" in their "ferocity".[46] Individual rovibronic components in the fluorescence spectra exhibit biexponential decay processes and show up to a 5-fold variation in lifetimes.[47,48] Further evidence of quantum interference among these low-lying states is provided by the Raman deenhancement of the totally symmetric C−S stretching vibration on 320 nm excitation.[49] This was attributed to interference between the

SCHEME 1



allowed $^1\Sigma_u$ state and two forbidden Renner−Teller components, but it could also arise from potential surface crossings.[50] These observations suggest that the quantum yields for product formation could be influenced by at least two nonradiative processes of the parent molecule. One would be the rate of intersystem crossing (k_{isc}) to the long-lived state that promotes polymerization, and the second would be the rate of nonradiative decay (k_{nr}) of the long-lived state (Scheme 1).

In the weak coupling model for nonradiative processes, both these rates would involve electronic or spin−orbit matrix elements that couple the electronic states involved in the nonradiative processes. There is also a Franck−Condon factor for overlap of the vibrational wave functions between the relevant electronic potential surfaces.[51] Both the electronic and vibronic couplings should depend on the specific placement of vibronic energy levels between the two potential surfaces involved in the nonradiative process. This should lead to different nonradiative rates for different isotopic species and yield mass fractionations that do not rely on thermally activated events.

In small gas-phase organic molecules, dramatic deuterium isotope effects have been observed for nonradiative decay rates from the lowest triplet state T_1 to the singlet ground-state S_0.[51] Poor Franck−Condon overlap between the $v = 0$ vibrational level of T_1 and high v levels of S_0 causes deuterated compounds to exhibit much longer excited-state lifetimes (and quantum yields for photochemistry) than corresponding hydrogen compounds. This effect, a consequence of the energy gap law, applies to both internal conversion and intersystem crossing rates.[52] In carbon disulfide, the C−S vibrations should be the primary modes involved in vibrational coupling. The dramatic increase in sulfur isotope fractionations by substituting ^{13}C for ^{12}C may reflect the increasing importance of this decay pathway in determining triplet lifetimes and thereby product quantum yields. If this were the case, then the frequency of C−S stretching (proportional to $1/\mu^{1/2}$, where μ is the reduced mass of a particular C−S isotopic combination) should correlate with the degree of isotopic enrichment. This is observed experimentally as shown in Figure 2. Data for ^{12}C isotopes are also included in this plot, and they show a similar trend, with the exception of the data for the ^{36}S isotope. The reduced enrichments observed in the ^{12}C case may reflect a greater importance of the initial intersystem crossing rate in determining product formation, but like ^{13}C the enrichment increases with increasing isotope mass, except for ^{36}S. The latter anomaly may reflect an accidental degeneracy of vibronic states for the ^{36}S isotopomer.

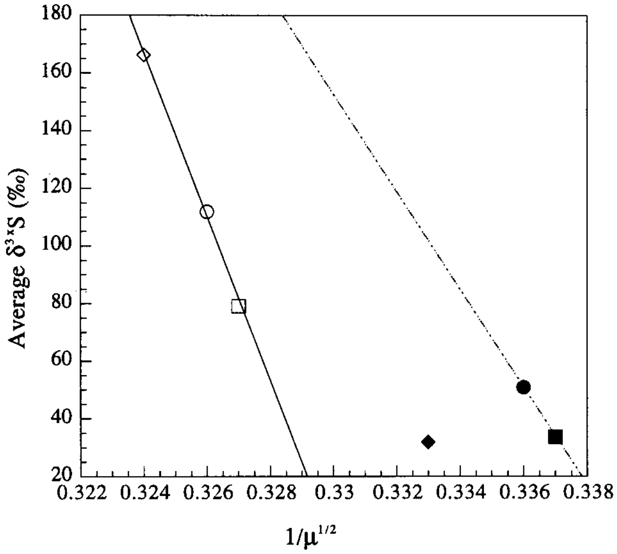


Figure 2. Plot of the average per mil shift measured for sulfur isotopes in $[^{12}CS_2]_x$ and $[^{13}CS_2]_x$ against the reciprocal of the square root of the reduced mass (proportional to the vibrational frequency of the C−S bond) for the corresponding $^{ij}C-^{kl}S$ bond. The symbols are $\delta^{34}S$ $[^{12}CS_2]_x$ (●), $\delta^{33}S$ $[^{12}CS_2]_x$ (■), $\delta^{36}S$ $[^{12}CS_2]_x$ (◆), $\delta^{34}S[^{13}CS_2]_x$ (○), $\delta^{33}S$ $[^{13}CS_2]_x$ (□), and $\delta^{36}S$ $[^{13}CS_2]_x$ (◇). The $[^{13}CS_2]_x$ sulfur isotope enrichments show a mass-dependent correlation among themselves even though they lie off the mass-dependent line of Figure 1.

Molecular vibronic effects on nonradiative pathways are of reduced importance in the liquid phase, since excited-state deactivation is dominated by collisions with the surrounding solvent. Low-frequency bending is predicted to be the gateway mode for deactivation of highly vibrationally excited CS_2.[50] Indeed, photolysis of liquid carbon disulfide yields a different polymer corresponding to the loss of a sulfur atom. This is suggestive of solution photochemistry occurring from a different electronic state, such as a short-lived singlet. Sulfur isotope fractionations observed in the photopolymers produced during liquid-phase photopolymerization are much smaller than for the gas-phase photopolymer and they exhibit a normal mass-dependent relationship (Figure 1).

In conclusion, these data show that dramatic mass-independent heavy atom isotope enrichments can result from gas-phase solar photolysis of small molecules. It could be an important factor that influences environmental isotope ratios and it offers a new mechanism for isotope enrichment.

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(28) A 2 L evacuated quartz Schlenk flask charged with 1.0 g of $^{13}CS_2$ was triply freeze−pump−thaw degassed. The reaction flask was back-filled with high purity nitrogen to a pressure slightly above 760 Torr to maintain a positive pressure during photolysis. The flask was exposed to direct sunlight (32° N latitude, February) for several days. Aerosols formed within 15 min and slowly settled. Photopolymer was collected and heated at 120 °C for several hours in vacuo to remove adsorbed CS_2. The yields obtained were 40−50 mg, which correspond to only 4−5% conversion. To observe the initial fractionations, the % conversion must be kept low.

(29) After fractionally distilling liquid CS_2, 2−3 mL was placed in a 250 mL round-bottom Pyrex or quartz Schlenk flask. The liquid was then freeze−pump−thaw degassed three times on a vacuum manifold. After the third freeze−pump−thaw sequence, the liquid, still under vacuum, was taken to the roof top and placed in direct sunlight. Solar heating provided a continuously refluxing film of liquid coating the walls of the flask. The yield after 60 h of irradiation was about 4 mg or 0.24%. Anal. Found: C, 26.08; S, 72.07%. Calcd for $(CS)_x$: C, 27.25; S, 72.72%.

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(32) Sodium chloride was added to the flask and the solution was then placed in an oil bath (120 °C) for about 2 h and 6 M HCl was added. The solution was heated to dryness, cooled, and then reheated with more HCl. This process was repeated four times. After the final drying step, a reducing solution containing hypophosphoric, hydrochloric, and hydroiodic acid was added to the flask. The mixture and flask from the previous step was attached to a condenser and heated, and the liberated H_2S was carried by high purity N_2 through a water trap into a tube containing a 0.2 M cadmium acetate solution. The CdS that formed was converted to Ag_2S by adding 0.1 M $AgNO_3$, and the precipitate was allowed to settle overnight. The Ag_2S was filtered, washed with 0.1 N $NH_3{\cdot}H_2O$, rinsed with low-conductivity water, and dried at 100 °C overnight. Addition of excess BrF_5 to Ag_2S in a nickel reaction system was performed at 550 °C for about 12−14 h. The product SF_6 was isolated from BrF_5 and other byproducts by cryogenically extracting it in stages at −119 °C.

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(35) The isotopic compositions are reported in the conventional delta notation where:

$$\delta^{34}S = \{[(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{std}] - 1\} \times 1000$$

refers to the $^{34}S/^{32}S$ ratio in a sample, with respect to a standard (std), which for sulfur is CDT (Cañon Diablo Troilite). The variations are reported in parts per thousand, or per mil (‰). The $\delta^{33}S$ ($^{33}S/^{32}S$) and $\delta^{36}S$ ($^{36}S/^{32}S$) ratios were also determined. Figure 1 shows the isotopic results, expressed with respect to the initial CS_2 isotopic composition (for $^{12}CS_2$: $\delta^{34}S = +4.63$, $\delta^{33}S = +2.44$ and $\delta^{36}S = +8.3$‰ with respect to CDT, and for $^{13}CS_2$: $\delta^{34}S = 3.43$, $\delta^{33}S = +1.87$ and $\delta^{36}S = +6.5$‰ with respect to CDT).

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