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THE FEASIBILITY OF LASER-SEPARATION
OF ^{36}S AND ITS USE AS AN
ATMOSPHERIC TRACER

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The Feasibility of Laser-Separation of ^{36}S and Its Use as an Atmospheric Tracer

This report addresses one of the possible uses of isotopic tracers, produced by laser-assisted isotope separation, in the investigation of pollution problems. Specifically, the use of laser-produced sulfur isotopes to analyze the acid rain situation is considered as it is a most important application of this technique.

I. Introduction

The United States releases approximately 35 megatonnes of man-made SO_2 into the atmosphere annually, of which two-thirds comes from stationary fuel combustion sources.^{1,2} This corresponds to about 1 tonne of SO_2 released from United States power plants every second. In eastern North America man-made sulfur emissions are estimated to exceed natural emissions by a factor of 10.³ SO_2 and its chemical descendents, SO_3 , H_2SO_4 , and various sulfates, are generally conceded to be hazardous to human health, to property, and to nature in general, with sulfuric acid and the sulfates widely thought to be the most harmful of all the sulfur oxides. The Federal Ambient Air Quality Standards for the maximum acceptable limits for SO_2 in the air have been established at 0.03 ppm annual average, 0.14 ppm for a 24 hour average, and the lesser standard of 0.5 ppm for a 3 hour period.¹

About 1 — 2% of a power plant's sulfur oxide emission is in the form SO_3 , the rest is SO_2 . Within the emission stack plume 0.2 — 5% of the SO_2 is oxidized to sulfate per hour.⁴⁻¹⁰ The details of the kinetics involved in the conversion of SO_2 to sulfate are still unclear. Sunlight is thought to have a strong direct or indirect effect since the observed oxidation rate is about an order of magnitude greater during the day than at night or early morning.¹⁰ There is also evidence for both homogeneous and heterogeneous contributions to the overall reaction mechanism.¹⁰ In particular, sulfuric acid can be produced from SO_3 hydrolysis, or instead by hydrolysis-oxidation of SO_2 , and this polluting acidic mist may further react to form various sulfates; this mist can be transported to ground level by precipitation—thus increasing the acidity of soil and local bodies of water. After sufficient deposition of sulfates, the natural acid-base buffers in lakes are overwhelmed, and the water's pH begins to drop. Below $\text{pH} = 4.5 - 5.0$ fish and other marine life die, and toxic metals trapped in sludge at lake-bottom then dissolve in the acidic water, thereby further killing the lake.¹¹ Sulfur-containing molecules and particulates can also reach ground level by dry deposition. As much as one third of all deposited

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sulfur may be due to this route¹²; the remainder is derived from acid rain (wet deposition)¹³.

Acid rain is by no means exclusively a local dilemma, as long distance (100 - several 1000 km) atmospheric transport of sulfur compounds may prove to make an important contribution to local sulfur levels. Actually, such long range transport further exacerbates the acid rain problem, since areas with little natural sulfur emission, and consequently little natural buffering, are especially sensitive to massive additional doses of sulfur compounds.¹³ In particular, areas in the United States Northeast and Northwest and in northern Europe have been severely hit by acid rain and its affect on marine life. Since much of the sulfur deposited in these regions is believed to be due to long range transport, inter-regional as well as international disputes have begun to surface as the devastation caused by acid rain has become better understood. For example, much of the sulfur agents in acid rain in the United States Northeast is suspected to be due to the sulfur emissions coming from the industrial Midwest, but this has yet to be conclusively proven. In this case, it appears that the emission of fossil fuel power plant waste through tall stacks in the Midwest has solved the problem of local dispersion of pollutants; however, the prevailing winds to the East may have merely geographically shifted the problem to an area with little natural buffering. In a quite similar situation, Scandinavian nations claim that British industry is to be blamed for the huge amounts of sulfur in their soil and lakes.¹⁴

The literature contains several references that espouse the hypothesis of long distance travel of SO_2 and other sulfur compounds. The early study by Zeedijk and Velds¹⁵ suggested transport of SO_2 from the German Ruhr to Eindhoven, Netherlands—a distance of ~ 100 km. More recently, Millan and Chung¹⁶ claim to have traced an SO_2 flow of 400 km. Several other studies also suggest such long range flow of SO_2 .¹⁷⁻²⁴ In one investigation Fisher¹⁷ claims that the British contribution to sulfur deposition over rural Sweden is about one-half the Swedish contribution, implying massive long-range transport. Chung¹⁸ concludes that high sulfate levels in Canada are often associated with S-SW airflows; this suggests that long-range transport of airborne sulfur pollutants, mainly from several United States industrial areas, is important. Altshuler¹⁹ has observed that while many adjacent areas in the United States have quite different SO_2 levels, they usually seem to have quite similar SO_4^{2-} concentrations; he has explained this by hypothesizing that long distance SO_2 transport with chemical conversion to sulfates is occurring over a range of hundreds of kilometers. This would also explain why several regions in the United States East have experienced only a small decline in SO_4^{2-} levels, despite recent great local reductions of the SO_2 concentration.¹⁹ Of particular interest to the United States Northeast acid rain situation is the study of SO_4^{2-} concentrations in New York State by Samson²⁰, who found a significant correlation between the SO_4^{2-} level and the inverse of windspeeds at least 24 hours prior to sampling; he also observed that

the highest concentrations of SO_4^- in New York State were associated with winds originating in the upper Ohio River valley. (Samson cites similar observations and conclusions by other investigation.) In a more recent study, Liou et al.²¹ found that exceedingly high sulfate concentrations, $\geq 15 \mu\text{g}/\text{m}^3$, were strongly correlated with backward-in-time traced westerly winds from the Ohio Valley; whereas, very low sulfate levels, $\leq 5 \mu\text{g}/\text{m}^3$, were associated with winds from other directions. It is the assertion of the present report that long-distance transport of sulfur compounds should be further investigated by sulfur isotope labelling of the pollutants. Whereas the above studies were based for the most part on accidental discharges into the atmosphere, well-designed experiments on atmospheric chemistry and transport can be performed on a local ($\sim 10 \text{ km}$) or regional ($100 \text{ to } > 1000 \text{ km}$) basis using rare sulfur isotope tracers, as discussed in more detail below.

Fossil fuels, in general, are notorious for their high sulfur contents, and among these fuels, coal is cursed with the highest sulfur levels, ranging from $< 0.2 \text{ to } > 5\%$ sulfur by weight. Presently mined coal has $2.0 - 2.5\%$ sulfur by weight, and is classified as "high-sulfur" coal (as is all coal with sulfur level $> 1\%$). Since coal is slated to be the United States' major energy resource in future years, the already high atmospheric levels of SO_2 , SO_3 and SO_4^- will increase, and the already significant decay of the environment will accelerate. There are several manners in which net sulfur emissions may be lessened. First, low sulfur fossil fuels can be utilized. The beginning of the use of low-sulfur coal in the mid-1960's in major urban areas helped to lower the SO_2 levels to the federal guidelines.^{1,10} However, most of the low-sulfur Eastern United States coal has already been consumed. There are also notable problems associated with using low-sulfur Western coal. Sulfur removal via coal gasification and subsequent processing is quite expensive. Direct control of sulfur release by the clean-up of stack emissions can eliminate $> 90\%$ of the sulfur from the plume; however, several problems plague this effort, such as the high expense, inability to modify existing power plants, and the huge amounts of removed sulfur-containing scavengers in the non-regenerative processes. For instance, if CaO/CaCO_3 is used to remove SO_2 via production of CaSO_4 , then clean-up of 5% sulfur coal involves storage of a quantity of CaSO_4 weighing 20% of the original amount of coal used—a truly huge amount.¹ However, if certain sources of sulfur pollution in specified geographical areas can be positively determined to have a major detrimental effect in the environment in a nearby or faraway location, these sites may be chosen for near-complete sulfur removal. Sulfur isotope labelled tracer experiments can help determine the sites where this intensive clean-up would be performed.

II. Prior Atmospheric Tracer Research

The study of atmospheric chemistry and transport with tracers has been intensive in the past decade. For instance, sulfur hexafluoride has been extensively used as a tracer to about 100 km; however, the ambient levels of SF_6 are becoming so high that SF_6 is no longer usable for highly sensitive work.⁴ The perfluorocarbons, perfluorodimethylcyclohexane, perfluoromethylcyclohexane, and perfluorodimethylcyclobutane, are considered ideal long range tracers for future work.⁴ In addition, due to the great sensitivity of mass spectrometric detection of CD_4 (1 part in 10^{18} of air), it too is an excellent atmospheric transport tracer; in fact, $^{13}\text{CD}_4$ has been traced to a distance of 2500 km.^{25,26} Of note is the joint study presently being conducted by the Electric Power Research Institute and Britain's Central Electricity Generating Board, in which SF_6 and the perfluorocarbons are being employed as tracers to determine if sulfur from British power plants is indeed strongly polluting Scandinavia.¹⁴

Only a few groups have performed notable investigation of atmospheric chemistry based on either the $^{34}\text{S}/^{32}\text{S}$ or the $^{18}\text{O}/^{16}\text{O}$ abundances in SO_2 or SO_4^{2-} ; this is in contrast to the extensive literature of atmospheric sulfur chemistry employing alternate techniques. In these isotopic studies, carefully monitored minute differences in the isotope ratio due to either natural sources or variations in the isotopic composition of fuel in power plants relative to the ambient ratio serve as the tracer. In this area of research the isotope ratios are identified by their "del" (delta) value relative to a standard. For instance for $^{34}\text{S}/^{32}\text{S}$,

$$\delta^{34}\text{S}/\text{‰} = \frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}} - (^{34}\text{S}/^{32}\text{S})_{\text{standard}}}{(^{34}\text{S}/^{32}\text{S})_{\text{standard}}} \times 1000,$$

where the fractional deviation per mil (‰) of the rare isotope concentration divided by the abundant isotope concentration in the examined sample is analyzed relative to a standard. For sulfur, the standard is the Canyon Diablo meteoritic troilite, whereas for oxygen it is Standard Mean Ocean Water. A group at the Argonne National Laboratory has conducted an investigation of atmospheric sulfates aimed at the mechanistic question of whether the hydrolysis-oxidation or oxidation-hydrolysis hypothesis better describes the transformation of SO_2 to sulfates.²⁷ Since near Argonne $\delta^{18}\text{O}$ for air oxygen is $+23\text{‰}$, while for precipitation water and water vapor the del values are -8‰ and -18‰ , respectively, these two mechanisms can be differentiated on the basis of the ^{18}O in SO_4^{2-} . This study concluded that both precipitation sulfates and particulate sulfates are formed by hydrolysis-oxidation (this is not universally accepted), and that particulate sulfates have a long atmospheric lifetime. Holt and collaborators²⁸ at Argonne have also studied the variation of sulfur isotope ratios in water and air samples near Chicago. This study showed a $\pm 2.5\text{‰}$ fluctuation in $^{34}\text{SO}_2$ in air samples over a three

month period, and a $\pm 5^\circ/00$ variation in precipitation sulfate at each of several specific locations. Also, the $\delta^{34}\text{S}$ of sulfate in different well locations was found to range from -14 to $+24^\circ/00$.

Newman and co-workers²⁹ at Brookhaven National Laboratory pioneered in methods of sampling $\delta^{34}\text{S}$, and used these techniques to determine that the conversion of SO_2 to sulfate, ($\equiv \text{SO}_4^{=}/\text{total S}$) is $\sim 1\text{ to }3\%$ within a stack's plume.^{4,5} Again, this study utilized the specific $^{34}\text{S}/^{32}\text{S}$ signature ratio of the SO_2 emitted by the particular studied power plant, which differed from the ambient ratio. In all these sulfur isotope labelling experiments, it is important to realize that at any given location, $\delta^{34}\text{S}$ can fluctuate rapidly because of changing winds and changing fuels used in nearby fossil fuel power plants. Different fuels have different $\delta^{34}\text{S}$, as exemplified by a study³⁰ of the isotopic composition of sulfur in Australian coal, in which $\delta^{34}\text{S}$ for organic sulfur was found to vary from $+4.8$ to $+24.4^\circ/00$. High sulfur content coal ($> 1\%$ S) exhibited a larger and much more variable $\delta^{34}\text{S}$ than did low sulfur coal. Still note that this variation represents only a $\pm 1\%$ variation in the 4.2% $^{34}\text{S}/^{32}\text{S}$ ratio.

III. The Use of ^{36}S as an Atmospheric Tracer

Release of $^{34}\text{SO}_2$ from a power plant exhaust stack has been suggested²⁵ as a possible tracing system to investigate atmospheric chemistry. However, since the natural abundance of ^{34}S is 4.2% , large amounts of ^{34}S would have to be produced, and, more significantly, huge amounts of noxious sulfur compounds would have to be released into the atmosphere for each experiment. However, since the natural abundance of the stable isotope ^{36}S is much lower, $140\text{ to }170$ ppm,^{31,32} equally sensitive tracing research could be undertaken with much lower ($300 \times$ lower) amounts of sulfur. The possibility exists of double labelling of SO_2 , such as using enriched $^{36}\text{S}^{18}\text{O}^{16}\text{O}$ relative to $^{32}\text{S}^{16}\text{O}_2$; but since oxygen exchange between water and SO_2 is rapid³³, the selective oxygen labeling would be quickly lost. However, oxygen exchange between sulfate and water vapor is slow and stack emitted, doubly labelled $\text{SO}_4^{=}$ may prove to be an important tracer. Use of either singly or doubly labeled $\text{SO}_4^{=}$ as a tracer may prove to be most illuminating because long range transport of $\text{SO}_4^{=}$ may be significant in the overall flow of sulfur.¹⁹ One slight disadvantage in employing ^{36}S —rather than ^{34}S —is that the ambient fluctuations in ^{36}S are expected to be twice the variation in $\delta^{36}\text{S}$. Also, for equivalent signal amplitudes longer sample collection times and/or larger volume samples are required. Recent advances by W. Roedel and W. Jundermann^{34a} in high volume sampling of SO_2 may assist ^{36}S processing. Mass spectrometric procedures would also probably have to be refined. The only other noted references to the

use of rare sulfur isotopes in atmospheric studies are the studies of Roedel and Junkermann^{34a,b} where cosmic ray-produced, radioactive ^{38}S (2.87 hour half-life) was being projected for a direct measurement of the rate of SO_2 oxidation in the atmosphere, and the limited use of radioactive ^{35}S in studies of dry deposition, as reviewed by Chamberlain.³⁵ For example, M. J. Owers and A. W. Powell³⁶ studied the absorption of SO_2 onto land and water surfaces (within a range of several 100 m) using radioactive ^{35}S labelled SO_2 .

The sulfur-labelling experiments suggested here would entail the release of sulfur from a single fossil fuel power plant stack during normal operation, probably in the form of $^{36}\text{SO}_2$ (or perhaps $^{36}\text{SO}_4^-$); because of the variation in short-term wind flows, experiments would be attempted at different times. Samples of SO_2 , SO_4^- and total S would be taken periodically before and after release, both at the site and at hundreds of stations throughout the neighboring regions. For instance, ^{36}S could be released in a U.S. Midwest plant and additional monitoring stations could be placed in the Northeast. Perhaps the sampling facilities being constructed for other large scale atmospheric sulfur studies, such as the EPRI-sponsored Sulfate Regional Experiment (SURE) project³⁷, could be utilized. (Of course, collaborative use of available sampling station facilities or the sharing of atmospheric chemistry and transport expertise with other ongoing projects, such as The Multistate Atmospheric Power Production Pollution Study (MAP3S)⁴ would be most beneficial to this program.) The sensitivity of such an experiment, as well as the cost of producing the ^{36}S isotope must be analyzed. In passing, two other possible uses of rare sulfur isotopes should be mentioned. First is the use of $^{34}\text{SF}_6$ or $^{36}\text{SF}_6$ as a long range atmospheric tracer in lieu of $^{32}\text{SF}_6$. Second is the use of isotopically labelled sulfur to trace the steps of oxidation of H_2S , methyl sulfide and dimethyl sulfide; this would help to elucidate the "short range" chemistry of marshes.

The magnitude of the proposed $^{36}\text{SO}_2$ labelling project can be estimated from the required sensitivity to measure a perturbation in $\delta^{36}\text{S}$ at the specific testing sites. Models to describe the trajectory of a spatial (and temporal) delta function ^{36}S source have appeared in the literature³⁸; however, at present two crude models are employed to ascertain the required amount of ^{36}S . These two (inter-related) estimates are hinged on determining the doses required to significantly perturb the ^{36}S level sufficiently from ambient, and are based on either the net U.S. emission of sulfur or on present-day ambient pollution levels. First, in the U.S. about $6 \times 10^{10} \text{ g}$ ($= 60,000$ tonnes) of S are released into the atmosphere daily. If a region is considered within the U.S. where, say, 25% of all S is released and if daily fluctuations of $\delta^{36}\text{S}$ at each test location are estimated to be $< \pm 40^\circ/00$, then assuming a 1-day characteristic time for sulfur compounds in the region— $\sim 100 \text{ kg}$ of ^{36}S must be released in < 1 day for adequate sensitivity. ($= 6 \times 10^{10} \text{ g} \times (1/6000 = ^{36}\text{S}/^{32}\text{S}) \times 25\% \times 40^\circ/00$). For smaller fluctuations in ^{36}S and shorter characteristic times, correspondingly less ^{36}S would be needed. This characteristic

time is actually that time that these sulfur compounds remain in the "local regional" atmosphere and maintain their identity. It is also referred to as the turn-over time or the regional residence time, and has been determined to be equal to roughly one day for sulfur oxides.³⁹ Note that the observed rate of atmospheric oxidation of SO₂ corresponds to the loss of half of initial SO₂ in about one day.⁴⁻¹⁰ Consider now the alternate approach. Suppose that the SO₂ levels at the monitoring stations are reasonably low, say only 0.01 ppm SO₂,¹⁰ compared to the 0.03 ppm annual average regulation. Imagine an atmospheric disc of 10 km height (atmospheric thickness) and 500 km radius (for long-range transport). Then the appropriate question is what amount of ³⁶S must be released within this disc to insure that upon uniform ³⁶S dispersal there is uniformly a $\delta^{36}\text{S} = +40\text{‰}$ (a quite generous statistically significant deviation) at all sampling stations due to this emission. Calculation shows that a quantity of 750 kg ³⁶S is required. For smaller than 40‰ fluctuations in $\delta^{36}\text{S}$, and for directed air flow (and therefore directional, non-uniform dispersion), a much smaller quantity is required. Still, note that this is of roughly the same order of magnitude as the other estimate. For comparison, note that a 1 GW_e (= 3GW_{th}) electrical power plant using 10,000 Btu/lb coal that contains 1% S by weight emits about 5,000 kg S/hour—for which the hourly emission amount is considerably greater than the amount of ³⁶S required for a 1 day experiment. Of course, if the sulfur tracer is only, say, 10% ³⁶S, then 10 times as much sulfur starting material (~ 90% ³²S, ~ 10% ³⁶S) is required.

IV. Sulfur Isotope Separation Considerations

Isotope separation of ³⁶S/³²S and D/H are similar in that the fractional abundance of the heavier species are both approximately the same, 150 ppm. However, since isotope shifts are generally much smaller in the sulfur case vis-a-vis hydrogen due to the smaller isotope mass ratio—and since there are many fewer small, gas phase, sulfur-containing molecules isotope separation of ³⁶S/³²S is a relatively harder and more expensive task than is D/H isotope separation. The separation of ³⁴S and ³²S by CO₂ laser multiple-photon dissociation (MPD) near 10.6μ has been studied by many investigators. (For example see Refs. 40 — 42.) Typical single-step enrichment factors of ~ 5 — 10 have been achieved. An enrichment factor of 5 in ³³S/³²S has been measured in CO₂ laser MPD in cooled (170 — 190°K) SF₆.⁴³ The possibility of ³⁶S separation has also been mentioned in the literature.⁴⁴ The ³⁶SF₆ ν₃ peak is considerably redshifted from that of ³²SF₆ [³²SF₆, 947;-³³SF₆, 939; ³⁴SF₆, 930; ³⁶SF₆, 914 cm⁻¹]⁴⁵. Despite the redshift in the MPD peak in ³²SF₆ at 943 cm⁻¹ relative to the peak linear absorption, good optical selectivity in absorption and dissociation selectivity in ³⁶SF₆ vis-a-vis ³²SF₆, in the range of 10 — 100 to 1, is expected at about 11μ; this wavelength is obtainable

using conventional TEA CO₂ lasers. Sulfur isotope separation by MPD of other molecules, such as SF₅Cl⁴⁶, is also possible.

Several other schemes of laser-initiated isotope separation are worthy of at least preliminary investigation. One example is vacuum-UV photopredissociation of CS₂ using a wave length tuned ArF laser⁴⁷, in which ¹²C³⁶S³²S is redshifted about 2 Å (to 1937 Å) from ¹²C³²S₂; note that in this type of experiment the enrichment factor will most probably be << 100, even after reasonable development.

The first overtone of the SO₂ bending mode, $2\nu_2 \leftarrow 0$, is considerably shifted from $\sim 1036\text{ cm}^{-1}$ ($2 \times 518\text{ cm}^{-1}$) in ³²S¹⁶O₂ to $\sim 1017\text{ cm}^{-1}$ ($2 \times 508.7\text{ cm}^{-1}$) in ³⁶S¹⁶O₂⁴⁸, and is thus still within the spectral reach of CO₂ lasers. The ν_1 symmetric stretching mode shifts from 1152 cm^{-1} in ³²S¹⁶O₂ to $\sim 1138\text{ cm}^{-1}$ in ³⁶S¹⁶O₂⁴⁸, to $\sim 1108\text{ cm}^{-1}$ in ³⁶S¹⁶O¹⁸O⁴⁹ to $\sim 1080\text{ cm}^{-1}$ in ³⁶S¹⁸O₂⁴⁹, consequently infrared resonances are barely outside the range of CO₂ lasers for the more useful isotopic varieties. The laser chemistry of vibrationally-excited SO₂ has not been investigated in much detail. Białkowski and Guillory did, however, observe collision-induced, and therefore isotopically non-selective, infrared photolysis of SO₂⁵⁰. SO₂ has a medium-intense, singlet-to-singlet electronic absorption band from 2500 — 3400 Å.⁵¹ The excited singlet state is rapidly quenched to the metastable ³B₁ triplet level⁵²; perhaps isotopic selectivity can be maintained. Additional, even stronger absorption begins at 2350 Å and continues beyond 2000 Å due to ¹B₂ $\leftarrow$ ¹A₁⁵³; the observed decrease in fluorescence for $\lambda < 2206\text{ Å}$ ⁵⁴ suggests predissociation of SO₂ to SO + O. Because of the small isotope shift and the great density of levels, isotopically-selective UV photopredissociation of SO₂ may prove to be difficult. Note that rare gas halide lasers or their Raman-shifted varieties lase in the indicated wavelengths regions (XeCl in the SO₂ 2500 — 3400 Å band; upshifted KrF, or perhaps ArF, in the ¹B₂ $\leftarrow$ ¹A₁ band).

OCS is another sulfur-containing triatomic molecule in which $2\nu_2 \leftarrow 0$ is resonant with CO₂ laser radiation. However, the isotope shift is quite small, with ¹⁶O¹²C³⁶S at 1043 cm^{-1} shifted only $\sim 4\text{ cm}^{-1}$ to the red relative to ¹⁶O¹²C³²S.⁵⁵ Collision-free CO₂ laser multiple-photon dissociation of normal OCS has been observed⁵⁶, however, only at high fluences (threshold at 50 J/cm², corresponding to $1.3 \times 10^8\text{ W/cm}^2$; saturation near 80 J/cm²).

Dimethyl sulfide, (CH₃)₂S, and thiophene, C₄H₄S, are two other compounds that may be amenable to sulfur isotope separation. Dimethyl sulfide has very strong infrared absorption bands at 1024 and 1037 cm^{-1} and a medium band at 975 cm^{-1} .^{57,58} Though these bands are accessible by the CO₂ laser, the expected small ³⁶S/³²S isotope shift combined with the broad and overlapping nature of these bands makes IR photolysis of dimethyl sulfide a possible, but doubtful, process for sulfur isotope separation. Thiophene has a strong band at 1035 cm^{-1} ,⁵⁹ and again, depending on the magnitude of the sulfur shift, may be worthy of

further investigation. The ultraviolet absorption spectrum of dimethyl sulfide shows sharp bands from 1850 — 1960 Å ($C \leftarrow X$) (ArF laser region), overlapped by a weak continuum,^{60,61} while thiophene exhibits sharp bands in 2100—2450 Å ($A \leftarrow X$) which become diffuse (photopredissociation) at shorter wavelengths;⁶² these molecules may be worthy of further investigation.

Based on prior research, CO_2 laser MPD of SF_6 presently appears to be most suitable for sulfur isotope separation; still, other systems may warrant study in the future. In contrast to the techniques employed in laser separation of deuterium⁵³, there must be a sufficiently large annual production of the regular working molecule, SF_6 in this case, for sulfur isotope separation, since replenishment of the depleted rare isotope cannot occur by simple chemical exchange. Present U.S. production of SF_6 is about 4.5 million pounds with a total capacity of about 6 million (bulk price = \$3.25/lb).⁶⁴ Therefore, from the present production capacity of SF_6 about 70 kg/yr of ^{36}S is available. The above estimate of 100 kg of ^{36}S needed for a large scale tracing experiment is probably a quite high upper bound, as the assumptions of large perturbations in $\delta^{36}S$, very large geographical areas, and unrealistically uniform dispersion of the tracer are quite conservative; consequently, the actual amounts required may be over an order of magnitude lower. In this case, there would be sufficient commercial production of SF_6 to extract enough ^{36}S for several large scale atmospheric tracer experiments a year; the rest of the SF_6 would be returned to the production stream following isotope separation for general industrial use. Of course, less ambitious tracer experiments involving smaller areas would be less dependent on SF_6 capacity. Note that the amount of SF_6 starting material required to produce sufficient ^{34}S for a tracing experiment with an equivalent sensitivity (i.e., equal perturbation in the appropriate atmospheric isotopic abundance vis-a-vis ^{36}S tracing) is as large as for ^{36}S separation. However, a much greater amount of sulfur would actually be released for a single tracing experiment using ^{34}S ; therefore, such experiments cost more because of the large number of molecules consumed and photons used (because of relatively inferior photochemical parameters), and also constitute a much greater environmental hazard.

V. Economic Estimates

An estimate of the cost of the electrical energy required in such MPD separation of ^{36}S from $^{32,33,34}S$ is necessary to determine whether the cost of producing sufficient ^{36}S for atmospheric tracing studies is within reason. It is assumed for this purpose that the 100 kg ^{36}S /experiment estimate obtained above is representative. In this estimate, the isotopic selectivity of dissociation and photon absorption will be assumed to be equal. The $^{36}S:^{32}S$ (and $^{36}S:^{33}S$) selectivity is taken to be 100 : 1, while for $^{36}S:^{34}S$ it is assumed to be 5 : 1. Therefore, after a single-step of

photochemical process, the ^{36}S abundance will be about 1%. To limit the overall emission of sulfur in performing a tracing experiment, a second photochemical enrichment stage may be deemed necessary. With 4 eV required to dissociate a single SF_6 molecule, about 100 times more net photon energy, 400 eV, is required in the first stage to separate one ^{36}S . With a laser efficiency of 5% and overall photon utilization factor of about 20%, at least 40 keV of electrical energy would be required to separate one ^{36}S atom. At 0.05\$/kw-hr, it would cost about 170K\$ to separate 100 kg of ^{36}S , which is diluted in 10^4 kg total S after the first stage. Second stage enrichment will cost significantly less than the first step. This figure is most sensitive to the laser efficiency at 11μ , the stated selectivities, and the actual quantity of ^{36}S tracer required.

Based on these parameters, a 40 KW average power pulsed CO_2 laser could separate the required first stage amounts of ^{36}S (100 kg) in a single month of continuous operation. At \$10/watt capital cost, which is perhaps somewhat low for operation at 11μ , the required laser costs $\sim 0.5M\$$. If 50 runs are made with this laser, the capital cost per run would be roughly 10K\$ (assuming no interest, but total depreciation).

Therefore, including a second enrichment stage, the photon-related operating costs alone will be about 200K\$ per 100 kg ^{36}S tracer experiment. If atmospheric tracing of stable isotope ^{36}S labelled SO_2 or SO_4^- is deemed a sufficiently valuable technique, the M\$-level cost of such a production facility appears to be reasonable enough to warrant further photochemical investigation.

VI. Concluding Remarks

The serious environmental problems associated with both wet and dry deposition of man-made sulfur are present by being fully recognized. Previously, atmospheric tracer studies have been performed specifically either to better understand the atmospheric chemical conversion of sulfur dioxide to sulfate or instead to monitor long-range transport. In contrast, the proposed use of isotopically-labelled SO_2 , in particular of $^{36}\text{SO}_2$, as a tracer can help elucidate the chemical and transport facets in a unified experiment. Separation of a sufficient quantity of the rare ^{36}S isotope to perform several of these tracer studies appears to be practical and economical. This overall process is certainly deserving of further investigation.

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