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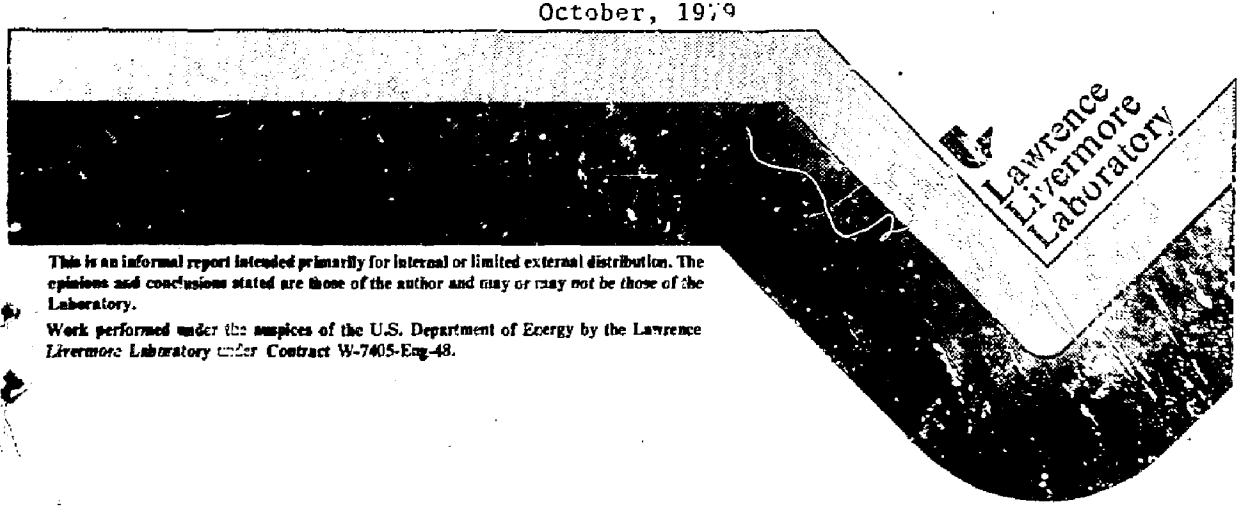

PROPOSAL TO REALIZE A COST BREAKTHORUGH IN CARBON-13 PRODUCTION BY PHOTOCHEMICAL SEPARATION*

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ABSTRACT

A cost breakthrough can now be made in photochemical production of the rare stable isotope carbon-13. This cost breakthrough is achieved by CO_2 laser infrared multiple-photon dissociation of any of several halocarbons (Freon derivatives) such as CF_3Cl, CF_3Br, or CF_2Cl_2. The single-step carbon-13 enrichment factor for this process is approximately 50, yielding 30% pure C-13 in one step, or up to 97% pure C-13 in two steps.

A three-fold carbon-13 cost reduction to below $20/gram is expected to be achieved in a small laboratory-scale demonstration facility capable of producing 4-8 kg/year of carbon-13, using presently available pulsed CO_2 TEA lasers at an average power level of 50 watts. Personnel costs dominate the attainable C-13 production costs in a small photochemical enrichment facility. A price reduction to $2/gm carbon-13 is feasible at carbon-13 production levels of 100-1000 kg/year, dominated by the Freon raw material costs.

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INTRODUCTION

The rare stable isotope carbon-13 is currently supplied by Mound Laboratory at a cost of about $60/gram (at 90% isotopic purity). Demand for this isotope is presently 4-5 kilograms/year, and it is currently needed as a stable isotopic tracer in medicine and biology and in NMR studies. An approximately 100-fold increase in level of demand for carbon-13 has been projected for when its cost drops by an order-of-magnitude. Present production technology for this isotope utilizes fractional distillation with potential for real, but limited economies-of-scale. By means of radically new technologies utilizing photochemical isotope separation, production costs of carbon-13 at the 1000 kg/year production level have the potential of dropping to $2/gram utilizing commercially available, inexpensive and efficient infrared CO_2 lasers. It is both technically feasible and economically realistic to anticipate C-13 production costs to drop below $20/gram in a small, several-kg-of-C-13-per-year facility which could begin operation in 1981, utilizing existing laboratory-scale CO_2 laser equipment and technology.

PHOTOCHEMISTRY

The photochemical basis of this new isotope separation technology is the infrared multiple-photon dissociation of Freon derivatives. Using CF_3Br (Freon 13B1) as an example, the photochemical steps are as follows, where $h\nu$ represents the energy of a single CO_2 laser infrared photon:

$$^{13}CF_3Br + nh\nu\ (9.65\mu) \rightarrow {}^{13}CF_3\cdot + Br\cdot \qquad (1)$$

$$2\ {}^{13}CF_3\cdot \rightarrow {}^{13}CF_3\text{-}{}^{13}CF_3 \qquad (2)$$

$$2Br \rightarrow Br_2 \qquad (3)$$

$^{13}CF_3Br$ selectively absorbs CO_2 laser radiation, n-photons near 9.6 micron in step (1), and dissociates yielding a $^{13}CF_3$ radical. These radicals recombine to form carbon-13-enriched hexafluoroethane in step (2) and bromine molecules in step (3). Alternately, a scavenger gas such as chlorine can react with the $^{13}CF_3$ radicals to form $^{13}CF_3Cl$ in steps (4) and (5).

$$^{13}CF_3\cdot + Cl_2 \rightarrow {}^{13}CF_3Cl + Cl \qquad (4)$$

$$^{13}CF_3\cdot + Cl \rightarrow {}^{13}CF_3Cl \qquad (5)$$

The single-step carbon-13 enrichment factor using this process has been measured to be 56 at room temperature, and 120 at -50°C[1]. Alternate primary photochemical processes may use other Freon derivatives, such as CF_2Cl_2(Freon-12)[2] or CF_3Cl (Freon-13)[1].

$$^{13}CF_3Cl + n\ h\nu\ (9.3\mu) \rightarrow {}^{13}CF_3\cdot + Cl \qquad (6)$$

$$^{13}CF_2Cl_2 + n\ h\nu\ (9.5\mu) \rightarrow {}^{13}CF_2: + Cl_2 \qquad (7)$$

The attainable carbon-13 single-step enrichment factors for these 3 primary processes, eq. (1), (6), (7), are summarized in Table I.

TABLE I

SINGLE-STEP CARBON-13 ENRICHMENT FACTOR IN FREONS[1,2]

COMPOUND	CO_2 LASER LINE	C-13 SINGLE-STEP ENRICHMENT, α	
		+22°C	-50°C
Freon-12, CF_2Cl_2	P(20), 9.55μ	22	---
Freon-13, CF_3Cl	R(8), 9.3μ	32	108
Freon-13B1, CF_3Br	P(24), 9.65μ	56	120
Freon-22, CF_2HCl	P(14), 9.50μ	38	---

The threshold for dissociation is 1 joule/cm^2 energy fluence[3] and dissociation yields $n \geq 0.5$ are easily obtained[2-4] at fluences of 10-20 joules/cm^2 as shown in Figure 1. The optical selectivity falls with operating pressure, and maximum operating pressure depends on wavelength as shown in Figure 2, and is in the range of 1-10 torr using standard CO_2 laser pulses of about 100 nanoseconds duration.[4,5] However, by using short CO_2 laser pulses of 2 nanoseconds duration, operating pressure may be extended to several hundred torr, as shown in Figure 3. The data for Figure 1 were obtained by the author from experiments performed at the Los Alamos Scientific Laboratory and at the Lawrence Livermore Laboratory.[4]

PROCESS REQUIREMENTS

Initial development of this process will require a reliable, high repetition rate CO_2 laser such as the Lumonics Model 820 TEA laser, which is rated at about 50 watts average power in pulses of 1-3 joules each of 0.5 microseconds duration. The absorption strength of, for example, CF_3Br is quite high,[5] being about $\alpha = 0.1$ torr^{-1} cm^{-1}. Hence, for carbon 13 at natural isotopic abundance (1.1% C-13), an optical path length of only about 2 meters will be required at a CF_3Br operating pressure of 5 torr, to insure adequate photon utilization. Note that this is a gas-phase process operating at reduced pressure.

The laser power required for a given production capability of a stable isotope may be estimated from the expression

$$P_{\substack{\text{Average Optical} \\ \text{Power}}} = \frac{3.175 \times 10^{-8} K}{\phi \cdot \eta} \left| \eta = \frac{91}{\alpha \cdot m} \right| \frac{\text{watts}}{(\text{kg C-13 per year})} \qquad (8)$$

$$\text{where } K = \frac{nhcN_a}{\lambda} = 9.20 \times 10^6 \, n/\lambda \qquad \text{(Joules/kg C-13)} \qquad (9)$$

N_a = Avogadro's number

n = Number of CO_2 photons required for dissociation of a single molecule

λ = CO_2 laser wavelength (in microns)

ϕ = Photon absorption efficiency fraction

η = Photodissociation yield fraction

α = C-13 isotopic selectivity in absorption at wavelength λ or σ_{13}/σ_{12}

m = Number of carbon atoms per molecule; m=1 here.

σ_i = Absorption cross-section of molecular isotopic species i at dissociation fluence

For a typical system, such as dissociation of CF_3Br at λ = 9.65 micron, typical values are α = 50, photon utilization $\phi.\eta$ = 0.37, and n = 28 photons. This leads to a value of k = 2.7 x 10^7 joules/kg C-13 and

$$P(CF_3Br) = 6.6 \text{ Watts/(kg C-13 per year)} \qquad (10)$$

Thus, only 5-10 watts of laser average power are required to produce one kg of carbon-13 per year via this photochemical process, assuming 24 hour/day laser operation. Since presently available high repetition rate industrial CO_2 lasers produce 25-50 watts, one may project an annual production capability of 4-8 kg carbon-13 per year per single laser unit in this output range.

As noted in Table I, the single-step carbon-13 enrichment factor for this process is about 50, leading to product containing about 30% carbon-13 in the first step. The second step will consist in "burning out" the residual carbon-12 as follows, using, for example, CF_2HCl:

$$CF_2HCl + 21\ h\nu\ (9.5\mu) \rightarrow CF_2: + HCl \qquad 30\%\ C\text{-}13 \qquad (11)$$

$$CF_2: + HI \rightarrow CF_2HI \qquad 30\%\ C\text{-}13 \qquad (12)$$

$$^{12}CF_2HI + 20\ h\nu\ (9.3\mu) \rightarrow \text{decomposition products} \qquad (13)$$

For example, if HI is used as a radical scavenger in reaction (12), then the stable molecule difluoroidomethane will be formed containing about 30% carbon-13. The activation energy of step (12) is about 5 $\pm$ 2 kcal/mole, and

occurs at room temperature. The unwanted carbon-12 will then be burned out, step (13), by irradiation at 9.3μ where $^{12}CHIF_2$ absorbs and dissociates, but where $^{13}CHIF_2$ does not dissociate. By this procedure, it is possible to prepare arbitrarily pure carbon-13, and 99% C-13 will be only slightly more costly to prepare than the (laser produced) standard carbon-13 purity of 90%. The nearly pure remaining carbon-13-bearing product ($^{13}CHIF_2$ in this example) is processed chemically into the desired end products.

ECONOMIC ANALYSIS

A. Laser Related Costs

The following economic analysis is only approximate, since this photochemical route to carbon isotope separation has not yet been put into production, although the cost elements are well-established. Cost may roughly be divided into laser-related costs, raw material costs, and chemical handling costs. A long-life high-repetition rate CO_2 laser costs about $66,000 and yields a tunable near-diffraction limited output of up to 150 watts.[6] Hence, we may assume that small laboratory-scale pulsed CO_2 laser costs are presently $500/watt. Since from expression (10), we estimate that 6.6 watts/kg C-13 per year laser power is required, the following laser-related costs are derived, where C = the capital cost in dollars/optical output watt for the CO_2 laser.

TABLE II

LASER-RELATED COSTS PER GRAM FOR C-13 SEPARATION BY CO_2 LASER MULTIPLE-PHOTON DISSOCIATION

ASSUMPTIONS	POWER COST	CAPITAL COST	LASER MAINTENANCE	TOTAL
C = $500/watt	$0.046	$0.50	$0.50	$1.05/gm C-13 Current Cost
C = $100/watt	$0.046	$0.099	Estimate $0.10	$0.25/gm C-13 Projected Cost

The current costs are dominated by capital and operating costs, based on 1 liter/minute gas usage = $0.30/hour and use of a small high power CO_2 TEA laser.[6] These current cost figures are based on a standard commercially available CO_2 TEA laser of 150 watts average power. The projected cost figures are appropriate for a 10 kw average power CO_2 laser based on electron beam-sustained electric discharge technology currently well developed at, for example, Avco Everett Research Laboratory in Everett, Massachusetts. These projected cost figures are thus appropriate only when carbon-13 demand approaches 1000 kg/year. The capital costs are based on a 15% capital charge, and power costs are based on 4¢/kWh electrical power costs at 5% laser electrical efficiency.

B. Materials Costs

The raw materials for this photochemical process are Freon derivatives, and the initial cost of the Freon raw material form a very significant portion of the total carbon-13 costs. This is due to the low natural abundance of 1.1% C-13 in natural carbon. These raw material costs are summarized in Table III, assuming no Freon recovery.

TABLE III

COST PER GRAM CARBON-13 DUE TO FREON RAW MATERIAL

WORKING MATERIAL	COST/KG IN TON LOTS	COST/GRAM CONTAINED C-13*
CF_3Cl, Freon-13	$6.86	$5.01
CF_3Br, Freon-13B1	$2.23	$2.32
CF_2Cl_2, Freon-12	$1.39	$1.18
CF_2Cl-CF_2Cl, Freon-114	$2.25	$1.36
CHF_2Cl, Freon-22	$2.14	$1.30
$CFCl_3$, Freon-11	$1.43	$1.38

*Assumes 100% carbon-13 removal

It is clear from Table III that raw material costs are important and that CF_2Cl_2(Freon 12) seems to be the best choice for a working material, based on raw material costs. If the approximately 98% Freon remaining after removal of the carbon-13 can be resold, then most of these material costs can be recovered.

OPERATING COSTS

Operating costs are only approximate, but one may assume that one full-time technician supervises operation of the laser, and subsequent chemical processing steps. Hence, 3 shift/day operation requires 4 man-years of technical personnel, which may cost $25,000/year each. A one-tenth-time supervisor adds an additional $4,000/year to which we may add perhaps $20,000/year for space, chemical apparatus, and pumps, etc. Thus, for a 50-watt laser yielding 8 kg/year of carbon-13, operating costs may be about $16/gm carbon-13.

Total carbon-13 production costs based on this photochemical process are thus summarized in Table IV.

TABLE IV

ANTICIPATED OVERALL PRODUCTION COSTS OF CARBON-13 BY CO_2-LASER MULTIPLE-PHOTON DISSOCIATION, $/gm C-13

	LASER-RELATED COSTS	RAW MATERIAL COSTS	OPERATING COSTS	TOTAL
50-watt Laser Present System	$2.77	$1.57	$16.00	$20.34/gm
150-watt Laser	$1.05	$1.57	$ 5.40	$ 8.02/gm
10 kw Laser	$0.25	$1.57	$ 0.32	$\leq$ $2.14/gm

CONCLUSIONS

Table IV shows that present photochemical production costs will be of the order of $20/gm (dominated by personnel costs), using existing off-the-shelf CO_2 laser technology. A very significant price reduction may be anticipated using much higher average power lasers, should carbon-13 demand reach the 100-1000 kg/year level. It is important to note that the present cost of carbon-13 is about $70/gram, and a three-fold price reduction to about $20/gram can be achieved even using small-scale existing lasers. This price reduction is not compelling, although it certainly will pay its own way in permitting photochemical technology to establish a foothold. The very large price reductions of over an order-of-magnitude below the current cost of $70/gram become achievable using a photochemical process scaled up in size to production levels of 100-1000 kg C-13/year using 1000-10,000 watt average power CO_2 laser technology. It may be noted that CW CO_2 lasers are available today at average powers of 10,000-20,000 watts for industrial processes such as welding. Ultimately, the cost of photochemical production of Carbon-13 will be determined by the raw material costs as a limiting factor, as indicated in Tables III and IV. Hence, a photochemical basis for a cost breakthrough in carbon-13 separation by CO_2 laser has been established. In a small laboratory-scale demonstration facility, it will be possible to produce 4-8 kg/year of high purity carbon-13 using a 50 watt pulsed CO_2 TEA laser. Production costs will be significantly below the present cost of $70/gm, and will actually be dominated by personnel costs.

1. M. Drouin, et al., Chemical Physics Letters 60, 16 (1978).

2. D. S. King and J. C. Stephenson, J. Am. Chem. Soc. 100, 7151 (1978).

3. E. Wurzberg, L. J. Kovalenko, and P. L. Houston, Chemical Physics 35, 317 (1978).

4. J. Marling, unpublished results.

5. M. Gauthier, et al., Can. J. Chem. 56, 2227 (1978).

6. Gen-Tec Model DD-300, STE-FOY, Quebec, Canada

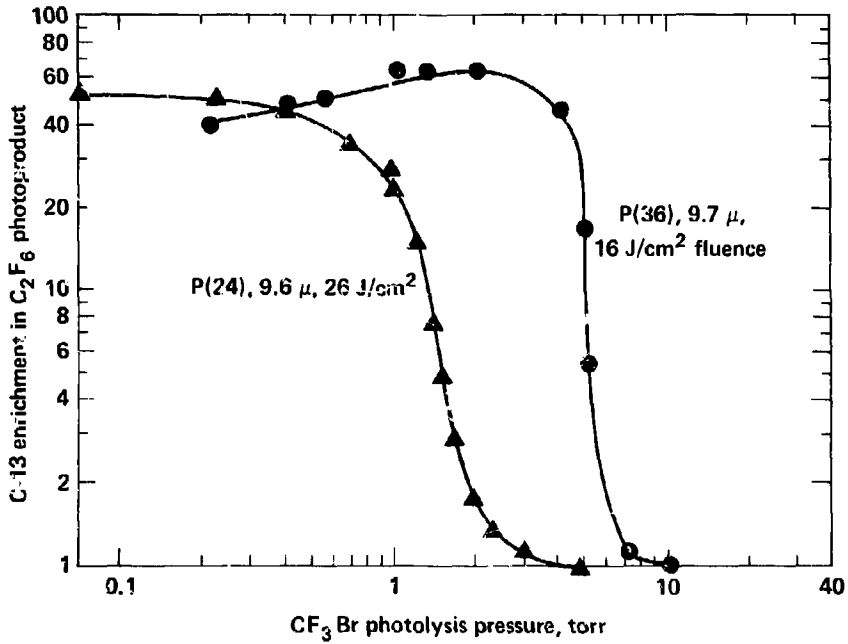

Figure 1. The CF_3Br single step carbon-13 enrichment factor remains high only below 1 torr pressure using the P(24) 10_2 laser line (solid triangles) and normal TEA pulse durations. Five-fold higher pressure is achieved using the P(36) CO_2 laser line as shown by the solid circles.

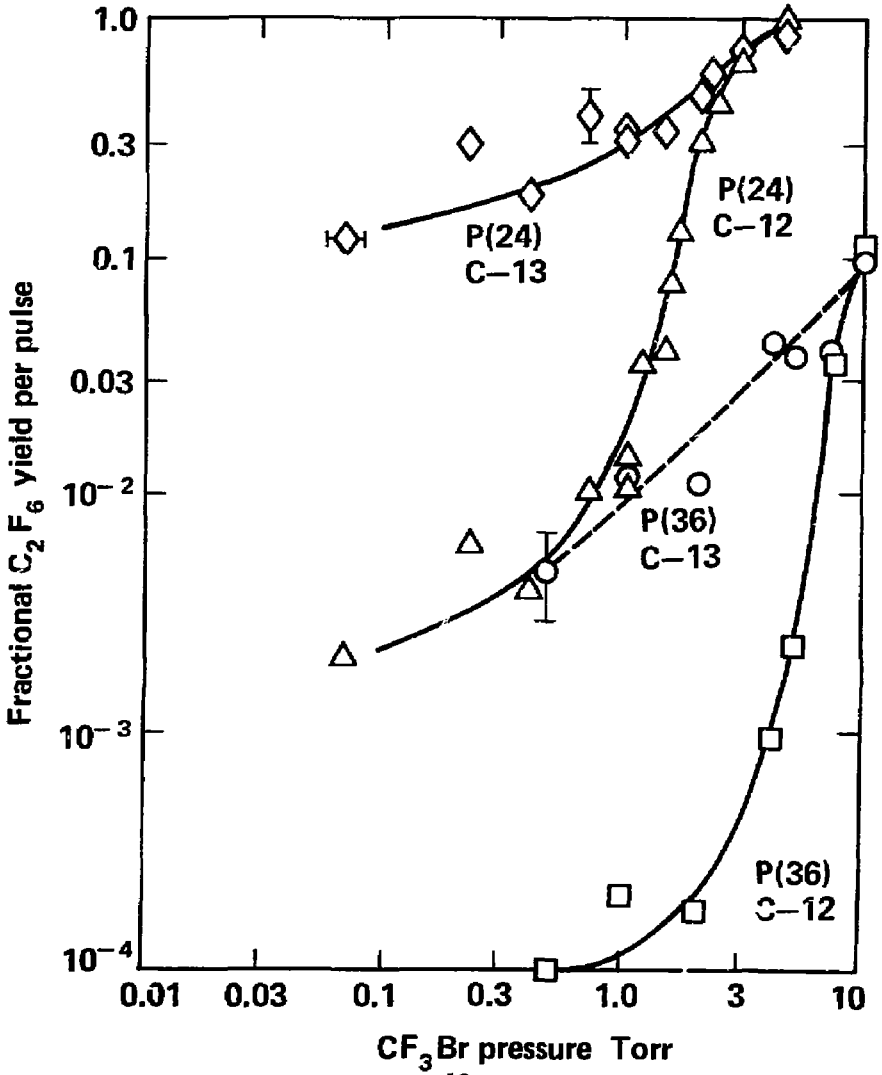

Figure 2. The fractions yield of $^{13}C_2F_6$ photoproduct is an order of magnitude higher using the P(24) CO_2 laser line at 263/cm^2 (open diamonds) compared to using the P(36) CO_2 laser line at 165/cm^2 (open circles). At P(24), yield approaches units above 3 torr pressure, and isotopic selectivity drops to 1 (non-selective).

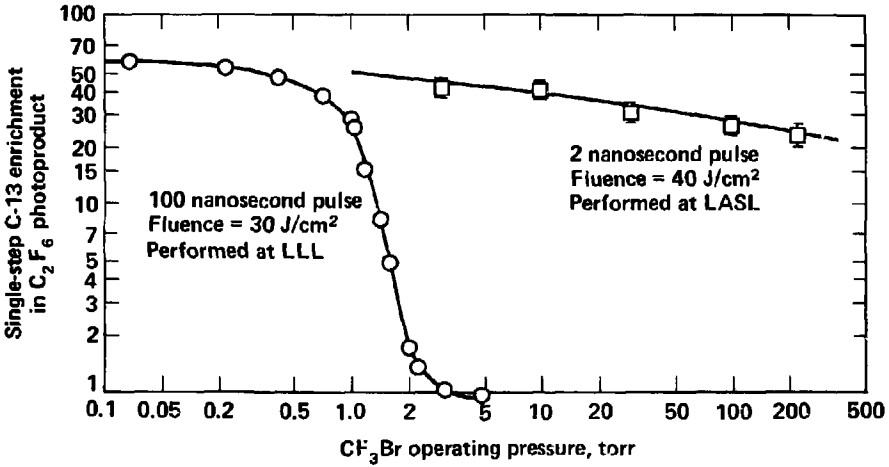

Figure 3. CO_2 laser techniques can be applied very effectively in separation of light isotopes such as carbon-13. This figure shows that the single-step carbon-13 enrichment factor is about 50 at low pressure using CF_3Br. The CF_3Br dissociates by high power pulsed CO_2 laser (P(24), 9.6μ) to yield carbon-13 enriched $^{13}CF_3$ fragments that recombine to produce $^{13}C_2F_6$. The $^{13}C_2F_6$ may be tnen converted into the desired C-13 bearing products, or it may undergo further laser enrichment to yield nearly pure carbon-13. The sharp decrease in C-13 enrichment at higher pressure may be greatly reduced by using shorter duration CO_2 laser pulses, as shown in the curve to the right. Higher pressure operation greatly increases the throughput and greatly reduces the photochemical reactor size.