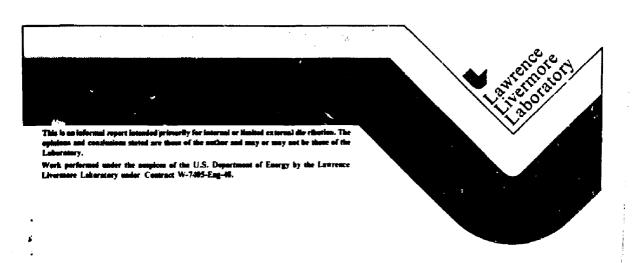
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DEVELOPMENT OF ADVANCED TECHNOLOGIES FOR PHOTOCHEMICAL TRITIUM RECOVERY Tri-Quarterly Progress Report For the Period October 1, 1980 through June 30, 1981

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September 1, 1981



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Tri-Quarterly Progress Report, 5 For the Period October 1, 1980-through June 30, 1981

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#### Abstract

The  ${\rm CTCl}_3$  and  ${\rm CTBr}_3$  working molecules were synthesized, and laser construction, photochemistry, and process engineering for T/D recovery began during this reporting period.



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#### I. Introduction

The past reporting period marked significant progress in tritium recovery experimentation. Tritiated chloroform and bromoform were synthesized, an ammonia laser for selective photolysis was constructed, the gas chromatograph product analysis system was completed, and initial photochemistry experiments began. In addition, chemical engineering study of the overall process commenced. Chloroform still appears to be a totally suitable working molecule for tritium recovery by selective infrared photolysis.

#### II. Synthesis of Monotritiated Working Molecules

CTF3

Several new inventory samples of tritiated trifluoromethane were synthesized employing either the gas phase UV or the Pt catalyst techniques described previously. Purified  ${\rm CTF}_3$  was obtained by successive distillation. (Run 30, see Table I).

CTCL

The intial attempts to synthesize tritiated chloroform involved the same noble metal catalysis techniques employed in CTF $_3$  synthesis. There was positive evidence for CTCl $_3$  formation using a room temperature, gas phase CDCl $_3$ /T $_2$  mixture interfaced with a platinum catalyst (Run 17) based on the product infrared spectrum, but an unidentified major peak at 1030 cm $^{-1}$  prevented definitive identification. Apparently some (possibly pure) CTCl $_3$  formed with CBrCl $_3$ /T $_2$ /platinum for short reaction times ( $\sim$  1 day, Run 20); a more complex set of products was formed during longer runs (5 days, Run 18).

Ultraviolet irradiation (1849Å and/or 2537Å) of CRrCl $_3/T_2$  mixtures produced many unidentified products, with little, if any, CTCl $_3$ . Initially, the UV photolysis kinetics scheme here was thought to be similar to that used in producing CTF $_2$  with:

$$CBrCl_3 + hv + CCl_3 + Br$$
 (1)

$$CCl_3 + T_2 + CTCl_3 + T.$$
 (2)

However, a much more complex reaction mechanism is clearly required to explain the results vis-a-vis the CTF<sub>3</sub> case. This is because the C-T, C-Cl and C-Br bonds have nearly equal strengths, whereas the C-F bond is significantly stronger; consequently, the mechanism involves many more competing reaction channels.

When platinum or palladium is used as the catalyst as above, the  $\mathbf{T}_2$  adsorbs onto the catalytic surface and dissociates into atoms, while the organic compound remains essentially in the gas phase. If an adsorbant material, such as a common laboratory

TABLE I.

Run no.	* Intend		Conditions	Remarks
16	CTF3	20t CF <sub>3</sub> J/67t T <sub>2</sub>	Pt/6 days	CTF3 formed, much
1 7	CTCI3	15t CDCl3/56t T2	Pt/6 days	Evidence for CTCl <sub>3</sub> , unidentified peak at 1030 cm <sup>-1</sup>
8 [	СТСІ3	22t CBrCl3/63t T2	Pt/5 deys	CBrCl3 consumed, many products, CTCl3
9	$CTF_3$	15t CF3I/10t T2	Pt/24 hours	Little product
20	стсі3	15t CBrCl3/63t Tg	Pt/25 hours	Less reaction, than Ru 18, evidence for CTC1 especially in distilled product
21	CTCl3	15t CBrCl3/63t T2	1849Å+2537Å/64°C/ 44/hours	C-T organics produced
2 2	CTC13	22t CBrCl3/63t T2	2537Å/47°C/3 days	Unidentified products
23	CTCl3	∿81 CBrCl3/741 T2	Mol. Sieve 5A/4 hrs	No product
2 4	CTCl3	∿7t CBrCl3/55t T2	Mol Sieve 5A/7 days	Unidentified product
25	CTCl3	∿8t CBrCl <sub>3</sub> /63t T <sub>2</sub>	Mol. sieve 4A/6 days	Unidentified product
6	CTCl3	∿17 CBrCl3/50t T2	Activated alumina/ 4 days	Unidentifed product
7	$\text{CTCl}_3$	∿16t CBrCl3/37t T2	Silica Gel/4 days	No products
8	$CTF_3$	161 CF3I/421 T2	2537Å/1 day	Many products
9	CTF3	12t CF31/70t T2	Pt/8 days	CTF3
0	CTF3	9t CF3I/83t T2	2537Å/1 day/no fan	CTF3; distillation purification
la	Test	CDCl3/NaOD		Glass/vacuum grease system used (to Run 37
lЬ	CTCl3	CDCl3/T20/NaOD	1 hour	Evidence for small amount of CTCl <sub>3</sub>

<sup>\*</sup> For Runs 1-15 see Table I in Ref. 1a.

TABLE I. (continued)

Run no.	Intend Produ		Conditions	Remarks
32	CTCl3	CDCl3/T20/NaOD		No products
33	сисі3	CDCl3/H20/NaOD	] hour	Some CHCl3 formed
34	CHCl3	CDCI3/H20/NaOD	4 hours	Some CHCl3 produced
35	CHCl3	CDCl3/H20/NaOD	2 1/2 hrs mixing in sonic cleaner	Little, if any, CHCl3
36		CDCl3		Test of CDCl <sub>3</sub> adsorption on Mol. Sieve 5A
37	CHCl3	100t CDCl3/H2O/NaOD	l hr/sonic cleaner	Much CDCl3 produced
38				CDCl3 infrared spectrum
39	СТСІ3	103t CDCl <sub>3</sub> /20 Ci T <sub>2</sub> O/∿1λ, 15M NaOD	l hour	Now stainless steel exchange vessels and apparatus used here and below, and much CTCl3 formed
40	CTCl3	800 t∙ee CDCl3/20 Ci T <sub>2</sub> O/NaOD	17 hours	Much CTCl <sub>3</sub> formed (T/D = 1.56)
4]	стсі3	700 tree CDCl <sub>3</sub> / T <sub>2</sub> 8/NaOD	19 hours	Much CTCl <sub>3</sub> formed (T/D = 3.2)
4 2	СТСІ3	360 t•ce CDCl3/ T <sub>2</sub> O/old base	(∿l day)	Very little exchange
43	СТС1 <sub>3</sub>	700 t°cc CDCl3/ T2O/NaOD	5 hours	CTCl <sub>3</sub> produced; no decomposition after 9 days (T/D = 0.45)
44		CDCl3		Transfer experiments test for CHCl <sub>3</sub> formation
15	CTCl3	750 t*ee CDCl3/ T <sub>2</sub> O/NaOD	∿20 hours	CTCl3 produced

TABLE I. (continued)

Run Intend		Conditions	Remarks
46	CDCl3		Transfer experiment
47	CDCI3		Only traces of CHCl3 observed; transfer system devoid of H <sub>2</sub> O
48b	90 mt CTCl <sub>3</sub> /CDCl <sub>3</sub> Run 41 sample used in Runs 48b-e	77 mJ 12µ/ 25 cm f.l.lens/ 930 pulses	IR spectrum unchanged
48c	90 mt CTCl3/CDCl3	103 mJ l 2µ/ 5:1 cm f1.lens/ 1680 pulses	IP spectrum unchanged
48d	90 mt CTCl <sub>3</sub> /CDCl <sub>3</sub> + 21.1 torr Ar	57 mJ 12µ/ 50 cm f.Llens/ 1690 pulses	IR spectrum unchanged
48e	90 mt CTCl3/CDCl3 + 21.2 torr Ar	38 mJ 12µ/ 25 cm f.l.lens/ 1225 pulses	IR spectrum unchanged
49	2.1t CHBr3	long IR cell (9.77 cm)	Spectrum test
50	5.26t CHBr3	long cell	Spectrum test
51	27 tee CHBr3	long cell	Spectrum test
52	178.6t CDC!3	long cell	Optical selectivity measurement
53 CTBr <sub>3</sub>	4λ CHBr3/20 Ci T <sub>2</sub> O/N4OD	long cell/20 hours	Evidence for CTBr3 formation

adsorbant or chromatograph column packing material, is instead used as a catalyst, then it is the organic molecule that binds to the catalyst, while the tritium remains in the gas phase. If any CTCl<sub>3</sub> is formed in this latter process, it will remain bound to the catalyst and will suffer no gas-phase collisions with other organic compounds; this would minimize the formation of the tritiated ethylenes and ethanes that can be produced using the Pt or UV catalysis techniques. In Runs 23-27, several common adsorbants were tested. Silica gel produced no reaction, whereas molecular sieves 4A and 5A, and activated alumina formed unidentified products, and no CTCl<sub>3</sub>. This route of CTCl<sub>3</sub> synthesis was then abandoned.

Though some CTCl<sub>3</sub> was formed using the platinum catalyst, a more efficient and reliable method was sought to obtain pure CTCl<sub>3</sub>. Deuteration of CHCl<sub>3</sub> by the overall reaction

$$CHCl3 + HDO + CDCl3 + H2O$$
 (3)

is known to be rapid when the hydroxide ion is added to catalyze the first and ratelimiting step of the exchange mechanism:

$$C HCl_3 + OH^{-} + CCl_2^{-} + H_2O$$
 (4)

$$CCl_3^- + HDO + CDCl_3 + OH^-$$
 (5)

The rate of this reaction is about 0.2 l/mole-sec, while the hydrolysis rate is  $10^4$  times slower. The rate for the  $CDCl_3/DTO$  D/T exchange process, which will be used to retritiate the working molecule in an actual tritium recovery plant, will also be extremely fast,  $\sim 0.2$  l/mole-sec. Synthesis of  $CTCl_3$  was accomplished utilizing D/T exchange between  $CDCl_3$  and laboratory produced  $T_2O$ , using NaOD as a catalyst. Extreme care was exercised in making and using the small quantities of  $T_2O$  in question.

The two initial exchange runs using  $T_2O$ ,  $CDCl_3$  and NaOD were made in an all glass system (Runs 31b, 32). The  $T_2O$  was made by passing a measured volume of  $T_2$  gas over CuO (wire form) at  $\sim 450\,^{\circ}\text{C}$  to produce  $3\lambda$   $(3x10^{-3}\text{ cc})$  of  $T_2O$  (10Ci). The water formed was cryogenically pumped into a  $\sim 0.2$  cc glass thimble, which had been pre-loaded with  $CDCl_3$  and NaOD in  $D_2O$ . Approximately 500 torrace of  $CDCl_3$  was loaded by vapor transfer in a vacuum apparatus, while about  $1\lambda$  of the 15M NaOD catalyst was added using a micro-pipette. After the water was transferred into the

thimble, the thimble was allowed to come to ambient temperature. The quantity of material within the thimble and the volume of the thimble were such that a significant fraction of the chloroform and water remained in the liquid phase. To assure mixing, the thimble was subjected to several freeze-thaw cycles. After approximately an hour (in these initial runs), the product was passed through a U-tube containing  $\sim 15g$  of Linde 5A molecular sieve to remove any water present, and was cryogenically pumped into a cell for infrared spectral analysis.

Four additional runs (runs 33, 34, 34, 37) were made with  $\rm H_2O$  in lieu of  $\rm T_2O$ . During these runs, it became apparent that  $\rm CDCl_3$  was very efficient at removing stopcocks grease (Apiezon, silicone, Kel-F), causing leaks which allowed a significant amount of air to enter the system. As a result, a new stainless-steel system was built. The vacuum stopcocks and greased joints were eliminated, and the thimble was redesigned to allow easier loading of the base catalyst. The thimble was constructed of stainless steel, except for the bottom of the tube which was terminated by a metal-glass seal and a glass tubing end. This allowed visual inspection of the transferred molecules.

Six runs with mixtures of  $T_2O$ ,  $CDCl_3$ , and NaOD were made with this new system. The quantity of  $T_2$  gas was increased to produce  $6\lambda$  of  $T_2O$ . Variations were made in the length of time allowed for the reaction to take place, which ranged from 1 to 20 hours. Though the rate of T/D exchange is extremely fast in mixed liquids, the low solubility of cholorform in water combined with the difficulty in stirring the small quantities involved led to poor mixing of the reactants (except for the several freeze-thaw cycles). In addition to varying the reaction time, the quantity of initial  $CDCl_3$  was varied in these runs.

As expected, this technique produced a mixture of  $\mathrm{CDCl}_3$  and  $\mathrm{CTCl}_3$  which was identified on the basis of the agreement of the observed infrared spectroscopic  $v_4$ ,  $v_5$ -0 peaks with our calculated values 3, and also on the basis of mass spectrometric measurements. In Run 41, 76% of the final chloroform was found to be tritiated. There was also evidence of a small amount of  $\mathrm{CHCl}_3$  formed, and in addition, there was a small unidentified peak at 794 cm<sup>-1</sup> in the infrared spectrum. The product composition of Run 43 remained unchanged (according to the infrared spectral analysis) even after storage in the infrared analysis cell for 9 days at ambient temperature. Therefore, the  $\mathrm{CTCl}_3/\mathrm{CDCl}_3$  gas mixture (10 torr) is stable, and does not react with itself or with the cell materials (stainless stee!, copper and KRS-5) by any radiation-induced homogeneous or heterogeneous mechanism with an observable rate.

## CTBr3

In Run 53 CHBr $_3$  was mixed with T $_2$ 0 and a NaOH catalyst according to the above method. Initial infrared spectral analysis shows that CTBr $_3$  was produced.

#### III. Molecular photochemistry and spectroscopy

#### Ammoria Laser Development

in these studies, a 12 m NH, laser is desired as the photolysis source in the isotopically selective multiple-photon dissociation (MPD) of CTCl2. The ammonia laser is optically pumped by the R(30), 9.22 $\mu$  line from a pulsed CO $_9$  laser. The sR(5,0) transition in  $NH_3$  absorbs this radiation; lasing occurs at the coupled sP(7,K) transition at 828 cm<sup>-1</sup>. Our Lumonics 103 laser delivers over 4 joules per pulse at the pump transtion. In the initial studies, the ammonia laser optical resonator was a three mirror folded cavity. A grating was positioned at the vertex and a 115 cm long, 35 mm 1D ammonia cell having KCl Brewster windows was placed in the longer resonator arm. The first order reflection off the grating effectively directed the incident, unfocused 9u radiation into the cell, and the optical cavity was aligned to permit 12µ oscillation with the grating used in first order. The 12µ and residual 9µ radiation were coupled out of the cavity reflection off the grating in zeroeth order. A 10 cm long cell filled with 25 torr of  $CF_2I$  served as a  $9\mu$  absorbing filter; this removed any transmitted  $CO_5$ laser energy. In this configuration, as much as 75% of the ouput power was found to be due to two-pass superradiant build-up. The 12µ laser power was insensitive to the curvature of the totally reflecting mirror in the cell arm (4, 10, 20 meter radius of curvature). Optimal operation occurred . ith  $\sim 1$  torr NH, and  $\sim 20$  torr added No buffer, leading to a maximum puise energy of 190 mJ.

The cavity configuration was altered to measure the single-pass superradiant output using the same 115 cm long ammonia cell. The 9 $\mu$  radiation was coupled into the NH $_3$  cell in three ways: (1) unfocused parallel beams, beam diameter ~2.9 cm; (2) telescoped down parallel beam (100 cm f.l. KCl lens, 40 cm f.l. BaF $_2$  Galilean telescope), beam diameter ~1.5 cm; (3) coaxially focused into the center of the cell by a 100 cm f.l. lens. Absorption at 9 $\mu$  and emission at 12  $\mu$  were monitored at the cell exit using the CF $_3$ l cold gas filter. In all cases adding 20-60 torr N $_2$  led to greatly improved 9 $\mu$  absorption and 12 $\mu$  emission.

Using configuration (1),  $9\mu$  absorption increased, though  $12\mu$  emission decreased when the NH $_3$  partial pressure was increased above 1.5 torr. In some cases when set-ups (2) and (3) were employed, overall performance was superior with 2-3 torr NH $_3$ 

than with lower  $NH_3$  pressure. As expected, more 9u energy was absorbed using (1) than with (2), and more with (2) than (3). Similarly, the fraction of absorbed 9u radiation converted to 12u increased from (1),  $\sim 0.15$ , to (2)  $\sim 0.26$ , to (3)  $\sim 0.33$ . A maximum 12u output of 350 mJ occurred with layout (3) with 2.4 torr  $NH_3/49$  torr  $N_2$ . In this case the 9 to 12u photon conversion fraction is 0.29. The output pulse energy could be straightforwardly increased to  $\simeq 450$  mj by cooling the  $NH_3$  medium to 220°K. A maximum photon conversion ratio of roughly 0.4 was observed using  $\sim 1$  torr  $NH_3/\sim 50$  torr  $N_2$  in configuration (3). Under these conditions, about 250 mJ of 12u was produced, and only 0.2 of the 9u pump was absorbed.

Further improvements in our 12p photolysis source will permit wavelength tuning, pulse energies approaching 1J, and perhaps short pulse operation (~2nsec FWHM).

#### Evaluation of Lasers for T/D recovery

Spectroscopic analysis of our recently synthesized CTCl $_3$  has confirmed that the CTCl $_3$   $v_1$ +0 mode infrared resonance is near 835 cm $^{-1}$ , in agreement with out normal mode calculations,  $^{1,3}$  CDCl $_3$  has only a very small absorption cross-section at this frequency. Consequently, both the T/D absorption and dissociation selectivity will be suitably high for successful tritium recovery in a process based on infrared laser multiple-photon dissociation (MPD) of chloroform.

As described above, the ammonia laser is optically-pumped by the pulsed CO<sub>2</sub> laser, and is capable of lasing at 30 wavelengths between 770.9 and 888.1 cm<sup>-1</sup>. <sup>4-8</sup> Notably, each of the 12 lasing wavelengths from 815.4 to 853.6 cm<sup>-1</sup> has 2 14-20% efficiency, of which 5 lines are between 828 and 835 cm<sup>-1</sup>. Despite the superior operating characteristics of the NH<sub>3</sub> laser and its apparent suitability for CTCl<sub>3</sub>/CDCl<sub>3</sub> recovery, <sup>1,3</sup> it is prudent to examine other possible laser systems which can also selectively decompose CTCl<sub>3</sub>. These alternate laser systems, as listed in Table II, should be compared to the NH<sub>3</sub> laser on the basis of their present stage of technological development, overall operational simplicity, electrical efficiency, overhead costs, and ability to operate in a short pulse (\*Insec FWHM) regime.

A sealed off  $^{9-12}$   $^{14}$ C $^{16}$ O $_2$  laser  $^{13}$  tuned to the P(34), (100)-(001) line lases at 836.2 cm $^{-1}$ ; both this and the neighboring rotational lines would be suitable for

the MPD of CTCl<sub>3</sub>. A closed cycle  $^{14}\mathrm{C}^{16}\mathrm{O}_2$  laser using current stockpiles of  $^{14}\mathrm{C}^{16}\mathrm{O}_2$   $^{14}$  would require minimum development to operate in the short pulse regime. However, the operation of a radioactively hot laser is a definite drawback, especially considering the small amounts of tritium that are actually recovered when decontaminating the coolant inventories in a heavy water fission plant (e.g., Savannah River).

Another prospective 12u laser system entails rotational Raman scattering of a  ${\rm CO_2}$  laser in high pressure hydrogen. <sup>15</sup> In one such system under intensive development for UF<sub>6</sub> photolysis,  ${\rm ^{12}C^{16}O_2}$  laser radiation [R(22), 10.2u] is downshifted to 16u by rotational Raman scattering in cooled para-H<sub>2</sub>. <sup>15-17</sup> An outstanding quantum conversion efficiency of  ${\rm ^{N85}S}$  is claimed for shifting these 10u photons to 16u. Three similar isotopic combinations hold promise as a 12u laser source.

Scattering the 9.81, P(48)  $^{12}C^{16}O_2$  laser line in cooled  $D_2$  (J=2+0, a shift of 179 cm<sup>-1</sup>) produces 840 cm<sup>-1</sup> radiation, near the peak of the CTCl<sub>3</sub> spectral resonance of interest. Note that in this case the  $CO_2$  laser must lase at a high J state, and therefore will operate at less than optimal efficiency; in addition, amplication of a short pulse will require a relatively long path length. Operation at a lower J transistion will produce  $12\mu$  radiation to the "blue" side of the CTCl<sub>3</sub>,  $V_4$ +0 transition, and this would most probably decrease the MPD cross section, whereas operation at higher J transitions will drastically lower the  $CO_2$  laser efficiency. Raman scattering the output of a sealed off  $^{9-12}$   $^{13}C^{16}O_2$  laser in cooled  $D_2$  (J=2+0) may, in fact, be preferred. For example, the P(12), (020)+(001) line at 9.92 $\mu$  will scatter to 828.6 cm<sup>-1</sup>; neighboring J lines will also be useful based on  $CO_2$  laser efficiency and CTCl<sub>2</sub> MPD considerations.

Raman scattering off of HD is also attractive. It the scattering cell materials are carefully chosen, it is quite possible that HD will not catalytically equilibriate with H $_2$  and D $_2$ . If HD does not equilibriate, there is then no need to spoil the gain at the H $_2$ - and D $_2$ -scattered frequencies. The  $^{12}\mathrm{C}^{16}\mathrm{O}_2$  laser line at R(40), 9.2 $\mu$  will scatter to 823.0 cm $^{-1}$  (J=2+0, 267.1 cm $^{-1}$  shift); R(50), 9.1 $\mu$  produces 827.7 cm $^{-1}$ . The  $^{12}\mathrm{C}^{18}\mathrm{O}_2$  R(20), 9.1 $\mu$  line scatters to 829.9 cm $^{-1}$ . Other things being equal, the CO $_2$  laser-hydrogen combination employing the fewest exotic isotopes would be preferred. Use of deuterated hydrogen would be probably less costly than isotopically rare CO $_2$ 

TABLE II. 12 $\mu$  Laser Sources for CTCl $_3$  MPD.

Pump läser, (λ representative)	Interaction	Pumped medium, Secondary laser, (cm <sup>-1</sup> )		Approximate Useful Range (cm <sup>-1</sup> )
12C16O2 [R(30),9.2µ]	Optical Pumping	NH3	(828-0)	815-954
14C16O <sub>2</sub> [P(34),12.0 <sub>14</sub> 836.2 cm <sup>-1</sup> ]	Direct			830-850
12C16O2 [P(48),9.8u]	Rotational Raman	D <sub>2</sub>	(839,9)	∿840
<sup>13</sup> С <sup>16</sup> О <sub>2</sub> (Р(12),9.9µ]	Rotational Raman	$D_2$	(828.6)	820-832
12 <sub>C</sub> 16 <sub>O 2</sub> (R(40),9.2)վ	Rotational Raman	НD	(823.0)	820-827
<sup>12</sup> C <sup>18</sup> O <sub>2</sub> [R(20),9.1µ]	Rotational Raman	НD	(829.9)	820-840

One advantage of  $\text{CO}_2$  laser-hydrogen Raman scattering laser sources over NH $_3$  laser systems is their possibly superior short pulse ( $^2$  nsec FWHM) operation. The Raman gain for short pulses will increase dramatically as the pulse width is shortened, so that the  $\text{CO}_2$  laser-hydrogen system will be efficient and simple in the short pulse regime. Though injection model-locked operation of an NH $_3$  laser has been demonstrated, the single pass, short pulse population-induced gain in NH $_3$  has not been measured. Perhaps, at high pulse intensities, the Raman gain in NH $_3$  may also be quite high.

The strong infrared absorption peak in CTBr $_3$  at 761 cm $^{-1}$  (13.1µ),  $^3$  due to  $v_6$ +0, should have a quite high T/D isotopic absorption selectivity. In this case, an attractive laser source for MPD and tritium recovery is the 13µ laser produced by Raman scattering 10.6µ radiation from a normal isotopic CO $_2$  laser in D $_2$ , where the laser frequency is downshifted by 179 cm $^{-1}$ . In particular, the P(24), 10.63µ line scatters to a frequency quite near the  $v_6$  CTBr $_3$  peak. The high electrical efficiency of these normal CO $_2$  laser lines combined with the high Raman conversion efficiency make this 13µ laser source very attractive for economically attractive T/D recovery. The relative merits of these various 12µ and 13µ lasers are under continued investigation.

#### Chloroform Studies

The observed CTCl<sub>3</sub> spectral frequencies are extremely close to those we previously calculated.<sup>3</sup> An infrared spectrum of 7.8 torr CTCl<sub>3</sub>/5.2 torr CDCl<sub>3</sub> from Run 49 in a 2.0 cm long cell is shown in Fig. 1. In particular, the important  $v_4$ +0 peak is at 835.3  $\pm$  0.3 cm<sup>-1</sup>, in very good agreement with the value of 837.1 cm<sup>-1</sup> calculated using the best available harmonic force field.<sup>3</sup> In CDCl<sub>3</sub> the  $v_4$  and  $v_5$  peaks are of approximately equal absorption strength. Fortuitously, in CTCl<sub>3</sub> the interesting  $v_4$  peak is stronger, while the  $v_5$  peak is weaker, than the  $v_4$  and  $v_5$  peaks in CDCl<sub>3</sub>. In fact, the peak absorption strength for CTCl<sub>3</sub>  $v_4$ +0 is measured to be  $v_10.2$  ( $\pm 0.7$ ) x  $10^{-2}$ /cm-torr (835 cm<sup>-1</sup>), or  $v_6$ 5% larger than the measured absorption coefficient at the CDCl<sub>3</sub>  $v_4$ +0 peak (914 cm<sup>-1</sup>), 6.2 x  $10^{-2}$ /cm-torr. The CTCl<sub>3</sub> absorption coefficient was determined from the infrared spectra of T/D chloroform mixtures for which the CTCl<sub>3</sub>/CDCl<sub>3</sub> concentration ratio was determined by mass spectrometry (Runs 40, 41, 43).

The low fluence T/D optical absorption selectivity for chloroform is determined by the ratio of the peak absorption coefficient of  $CTCl_3$  at 835 cm<sup>-1</sup> to that of  $CDCl_3$  at that same photon energy. New infrared analysis puts this  $CDCl_3$  absorption coefficient at  $\stackrel{<}{\sim} 1.1$  ( $\stackrel{+0.5}{\sim}$ ) x  $10^{-6}$ /cm-torr. This absorption is extremely weak and the exact value of this cross-section is still uncertain. Using the cited values, the low fluence optical selectivity is  $\sim 9000(\stackrel{+2}{\sim} 5000)$  to 1 at 835 cm<sup>-1</sup>. At the ammonia laser wavelength,  $12.08\mu$ , the low fluence selectivity is about half this value. At higher fluences, the excited state absorption cross section of  $CTCl_3$  contributes quite strongly to isotopic selectivity. Though when  $CTCl_3$  is highly vibrationally excited, the  $\vee_4$  fundamental peak will most probably broaden and so decrease (as well as shift to the red), the suitably level-averaged T/D absorption selectivity should remain quite high: >1000:1.

Initial IR photolysis studies began using the  $\sim 100$  mJ pulse energies available from the earlier versions of the ammonia laser by tightly focusing this radiation into a photolysis cell containing the CTCl3 synthesized in Run 41 [Run 48 (25 or 50 cm f.l. lenses)]. No definite product formation was observed using the crude infrared spectroscopic detection technique. Based on our earlier CDCl3 MPD studies, only marginally observable amounts of product formation would be expected here. (Note that reactant removal was being actually monitored). With the much higher 12 $\mu$  pulse energies now available, and with the use of the sensitive gas chromatographic analysis system, much higher sensitivity experiments will be performed in the coming reporting period. Notably, it was observed during these runs that CDCl3 rapidly exchanges with H2O residing on the walls of the vacuum system, thus converting much of the initial CDCl3 to CHCl3 as determined by infrared spectroscopy. This D/H exchange reaction ceased once the vacuum system was suitably baked out.

#### IV. Process Development

Tritium removal from heavy water based on MPD will require a process that includes the unit operations shown in Fig. 2. Heavy water contaminated with tritium (DTO) is passed through an exchange unit where the tritium is exchanged with deuterated chloroform (or a similar working moledule). The decontaminated water is then returned to the source. Deuterated chloroform is fed into the exchange unit, where it becomes partially tritiated by exchange with the heavy water. The chloroform then passes through a let-down valve into the photo-reaction tube (the exchanger pressure will be atmospheric or above, while the photo-reaction pressure will likely be approximately 100 torr), where the laser preferentially dissociates the tritiated molecules. Passing from the photo-reaction tube, the products and remaining reactants are compressed before entry to the photoproduct stripper, where the products from the laser-induced reaction are removed. Then the pure deuterated chloroform (plus the small fraction of tritiated chloroform which was not dissociated by the laser) is recycled to the exchanger unit, with sone additional chloroform to replace that removed by the laser MPD process.

Our efforts have to date been focused on the identification of operating parameters and potential problems for each unit. We have also constructed a system mass balance to identify the relevant scale of operation. A few general considerations are discussed below.

In the exchange unit, the tritium exchange between water and chloroform must be accomplished rapidly, to minimize the size and holdup of equipment. The use of a liquid catalyst (dimethyl sulfoxide with sodium hydroxide promoter for trifluoromethane; only sodium hydroxide or equivalent base for chloroform) has been shown to be effective. In some cases (CTF<sub>3</sub>), the necessary catalyst-water separation may require a relatively large expenditure of energy. However, the energy consumption in the CTCl<sub>3</sub> case is expected to be small. Still, exploration of potential catalysts is crucial to design of an economical exchange reactor.

The photo-reaction tube will operate at sub-atmospheric pressure, because of more favorable photophysics at lower pressures. The optimal reaction pressure (trading reactor size and compressor duty for lower reaction yields) must be identified. The compressor at the reactor outlet will be a major capital expense and energy user, and suitable care must be taken in optimizing the reactor operating pressure.

Removal of the photoproducts must be highly efficient in order to maximize the desired decontamination. Handling the somewhat corrosive TCl (or TF for the trifluoromethane working molecule) must be done with the best commercial techniques. The photoproduct stripper can be designed to either allow recovery of tritium for use elsewhere or to immobilize it for disposal; the two options imply quite different designs.

To give an indication of the necessary size of the system, a mass balance was performed for the case of greatest interest, namely the cleanup of a Savannah River Plant Heavy Water Reactor. Specifications are given in Table 3. Several assumptions made in the course of the calculation are in Table 4. Outte conservative photochemical parameters for chloroform photolysis are given in this table. The resulting system flows and power consumptions are shown in Table 5. The volumetric flow rates are quite modest, and the power consumption is rather negligible (involving an electricity cost of about \$60K during the assumed one-year operation).

We plan to identify in more detail the process development areas of greatest concern; with this information we will plan an orderly research and development program to address the areas of most interest. We will have an engineer from the Savannah River Plant working with us soon, to ensure that the developed T/D recovery process will be well-tailored to Savannah River Plant needs and requirements.

TABLE 3: Initial Specifications - Cleanup of Savannah River Plant Heavy Water Reactor.

Reactor volume: 500 tonne DoO Tritium concentration: 20 Ci/liter Desired Tritium level: 2 Ci/liter (10% of initial concentration) Time allowed to reach desired level: I year

TABLE 4: Assumptions used in calculation of mass balance data shown in Table 5.

- o Exchange unit reaches equilibrium with T concentration equal in water and chloreform
- o Photoproduct stripper efficiency is 100%

o Optical selectivity: S = 650 for laser-induced reaction

o Enrichment factor:

E = 1000 for laser-induced reaction

TABLE 5. Process parameters for the cleanup of Savannah River Plant Heavy Water Reactor.

Heavy water flow through exchanger 6.64 1/min Chloroform flow through exchanger 29.4 1/min Photoproduct formation rate: 0.04 ee/min DCL 3.5 cc/min  $C_{\mathbf{x}}Cl_{\mathbf{v}}$ 5.7 cc/min Make-up chloroform flow 8.9 cc/min Electric power to laser (1.25% efficiency) 87 kW Pumping power (reactor at 100 torr. rest of process at 1 atm) 31 kW

#### V. Program Personnel

The LLNL photochemical tritium recovery project is a collaborative effort of the program's principal investigators, who are members of the Special Studies Group of the Physics Department, and the LLNL Tritium Facility of the Chemical and Material Sciences Department. Terrance Biel, Jon Maienschein, Clyde Griffith, and other members of the Tritium Facility have been instrumental in the synthesis of the tritiated molecules, the chemical engineering analysis, and related program efforts. Our contacts at the Savannah River Plant Heavy Water Reactor are James Bosvell, John Church, and Chet Thayer, who have been kept informed of our progress; we will continue to work closely with them on establishing the tritium recovery requirements of the reactor, and on interfacing our photochemical tritium separation unit with the reactor.

#### VI. Concluding Remarks

Chloroform appears to be an ideal molecule for photochemical tritium-from-deuterium separation. Intensive photochemical evaluation and process engineering studies of the CTCl<sub>3</sub> MPD route of T/D recovery will continue during the coming reporting period. The properties of the 12µ laser sources required for this process will also be studied further.

### VII. Patent activity

A patent application entitled "Laser-Assisted Isotope Separation of Tritium" (S-53,693; RL-7890; IL-6619/IL-6729) was filed by the Department of Energy on March 11, 1981.

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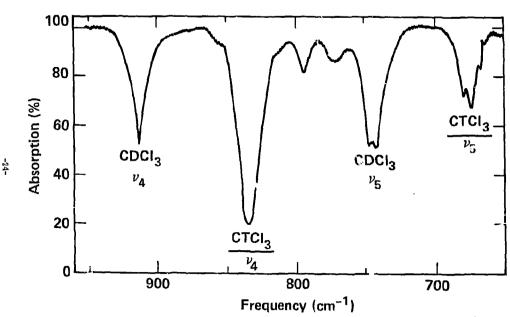


FIG. 1. The absorption spectrum of CTCl3 which was produced by based catalyzed aqueous exchange in Run 40.

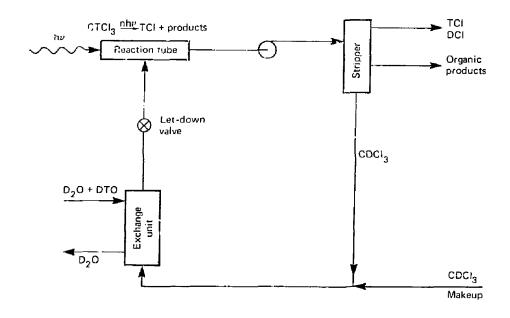


FIG. 2. Process flow diagram for tritium recovery by MPD of chloroform.