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FOR PHOTOCHEMICAL TRITIUM RECOVERYBi-Quarterly Progress Report
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ABSTRACT

Mixtures of $\text{CTCl}_3/\text{CDCl}_3$ were successfully detritiated by 1μ laser multiple-photon dissociation. The lower limit of the T/D enrichment factor was determined to be ~ 165 . Additional studies concerning the effects of pulse energy, irradiation geometry and sample pressure were conducted. Characterization of both untuned and tuned NH_3 laser configurations were completed. Further laser studies considered implementation of a short pulse CO_2 laser pump source for either the current NH_3 laser or for possible use in a rotational Raman laser. Process engineering requirements for T/D separation at Savannah River were studied in detail and the first complete process design for implementation is presented.

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I. INTRODUCTION

Chloroform was successfully detritiated by infrared laser multiple-photon dissociation in this reporting period. A lower limit value of the T/D enrichment factor of 165 was obtained, limited by experimental sensitivity. Experimental evidence implies that it is indeed much larger than this estimate. Additional studies of chloroform MPD were conducted, and the 12 μ laser sources that are required for practical tritium recovery were further considered. Process engineering studies for implementing laser MPD tritium recovery at Savannah River continued at LLNL and began at the Savannah River Laboratory.

II. MOLECULAR PHOTOCHEMISTRY

Tritium Enrichment

As described in an earlier report,⁽¹⁾ CTCl_3 was synthesized by base-catalyzed aqueous exchange between CDCl_3 and T_2O

(0.21 l/mole-sec for D/H exchange at 20°C for dissolved chloroform) ⁽²⁾

A premeasured quantity of T_2 was passed over CuO wire at 450°C to produce about 6×10^{-3} cc T_2O . Approximately 1×10^{-3} cc of 15M NaOD in D_2O was preloaded into a 0.2cc stainless steel/glass thimble. Then about 500 torr-cc of CDCl_3 vapor and the T_2O were cryogenically transferred to the thimble. These cited dimensions and quantities allowed a significant fraction of the chloroform and water to remain in the liquid phase to permit exchange; CTCl_3 production was accelerated via mixing by several freeze-thaw cycles. After exchange, the products were passed through molecular sieve 5A to remove the water, and were then analyzed by infrared spectroscopy and mass spectrometry. Typically, 20-70% of the chloroform was CTCl_3 ; the remainder was CDCl_3 , with about 2% of CHCl_3 . At times CCl_4 was observed in the tritiated samples due to radiolysis in high specific activity mixtures. The CCl_4 fraction increased noticeably after many weeks of storage. It was therefore preferable to dilute samples to the desired $\text{CTCl}_3/\text{CDCl}_3$ ratios immediately after CTCl_3 synthesis.

The grease-free main vacuum apparatus consisted of glassware, O-ring/glass plug/stopcocks, and stainless steel tubing and valves. The pyrex reaction cell (8.5 cm long, 1.3 cm ID), had KCl Brewster angle windows. After photolysis, the products were cryogenically transferred to the gas sampling valve loop of a temperature-programmed gas chromatograph. A 6 foot n-octane on porasil-C column was used for separation. The effluent of the gas chromatograph thermal conductivity detector was directly coupled to a 200 cc ionization chamber.

Laser photolysis of CTCl_3 was monitored by a decrease in the ionization chamber output, as compared to an unphotolyzed sample; depletion of CDCl_3 was similarly monitored by the thermal conductivity detector. Run-to-run variations in the detection of identical quantities of a molecule were typically $\pm 3\%$. In some cases $\sim 2\%$ of $\text{c-C}_4\text{F}_8$ was added to $\text{CTCl}_3/\text{CDCl}_3$ mixtures for internal calibration.

A 0.3 Hz repetition rate, pulsed CO_2 laser delivering 4 J at R(30), 9.22μ in a 100 nsec FWHM pulse was coupled off a grating into a 120 cm long cell filled with 1 torr NH_3 /20 torr N_2 . As described in greater detail in the next section, the ammonia laser resonator consisted of this grating, a totally reflecting 15 m radius concave mirror (in the cell arm), and a partially reflective (ranging from 35-80% reflecting) 10 m concave output mirror.⁽³⁾ Typical operating characteristics were 350 mJ output in 1.5 μ sec FWHM pulses at the 12.08μ [828 cm^{-1} , $\text{SP}(7, \text{K})$] line used. No radiation ($<0.1\%$) was observed near 11.7 , 12.0 , 12.3 , and 12.5μ , which are the strongest wavelengths of NH_3 superradiant emission. The 12.08μ pulse was focused into the center of the reaction cell by either a 25 or 50 cm focal length KCl lens.

In some cases, the photolyzing fluence was doubled by retroreflecting the transmitted beam with a totally reflecting concave mirror, with radius of curvature approximately equal to the lens focal length, placed a distance of one lens focal length past the cell focus. In such cases, the effectively-doubled laser energy per pulse incident on the cell is cited as the net incident energy. This retroreflection did not couple back into the NH_3 laser.

The infrared spectrum of a typical $\text{CTCl}_3/\text{CDCl}_3$ gas mixture ($\sim 25\%$ tritiated) is shown in Fig. 1. The CTCl_3 ν_4 peak occurs at $835.3 \pm 0.3\text{ cm}^{-1}$ and ν_5 at 674 cm^{-1} , as predicted by the normal mode calculations, with the Ruoff and Burger⁽⁴⁾ force field providing the best spectral fit. In new measurements, there is no discernable infrared absorption in 1800 torr $\cdot$ cm path lengths in CDCl_3 from $815\text{--}842\text{ cm}^{-1}$ [$< 8 \begin{pmatrix} +3 \\ -8 \end{pmatrix} \times 10^{-6}/\text{cm-torr}$]. The low-fluence optical selectivity for $\text{CTCl}_3/\text{CDCl}_3$ at 835 cm^{-1} is 12,000 $\begin{pmatrix} +\infty \\ -3000 \end{pmatrix}$, while at the ammonia laser photon energy, 828 cm^{-1} , it is 6,500 $\begin{pmatrix} +\infty \\ -1900 \end{pmatrix}$.

When CTCl_3 was irradiated by 12.08μ , a large, highly selective depletion of CTCl_3 occurred, though, in no case did any tritiated product appear in the ionization chamber due to laser photolysis. In some samples, small amounts (ppm level) of tritiated impurities, such as dichloromethane and trichloroethylene, and non-tritiated products ($<0.1\%$), such as carbon tetrachloride and dichloromethane, were present in equal quantities in photolyzed and null samples. Since the absolute quantities of irradiated CTCl_3 were purposely kept small, no CTCl_3 product was expected or appeared using the thermal conductivity detector. No CDCl_3 reactant depletion (within $\pm 3\%$) or CDCl_3 decomposition products were observed with 12.08μ laser irradiation.

The extent of CTCl_3 and CDCl_3 reagent depletion versus the number of irradiating pulses is shown in Fig. 2. In the 25 cm focus plots of remaining CTCl_3 and CDCl_3 , a net of 460 mJ per pulse irradiated the cell (including retroreflection); the 200 mtorr chloroform sample had T/D ratio, η , of 200 ppm. A 50 cm focal length lens focused a net of 505 mJ per pulse of 12.08μ radiation into the cell containing 200 mtorr with $\eta = 200$ ppm in the 50 cm focus CTCl_3 curves. For the 25 cm focusing case 0.32% of the present CTCl_3 decomposed per shot. Based on the 2.0% standard deviation from the best fit line in the CDCl_3 plot (which is horizontal), CDCl_3 depletion per shot is $<2.0 \times 10^{-5}$.

The laser pulse energy dependence of infrared photolysis of the CTCl_3 in 200 mtorr with $\eta = 200$ ppm (50 cm lens) is shown in Fig. 3, data being taken both with and without retroreflection. This plot depicts the fractional decomposition of the cell contents per shot. The laser swept about 2.5% of the cell volume. With 400 mJ of energy incident on the cell, the fluence near the focus was $\sim 20 \text{ J/cm}^2$, while at the windows it was $\sim 6 \text{ J/cm}^2$.

Figure 4 portrays the dependence of CTCl_3 dissociation on added CDCl_3 . The fractional decomposition per pulse is shown for 50 cm focal length optics with 270 mJ incident (one-pass) and a net of 535 mJ in the cell (retroreflection). For all data the CTCl_3 partial pressure was ≤ 0.15 mtorr, so CTCl_3 - CTCl_3 collisions are unimportant. For the 270 mJ data, T/D was fixed at 195 ppm for CDCl_3 pressures below 0.75 torr and at 19 ppm above 0.75 torr. For the 535 mJ data, $\eta = 150$ ppm for total pressures below 0.75 torr and 24 ppm at higher pressures. The CTCl_3 dissociation probability is quenched to one half its low pressure value with 1.7 torr of added CDCl_3 when 270 mJ is incident, and with 3.0 torr CDCl_3 when 535 mJ impinges on the cell.

Several more 12μ laser experiments on $\text{CTCl}_3/\text{CDCl}_3$ mixtures and neat CDCl_3 were performed, similar to those described above except many more pulses irradiated the sample in order to search for CDCl_3 decomposition; no CDCl_3 photolysis products were detected. As reported earlier,⁽⁵⁾ only by using large reaction vessels (300 cc volume) and CDCl_3 pressures over 1 torr could enough of the reactive deuterium chloride be formed in P(48), 10.91μ photolysis of CDCl_3 to be observed on the thermal conductivity detector. This explains why no TCl , the major tritium-bearing product, was observed in the ionization chamber traces here.

Since no CDCl_3 photolysis products were ever seen with 12μ photolysis, the system collection capability of small amounts of products was tested. 200 mtorr $\text{C}_2\text{Cl}_4/\text{CDCl}_3$ mixtures were placed in the reaction cell, and then transferred to the gas chromatograph; C_2Cl_4 mole fractions down to the lowest measured point of 0.1% were easily seen.

Studies of the 10.91 μ photolysis of 200 mtorr CDCl_3 in the same 14 cc volume reaction cell showed that <1% deuterated chloroform conversion to any product should have been seen. For experiments at higher pressure, smaller conversion can be observed; for instance, it was confirmed that at 2 torr total pressure (as in Fig. 4), <0.1% product formation from CDCl_3 decomposition is detectable.

The single step T/D enrichment factor, β , is defined as the ratio of the fractional CTCl_3 decomposition per pulse, σ_T , to that of CDCl_3 , σ_D . From the short focus data of Fig. 2 ($\eta = 200$ ppm), β is conservatively >165, limited by the uncertainty in the run-to-run CDCl_3 reagent depletion measurements. Higher lower limit estimates come from the fact that no products ever appeared, although for runs at 2 torr it is estimated that products arising from 0.1% CDCl_3 decomposition would have been observed. Data near 2 torr CDCl_3 in Fig. 4 (75 pulses, 53J mJ) suggest $\beta > 540$; similar experiments with more pulses (250 pulses, 570 mJ) puts $\beta > 2200$. (In these cases, 42% and 89% of initial CTCl_3 was decomposed.) It should be noted that these two values are quite sensitive to the minimum detectable product.

There are three important modes of CDCl_3 decomposition with 12 μ irradiation: (1) direct MPD (possibly assisted by CDCl_3 - CDCl_3 collisions), (2) MPD after collisional excitation by hot CTCl_3 , and (3) reaction with CTCl_3 dissociation products. For the last two cases σ_D is proportional to the CTCl_3 partial pressure. (Of course, if these two mechanisms were significant, the above-cited lower limits for β would actually correspond to mixtures with η somewhat smaller than the pre-photolysis values.)

Since CDCl_3 is highly transparent near 12.08 μ , direct MPD cannot be very important. If only direct MPD leads to CDCl_3 dissociation, β should be greater than the high fluence optical selectivity; however, previous studies have shown that β can be even larger than the low fluence optical selectivity⁽⁶⁻⁸⁾ (>4600 at 828 cm^{-1}). In experiments in which 2800 pulses of 12 μ were incident on neat CDCl_3 (1 torr, net 520 mJ, 50 cm focus) there was still no evidence of CDCl_3 depletion or products; in the worst case these data imply $\beta \gg 400$ if only direct MPD is important.

If $\beta = 160$ (Fig. 2, 25 cm focus, 200 mtorr, $\eta = 200$ ppm) and if σ_D were CTCl_3 dependent, then ~ 30 CDCl_3 would be lost per removed CTCl_3 . Since there are only ~ 5 CTCl_3 - CDCl_3 collisions during the laser pulse under these conditions, and since at room temperature there is no apparent mechanism for a chain reaction (though for (2) or (3) one CDCl_3 may decompose per CTCl_3 , as in (5)), neither CTCl_3 -dependent σ_D mode can support such a small β . (Still, if σ_D depends linearly on η and $\beta(\eta = 200 \text{ ppm}) = 160$, then at the typical heavy water reactor T/D value of 5 ppm, β would be ~ 6400 .)

Kinetics Characterization

The determination of the nascent and subsequent steps of chloroform pyrolysis has been the subject of numerous investigations for over forty years. Both flow and shock-tube techniques have been employed, using various types of isotopic scavengers and detection methods to resolve the kinetics. Still, these studies do not definitively conclude whether hydrogen chloride⁽⁹⁻¹²⁾ or chlorine atom^(13,14) elimination (or both) is the nascent step.

In the most recent shock tube study of CHCl_3 pyrolysis,⁽¹²⁾ Reaction (2) is claimed to be the nascent step, with a measured activation energy of 54.5 ± 2.9 Kcal/mole. Based on the latest measured enthalpy of CCl_2 , 53.5 ± 2.3 Kcal/mole,⁽¹⁵⁾ Reaction (2) is 56 Kcal/mole endoergic. A typical barrier for a 3-center hydrogen chloride elimination back reaction in a halogenated methane is about 6 Kcal/mole,⁽¹⁶⁾ so Reaction (2) should have an activation energy of 62 Kcal/mole, significantly higher than the measured value; that of Reaction (3) should be about 70 Kcal/mole.⁽⁹⁾ According to quantum RRK theory, CTCl_3 molecules excited ~ 8 Kcal/mole above the dissociation energy decompose by Reaction (2) in about 5 nsec, slow enough for (2) and (3) to be competitive. A definitive experiment testing the relative contributions of Reactions (2) and (3) is underway.

The appearance of large amounts of C_2Cl_4 in CDCl_3 IR laser photolysis, reported earlier, suggests the contribution of Eq. (2) through Eqs. (4) or (5):

Since CCl_4 , though not C_2Cl_4 at room temperature can be formed as a result of Reaction (3),^(13,14) apparently both (2) and (3) are important. Depending on the route of C_2Cl_4 formation [(4) or (5)], C_2Cl_2 may be formed by $\text{Cl} + \text{Cl}$ or Cl_2 elimination or by secondary photolysis (only in the 10.9μ studies). In the $\text{CTCl}_3/\text{CDCl}_3$ experiments there was no evidence for TCI/CDCl_3 isotope scrambling.

In order to fully identify the products of multiple photon dissociation and to obtain the ability to examine the isotopic composition of each reaction product, the gas chromatograph and a quadrupole mass spectrometer have been modified so that GC-MS analysis can now be performed.

A Hewlett-Packard 5830-A gas chromatograph has been modified so that part of the column effluent bypasses the detector. This effluent is then introduced through a two stage pressure reduction system, into the inlet of an Inficon IQ200 quadrupole mass spectrometer. The gas flows continuously through the mass spectrometer, and the mass spectrum of the effluent is continuously displayed. The mass spectrometer has been interfaced with and is controlled by an LSI-11 computer. The mass spectrum of each chromatographic peak is read out by the computer and stored on a disk, so that a complete mass spectral record of the chromatographic run is obtained.

Since the gas chromatograph, mass spectrometer, and computer were already in use in the laboratory, the system was built without additional capital expenditure. The system has been built so that each of the components can still be used independently of the others. The system is now complete and debugged and experimental work using it is beginning.

Returning to the data presented in the previous section, note that the fluence dependence depicted in Fig. 3 is consistent with a multiple-photon dissociation probability that rises as the 2.5 ± 0.5 power of the local fluence until it reaches unity at and stays at unity above the saturation fluence, ϕ_{sat} , of about $23 \pm 3 \text{ J/cm}^2$. This characterization was obtained using the burn patterns of the focused beam at various positions in the photolysis cell path to determine that local fluence, assuming a flat transverse profile. The dissociation probability $P(\phi)$ was:

$$P(\phi) = \left(\frac{\phi}{\phi_{\text{sat}}} \right)^m \quad \phi < \phi_{\text{sat}}$$

$$1 \quad \phi \geq \phi_{\text{sat}} \quad (6)$$

where m is an integer in this characterization. The fractional conversion of reactant to product per pulse is given in the Appendix.

Since a flat profile was assumed here, the result cited in the Appendix differs slightly from that in Ref. (17). The values $m = 2.5 \pm 0.5$, $\phi_{\text{sat}} \approx 23 \pm 3 \text{ J/cm}^2$ for 12.08μ photolysis of CTCl_3 , were fairly insensitive to the interpretation of the burn patterns to obtain the local fluence. More precise measurement of these parameters is underway.

At low fluences, the net absorption cross-section, α , of a polyatomic molecule is typically constant, α_0 ; above a given fluence, ϕ_c , it decreases as

$$\alpha = \alpha_0 \left(\frac{\phi}{\phi_c} \right)^p; \quad (7)$$

in most cases $p \sim 1/3$.⁽¹⁸⁾ For $\phi > \phi_c$ the number of absorbed quanta, n , is

$$n = \frac{\alpha_0 \phi}{\hbar \omega} \left(\frac{\phi_c}{\phi} \right)^{1/3} \quad (8)$$

where $\hbar \omega$ is the photon energy. This low-to-high fluence cross-over in the absorption cross-section expression should occur at $\phi_c \approx 0.005 \text{ J/cm}^2$ here (which corresponds to ~ 1 quantum absorbed per molecule with $\alpha = \alpha_0$). Using $\phi = 23 \text{ J/cm}^2$ and α_0 as measured for 828 cm^{-1} , then $n \sim 140$ photons. This estimate is good to a factor of two, and within this limit it is insensitive to the precise value of ϕ_c . Since CTCl_3 will rapidly decompose after 35 quanta of 828 cm^{-1} are absorbed, it is clear that the actual decrease in excited state cross-section is more pronounced than expected.

In this study, the 12.08μ line of the ammonia laser was used since it is red shifted 7 cm^{-1} from the CTCl_3 ν_4 peak, and the red shift in the ν_4 ladder is large. The X_{44} anharmonicity constant for ν_4 in CTCl_3 is estimated to be -8.9 cm^{-1} , using Dennison's isotope shifting rule and X_{44} measured in CDCl_3 .⁽¹⁹⁾ This large anharmonicity in the pumped mode may well further lessen excited-state absorption in CTCl_3 . The wavelength dependence of CTCl_3 is presently being studied to further analyze this, using the tunable output of the NH_3 laser ($780\text{--}850 \text{ cm}^{-1}$). Note that CDCl_3 is extremely transparent from $815\text{--}842 \text{ cm}^{-1}$ so use of laser radiation (in single or dual frequency MPD) up to 20 cm^{-1} to the red of the ν_4 CTCl_3 peak is acceptable. In fact, the high power 12μ source obtained by rotational Raman scattering CO_2 laser radiation off of $\text{HD}^{(1)}$ is quite efficient at 815 cm^{-1} where the R(26), 9.2μ is used.

III. LASER DEVELOPMENT

The photolysis source for isotopically selective multiple photon dissociation of CTCl_3 currently is an optically pumped ammonia laser. While the recent literature⁽³⁾ aptly describes the qualitative aspects of the tuned resonator, the characteristics of superradiant NH_3 emissions are less well known. Studies involving superradiant emission imply that the primary emission line is at 828 cm^{-1} , the coupled $\text{sp}(7,k)$ transition. Initial MPD experiments attempted to make use of this 828 cm^{-1} emission from an untuned cavity, with negative results.⁽¹⁾ At this point an effort was undertaken to more fully characterize this laser system, since the actual operating parameters are configuration dependent.

Untuned NH_3 Laser

Initial experiments were aimed at optimizing both the 828 cm^{-1} as well as the total multi-line output. Figure 5 depicts an energy level diagram for NH_3 . The $\text{R}(30), 9.22\mu$ CO_2 laser pump line is displaced approximately 190 MHz from the $\text{sr}(5,0), \nu_2$ absorption in NH_3 . Pressure broadening with either N_2 or He serves to minimize the mismatch. Relaxation due to added buffer rotationally relaxes the initially pumped level and also results in V-V and V-T transfer. Taking the 1 GHz width of the CO_2 laser into account, addition of only moderate amounts of buffer tends to merge the various K sublevels such that $K=0-5$ are pumped simultaneously, enhancing the absorption by the increase in absorbing lines. By varying both the mixing ratio and the total pressure, the total output and/or the 828 cm^{-1} output can be optimized. The CO_2 pump line was focused $\sim 2\text{m}$ inside a 2.9 m long cell, dispersed through a monochromator, and terminated onto the pyroelectric detector. The dependence of total output versus both mixing ratio and total pressure is shown in Fig. 6. The 828 cm^{-1} output tracked the total output closely but surprisingly was only $\sim 5\%$ of the total emission. It is also apparent that the 2.9 m path length is sufficient to saturate the transition. Using a 1:40 mixture at 20 torr N_2 , the apparent pressure broadened absorption cross section of ammonia is $\sim 1.0 \times 10^{-19}\text{ cm}^2$ which results in 35% transmission. With 4 Joules of pump energy, E_0 (pulse fluence $\times$ absorption cross-section) is about 20 quanta, well in the saturated regime, and the output energy is somewhat insensitive to input energy.

The dispersed, superradiant output using both He and N_2 optimized buffer concentration is shown in Figs. 7 and 8. Switching from the 2.9 m to a 1.2 m cell did not significantly alter these distributions. Except for the emission from the initially pumped asymmetric $\text{R}(6,K)$ resonant transition at 828 cm^{-1} , the remaining strong emission

lines are identified as $v_2^S + 0^a$ transitions, i.e., originating from symmetric sublevels. This can be rationalized by invoking efficient $a + s$ collisional energy transfer or by postulating FIR emission from the v_2^a levels to the v_2^S levels (since FIR transitions have high optical gains). Such FIR emission has been recently observed in R(30) pumped NH_3 lasers.⁽²⁰⁾ The relevant energy levels responsible for the observed emission are shown in Fig. 4.

Tuned NH_3 Laser

Due to the low superradiant 828 cm^{-1} emission, the output characteristics of a simple, one pass tuned cavity were investigated, using 0.7 torr NH_3 /90 torr N_2 in a 1.2 m long cell. The ammonia laser resonator consisted of a grating, a totally reflecting 15 m radius concave mirror (in the cell arm), and a partially reflective 10 m concave output mirror. Varying the output coupler reflectivity from 35-70% did not significantly change the output power on the 828 cm^{-1} line. No radiation (<0.1%) was observed near 11.7, 12.0, 12.3, or 12.5μ , which are the strongest wavelengths of the NH_3 superradiant emission (Figs. 7 and 8). At 0.3 Hz repetition rate, an input power of 4 Joules [R(30), 9.22μ] in a 100 ns FWHM pulse ($\sim 1\mu$ s tail) produced $\sim 500\text{ mJ}$ output at 828 cm^{-1} . The temporal profile of the pulse consists of a double humped feature with a total FWHM of $\sim 1.5\mu$ s, which is virtually unchanged using either a 35% or 80% output coupler.

The 828 cm^{-1} pulse was focused into the center of an 86 mm long reaction cell by either a 25 or 50 cm focal length KCl lens. In certain photolysis runs, the fluence was doubled by means of a retroreflector. In a configuration using the 50 cm fl lens and a 40 cm radius of curvature retromirror, burn patterns on heat sensitive paper were measured in 2 dimensions using a microscope and reticle, at 5 positions along the cell length.

Additional Laser Studies

Further experimental work was done on the laboratory short pulse CO_2 laser system. The properties of a large scale 12μ laser system with $^{12}\text{C}^{16}\text{O}_2$ laser radiation Raman scattering in HD or D_2 $J=0$ molecules were also investigated.

Prior studies [referenced in (1)] show that Raman scattering is efficient in H_2 . Gain estimates for HD or D_2 scattering are equally promising. An oscillator-amplifier system may be used to obtain the $\sim 10\text{ kW}$ average pulsed power, that is estimated to be needed for T/D recovery at Savannah River. The oscillator would be a multi-pass

HD/D₂ cell pumped by 100 nsec long CO₂ laser pulses, that would deliver $\lesssim$ 100 nsec long 12 μ pulses (seeded by spontaneous Raman scattering). Other Stokes and anti-Stokes scattering processes have much lower gains; their quite weak beams could be further attenuated after the oscillator by (coated or non-coated) infrared transmitting windows placed in the beam path. This 12 μ seed beam is then directed into the amplifier, possibly collinearly with a strong CO₂ laser pump beam having a variable pulse width. The data portrayed in Fig. 4, obtained with 1.5 μ sec FWHM 12 μ pulses, suggests that 10-50 nsec long 12 μ pulses may selectively decompose CTCI₃ without severe quenching by $\sim$ 100 torr of added CDCI₃. (This relatively "long" pulse is advantageous since it becomes more difficult to efficiently extract energy from the CO₂ laser discharge when the desired pulse width is $<$ 5 nsec.)

Operation of this type of laser requires a large population of Raman scatterers in $J=0$. This necessitates operation at 77°K, where the fraction of molecules in $J=0$ are 0.61/HD, 0.59/D₂, 0.49/H₂ (ortho-para mixtures assumed for H₂/D₂). The cost of maintaining laser pumped hydro 77°K is relatively insignificant. For instance, if the CO₂ laser is 10% efficient, then an incident laser power of 10 kW requires 100 kW electrical energy. The steady state thermal load in the Raman scattering cell is mainly due to pumping HD from $J=2 \leftarrow 0$. With 10kW incident on HD and complete conversion of 9 μ to 12 μ , 2.5kW is absorbed. It is estimated that $\sim$ 15 kW refrigeration power is then required to maintain the medium at 77°K; this is quite small compared to the power required to drive the laser.

IV. PROCESS ENGINEERING

During this reporting period the overall process requirements for tritium recovery from the D_2O in the Savannah River Heavy Water Reactors were studied in detail. The specific details regarding the special requirements for tritium recovery at the Savannah River Plant (SRP) are discussed here along with the first (preliminary) complete process design for implementation at SRP.

Savannah River Plant: Overall Considerations

To obtain specific definition of SRP requirements for moderator detritiation, the Savannah River Laboratory (SRL) has been providing information on process requirements and potential implementation problems, including safety requirements for use of lasers and experimental substances (chloroform). Tritium handling, mobility of process hardware, construction and operation costs/benefits, plant size and location, and purity specifications for the detritiated moderator have also been considered. The last three items have been studied most exclusively at SRL thus far, with the *general conclusions* from this study detailed below.

The Combined Electrolysis and Catalytic Exchange (CECE), the Bipolar Electrolysis, and the Sulzer (catalytic exchange coupled with cryogenic distillation) detritiation processes have previously been considered for reduction of tritium inventory in the fission reactors at the Savannah River Plant. These processes were not used, primarily due to the high estimated cost of construction.

Potential economic advantages of a laser-based MPD process over other processes include reduction in containment and automatic shutdown equipment needed to handle the highly tritiated water streams. Calculations presented below indicate that none of the aqueous or organic streams in the MPD process have concentrations of tritium in excess of that found in the reactor moderator. The TCl/DCI photolysis product would contain $\sim 10^4$ Ci/L if isolated as a liquid; however, *current plans are to separate TCl/DCI from the photochemical reactor effluent (overwhelmingly $CDCl_3$) by formation of a metal tritide in a gettering bed*. While the tritium content will be high in the contained bed, immobilization of the tritium as a tritide will significantly reduce containment requirements since the activity of the most highly contaminated volatile process stream will be only ~ 4 Ci/L.

Two areas at SRP are possible sites for an MPD detritiation facility. Continuous (on-line) detritiation would require integration of MPD into the distillation area of each reactor. Some space exists inside the purification wing of each reactor for new equipment, but most of the MPD construction must be located outdoors and/or in a new

building. To retain access to the D_2O drum loading docks, any equipment outside the reactor building would probably be constructed over 100 ft from the distillation columns.

Siting of an MPD detritiation facility at a reactor may be accompanied by potential problems. The most detrimental would be possible chloride contamination of the reactor tank influent. Chlorides have been strictly forbidden in the reactor areas as a precaution in the prevention of stress corrosion cracking of stainless steel components. Stress corrosion cracking has been controlled by regulating moderator acidity and maintaining very low chloride levels. An on-line MPD process based on chloroform photolysis would require rapid, extensive monitoring to ensure that processed moderator is stripped of all chlorinated organics and chlorides.

Potential degradation of the carbon beds used to remove accidentally released radioactive iodine from the reactor building exhaust system could result from location of MPD process equipment inside a reactor building. Leakage from any volatile chlorinated stream would be trapped by material exclusively allocated for iodine removal.

Finally, cost might be prohibitive if on-line detritiation is pursued since three or four facilities would be needed. Cost could be significantly reduced by construction of one on-line system perhaps at C reactor with drum transport of moderator to and from P and K reactors.

An alternative would be construction of an off-line facility at the central moderator rework facility, where moderator processing is the exclusive function. Regulated drumming facilities are already in place for loading and unloading tritiated moderator as are laboratory facilities for quality control of the reworked moderator. Moderator to be detritiated could be passed through the MPD process on arrival at the central facility, stripped of any introduced hydrocarbon impurities, and analyzed before entering the feed step to the existing rework facility. Any detritiated moderator with abnormally high chloride content could be reprocessed through the stripping section of the MPD process. Space is available in the proximity of the rework facility distillation columns for construction of new equipment and buildings.

Regardless of the location of an MPD process, the detritiated moderator must meet stringent purity standards before it can be returned to the reactor tank. Regulation of moderator pD [$-\log(D^+)$] is crucial for control of turbidity (aluminum hydroxide formed by corrosion of fuel tube cladding). Turbidity figures heavily, along with chloride ions, in stress corrosion cracking of stainless steel. The exchange step between DTO and $CDCl_3$ in MPD is base-catalyzed so pD adjustment will be necessary following detritiation. Addition of HNO_3 should be satisfactory for this adjustment, but the ultimate conductivity, a measure of gross ionic impurities, must be carefully controlled in the reworked moderator.

Maximum chloride content for the final product of the MPD process unit would be about 0.1 ppm. Concentration limits for other anions have not been individually specified, but their aggregate contribution to the conductivity should be small so as not to interfere with the determination of pD. Organic materials, which might reduce the nitric acid used for pD control, must satisfy a qualitative limit to qualify for rework. Limits on chlorinated organics from MPD will need more careful definition since radiolysis of these materials in the reactors could release chloride ions.

Process Design

Tritium removal from heavy water based on MPD will require a process that includes the unit operations shown in Fig. 9. As discussed in previous reports,^(1,5) heavy water contaminated with tritium (DTO) is passed through an exchange unit where the tritium is exchanged with deuterated chloroform (or a similar working molecule). 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 be perhaps 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 some additional chloroform to replace that removed by the laser MPD process.

Estimated mass balances reported in earlier progress reports^(1,5) have been updated to more accurately reflect tritium recovery at Savannah River. Specifications are given in Table 1. Several assumptions made in the course of the calculation are shown in Table 2. Quite conservative photochemical parameters for chloroform photolysis are given in this table. The resulting system flows and power consumptions are shown in Table 3. The volumetric flow rates are modest, and the power consumption is small (involving an electricity cost of about \$25K per year at current rates).

In the detritiation process, the tritium concentration in chloroform will be roughly equal to that in the feed heavy water; tritium is concentrated to a higher isotopic purity only in the products from the photoreactor. Therefore the tritium concentration is sufficiently low in most process streams that containment problems will not be severe; Savannah River currently handles streams of similar tritium concentrations without unusual containment provisions. Only the photoproduct stream has a high tritium

TABLE 1. Initial specifications - Cleanup of Savannah River Plant Heavy Water Reactor.

Reactor volume:	690 tonnes D ₂ O
Tritium concentration:	20 Ci/liter
Desired Tritium level:	3.3 Ci/liter (17% of initial concentration)
Time allowed to reach desired level:	3 years

TABLE 2. Assumptions used in calculation of mass balance data shown in Table 3.

-
- o Chloroform flow in exchange unit is 130% of theoretical minimum.
 - o Photoproduct stripper efficiency is 100%
 - o Optical selectivity: S = 650 for laser-induced reaction
 - o Enrichment factor: β = 1000 for laser-induced reaction
-

TABLE 3. Process parameters for the cleanup of Savannah River Plant Heavy Water Reactor.

Heavy water flow through exchanger	2.6 liter/min (142 moles/min)
Chloroform flow through exchanger	15.0 liter/min (184 moles/min)
Protoproduct formation rate:	
TCl	0.02 cc/min (6 x 10 ⁻⁴ moles/min)
DCI	1.8 cc/min (0.06 moles/min)
C _x Cl _y	2.9 cc/min (0.03 moles/min)
Make-up chloroform flow	4.5 cc/min (0.06 moles/min)
Electric power to laser (1.25% efficiency)	55 kW
Pumping power (reactor at 100 torr, rest of process at 1 atm)	16 kW

concentration (about 1%) and must be treated carefully. If we can capture the tritiated products in a solid form by using a suitable selective absorbant (and this appears to be feasible), the hazards of handling the photoproduct stream will be greatly reduced. Tritium concentrations for each stream of the process are shown in Table 4.

TABLE 4. Tritium Concentration in Process Streams for Initial Operations.

1. Heavy water feed	DTO mole fraction = 1.24×10^{-5}	(20 Ci/liter)
2. Heavy water return	DTO mole fraction = 0.81×10^{-5}	(13 Ci/liter)
3. Chloroform from exchange unit	CTCl ₃ mole fraction = 1.11×10^{-5}	(4.1 Ci/liter for liquid CDCl ₃ ; 0.013 Ci/liter for gaseous CDCl ₃ at 300°K, 1 atm)
4. Chloroform from reaction tube	CTCl ₃ mole fraction = 0.77×10^{-5}	(2.8 Ci/liter for liquid CDCl ₃ ; 0.009 Ci/liter for gaseous CDCl ₃ at 300°K, 1 atm)
(Note: this stream also contains additional tritium as TCl as indicated in stream 5.)		
5. TCl/DCI product stream	TCl mole fraction = 0.011	(10 Ci/cc for liquid)
6. Organic product stream, containing mostly C ₂ Cl ₄ , perhaps some tritiated ethane. Tritium levels will be lower than for stream 5, since most reaction products will not contain hydrogen.		
7. Chloroform stream from photoproduct stripper - identical to stream 4, except that photoproducts have been removed.		
8. Chloroform makeup stream contains no tritium.		
9. Chloroform stream to exchange unit - virtually identical to stream 7.		

The process for water detritiation contains three individual units (the exchange unit, the reaction tube, and the photoproduct stripper) and a compressor; those four items constitute the major capital expense. Revised approximate capital costs for each item and for the integrated process are shown in Table 5. For the capital cost of \$415,000 and the electricity costs of \$75,000 for 3 years, the cost of tritium removal ($\sim 10^7$ Ci recovered) is about \$0.05/Ci (excluding laser costs). A discussion of each unit and their integration into an overall process is presented below.

TABLE 5. Approximate Capital Costs of Tritium Cleanup System for Savannah River Plant.

Exchange Unit	\$22,000
Reaction Tube	\$12,000
Compressor	\$32,000
Photoproduct Stripper	<u>\$20,000</u>
Cost of major units	\$86,000

Applying Lang factor of 4.8 (Peters and Timmerhaus, Plant Design and Economics for Chemical Engineers, 3rd edition, p 181) gives total capital cost estimate of \$415,000 (excluding laser cost).

Exchange Unit

In the exchange unit the tritium exchange between water and chloroform must be accomplished rapidly to minimize the size and holdup of equipment. A packed tower in which heavy water is in countercurrent flow with chloroform is the most likely configuration; the chloroform may be either liquid or gas. Since water and chloroform are mutually soluble to small extents, the streams leaving the tower will have to be purified.

In designing an exchange unit, the kinetics and equilibrium conversion must be determined for the tritium exchange reaction. The exchange reaction is catalyzed by sodium hydroxide; a few studies have indicated that the exchange reaction is rapid for chloroform dissolved in water (0.21 l/mole-sec at 20°C for D/H exchange).^(2,21,22) No results have been reported for tritium exchange between DTO and deuterated chloroform; the kinetics and equilibrium parameters are presently being measured here. With this information we can accurately assess the significance of mass transfer limitations vs kinetic limitations, and design the exchange unit packed tower accordingly. (For the cost estimate in Table 5, mass transfer was assumed to be limiting. Because of the small solubility of chloroform in water, the flows in Table 3 and the Exchange Unit cost in Table 5 may have to be increased accordingly.)

Design of the exchange unit is complicated by the formation of an azeotrope of chloroform and water at 56.1°C; the aqueous phase of the azeotrope contains 0.8% chloroform, and the organic phase contains 0.2% water. The azeotrope composition and temperature will be somewhat different for deuterated species. However, the presence

of the azeotrope will not cause severe problems, since it can be broken by physical separation of the two phases. In addition, the method of Nutting and Horsley⁽²³⁾ indicates that it can be broken by modest vacuum (~ 230 torr total pressure). Still, the azeotrope must be properly considered in designing the exchange unit.

Leaving the packed tower will be a chloroform stream with a small amount of water and a water stream containing chloroform and sodium deuteroxide. A molecular sieve dryer should adequately remove water from the chloroform; the heavy water can be recovered from the dryer by periodic bed regeneration.

The heavy water stream containing sodium deuteroxide and chloroform must be purified to stringent specification; to minimize reactor corrosion, Savannah River limits chloride ion concentration to a maximum of 100 parts per billion (ppb). To be conservative, one must assume that any chloroform reaching the reactor is decomposed. Therefore, to meet current Savannah River limits, the heavy water returning from the exchange unit must contain no more than 33 ppb chloroform ($200\mu\text{g/l}$). Water can be purified to this level by standard treatment with granular activated carbon, but the adsorbed capacity for chloroform at these levels is small.⁽²⁴⁾ Some means of pretreatment to reduce chloroform levels from its initial solubility in water of 0.5-1% to perhaps one-hundredth to one-thousandth of that will be necessary. Distillation and reverse osmosis are two possibilities for pretreatment. Perhaps the presence of sodium deuteroxide reduces chloroform solubility - - this would diminish the pretreatment problem. Further research into water cleanup is needed since it is clear that maintaining water purity is an important concern for this process.

Reaction Tube

A variety of reactor configurations will be considered to achieve efficient utilization of the laser pulse energy and maximum enrichment of T with respect to D. The desired extent of reaction for CTCl_3 and CDCl_3 , along with laser parameters such as pulse power, duration, and repetition rate, will determine the gas residence time in the reaction tube, and hence the reaction tube volume.

Present experimental results suggest that 20 J/cm^2 fluences will be needed to dissociate CTCl_3 at 12μ . Since infrared transmitting windows suffer damage at such high fluences, some laser focusing may be required inside the reaction tube, probably by curved copper-based mirrors. Further wavelength studies of one and two frequency MPD of CTCl_3 should, however, lower this fluence requirement.

Photoproduct Stripper

Photoproducts from the reaction tube take two major forms: C_xCl_y compounds and TCl/DCI. The removal of the two forms may be undertaken separately.

The C_xCl_y compounds (mostly CCl_4 and C_2Cl_2) may contain little tritium (some tritiated chlorinated ethanes may appear). These components will gradually build up in the recirculating chloroform. The solubility of these compounds in water is sufficiently high that all C_xCl_y formed could be removed by dissolution in water in the exchange unit, followed by removal from the water along with dissolved $CDCl_3$; then only a small distillation unit would be required to separate C_xCl_y from chloroform. Alternatively, a drag stream could be taken from the main chloroform flow and distilled to remove the C_xCl_y compounds. Either option seems practical at this point - - removal of C_xCl_y compounds should not be a problem.

The TCl/DCI formed in the reaction tube is corrosive (though not excessively so in the absence of water). In addition, if isolated as a separate stream, the TCl/DCI would have about 1% T, or about 10 Ci/cc liquid. Handling this corrosive, radioactive mixture directly as a liquid or gas is not desirable; if it could be converted to a solid, it could be easily recovered and transported elsewhere for tritium recovery. Two concepts have been identified for solidification of this stream, and will be investigated further. The first involves the reaction of TCl/DCI with a reactive metal or other substance to release T_2 or DT; the gaseous hydrogen isotopes would then be chemically captured by an organic getter and immobilized. In the second concept, a selective adsorbant removes TCl/DCI directly from chloroform. Bratolyubov and Solov'eva have removed HCl from liquid methyl chloroform using silica gel and a variety of other adsorbants;⁽²⁵⁾ the recovery of TCl/DCI should be straightforward once the suitable adsorbant for removal of TCl/DCI from $CDCl_3$ is found.

Process Integration

Several additional questions must be resolved to successfully combine these three major units into an integrated process. Some of these are discussed here.

The chemical stability of chloroform in the presence of water, sodium deuterioxide, tritium, and the various materials of construction is of obvious importance. Since deuterated chloroform is as costly as heavy water, the makeup requirements should be as low as possible. Chloroform is known to slowly degrade in the presence of sunlight or air;⁽²⁶⁾ this should not be a problem here, however, since chloroform will be contained

in an enclosed system which will exclude both. The hydrolysis of chloroform by water is catalyzed by hydroxide ion, fortunately the hydrolysis rate data of Hine and Dowell⁽²⁷⁾ indicate that hydrolysis losses will be very small, and in fact, less than 3% of the photolysis makeup requirement. Still, to minimize hydrolysis, the hydroxide ion concentration should be kept as low as possible (it is required in small amounts to catalyze the D/T exchange reaction). The stability of chloroform in metal systems is expected to be good, but the tritium radioactivity presents unexplored degradation mechanisms which must be studied. Our laboratory experience to date suggests that for the dilute chloroform mixtures of interest ($<10\text{ppm CTCl}_3/\text{CDCl}_3$), chloroform degradation should pose no problem.

Chloroform circulating through the process will be in the gas phase in the photo-reaction tube; however, it is not clear whether liquid or gas would be better for the rest of the process. Process volume would probably be smaller with liquid chloroform, but a condenser and evaporator would be needed. The kinetic and mass transfer rates in the exchange unit and the feasibility of TCl/DCl removal from gas or liquid chloroform will be major factors in selecting the optimum phase.

The operating pressure of the photo-reaction tube will have a major impact on system cost, because the single most expensive capital item is the compressor (Table 5). To illustrate the importance of this parameter, cost estimates for the compressor and the complete system for several reaction tube pressures are shown in Table 6. Decreasing reactor pressure from 10 torr to 1 torr increases the estimated system capital cost by 20%; therefore, in selecting the reaction tube operating pressure, system design and economics must be considered along with reaction physics and chemistry. Note that the experimental studies reported earlier in this document (Fig. 4) show that even with quite long 12μ laser pulses (1.5 μsec FWHM), the CTCl_3 decomposition probability does not decrease until total $\text{CTCl}_3/\text{CDCl}_3$ pressure reaches several torr. With easily obtainable shorter pulses, even higher pressure operation will be practical.

The presence of chloroform, water, sodium deuterioxide, TCl, DCl, C_xCl_y , and possibly other compounds requires a careful selection of construction materials. All cost estimates were based on the use of Type 316 stainless steel throughout; whether this is necessary (or even adequate) must be carefully determined.

As detailed in the previous section, constraints that must be considered in designing a detritiation unit for the Savannah River Heavy Water Reactor may include: construction specifications to give adequate tritium containment; limitations on unit size or overall process size because of limited available space; chemical purity of detritiated heavy

TABLE 6. Variation in System Estimated Capital Cost with Reaction Tube Pressure.

Reaction tube Pressure	Compressor Power	Compressor Cost	System Cost*
0.1 torr	113 kW	\$70,000	\$595,000
1 torr	70 kW	\$49,000	\$495,000
10 torr	39 kW	\$32,000	\$415,000
100 torr	15 kW	\$16,000	\$340,000

* System cost estimated using data from Table 5; only compressor cost is changing. System pressure is atmospheric except for reaction tube.

water; and overall cost. Of the above-mentioned factors, tritium containment should not be a serious problem, since, as mentioned above, most process streams do not contain concentrated tritium. The overall cost is considerably reduced or eliminated if the tritium can be recovered for further use; at \$1.00/Ci, the 10^7 Ci to be removed represent a large economic incentive for heavy water detritiation.

V. PRESENT PLANS

The wavelength dependence of CTCl_3 MPD will be investigated. Additional experiments will lead to a better understanding of nascent CTCl_3 decomposition and the subsequent chemistry. High power laser systems will be further developed.

All the areas discussed in the process engineering report (Section IV) need further study before definite process decisions can be made. Initial efforts will focus on the following:

1. Kinetics and equilibrium of the DTO/CDCl_3 exchange reaction. A summer student will undertake this work for us.
2. TCI/DCI removal for chloroform.
3. Purification of heavy water for return to reactor.
4. Chloroform stability under process conditions.

Future work at SRL will ascertain requirements for tritium and chloroform handling and containment, for laser safety, and for speed of recovery and desired ultimate concentrations of tritium. Cost/benefits, which will include an assessment of potential damage to reactor equipment caused by accidentally high chloride levels from the MPD process, will be further developed.

VI. APPENDIX

The fractional conversion of reagent to product per pulse is obtained by integrating the MPD probability, Eq. (6), over the region of the reactant cell intercepted by the laser to obtain V , and then dividing this by the cell volume.

With a flat-profiled laser focused in the center of a cell ($z=0$) of length, l , the cross sectional area of the beam at z , $A(z)$, and cumulative subtended volume from $-z$ to $+z$, $V_0(z)$, are:

$$A(z) \approx a + bz^2 \quad (A.1)$$

$$V_0(z) = 2az + \frac{2}{3}bz^3 \quad (A.2)$$

A pulse of incident energy U , will have a local fluence $\phi(z) = U/A(z)$. With $z_t \equiv l/2$, an axial parameter z_c may be defined as:

$$\begin{aligned} z_c = 0 & \quad \frac{U}{\phi_c} < a \\ \sqrt{\frac{\frac{U}{\phi_c} - a}{b}} & \quad a + bz_t^2 > \frac{U}{\phi_c} > a \\ z_t & \quad \frac{U}{\phi_c} > a + bz_t^2 \end{aligned} \quad (A.3)$$

V may be written as

$$V = V_0(z_c) + V_1(z_t, z_c), \quad (A.4)$$

where the first term is the contribution for $|z| < z_c$ and $\phi > \phi_c$ so $P=1$, and the second term gives the reaction volume from $\pm z_c$ to the ends of the cell using the power law dependence of Eq. (6).

V_1 is given by

$$\text{for } m = 1 \quad V_1 = 2\left(\frac{U}{\phi_c}\right) (z_t - z_c)$$

$$m = 2 \quad V_1 = \frac{2}{\sqrt{ab}} \left(\frac{U}{\phi_c}\right)^2 \left[\tan^{-1}\left(\frac{z_t}{c}\right) - \tan^{-1}\left(\frac{z_c}{c}\right) \right]$$

$$\begin{aligned}
 m > 2 \quad V_I = & \frac{2}{b^{m-1}} \left(\frac{U}{\phi_c} \right)^m \left[\sum_{k=1}^{m-1} \frac{1}{(2c)^k} \frac{(m-k-1)!}{(m-1)!} \frac{(2m-3)!!}{(2m-2k-1)!!} \frac{x}{(c^2 + x^2)^{m-k}} \right. \\
 & \left. + \frac{1}{(2c)^{m-1}} \frac{(2m-3)!!}{(m-1)!} \frac{1}{c} \tan^{-1} \frac{x}{c} \right] \frac{z_t}{z_c} \quad (A.5)
 \end{aligned}$$

where $c \equiv \sqrt{\frac{a}{b}}$.

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FIG. 1. The infrared spectrum of CTCl_3 synthesized by $\text{CDCl}_3/\text{T}_2\text{O}/\text{OD}^-$ exchange. In this undiluted sample about 25% of the chloroform is tritiated.

FIG. 2. Reactant depletion vs number of irradiating pulses for CTCl_3 and CDCl_3 with a 25 cm focus with retroreflection (200 mtorr, 200 ppm T/D, 460 mJ net pulse energy), and for CTCl_3 with a 50 cm focus (200 mtorr, $\eta = 200$ ppm, 505 mJ net laser pulse energy).

FIG. 3. CTCI₃ decomposition vs laser pulse energy (200 mtorr, 200 ppm T/D, 50 cm focal length lens).

FIG. 4. CTCl_3 dissociation probability vs added CDCl_3 with either 270 mJ or a net 535 mJ per pulse incident (see text for details).

FIG. 5. Energy level diagram of the NH_3 laser.

FIG. 6. The dependence of total untuned NH_3 laser output versus the mixing ratio of $NH_3:N_2$ and the total pressure.

FIG. 7. Dispersed superradiant radiation from an NH_3 laser with He buffer added to obtain maximum output. Total pressure is 65 torr and NH_3 : He = 1 : 50.

FIG. 8. Dispersed superradiant radiation from an untuned NH_3 laser with N_2 added to optimize output. The total pressure is 40 torr and $\text{NH}_3 : \text{N}_2 = 1 : 40$.

FIG. 9. Process flow diagram for tritium recovery by MPD of chloroform, with flow streams labelled as in Table 4.