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Infrared Multiphoton Decomposition and the Possibilities of Laser-Based Heavy Water Processes

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Abstract

The selective multiphoton decomposition (MPD) process has the potential to provide a stand-alone heavy water process which is competitive with conventional processes. Twelve criteria are discussed for selecting a working molecule to give a process economically competitive with the Girdler-Sulphide process. The dependence of the MPD process on interacting parameters such as laser fluence, intensity and bandwidth as well as collisional effects are discussed. Finally, several potential working molecules are reviewed.

1 Introduction

Since the early 1970's, laser-based isotope separation processes have been the subject of much scientific study. However, almost 20 years after multiphoton decomposition (MPD) was first reported [1], no production scale laser-based separation plant exists. The atomic vapour laser isotope separation (AVLIS) uranium process appears poised to challenge the conventional process of gaseous diffusion and the newer gaseous centrifuges for a place in uranium enrichment; but to what extent laser-based processes will displace conventional enrichment methods for other isotopes is unknown.

Next to uranium, the largest market for isotope enrichment is the production of reactor-grade heavy water, however, the problems associated with laser isotope separation (LIS) of hydrogen isotopes are quite different from those of uranium enrichment. For instance, deuterium is enriched from one in 7000 in the feed to 99.8% in the product. This compares to only 4-fold enrichment of the relatively abundant isotope, ^{235}U, in natural uranium, from one in 140 up to about 3% in the product. The value of the enriched uranium is also much higher than that of D_2O. Thus with deuterium LIS, isotopic selectivity and photon utilisation are of much greater concern. With uranium enrichment, the isotope shifts are only fractions of a wavenumber compared to tens or hundreds of wavenumbers for deuterium containing molecules; the advantages of this larger shift for hydrogen/deuterium is offset by the anharmonicity of the pumped mode. In uranium LIS, therefore, power broadening can seriously degrade the selectivity but such is not usually true for hydrogen LIS. In fact, in the latter, power broadening transitions may give access to more rotational levels and overcome anharmonic bottlenecking, thereby increasing the fraction of molecules excited to decomposition. Also, because of the low cost of competing heavy water production processes, visible/UV lasers cannot be used for deuterium LIS, unless the efficiency of those sources increases greatly. For reasons such as these the emphasis of much of the underlying research for deuterium LIS is quite different from uranium LIS.

The criteria for an economic heavy water process, based on selective MPD, are examined in this review. The parameters controlling MPD are often strongly coupled in the sense that the effects of one parameter are difficult to distinguish from those of another. These problems, where they are relevant to isotope separation, are discussed and a number of experiments that have been devised to deconvolute the effects of interacting parameters are reviewed.

1.1 Conventional D_2O Processes

Most of the world's current inventory of heavy water was made using the Girdler-Sulphide (GS) process [2]. In this process water is exchanged with gaseous H_2S in bithermal countercurrent ex-

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change towers. Construction of a new GS plant would produce expensive D_2O. The major market for D_2O is as moderator and coolant for CANDU type reactors and there is a need for an alternative, inexpensive large-scale D_2O process.

Other D_2O exchange processes include bithermal (H_2/H_2O) exchange, ammonia (H_2/NH_3) exchange, and amine (H_2/CH_3NH_2) exchange. With the exception of the H_2/H_2O process, for which suitable catalysts have not yet been developed, these exchange processes are all currently parasitic to some other industrial process [2].

Several hybrid methods, such as the Combined Electrolysis and Catalytic Exchange (CECE) and the Combined Industrially Reformed hydrogen and Catalytic Exchange (CIRCE) processes could produce D_2O at a substantially lower cost than the GS process. But, because they are parasitic to other industrial processes, they are both limited in scale and vulnerable to external market forces.

The interest in LIS techniques arises from the possibility that this approach could provide an economic stand-alone plant producing D_2O cheaper than a new GS plant.

1.2 Laser-Based D_2O Processes

Many laser-based D_2O processes have been proposed over the years. For a variety of reasons, most of them have been ruled out as economically viable alternatives to the GS process. In most instances, either the photons used to do the separative work are too expensive or the isotopic selectivity of the process is too low.

One such laser-based process is the selective predissociation process, illustrated schematically in Fig. 1a. Selective vibronic excitation followed by predissociation is possible if the predissociative state is *sharp* enough to show isotopic selectivity and if the predissociation occurs faster than collisional degradation of selectivity. The earliest observation of this process was for separation of carbon isotopes using H_2CO [3-7]. The $\tilde{A}$ state of formaldehyde predissociates giving H_2 and CO products. Although this scheme may potentially be a useful way of separating carbon isotopes it is not suitable for D_2O for various reasons: the cost of generating UV laser photons is prohibitively expensive; H_2CO undergoes explosive polymerization at pressures above 1.3 kPa and formaldehyde is not easily redeuterated by exchange with water or methane.

A second method is the selective two-step process [8,9], illustrated in Fig. 1b. In this process a specific isotopic species, in a mixture, is excited vibrationally, with an infrared (IR) laser. A visible or UV photon then further excites the molecule to dissociation. The energy of the visible or UV photon is not large enough to cause absorption from thermally populated ground state vibrational levels. This method was initially considered for use directly on water but the dissociation of water does not have a sufficiently sharp spectral onset. Furthermore, the products of water photodecomposition are free-radicals which react with undecomposed water degrading isotopic selectivity and, again, visible or UV laser photons are currently too expensive.

Another laser-based process, still under active investigation, is the selective infrared MPD (Fig. 1c) process [1,10-14]. A specific isotopic species, in a mixture, absorbs successive IR photons until its internal vibrational energy exceeds the dissociation threshold of the ground electronic state. The isotopic selectivity is provided by the first few absorption steps and can, therefore, be much higher than a one-photon optical selectivity. IR photons, if provided by a high efficiency laser (CO_2 or HF for instance), may be inexpensive enough to allow economic production of a low cost isotope such as deuterium.

2 Selective MPD as a Potential D_2O Process

The largest deuterium sources are water and methane. However, these molecules are very difficult to decompose by MPD. An intermediate, or *working molecule* (WM), must therefore be used for selective MPD. The depleted WM is redeuterated by exchange with a deuterium source so that it can be reused. The criteria for selecting a working molecule for an economic, relative to a new GS plant, laser-based process are reviewed below. The criteria for selection of WM's are minimum requirements to give D_2O from a LIS process roughly comparable in cost to that from a new GS plant. It is expected that successful WM's will be significantly better than the minimum requirements in some criteria and thereby yield a LIS process significantly cheaper than the GS process.

(i) ***The WM should have selective absorption near an accessible laser line.*** This is largely an economic and operational requirement, as coherent light can, in principle, be generated at almost any wavelength. For D_2O production, the allowable costs require a high power, inexpensive and efficient laser.

(ii) ***Maximize photon efficiency ϵ_p.*** The photon efficiency can be approximated [12] in terms of the optical selectivity, $S(\phi)$, defined as the ratio of the measured absorption, at fluence ϕ, of the deuterated to the protiated WM, and δ, the fraction of the molecules containing a deuterium by

$$\epsilon_p = \left[1 + \frac{1}{\delta S(\phi)}\right]^{-1} \tag{1}$$

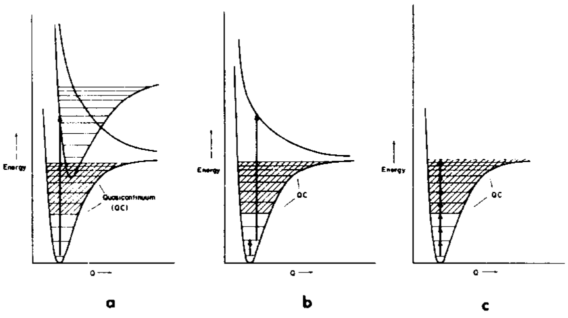

Figure 1: a. Selective, one-photon predissociation process; b. Selective two-step, two-photon, process; c. Selective MPD process

An economic process requires $\epsilon_p \geq 0.2$. For natural abundance deuterium in hydrogen this defines the lower limit for the required optical selectivity to be 10^3. The efficiency, ϵ_p, can be improved for molecules containing multiple equivalent hydrogens where δ is greater.

(iii) *Minimize WM makeup costs.* The WM makeup, R (in units of kg of WM per kg of D_2O produced), can be defined in terms of β, the heads separation factor, and δ by

$$R = \frac{M}{10\epsilon_x}\left[1 + \frac{1}{\delta\beta}\right] \qquad (2)$$

where M is the molecular weight of the working molecule and ϵ_x is an extraction efficiency which equals 1.0 if the deuterium enriched photoproduct, can be completely separated from the parent molecules. If β is less than 10^4, then so many working molecules will be destroyed for each deuterium atom separated, that makeup costs would be unacceptable [12]. Again as in (ii), this can be improved if δ is increased by multiple equivalent hydrogens.

(iv) *The bulk cost of WM $\leq$ \$ 2/kg.* For example a WM with one hydrogen, a β of 10^4 and a molecular weight of 100 amu will have a makeup cost of \$ 34 per kg of D_2O produced, given a bulk WM cost of \$ 2/kg.

(v) *Deuterated products must be easily separated.* The stable deuterium enriched product(s) should be sufficiently chemically different from the WM to reduce the problem of isotope separation to one of chemical separation.

(vi) *The WM should have a vapour pressure $\geq$ 13 kPa at or near room temperature.* This criterion comes from a consideration of the cost required to move the WM through the optical system. This will be the sum of the cost required to get a pressure of the WM that can be economically pumped, plus the cost of that pumping. However, the costs associated with pumping gases escalate rapidly as the gas pressure is lowered much below 13 kPa [15], hence the criterion.

(vii) *The WM should be relatively non-toxic and non- explosive.*

(viii) *Chemical exchange with a bulk feed-source of deuterium must be rapid, and nondestructive of WM's.* The WM must undergo a rapid, and relatively inexpensive redeuteration step with water or methane. At the same time, significant WM destruction by reaction with the bulk source, hydrolysis for instance, cannot be tolerated. Redeuteration is a major consideration in the design of a process and will likely be up to 25% of the cost of a heavy water process.

(ix) *The WM must undergo efficient MPD at intensities less than those which damage optical materials.* Laser intensity must be kept low for several reasons. Operationally, high intensities damage optical components and thereby complicate the design of a photolysis cell. To minimize collisional degradation of selectivilty, at pressures > 13 kPa, most likely short, intense laser pulses will be required. To reduce the problem of laser damage, WM's should undergo MPD at low fluences, a few J/cm^2, so the intensity of the short pulse will not exceed damage thresholds.

(x) *The MPD products must preserve the initial selectivity.* If the nascent MPD products are free radicals or stable molecular species which freely exchange the deuterium with the remaining WM's, then separative work will be lost. Free radical chemistry is potentially acceptable if a suitable means of preserving the selectivity can be found. One possibility is the use of efficient scavengers, but at the cost of increased system complexity. If the deuterium occurs in a stable, non-exchanging, product then the other products of the photochemistry may be free-radicals. One of the early promising molecules studied was fluoroform, CDF_3, which undergoes the following reactions.

$$CDF_3 \xrightarrow{nh\nu} CF_2 + DF \qquad (3)$$

$$2CF_2 \longrightarrow C_2F_4 \qquad (4)$$

The CF_2 radicals combine cleanly to form tetrafluoroethene and do not have any effect on the selective enrichment in the DF [12,16,17]. Similar chemistry is seen in $CDCl_3$ MPD [18-23]; but selective MPD studies have not been done.

An example of one approach to determining a reaction mechanism is a MPD study of isotopic variants of ethanol [24,25], in the presence of a scavenger. This work was aimed at elucidating the relative roles of the suggested decomposition channels:

$$CH_3CH_2OH \xrightarrow{nh\nu} CH_2CH_2 + H_2O \qquad (5)$$

$$\xrightarrow{nh\nu} CH_3 + CH_2OH \qquad (6)$$

$$\xrightarrow{nh\nu} CH_3CHO + H_2 \qquad (7)$$

$$\xrightarrow{nh\nu} CH_4 + CH_2O \qquad (8)$$

$$\xrightarrow{nh\nu} CH_3CH_2 + OH \qquad (9)$$

In particular, the question arises whether ethene is produced from a concerted molecular elimination or from a subsequent elimination of hydrogen from hot ethane formed from two methyl radicals. When the isotopic form CH_3CD_2OH was decomposed, analysis of the products using a gas chromatograph/mass spectrometer showed only CH_2CD_2 and no CH_2CH_2. This suggests that the principle source of ethene in the decomposition of ethanol is from the concerted reaction [25].

(xi) *The potential WM must have suitable non-linear optical properties.* If there is self focussing or defocussing of the laser beam, then the beam characteristics will vary along the optical path. In many instances a constant laser fluence over long distances would greatly simplify optical design so that self focussing is potentially useful if the beam is reduced in size by just the right amount to maintain the fluence in the presence of absorption or other losses.

A generalization of the theory of self-focussing was formulated for MPA of CDF_3 [26]. It shows the beam variation available, depending on the laser frequency, compared to the *optical centre of gravity* of the transition. The effect on the beam is a combination of the focussing or defocussing resulting from anomalous dispersion near the absorption frequency. In a study of the propagation of CO_2 laser beams through CDF_3, it was possible to change from self-focussing through a null effect to self-defocussing by varying the fluence.

(xii) *Other Factors.* There are a number of chemical properties of molecules which can have a profound effect on the utility of any potential D_2O LIS process. Among these are: WM isomerization, below the dissociation threshold, such as takes place with $C_2H_2Cl_2$ [27]; and dimerization or polymerization. These can act as a "sink" for laser photons, or reduce the photon efficiency.

3 Underlying Studies of Potential WM's

Investigation of MPD with a view to developing a LIS process involves a variety of parametric studies to determine which variables are the most important for promoting efficient MPD and obtaining the desired enrichment. The influence of the multitude of variables on MPD is often difficult to fathom because these variables are inherently coupled. For instance, with a conventional laser, the fluence ϕ cannot be changed without a concomitant change in intensity I_L. The pulse duration of a laser, τ_L cannot be changed without a change in laser bandwidth, $\Delta\nu_L$. The intensity of a laser cannot be changed without power broadening transitions, to some extent. In some pressure regimes, τ_L cannot be changed without affecting the number of molecules that interact with the beam; due to rotational relaxation and intermolecular V-V effects. As already mentioned, because of non-linear effects in high laser-intensity regimes, the target molecules can affect the spatial and temporal characteristics of the laser which, in turn, affects ϕ and I_L.

In the following section some methods of deconvoluting the influence of some important coupled parameters are examined. Note that these are only examples of parametric dependences and all possible interactions must be considered.

3.1 The Interaction Between Fluence and Intensity

When ϕ is increased, for a given laser pulse duration, I_L also increases so that an ambiguity exists in deciding whether the MPD is fluence (J/cm^2) or intensity (W/cm^2) dependent. Dependence of MPD on I_L can be determined from experiments at constant ϕ but different I_L. If the CO_2 laser has a single longitudinal mode (SLM) output, then the

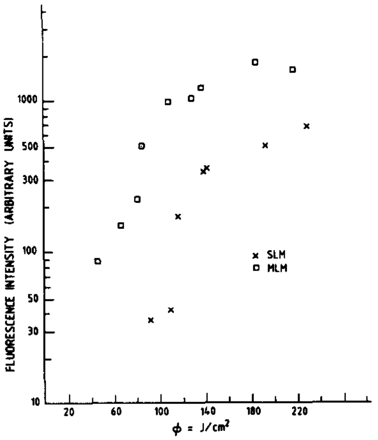

Figure 2: Integrated Fluorescence Intensity vs CO_2 Laser Fluence for different pulse intensities under collisionless conditions.

MPD or MPA induced by SLM compared to multilongitudinal mode (MLM) pulses can be compared. MLM pulses are more intense than SLM pulses because of mode beating which is seen as *spiking* of the laser pulse in the time domain. The increase in intensity is approximately equal to the SLM intensity multiplied by the number of modes that are beating together [28]. It is also important to perform such experiments under collisionless conditions if possible. Collisions can mask the effects of an intensity dependence [29], if the collisions augment MPD or exaggerate an intensity dependence if the collisions are deactivating.

Figure 2 shows the results of one such experiment [30] on the MPD of CH_3NH_2. This experiment was carried out using a pulsed supersonic expansion so that the effects of collisions on MPD could be ignored. The methylamine was coexpanded with helium achieving rotational cooling to approximately 5 K. The MPD was monitored by observing NH_2 fragment fluorescence. The probe laser was a Nd:YAG pumped dye, synchronised to a CO_2 pump laser (9P(22) line). The points in Fig. 2 represent the integrated intensity of 6 rotational transitions in the $\tilde{A}^2A_1$ (0,9,0) $\rightarrow$ $\tilde{X}^2B_1$ (0,0,0) vibronic band of NH_2. There is a very pronounced effect of I_L on MPD of this molecule, an order of magnitude or more at the lower fluences in Fig. 2.

The origin of this intensity dependence is not clear, but because CH_3NH_2 is a small molecule, with many high frequency vibrations, quasicontinuous behaviour may not appear until a high level of vibrational excitation is achieved. Hence, anharmonicity bottlenecking in the discrete lower levels is one possible origin of the intensity dependence. Alternatively, since the excitation of CH_3NH_2 is in the Q-branch, where different rotational bands cluster, power broadening may allow a larger fraction of molecules to be accessed by the CO_2 laser. It is not yet possible to say which of these factors is responsible for the observed intensity dependence.

3.2 The Interaction Between Intensity and Bandwidth

When I_L is changed, by going from SLM to MLM pulses, by temporally chopping out square wave portions of the laser pulse with an electrooptic switch, or by truncation with a plasma shutter, the conjugate frequency bandwidth, $\Delta\nu_L$, is also changed. It is possible that the change in $\Delta\nu_L$ due to modifying the laser pulse temporally can affect MPA or MPD.

Generally, lasers used in early MPD studies had an initial spike, of between 100 and 200 ns duration, followed by a low intensity tail which could last several microseconds. The laser pulses were MLM, with the attendant intensity fluctuations. Early studies of larger molecules showed that MPD seemed to be only fluence dependent. As better CO_2 lasers, with smooth SLM pulses, became available studies on smaller molecules showed that the laser pulse characteristics were important factors in MPA and MPD. In studies of SF_6 MPA, there had been a controversy about whether the excitation was dependent on ϕ or I_L. Instead it was found, that the MPA was significantly dependent on $\Delta\nu_L$ [31].

3.3 Collisional Energy Transfer

Most parametric studies of MPD involve experiments that take place in the collisional regime. For studies that require many laser pulses in order to see a measurable decomposition yield, a major point, not usually emphasised in such studies, is that the composition of the mixture changes from pulse to pulse. Gas partial pressures change during the pulse because of product formation. The products, in turn, can enhance MPD, inhibit MPD or, perhaps, have no effect on MPD depending on whether they absorb the CO_2 laser photons and are vibrationally excited themselves, and on whether V-V energy transfer is efficient. It is important that the effect of collisions is well understood because of the significant impact that it may have on isotopic selectivities in an LIS process.

Intermolecular transfer of vibrational energy will generally have a negative impact on isotopic selectivity and will be pronounced when one of the isotopes is very dilute, as in deuterium enrichment; except under unusual circumstances, such as when the buffer gas is an inert monatomic [32].

Although collisions significantly complicate the MPD picture, it is possible to get an idea of the relative importance of different collisional processes using a new method of analysis [23]. This analysis is briefly outlined below and its implications for the MPD of $CDCl_3$ discussed.

In general, to observe any measurable change in decomposition in an MPD experiment, a cell filled with the sample target molecule must be irradiated with a large number of pulses. The total number of target molecules left after m pulses, N_m, is:

$$N_m = Nc\prod_{i=1}^{m}(1 - \frac{Vo}{Vc}f_i(\phi_i, a_{i-1}, b_{i-1})) \qquad (10)$$

where Vo is the cylindrical optical reaction volume, Vc is the total cell volume, Nc is the initial number of molecules in the cell and $f(\phi, a, b)$ is the decomposition probability per pulse: a function of fluence, the partial pressure of the target gas, a, and the partial pressure of the fragments, or buffer molecules b (all the various fragment molecules are treated as a single entity for $CDCl_3$ decomposition).

The target gas partial pressure after m pulses, a_m, is given by:

$$a_m = \frac{N_m}{Nc}a_0 \qquad (11)$$

The buffer gas pressure can be computed from:

$$b_m \propto (a_0 - a_{m-1}) \qquad (12)$$

The proportionality constant depends on the stoichiometry of the decomposition. For example, where one volatile fragment is produced for each molecule decomposed the proportionality constant equals one.

The decomposition probability can be fitted to a power series of the form:

$$f(\phi, a, b) = \sum_{i=1}\sum_{j=0} h_{ij}(\phi)a^{i-1}b^j \qquad (13)$$

The pressure dependence can be understood in terms of three processes: rotational hole filling, and the V-V processes; circumvention of an anharmonic bottleneck and vibrational energy pooling. The pressures investigated in these studies were in the regime where V-V effects must be considered (above $\approx$ 0.1 kPa). It is useful to associate the h_{ij} parameters with Lindemann-like collision reactions, for example vibrational energy pooling can be described by:

$$A \overset{h\nu}{\Longrightarrow} A^*$$

$$\left.A^* \overset{k_1^*}{\Longrightarrow} B\right\}h_{10}$$

$$\left.\begin{array}{ccc} A^* + A^* & \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} & A^{**} + A \\ A^{**} & \overset{k_1^{**}}{\Longrightarrow} & B \end{array}\right\}h_{20}$$

Collisions with the reaction fragments can also effect the energy of the target molecule. In this instance the fragment C_2Cl_4 also absorbs at the wavelength used to decompose the target $CDCl_3$ so that it too is hot. It can transfer some of its vibrational energy to the target through collisions of the type:

$$\left.\begin{array}{ccc} B & \overset{h\nu}{\Longrightarrow} & B^* \\ A^* + B^* & \underset{k'_{-2}}{\overset{k'_2}{\rightleftarrows}} & A^{**} + B \\ A^{**} & \overset{k_1^{**}}{\Longrightarrow} & B \end{array}\right\}h_{11}$$

where, in the above collision sequences, the superscript *'s indicate a generalized excitation energy distribution due to photon absorption or collision. The k_1 is the energy dependent unimolecular kinetic rate constant and the k_2's are generalised bimolecular rate constants. The model parameters associated with each reaction are also listed. For an h_{ij} the sum of $i+j-1$ is the number of collisions in the reaction sequence where i molecules of A and j molecules of B collide. For example, in a collisionless environment, only the sequence identified here by the h_{10} term would take place. The process of overcoming an anharmonic bottleneck can be described using the above sequences if, after each collision, the possibility of further photon absorption is included.

Chloroform-d was chosen as a model system to study these interactions because it was considered as a potential working molecule for heavy water LIS and because it has simple photochemistry. At low to moderate CO_2 laser fluences, $CDCl_3$ decomposes to form DCl, which is not volatile at ambient temperatures, and, among other things, C_2Cl_4. This latter decomposition product absorbs the same light as the $CDCl_3$ producing a hot fragment that might be expected to have an effect on MPD in a collisional regime after a substantial number of products have built up.

The results of a MPD study of chloroform-d in the pressure range 0.3 to 2.0 kPa is shown in

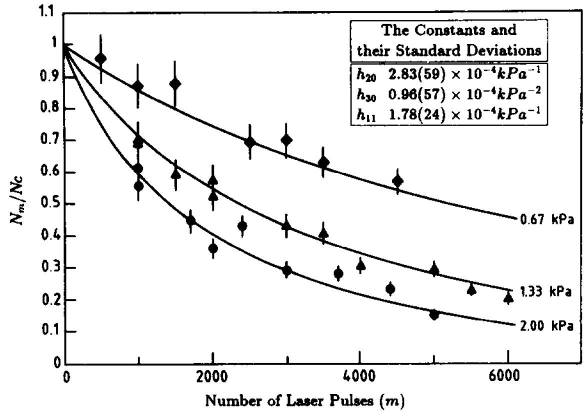

Figure 3: Fraction of $CDCl_3$ remaining versus number of pulses for various initial pressures of $CDCl_3$. The initial pressures in kPa are represented by a, ◆ for 0.67, ▲ for 1.33 and • for 2.00 respectively.

Figure 3. The table in the figure gives the coefficients of the power expansion determined from a fit of the experimental data to eqns (10-13). The calculated values of N_m/Nc, given the best fit parameters, appear as continuous lines in the figure. The startling result of these experiments is that the h_{10} coefficient is insignificant. Previous studies of $CDCl_3$ decomposition generally used a first-order-kinetic analysis which assumed that the average decomposition probability per pulse, which can be related to $f(\phi, a, b)$, is independent of pulse number. Further analysis shows that this is not true generally, and that a kinetic scheme is not appropriate for these pulsed photodecomposition processes. All of the decomposition that takes place, at the fluences used in this study, $\approx 8 J/cm^2$, is caused by higher order collision processes. Because of the pressure regime studied the results cannot be explained by rotational hole-filling alone.

The above results, of course, have profound implications for any heavy water LIS scheme based on this molecule. If the h_{10} sequence does not produce a significant amount of the product, then there is a likelihood of isotopic scrambling in the production of DCl because of the importance of collisions in the decomposition. In addition, in a natural abundance mixture, the most likely process for a vibrationally excited chloroform-d molecule to undergo is vibrational deactivation by undeuterated chloroform, since it is outnumbered by a factor of 7000 to 1. This will make it much harder to pump chloroform-d to decomposition.

This analysis also predicts that the collisional mechanisms leading to decomposition are dependent on ν_L. If a laser line is used which is absorbed by the parent molecule but not absorbed by the buffer, for instance, one would expect the h_{11} terms to be negative.

Experiments are under way with other potential working molecules, in collisional regimes, where many of the parameters are different than in the chloroform case, to test the predictive capability of this model. It serves to show how many different parameters, normally thought to be independent, are indeed strongly coupled.

4 Synopsis of Studies of Potential Working Molecules

Over 200 molecules have been considered for a D_2O LIS process. They have been evaluated on the basis of the criteria given in section 2. Many of these were eliminated relatively easily and a short list of approximately 20 molecules was established for further study. Table 1 lists 6 of the promising molecules that are under active investigation. They are ranked on a scale of -3 to +3 depending on the degree to which they satisfy the respective criteria; -3 being highly unfavorable and +3 being highly favorable.

Molecules were removed from the list based on

Table 1: Six Potential Working Molecules

Criteria	TCE	MeOEt	AcOH	TBOH	EtOAc	TBME
i. Sel.Abs.	+3	+3				
ii.,iii Max ϵ_p, Min R						
Opt Sel.	+1					
Heads Sep						
Symm Eqv H's	+1	+2	+1	+3	+1	+3
iv. Bulk Cost	+3	+3	+1	+2	+3	+1
v. Sep. Chem	+1		+2		+1	+1
vi. Vap. Press	+1	0	+1	0	0	+2
vii. Tox./Expl	+1	+3	+1	+1	+1	+1
viii. Chem Exch.	-1	+1			+1	
ix. Fluence Dep.	+1	-1	+2	+2	+3	+1
x. Stab of Prod.	+2	-1	-1	+2	+2	+3
xi. Non lin Opt						
xii. Others						

Where the following abbreviations have been used: TCE, CH_3CCl_3; MeOEt, methylethylether; AcOH, acetic acid; TBOH, $(CH_3)_3COH$; EtOAc, ethyl acetate; TBME, t-butyl methylether

extreme expense, non-volatility or extreme danger of handling. Next, molecules with simple photochemistry were sought. Research is currently under way to fill in the gaps in knowledge in Table 1. The molecules in Table 1 satisfy most of the criteria, to greater or lesser degrees, but a strongly unfavorable rating for any criterion would rule a molecule out from serious consideration for a heavy water LIS process. In the absence of any other information it would seem that first consideration should be given to molecules with a large number of symmetry equivalent hydrogens, because of the dramatic effect δ has on both photon efficiency and WM makeup costs.

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