D_2O PRODUCTION BY LASER-INDUCED SELECTIVE MULTIPHOTON DECOMPOSITION

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INTRODUCTION

All of the Canadian (and most of the world's) production of heavy water is done by the Girdler Sulphide (GS) H_2S/H_2O exchange process (1). This process requires both a large energy investment (36 GJ/kg D_2O) and the handling of large quantities of H_2S. The heavy water production of existing GS plants is expected to be insufficient to meet the demand created by new CANDU reactors, around the turn of the century. This could provide an opportunity to introduce a new heavy water process technology. The competing stand-alone heavy water processes include: a new GS plant; a yet to be developed bi-thermal H_2O/H_2 exchange process; and a laser-induced process - based on selective multiphoton decomposition (MPD). In addition, there are several parasitic methods (i.e. processes coupled to other industrial processes) of limited production capacity, such as the well-defined ammonia/H_2 process, the Combined Industrial Reformed hydrogen Catalytic Exchange (CIRCE) process, and the Combined Electrolysis Catalytic Exchange (CECE) process. The latter two are nearing the pilot plant stage.

As an alternative to the more conventional processes, lasers can be used to separate isotopes. The atomic vapour laser isotope separation (AVLIS) uranium process (2) is the most highly developed of these laser-based schemes and appears to be competitive with gaseous diffusion and the newer advanced gas centrifuge methods for ^{235}U enrichment. Its proponents claim that it will eventually produce enriched uranium for reactor fuel more cheaply than either of the non-laser based methods, but these claims have not yet been realized.

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 of hydrogen isotopes are quite different from those associated with uranium enrichment. For instance, deuterium is enriched from one in 7000 in the feed to 99.8% in the product compared to only a 4-fold enrichment of the relatively abundant (one in 140) ^{235}U isotope. Furthermore, the value of enriched uranium is much higher than that of D_2O. A laser-based deuterium enrichment process is subject to much more stringent economic constraints than a uranium process. These constraints make the AVLIS process too expensive for deuterium production for many reasons; but primarily because of the cost of producing a vapour of hydrogen atoms and the cost of ultraviolet photons.

In 1971 it was discovered that molecules could be dissociated by the successive absorption of infrared photons (3) and since then multiphoton decomposition (MPD) has been the subject of much scientific study. Isotope separation was soon recognized as a potential application of this phenomenon (4), and a new acronym, MLIS, was coined for the new process of <u>molecular</u> <u>laser</u> <u>isotope</u> <u>separation</u>. However, almost 20 years after the phenomenon was first reported, no production scale laser-based separation plant exists, although MLIS pilot plants do exist in Russia (5) and Germany (6) for the separation of carbon isotopes and in South Africa for the separation of uranium isotopes (7).

The MPD process is shown schematically in Fig. 1. An infrared laser is tuned to the transition frequency between the quantized vibrational energy levels of a gaseous molecule. The molecule absorbs a photon (Molecule A) and is raised to its first excited vibrational state, where, if the photon density is large enough, it can absorb successive photons as it rises up the 'ladder' of quantized vibrational energy levels until it has sufficient vibrational energy to dissociate. However, if the photon energy does not match the vibrational level spacing (Molecules B) in the molecule, no excitation takes place. This is thge esseence of the isotope selectivity. For a polyatomic molecule, where there are many vibrational modes, it is found that the photon energy does not generally stay in the mode that is initially pumped. Instead the energy is quickly randomized over all the modes of the molecule. At this point the reaction proceeds as in a standard thermal reaction. The main difference being that in a thermal reaction the molecules are promoted into excited vibrational states by a transfer of translational energy into vibrational energy during molecular collisions. With all the modes vibrating, it is generally found that the weakest bond is the first to break. For the MPD process, the molecules can be translationally cold (i.e. low kinetic temperature) and still undergo reactions that would only happen at a much higher thermal temperature, because the pumped mode acts like a conduit through which energy can be transferred into the molecule. Gone are the days of 'bunsen burner' chemistry; judiciously tuned lasers have allowed new chemistry through the selective heating of specific molecules in a reaction mixture (8).

The MLIS process takes advantage of the mass dependence of the molecular vibration frequency, which for a classical vibrator varies as the inverse of the square-root of the reduced-mass. For molecules containing hydrogen and deuterium, the effect on the shift of the vibration frequencies is the largest possible and is many orders of magnitude larger than the frequency bandwidths of the lasers used to excite, and selectively decompose, molecules containing deuterium.

The largest deuterium sources are water and methane, however, these molecules are not suitable for a MLIS process because they are difficult to decompose by MPD and the decomposition products are reactive free radicals. These radicals will tend to react with the surrounding non-absorbing hydrogen-containing molecular species and initiate chain reactions that will nullify the isotopic selectivity created, with the laser, in the initial decomposition.

Since bulk chemical sources of deuterium (i.e. water or methane) are not suitable for MPD directly, a working molecule (WM) is used on which the selective MPD step is performed. The laser-based heavy water process is shown schematically in Fig. 2. Non-decomposed WM's are redeuterated in a front end exchange step and fed back into the stream for selective MPD. A suitable laser source (dependent on the choice of the WM) is tuned in frequency to be absorbed only by those WM's containing a deuterium atom. Under certain conditions, only the deuterated species will absorb the many laser photons required for decomposition. As a consequence, the MPD products will be highly enriched in deuterium.

In studies of MLIS the emphasis is on understanding and optimizing the parameters which control an efficient and highly selective MPD process. The criteria for selection of a suitable WM have been defined (9) and include requiring the WM to have selective absorption at reasonable intensities in the region of a high efficiency infrared laser, (such as a CO or a CO_2 laser), in order to maximize photon efficiency and minimize WM make-up costs. Further, the WM must be relatively non-toxic and non-explosive and have a vapour pressure of at least 13 kPa at, or near, room temperature. The bulk cost of the WM should be less than \$2/Kg and the deuterated decomposition products must preserve the initial laser-induced selectivity and be easily separated from the parent molecule. The chemical exchange with a bulk source of deuterium must be rapid and non-destructive of the WM.

A parametric model of the MPD process has been developed (10) and this is providing essential insight into the design of a heavy water process. The model recognizes the importance of collisional energy transfer in moderating the efficiency and selectivity of the MPD process. The decomposition probability is written as:

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

where Φ is the photon fluence (intensity x pulse duration), 'a' is the partial pressure of the WM and 'b' is the partial pressure of a buffer gas. For isotope separation a separate 'b', and corresponding sum and subscript on the h parameter, would be required for the protiated WM as well as any gaseous decomposition products.

The h_{ij} parameters have been successfully associated with various collision mechanisms. As an example, in Fig. 3 is shown the processes associated with the first few terms in the expansion of equation 1. In general, the h_{ij} reflect the relative contribution, to the amount of reagent decomposed, by collisions between 'i' WM's and 'j' buffer molecules. For efficient isotope separation it is important to monitor the competition between the h_{10} process and the h_{11} processes. The h_{11} parameter will often be negative, which reflects deactivation of the selectively-excited deuterated molecules by the protiated, and the decomposition product, molecules. Detailed studies, using this new method, of a number of candidate working molecules have been carried out. These include chloroform (10)(11), 1-bromo 2-fluoroethane (12), 1,1,1-trichloroethane (13), t-butyl methyl ether (14), t-butyl bromide (15) and t-butyl chloride (16), among others.

For an efficient D-MLIS process it is necessary but not sufficient (13) that the h_{10} parameter yield the dominant contribution to the decomposition probability of the deuterated molecules. Collisional processes tend to channel energy into the protiated molecules which degrades photon efficiency as well as isotopic selectivity. This requirement of an essentially pressure-independent decomposition probability lead many researchers to assume that in order to have high isotopically selective MPD it was necessary that there were no molecular collisions during the laser pulse. For standard collision frequencies of 10 MHz/Torr this translated into lasers capable of nanosecond pulses in order to accommodate the required high pressures (> 13 kPa), determined by pumping costs. Although laser development has progressed to a state where high power short pulse lasers can be expected to produce reasonably priced photons, recent understanding gained from studies at Chalk River (13) allows us to relax the constraint that the pulse be of nanosecond duration.

This has a major impact on a LIS process. If we can use a longer pulse length then it should be possible to use Q-switched CO_2

lasers running with continuous wave (CW) discharges. Such lasers currently produce photons at over fifty times less cost than conventional TEA CO_2 lasers (17). This should translate into significant reductions in capital costs, which is particularly important when comparisons are made between this and other deuterium separation processes as it is generally agreed that the major cost component of D-MLIS is the initial capital outlay (see the next section on engineering costs).

In a continuing effort to understand the underlying principles that govern the LIS process, new insights emerged that enabled us to relax numerous process related constraints. Recently, we have shown that we can eliminate high energy radical channels by a judicious choice of LIS variables (14,15). In the past, molecules were eliminated from the list of potential WM's if they showed signs of radical products upon decomposition. This is because subsequent radical reactions are not isotopically selective and decrease the selectivity produced in the initial decomposition. From studies using the (h_{ij}) model, we have shown that the radical channel can be pumped by collisional energy transfer between two excited target molecules: a so-called h_{20} process. The importance of this for LIS is that for natural abundance samples the contribution to the decomposition from the h_{20} process is vanishingly small so that, by a judicious choice of fluence and pressure, the concern of free-radical chemistry can be essentially eliminated. Molecules that were taken off the list of potential WM's because studies with neat samples showed radical products can now be re-evaluated. Some of these molecules exhibited very promising properties. This means that a re-examination of WM's, previously discarded because of radical products, is now justified.

Recently, it has been demonstrated that very high selectivities can be obtained at the high gas pressures required for an economical LIS process and, that the selectivity increases with increasing dilution (13) (18). Selectivities as high as 10^4 have been measured and were found to vary as the dilution of D in H over three orders of magnitude. This dilution dependence is understood and modeled. Experiments to elucidate the selectivity at natural abundance have not yet been finished, however, extrapolation of the dilution dependence predicts a selectivity of 10^5 should be obtained for natural abundance samples. This is an extraordinarily large selectivity that was unexpected by many people. Furthermore, we believe this result to be quite general so that, as long as the optical selectivity is there, large selectivities should be obtainable.

This recent result has important ramifications for the deuterium MLIS process. For selectivities of 10^4, or greater, the cost associated with make-up of the destroyed WM is negligible and a further increase in selectivity does not significantly lower make-up costs (see next section). In the late 1980's a selectivity of only 10^3 had been demonstrated and selectivities as high as 10^4 were considered optimistic. At that time, economic production of heavy water by MPD was in doubt because of the exorbitant costs associated with the make-up of the WM if the selectivities were as low as 10^3. Given the measured, and predicted, selectivities we now believe are obtainable with any WM, the concern about high make-up costs has been eliminated.

This is a continuation of a trend; a few years ago, goals that were considered optimistic have now been reached and, in some circumstances, surpassed. The experiments in our laboratory, which were aimed at testing our improved (h_{ij}) model and in assessing potential working molecules, have shed light on the nature of the MPD process; allowed us to achieve a number of the target parameter values for an economic process, and to relax a number of the criteria for the selection of a working molecule. Furthermore, this advancing trend is also evident in parallel work in the development of IR lasers. Fuelled by the possibilities of Uranium-MLIS on UF_6, high-power CO_2 lasers with high repetition rates have been developed in South Africa (7) and Japan. All these advances have had a significant impact on both the viability of a future laser-based heavy water process and on its expected cost.

ENGINEERING COST ESTIMATES

In 1988 a cost estimate was carried out to obtain an approximate cost for heavy water resulting from a potential laser-based isotope separation process (19). This was a difficult endeavour since a working molecule had not yet been identified and the "process", strictly speaking, did not exist. As a result, the approach used in that study was to use a better established heavy water processes as a "yardstick" by which to determine the cost of heavy water from a potential LIS process. The more established, though not yet installed process, was the Combined Industrial Reformed hydrogen Catalytic Exchange (CIRCE) process, developed at Chalk River. A detailed economic evaluation of the CIRCE process had been carried out at CRL in the Chemical Engineering Branch in 1986 (20) and a useful algorithm developed.

In the 1988 costing study of the MLIS process the algorithm from the CIRCE study was used as a guide from which to develop a new one for LIS. The methodology in this approach was to use the state-of-the-art photochemistry parameters to determine the laser power required and the process flow rates. These, in turn, define a number of other costs both capital and operating, such as gas compression, laser costs, electrical, refrigeration, gas make-up for the laser, working molecule make-up, overheads and contingency and complexity cost estimates. The plant size was chosen to be 400 Mg/annum, the same as a GS plant. The economics of scale, for MLIS are not known, however. It could be that some other plant size would make more sense for MLIS, but this has not been studied thus far.

Using what were believed to be the appropriate parameters in 1988 it was estimated that, optimistically, a heavy water plant based on the MLIS process, might be about as economical as a GS plant. This was seen as economically unattractive at the time but there was considerable hope that the eventual costs could be made much lower, rather than higher, by future scientific and technical advances.

We recently re-investigated the costs to take into account scientific advances within our underlying research program and technological advances in the outside world. The first step was to look at the relevant photochemical parameters and adjust them so that they were state-of-the-art, for 1992. The relevant photochemistry parameters for the costing study are; ϵ_ℓ (Wall Plug Efficiency of the laser); ϵ_D (Molecule Dissociation Efficiency); ϵ_x (Product Extraction Efficiency); ϵ_c (Absorption Cell Efficiency); n (Number of IR photons absorbed); υ (IR laser frequency); S(Φ) (Optical Selectivity); ϵ_P (Photon Efficiency); β (Heads Separation Factor); Gas Pressure and Laser Cost in $/W. The values of these parameters are given in Appendix 1. The costs, as a function of the number of symmetry-equivalent-hydrogen atoms in the working molecule, are given in Table 1.

The plant capacity was modified in the new study. The calculations were performed for a 400 Mg/annum plant running at 80 percent capacity; effectively 320 Mg/annum. In addition, the costs of using a Pressure Swing Absorption unit for drying the gas after redeuteration, but prior to irradiation, was included; although the need for drying has not yet been established.

Table 1
MLIS Process Costs*

#SEH atoms =	1	2	3	4	6	9
With drying stage	.90	.56	.45	.39	.35	.32
Without drying stage	.54	.37[†]	.31	.29	.27	.27

*Costs are given relative to the cost of heavy water from a new GS Plant; i.e. 1.0 = cost of heavy water from a new GS Plant.

[†] The conditions for this calculation are essentially the same as those for the "base case" of the 1988 study, which showed that the cost of heavy water from MLIS was equal to that from GS. The reason for the lower cost in 1992 is because some of the parameters are updated.

In the calculation of the costs in Table 1, all other charges applied to the process are consistent with those applied to the CIRCE process (21). In particular, utility financing is used, with a 20 year write-off period for capital equipment. A 36.5% contingency charge is applied to the LIS process, also consistent with the CIRCE study[1].

Table 3 illustrates four important aspects of the new costing study:

1) Because a decision on the optimum WM, has not yet been made, it is unknown whether the feed gas requires drying prior to laser irradiation. If the products of MPD react with H_2O, in a way that scrambles isotopic selectivity, or if the products of reaction with H_2O make it more difficult to separate out the deuterium after the irradiation step, then drying may be necessary.
2) The predicted costs are significantly lower than for a new GS process, especially if the working molecule has more than one symmetry-equivalent-hydrogen (SEH) atom.
3) For molecules with 3 or more SEH atoms, the costs do not change very much, as a function of the number of SEH atoms.
4) The new cost calculation for the "base-case" of heavy water (Column 2, row 2 of Table 1) is only 0.37, whereas it was 1.0 in 1988. There are many reasons for this considerable drop in the predicted cost. In the 1988 study, Chemical Industry Financing was used; i.e. the capital cost component was written off over 4 years instead of 20 years (Utility Financing). The MLIS process is much more heavily "front-loaded" with capital than the GS process, or indeed any of the others. Hence, using utility financing brings the cost of heavy water from an MLIS process down more than any of the others. In addition, the largest capital cost component of an MLIS process would be the cost of lasers, and these are relatively inflation-proof. In fact, the cost of high-power CO_2 lasers has almost been halved in the last four years. Finally, advances in our underlying research program have justified the upgrading of several photochemical parameters.
5) One point not shown in Table 1 is that the cost is actually lower for a molecule with 7 or 8 SEH atoms. The costs go up again as the number of SEH atoms is greater than 7 in some cases because of DW finishing costs. This is because the deuterium enrichment in the product cannot be as high with multiple SEH atoms. Hence, the DW finishing costs, by conventional distillation methods, go up with the # of SEH atoms. Extensive calculations were not carried out for molecules with 7 or 8 SEH atoms, however, because so few of these exist in nature.

The next step in the costing study was to vary several of the relevant parameters to assess the impact on costs. This was

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[1] In discussions with Chemical Engineering Branch at CRL, they have suggested that a higher, 51 %, contingency factor is more appropriate for a less developed process such as LIS. The effect of the higher contingency charge is to raise the costs by between 5 and 7 %.

done, primarily, to help direct our research in areas which have the greatest impact on process costs. This sampling of parameter space gives a number of insights into those factors which are most important.

The most important message given in Table 2 is that, without a drying stage, the process costs are relatively insensitive to significant parameter changes, provided the molecule has 3 or more SEH atoms; the costs ranging from 0.23 to 0.45. Significantly, the cost of IR laser photons, which was believed to be the biggest obstacle to a viable MLIS process in 1988, does not effect process costs very much if the working molecule has 3 or more SEH atoms.

Table 2
MLIS Process Costs as a Function of Various Parameter Changes, Without a Drying Stage

Row #	# SEH atoms =	1	2	3	4	6	9
1	Process costs without dryer	.54	.37	.31	.29	.27	.27
2	ϵ_D = 0.5	.72	.47	.39	.35	.32	.31
3	ϵ_D = 0.9	.51	.35	.30	.28	.26	.26
4	$S(\Phi) = 10^4$	.32	.26	.24	.23	.23	.25
5	Selectivity = 5×10^2	.80	.50	.40	.35	.31	.30
6	Laser Cost = \$10/W	.47	.33	.29	.27	.25	.26
7	Laser Cost = \$30/W	.61	.41	.34	.31	.29	.29
8	WM Cost = \$10/kg	.73	.52	.45	.42	.40	.39

If the potential working molecule has 1 or 2 SEH atoms, some of the process costs are extremely sensitive to parameter variations. The costs are the most sensitive to $S(\Phi)$. However, this is a parameter that one can exercise very little control over. The optical selectivity is the ratio of one-photon absorption cross-sections for the deuterated/protonated molecule. The only way to improve this factor is to lower the temperature of the process. For most molecules under study, the process temperature cannot be significantly lowered without lowering the gas pressure well below 13 kPa (100 Torr), where a process is not viable. It is possible, though, to screen potential working molecules with 1 or 2 SEH atoms to see if they have high enough $S(\Phi)$'s. If $S(\Phi)$ is significantly less than 1000, then a molecule with 1 or 2 SEH's can likely be ruled out for a viable process. However, if $S(\Phi)$ is on the order of 10^4, a process based on only

1 SEH atom may be viable.

If the process requires a (PSA) drying stage, following redeuteration, and before irradiation, the costs are slightly higher but the sensitivity of costs to parameter changes is not much different, provided that the potential WM has 3 or more SEH atoms. If the working molecule has 2 SEH atoms, the costs can be reasonable if the photochemical parameters are favourable. However, if the process requires a PSA drying stage, a WM with only 1 SEH atom can all but be ruled out, because of the high costs.

Table 3
MLIS Process Costs as a Function of Various Parameter Changes, With a Drying Stage Included

Row #	# SEH atoms =	1	2	3	4	6	9
1	Process costs with dryer	.90	.56	.45	.39	.35	.32
2	$\epsilon_D = 0.5$	1.07	.66	.52	.45	.39	.36
3	$\epsilon_D = 0.9$	.87	.54	.43	.38	.34	.31
4	Selectivity = 10_4	.67	.44	.37	.33	.31	.30
5	Selectivity = 5×10^2	1.15	.68	.53	.45	.39	.35
6	Laser Cost = $10/W	.83	.52	.42	.37	.33	.31
7	Laser Cost = $30/W	.97	.60	.475	.41	.37	.34
8	WM Cost = $10/kg	1.09	.71	.58	.52	.47	.44

The reason for the relative insensitivity of costs to parameter changes, for WM's that have 3 or more SEH atoms is quite straightforward. If the WM has more SEH atoms, then the effective concentration of deuterated WM's in the feed goes up. Hence, the power required for the laser goes down, and the capital and operating costs of the process also decrease. In addition, if the concentration of deuterated WM's is higher, the process flows do not have to be as large. Hence, the pumps and compressors required are not as large, and the capital and operating costs for these components goes down as well. If the process requires a PSA unit, for instance, then for a process based on a WM with 1 or 2 SEH atoms, the costs of the compressors required is comparable to that of the lasers.

CONCLUSIONS

Advances in our underlying research program have had a significant impact on the expected costs, as have technological advances in the development of lasers in industry. We believe that a laser-based isotope separation process for deuterium seems much more viable now than in 1988.

The LIS process is still not as well defined as its "yardsticks" and this is both a good thing and a bad thing. On the positive side, it means that there is the potential of future advances that may drive the expected costs down even further. Unfortunately, its relative stage of immaturity makes it much less likely that it could deliver heavy water, on as short a time scale, as more conventional competing processes. Because of financial constraints, and limitations on time imposed by the expected demand for heavy water, at the turn of the century, work on this program has been suspended.

However, the technological base that AECL has built up may be useful for other isotope separation processes and our experience in this area has given us a big lead over other countries in the area of MLIS of light isotopes.

APPENDIX 1

The following are the relevant (photochemistry parameters used in the costing study as well as a few other key parameters:

1) Annual Production = 320 Mg/annum
2) Hours of operation per annum = 7000
3) Electrical Power Costs = 0.030 \$/kWh
4) Helium Cost = 4.0\$/m^3
5) Steam = 1.70\$/GJ
6) Feed Concentration = 148 ppm
7) Extraction Fraction = 0.5
8) Number of Symmetry-Equivalent H Atoms = 1 to 9.
9) Cost of Working Molecule = 2\$/kg except where noted.
10) Molecular Weight of the Working Molecule = 100
11) Pressure at Redeuteration = 101.1 kPa without a PSA drying unit or 2500 kPa with a drying unit.
12) Laser Cost/Watt = 20\$(US-1990)/W except where noted.
13) Optical Selectivity-$S(\Phi)$ = 1000 except where noted.
14) Electrical to Photon Conversion Efficiency $\epsilon\ell$ = 0.1
15) Extraction Efficiency ϵ_x = 0.9
16) Dissociation Efficiency ϵ_D = 0.8
17) Absorption Efficiency ϵ_c = 0.8
18) Heads Separation Factor ϵ_β = 10^4
19) Number of Photons for Dissociation = 30
20) Laser Wavenumber = 1000 cm^{-1}
21) Recovery Efficiency = 1.0
22) Temperature of Irradiation = 25°C
23) Pressure of Irradiation = 26 kPa
24) Cost Indices: (IND1) = 392.2
(IND2) = 502.9
25) Canadian/US Currency Exchange Rate = 1.17
26) Interest During Construction = 23.7%
27) Front End Exchange Capital = 43.38 M\$
28) Driving Temp. Difference for Cooling = 10°C
29) Return on Capital = 0.1175
The value of 0.1175 assumes depreciation of capital over 20 years.

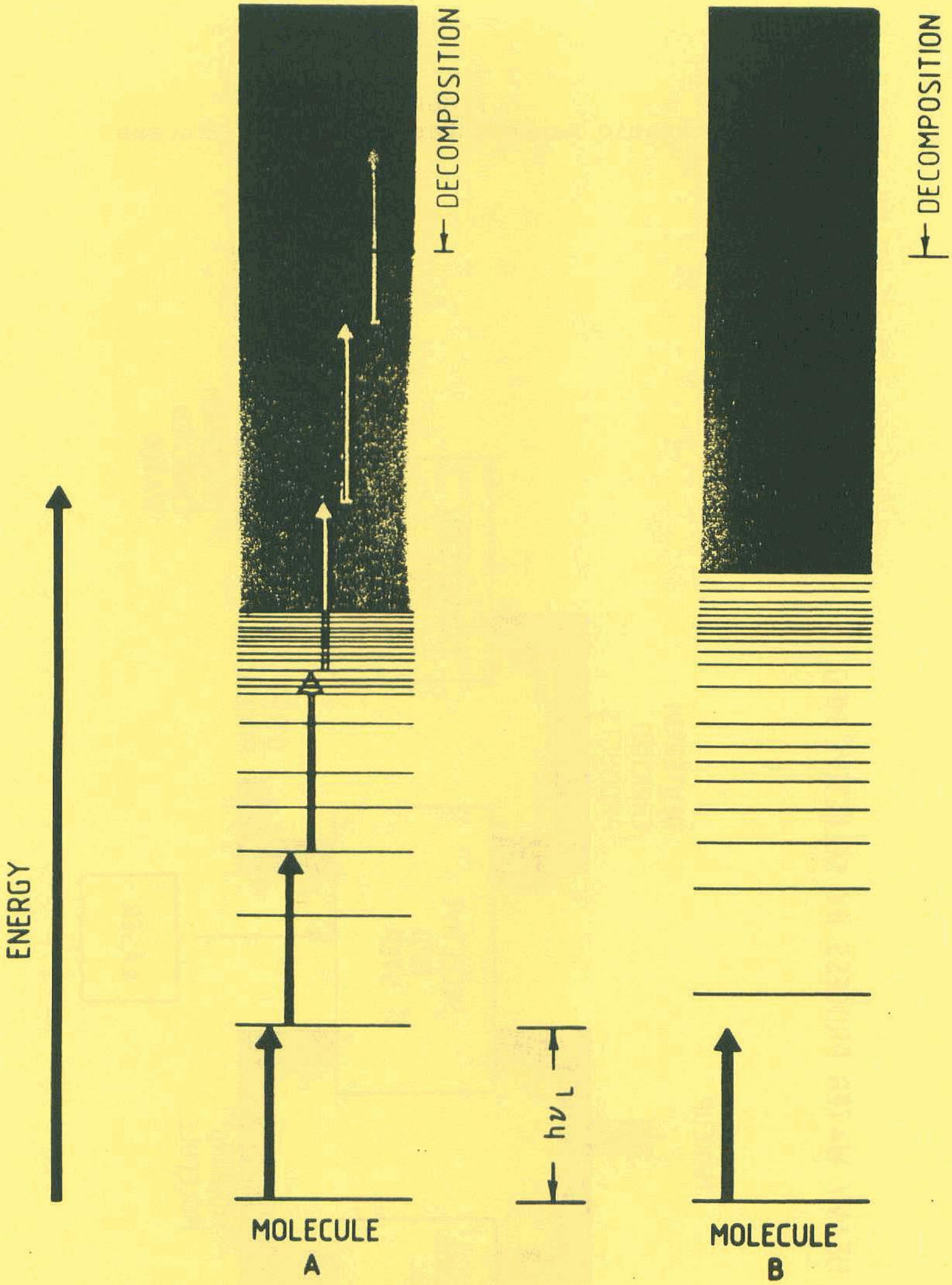

FIGURE 1
Selective Multiphoton Dissociation

The photon energy is matched to molecule A which undergoes subsequent absorption of photons, to dissociation. However, the energy mismatch between the photon and molecule B prevents its excitation.

FIGURE 2
Schematic Representation of MLIS Process

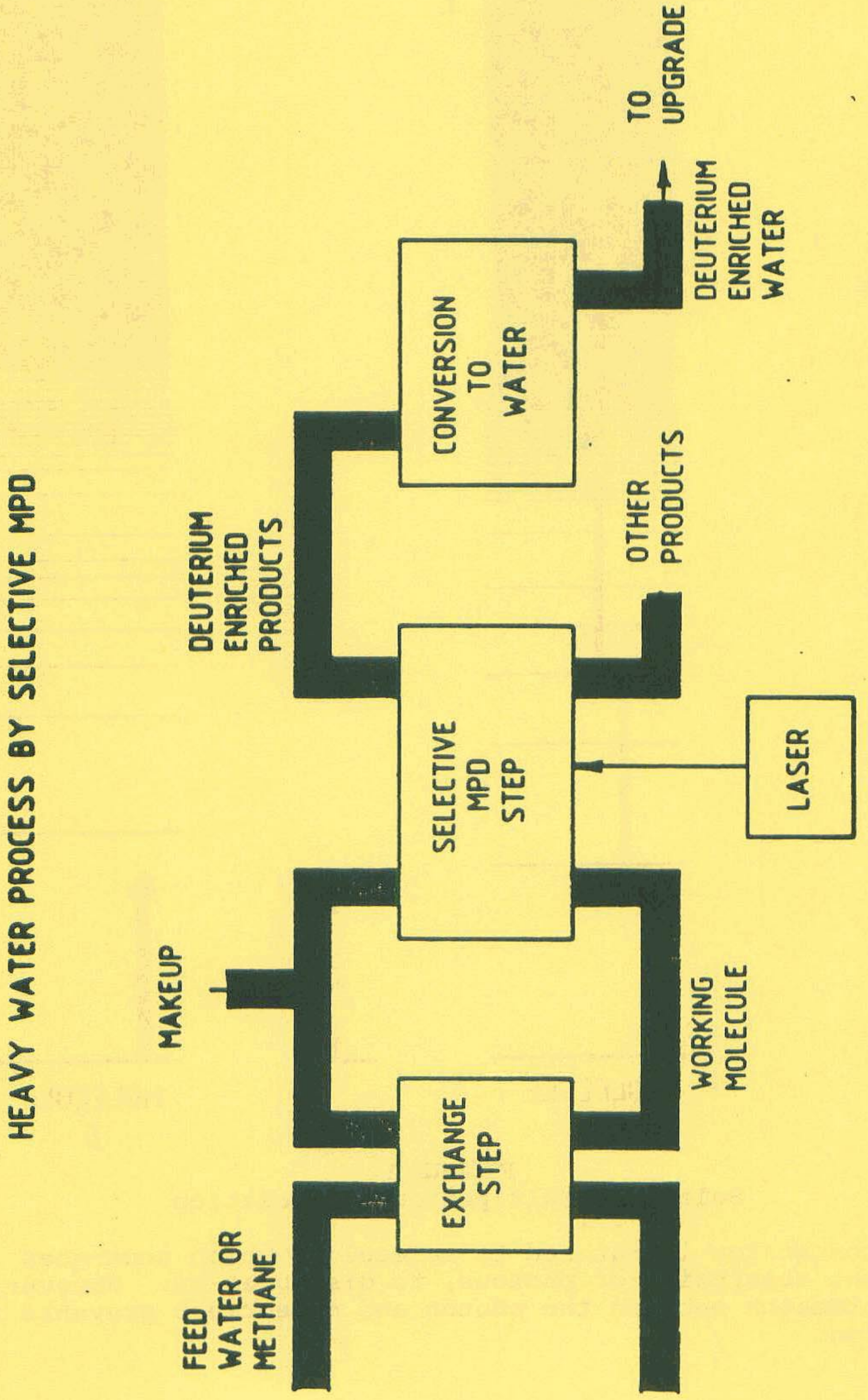

FIGURE 3
Collision Sequences Associated with h_{ij} Parameters

'A' is a target molecule while 'B' is a buffer. The asterisks represent the 'qualitative' level of excitation. Eg: A^{**} is a molecule that is energetic enough to decompose whereas A^{*} is not.

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

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

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

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

1. For a review of various heavy water processes see papers in: Separation of Hydrogen Isotopes, H.K. Rae ed., ACS Symposium #68, Wash. (1978)

2. AVLIS Advanced Enrichment Technology in the United States, Lawrence Livermore Laboratories, LLL-TB-072.

3. N.R. Isenor and M.C. Richardson, Appl. Phys. Lett. 18, 224 (1971)

4. a. V.S. Letokhov, Chem. Phys. Lett., 15, 221 (1972)
b. E.S. Yeung and C.B. Moore, Appl. Phys. Lett., 21, 109 (1972)

5. Private communication with Jim O'Niell at Ontario Hydro

6. W. Fuss, in the Proceedings of the Int. Symp. on Isotope Separation and Chem. Exch. Uranium Enrichment, Tokyo, Oct 29-Nov 1 (1990)

7. D.M. Kemp, P.J. Bredell, A.A. Ponelis, E.Ronander, in the Proceedings of the Int. Symp. on Isotope Separation and Chem. Exch. Uranium Enrichment, Tokyo, Oct 29-Nov 1 (1990)

8. M.C. Hsiao, A. Sinha and F.F. Crim, J. Chem. Phys., 92, 6333 (1990).

9. M. Ivanco, D.K. Evans, R.D. McAlpine, G.A. McRae, A.B. Yamashita, Spectro. Chem. Acta., 46A, 635 (1990)

10. G.A. McRae, A.B. Yamashita, J.W. Goodale, J.Chem. Phys. 92, 5997 (1990)

11. M. Ivanco, G.A. McRae, R.A. Back, J.W. Goodale, P.E. Lee, J. Chem. Phys. 96, 5191 (1992)

12. G.A. McRae, D.K. Evans, J.W. Goodale, J. Phys. Chem., 93, 1689, (1990)

13. G.A. McRae, M. Ivanco, R.A. Back, Chem. Phys. Lett. 185, 95 (1991)

14. G.A. McRae, P.E. Lee, R.D. McAlpine, J. Phys. Chem. 95, 9332 (1991)

15. B.M. Toselli, G.A. McRae, M. Ivanco, R.D. McAlpine, (to be published) J. Phys. Chem. June (1992)

16. G.A. McRae, R.D. McAlpine, J.W. Goodale (to be published)

17. W. Fuss, M. Ivanenko, W.E. Schmid, S. Trusin, in the Proceedings of the Int. Symp. on Isotope Separation and Chem. Exch. Uranium Enrichment, Tokyo, Oct 29-Nov 1 (1990)

18. a. G.A. McRae, M. Ivanco, P.E. Lee, J.W. Goodale, in the Proceedings of the Int. Symp. on Isotope Separation and Chem. Exch. Uranium Enrichment, Tokyo, Oct 29-Nov 1 (1990)

b. M. Ivanco, G.A. McRae, P.E. Lee and D.B. Grice (to be published)

19. R.D. McAlpine, A.I. Miller and D.A. Spagnolo, Chalk River Laboratories Internal Report, April 1988 (CRNL-4190).

20. D.A. Spagnolo, A.E. Everatt and G.W. Myles, Chalk River Laboratories Internal Report, April 1986 (HWP-HW-R-25).

21. D.A. Spagnolo, Chalk River Laboratories Internal Report, August 1991 (HWP-HW-R-30).