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STUDY OF THE PROSPECTS FOR HEAVY WATER PRODUCTION VIA

LASER ISOTOPE SEPARATION

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ABSTRACT

General considerations relevant to heavy water production via laser-induced vibrational catalysis are discussed. The problems and prospects inherent in utilizing the accelerating effect of reagent vibrational energy on chemical reaction rates are discussed for two reaction classes: isotopic exchange reactions and hydrogen halide additions to unsaturated hydrocarbons. Finally, the process of multiple photon molecular dissociation is considered with reference to two specific molecules: monodeuterated ammonia and formaldehyde.

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1.0 GENERAL

To quote from a recent review article[1]: "The attractive feature of vibrational photochemistry for isotope separation is the promise of using low energy IR photons from an efficient molecular laser to get a good yield of product. Since 1 mole of photons at 3000 cm^{-1} is 10^{-2} kWh and some IR lasers are about 10 percent efficient, processing of bulk chemicals might even be economic. There are many problems to overcome: thermal reaction rates, vibrational energy transfer, surface catalyzed reactions, fixed frequency sources and so on. The methods which rely on $V \rightarrow V$ transfer to enhance the excitation of heavy isotopes appear quite promising for systems with anharmonicities and isotopic shifts larger than kT at temperatures where the vapor pressure is sufficient."

The relevance of these remaks to deuterium separation is as follows:

1. A process which utilizes $10\,\mu$ photons from a 10 percent efficient CO_2 laser and which has a quantum efficiency

$$\left(\frac{photons}{separated\ D\ atom}\right)$$

of 1 percent would require a laser process energy of 3 kWh, equivalent to a laser process cost of approximately $\frac{7.5\ ¢}{mole\ D}$ or $\frac{\$7.5}{kg\ D_2O}$, assuming the availability of electric power at a cost of 25 mills/kWh. The laser capital cost, assuming a price of $20/watt CO_2 and a useful laser lifetime of two years, would be approximately $35/kg D_2O. This should be compared with the current Canadian price for heavy water made by the G-S process of $100/kg $D_2O \equiv$ $1/mole D, of which 60 percent is due to capital charges, 25 percent due to energy, and 15 percent for operations and maintenance[2]. The moral of this approximate calculation is

that since heavy water is a much cheaper commodity than U-235, the prospects for the economic viability of a heavy water laser separation process are much more uncertain.

2.   The methods which rely on V – V transfer to enhance the excitation of heavy isotopes[3] appear, at first glance, to be quite attractive for deuterium separation since the isotope shifts in diatomic and small polyatomic molecules containing hydrogen atoms can be large compared with kT, e.g., the difference between the fundamental frequencies of H_2O and DHO in the symmetric stretch mode is ≈ 700 cm^{-1}. Thus, on uncritical application of the formula for the isotopic selectivity S as given by Belenov et al.[4] and Basov et al. [5]

$$S = \exp \frac{E_a}{h\nu_\ell} \frac{\Delta E}{kT} , \tag{1}$$

where $h\nu_\ell$, $h\nu_h$ are the vibrational energies of the light and heavy species, respectively,

$$\Delta E = h\nu_\ell - h\nu_h , \text{ and}$$

$E_a >> h\nu_\ell$, $h\nu_h$ is the activation energy for the reaction,

leads to the prediction of large effects. The flaw in the argument – when applied to deuterium separation – is the erroneous assumption that saturation of the $0 \to 1$ transition of the heavy isotope by the laser will lead to high vibrational temperatures, i.e., Th, $T_\ell >> h\nu_h/k$[6]. Physically, the problem stems from the small natural abundance of deuterium; i.e., the optical energy pumped into the deuterated isotope is so diluted by $V \to V$ transfer into the surrounding "bath" of hydrogenerated isotopes that the average vibrational energy per molecule, and hence the vibrational temperatures are small compared with $h\nu_h$. The heavier isotope

still reacts faster, but the reaction rates of both heavy and light isotopes are very small, and the selectivity is not appreciably greater than one. As an example, consider a reaction which is initiated by saturating the symmetric stretch mode of HDO. Then $\Delta E = 700 \text{ cm}^{-1}$, and assuming that $kT = 300^{\circ}K = 200 \text{ cm}^{-1}$ and the ratio of $V \rightarrow T$ to $V \rightarrow V$ relaxation time constants, $\left(\dfrac{\tau V \rightarrow T}{\tau V \rightarrow v}\right) \approx 50$, we calculate the average vibrational energy per molecule θ to be[7]

$$\frac{\theta}{h\nu_h} \approx \frac{N_D/N_H}{N_D/N_H + 1} \left(\frac{\tau V \rightarrow T}{\tau V \rightarrow v} \left\{ 1 + \frac{N_H}{N_D} e^{-\Delta E/kT} \right\}^{1/2} \right)$$

$$\qquad\qquad (2)$$

$$\simeq \left\{ \frac{N_D}{N_H} \frac{\tau V \rightarrow T}{\tau V \rightarrow V} e^{-\Delta E/kT} \right\}^{1/2} \simeq 0.02 ,$$

This implies that

$$\frac{h\nu_h}{kT_h} = \ln\left(1 + \frac{h\nu_h}{\theta}\right) \simeq 3.93,$$

contrary to the assumption that $kT_h \gg h\nu_h$. The "moral" here is that one can not use methods which rely on $V \rightarrow V$ "ladder-climbing" to reach reaction thresholds to separate deuterium isotopes. Of course, it may be possible to find a bimolecular reaction in which a collision preferentially leads to an isotopically selective reaction rather than $V \rightarrow V$ or $V \rightarrow T$ trasfer. However, this is non-trivial (Section 2.0), and explains the attraction of unimolecular reactions which (hopefully) can be carried out in less than a collision time simply by absorption of radiation (Section 3.0).

## 2.0 VIBRATIONALLY CATALYZED PHOTOCHEMICAL REACTIONS IN THE GAS PHASE

The rationale of research in this area is the expectation that vibrational excitation of one of the reactants in a bimolecular reaction will reduce the activation energy, and hence enhance the reaction rate of the isotope of interest sufficiently to permit effective separation. For this to be the case, the vibrationally enhanced reaction rate k^+ must be large compared with the reaction rate under conditions of thermal equilibrium, k, and must also be sufficient to beat those $V \rightarrow V$ energy transfer processes which destroy the isotope selectivity. The experimental evidence on the efficiency of vibrational catalysis has been reviewed recently by Birely and Lyman[8]. Their conclusions may be summarized as follows:

1.   The simplifying assumption that the effect of vibrational excitation can be rationalized solely by a change in the exponential factor of the Arrenhuis rate expression is probably incorrect, i.e., changes in the pre-exponential factor seem to be the dominant effect in certain reactions.

2.   The fact that, for the reactions of vibrationally excited H_2, HCℓ, OH and O_3 which were studied, the rate enhancement is less than exp $(\Delta E_v/kT)$ where ΔE_v is the excess vibrational energy deposited by the laser, and moreover, that it is uncorrelated with the activation energy, E_a, the vibrational energy, E_v, ΔE_v, or the reaction exothermicity, ΔH, may be _partially_ explained by the intuitively "obvious" notion that the rate enhancement is _mode specific_. That is, if the reaction involves the breaking of a specific molecular bond and the vibrational excitation leads to insignificant excitation of that bond, the rate enhancement would be negligible. As an example, consider the isotopic exchange reaction

$$NH_2D^+ + H_2O \rightarrow NH_3 + HDO, \qquad (3)$$
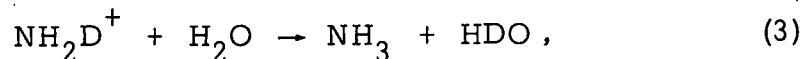
where NH_2D^+ represents the effect of exciting a $(\nu_2 = 0, J = 4)$ $\rightarrow (\nu_2 = 1, J = 5)$ transition of NH_2D using a CO_2 laser[9]. If the reaction (3) involves the breaking of the N-D bond, then the excitation of a mode such as ν_2 which leads to insignificant energy in the N-D stretch would be expected to be ineffective in promoting this reaction.

The thermal equilibrim analog of reaction (3) is one of a class of isotopic exchange reactions which have been considered theoretically and in some cases actually used to separate deuterium[10]. In fact, over 90 percent of the heavy water separated to date worldwide has been produced by a combination of hydrogen sulfide-water thermal equilibrium chemical exchange

$$HDS + H_2O \rightleftarrows H_2S + HDO \qquad (4)$$
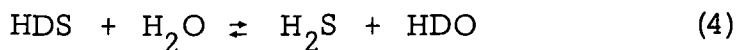
and fractional distillation. The possibility of separating isotopes using reactions such as (4) stems from the fact that the reaction equilibrium constant, $k(T)$, differs from unity[11], i.e., it is easy to show that the separation factor, $\alpha = K$

$$\alpha \equiv \frac{\left(\dfrac{D}{H}\right)_{H_2O}}{\left(\dfrac{D}{H}\right)_{H_2S}} = \frac{\left[\dfrac{HDO}{H_2O}\right]}{\left[\dfrac{HDS}{H_2S}\right]} \equiv K. \qquad (5)$$

Although practically all the thermal equilibrium exchanges considered to date for commercial heavy water production are liquid-vapor systems[12], it is intriguing to consider the possibility of vibrationally catalyzed isotope exchange reactions in the gas phase. For example, reaction (3), plus the V $\rightarrow$ V energy transfer

$$NH_2D^+ + NH_3 \rightarrow NH_2D + NH_3^+, \qquad (6)$$
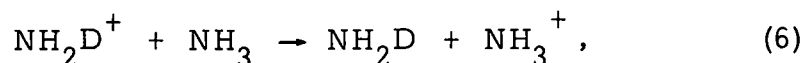
and the inverse reaction resulting from vibrationally excited NH_3 produced in (3)

$$NH_3^+ + H_2O \rightarrow NH_2D + HDO, \qquad (7)$$
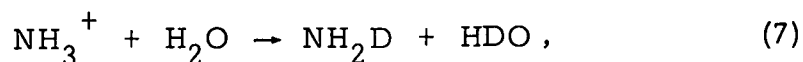
can be summarized by

$$NH_2D^+ + HDO \rightleftarrows NH_3^+ + H_2O, \qquad (8)$$
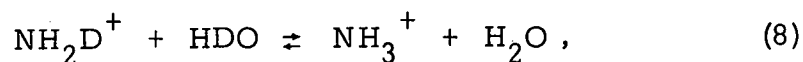
which may have a large steady state reaction constant, and hence a large separation factor. The fact that reactions involving exchange of the hydrogen isotopes can be vibrationally catalyzed in the gas phase has been established in the classic shock tube and Raman laser experiments of Bauer and co-workers[13]. This area certainly merits futher attention; here we wish to point out a basic impediment to effective isotope separation via this technique. Let us suppose that the rate enhancement due to vibrational excitation is such that in steady state the reaction constant for Equation (8) $K = 10$, and $\alpha = \frac{3}{2} K = 15$. Then, assuming that the initial deuterium concentrations in the water and ammonia are both equal to the natural concentrations, i.e.,

$$\left(\frac{D}{H}\right)_i^{H_2O} = \left(\frac{D}{H}\right)_i^{NH_3} = 1.5 \times 10^{-4}, \qquad (9)$$

It is easy to show that the water enrishment factor E is given by

$$E = \frac{\left(\frac{D}{H}\right)_f^{H_2O}}{\left(\frac{D}{H}\right)_i^{H_2O}} = \left(\frac{1+\eta}{1+\frac{\eta}{\alpha}}\right) = \left(\frac{1+\eta}{1+\frac{\eta}{15}}\right), \qquad (10)$$

where $\eta = \left[\dfrac{NH_3}{H_2O}\right]$ = the relative concentrations of ammonia and water in the reaction mixture. From Equation (10) it is obvious that we must make η large in order to take advantage of the large

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separation factor α. For example, if $\eta = 1$, $E \simeq 1.87$, while if $\eta = 30$, $E \simeq 10.33$, and $E \to 15$ in the limit $\eta \gg 15$. However, the condition $\eta \gg 1$ is that which enhances the scrambling reaction, eq. (5); in fact, experimental practice is to reduce the relative concentration of the vibrationa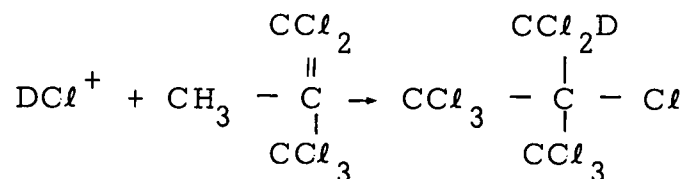lly excited reactant in order to enhance the reaction rate relative to the rate of $V \to V$ energy transfer. Thus, we see that while a large reaction constant presupposes a small scrambling rate, in order to take advantage of this rate enhancement, one must adjust the relative reactant concentrations in a manner which maximizes the scrambling probability.

Because of this and other difficulties[14], we consider another class of isotopically selective reactions which may be vibrationally catalyzed: hydrogen halide additions to unsaturated hydrocarbons in the gas phase[15]. As a specific example, consider the gaseous addition of hydrogen chloride to isobutene and the inverse reaction, the thermal decomposition of tertiary butyl chloride[16], i.e.,

$$HC\ell + CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_2}{||}}{C}} \rightleftarrows CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - C\ell \qquad (11)$$
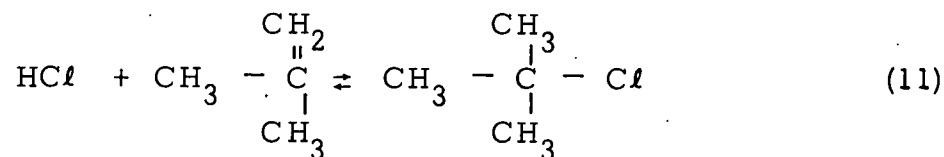
In analogy with the above, we suppose that the addition reaction can be made isotopically selective by the addition of vibrational excited $DC\ell$ to chlorinated isobutene, i.e.,

$$DC\ell^{+} + CH_3 - \underset{\underset{CC\ell_3}{|}}{\overset{\overset{CC\ell_2}{||}}{C}} \rightarrow CC\ell_3 - \underset{\underset{CC\ell_3}{|}}{\overset{\overset{CC\ell_2 D}{|}}{C}} - C\ell$$

Thermal decomposition of the product of reaction (11) would then yield isotopically pure $DC\ell$.

$$CCl_3 - \overset{\overset{\displaystyle CCl_2D}{|}}{\underset{\underset{\displaystyle CCl_3}{|}}{C}} - Cl \;\rightarrow\; CCl_3 - \overset{\overset{\displaystyle CCl_2}{\|}}{\underset{\underset{\displaystyle Cll_3}{|}}{C}} + DCl \tag{12}$$
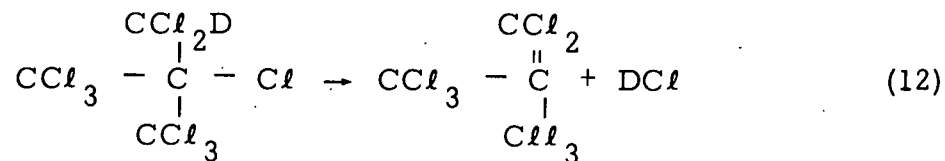
which can be exchanged with water. The block diagram of a prototype system to produce heavy water based on reactions (11) and (12) is shown in Figure 1 below:
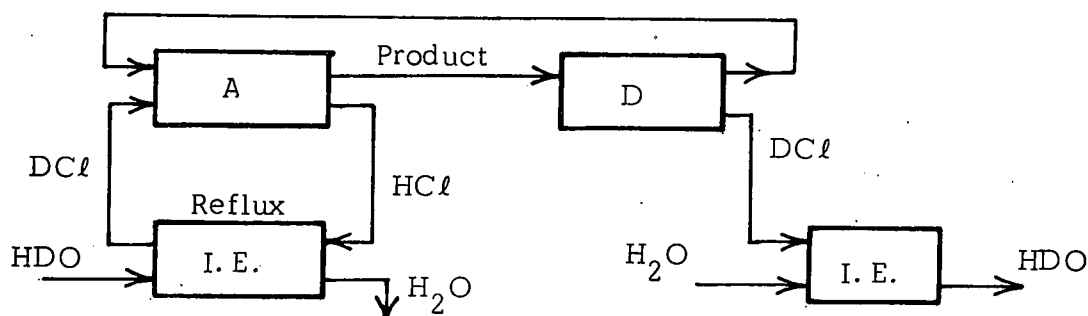
A = laser-driven association reaction

B = thermal dissociation reaction

I.E. = isotopic exchange interaction

Figure 1

Obviously, many variations on this prototype addition reaction are possible; some of the basic requirements for an effective separation process based on this scheme are:

a.   A reaction activation energy of magnitude such that excitation of the hydrogen halide to a low-lying vibrational level results in a reaction rate sufficient to compete with energy transfer processes which decrease the isotopic selectivity[17].

b.   A scavenger molecule which has no equivalent H atom. This requirement lies behind the choice of chlorinated isobutene as the scavenger in the prototype reaction (11). That is,

the thermal decomposition of the reaction product of $DC\ell^+$ and ordinary isobutene would yield $H\,C\ell$ rather than $DC\ell$, due to the kinetic isotope effect[18].

c.   Favorable conditions in the non-laser part of the separation process: In common with many other separation schemes, e.g., photodissociation of formaldehyde and H_2S/H_2O chemical exchange, the economic viability of this process depends on refluxing the reactant which is depleted of deuterium. Unfortunately, the hydrogen halides are not ideal in this respect since each of the hydrogen halide-water systems is very corrosive, has an unfavorable equilibrium constant for reflux, and forms a constant boiling mixture which complicates the design of the reflux process.

3.0   MULTIPLE PHOTON DISSOCIATION

There are two prime candidates at the present time: monodeute-
rated formaldehyde HDCO, and monodeuterated ammonia, NH_2D.
Relatively speaking, the former looks better from the point of view
of the primary photochemical reactions, while the latter has the
advantage of a straightforward reflux reaction with water to rein-
rich the depleted feedstock. To elaborate: multiple photon
dissociation of formaldehyde leads to stable reaction products,
i.e.,

$$HDCO + nh\nu \rightarrow HD + CO \tag{13}$$

while a similar reaction in ammonia would lead to radical forma-
tion[19], necessitating the use of a scavenger to trap the D atom.
In addition, it may be difficult to compensate for the "anharmonicity"
due to inversion doubling in the ν_2 mode of NH_2D. Analysis of
available spectroscopic information is in progress to shed light on
the possible mechanism(s) for NH_2D dissociation. Experimental
evidence for reaction (13) has recently been reported[20]. Un-
fortunately, the primary quantum efficiency, i.e., HD molecules
separated/CO_2 photons absorbed $\simeq 10^{-7}$, which is several orders
of magnitude too small to be economically viable. It is not clear
at this time whether this low value is due solely to the use of a
focused beam. However, the intensive research effect devoted
to U-235 separation via multiple photon dissociation of $^{235}UF_6$
should provide useful "spillover," e.g., the use of light wave-
guides to improve the quantum efficiency of separation using a
single frequency focused beam, or the possibility of using colli-
mated beams in separation schemes utilizing two lasers. This
is clearly a fruitful area for further investigations.

As for reflux: ammonia is ideal, i.e., the equilibrium constant
for the reaction

$$NH_2D + H_2O \rightleftharpoons NH_3 + HDO \qquad (14)$$
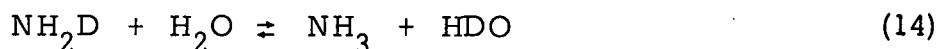
is close to unity and no catalyst is required.

Unfortunately, formaldehyde reflux is a more difficult process. In the first place, catalysis is required. Basically the reason for this is that, as compared with N - H, O - H, S - H and Halogen atom - H bonds, the exchange of the H atom in a C - H bond is difficult due to the absence of electrons not involved in the bonding. That is, O, N, S and Halogen atoms in electrically neutral molecules have a free pair of electrons, so that a deuteron may attach with the simultaneous elimination of a proton. In contrast there are no free electrons in the electron cloud of a carbon atom of an organic compound. Therefore exchange is possible only by breaking the C — H bond. Since this requires considerable activation energy, exchange is very slow without catalysis. Recently, evidence that formaldehyde exchanges with _heavy_ water over a platinum catalyst has been obtained by investigators at the Ontario Hydro Research Division in Toronto[21]. This is an important first step; however, there are problems, e.g., cracking of the formaldehyde by the platinum, and a good deal of further work is necessary before the commercial feasibility of this process is established.

4.0 CONCLUSION

In this report we have indicated some promising lines of research on methods for producing heavy water by using lasers to selectively excite vibrational modes of isotopic molecules. Besides the processes discussed in Sections II and III, we have also started work on a promising new area—vibrationally catalyzed adsorption and desorption. A full description of these efforts as well as further research in vibrational photochemistry, and a detailed analysis of the economics and engineering of heavy water laser isotope separation will appear in the final report.

5.0 REFERENCES

1.   V. S. Letokkov and C. B. Moore, "Laser Isotope Separation," preprint LBL-4904, University of California, Berkeley.

2.   A. I. Miller and H. K. Rae, "The Search for an Improved Heavy Water Proces," Chemistry in Canada, March 1975, p. 28. The cost of heavy water produced by a plant using the G-S process built today would be approximately $200/kg.

3.   The rationale for this method is that for two isotopic species strongly coupled by V → V energy transfer processes, the heavier isotope, with a lower energy of the vibrational quanta, and, consequently, with a higher vibrational temperature, reacts faster during the period of quasi-equilibrium which exists from the time of the intiial laser excitation of the heavier isotope until V → T relaxation processes became important.

4.   E. M. Belenov et al., JETP Letters 18, 116 (1973).

5.   N. G. Basov et al., Sov. J. Quant. Electron. 5, 510 (1975).

6.   V. S. Letokhov and A. A. Makarov, J. of Photochemistry 3, 249 (1974). See, in particular, p. 259 and p. 261, where the condition for the validity of Eq. (1) is given as $\frac{\Delta E}{kT} \gg \frac{h\nu_h}{E_a}$. Physically, this is equivalent to the fact that the selectivity due of the pumping of the heavier isotope is lost due to V → V energy transfer, and hence that a wide-band pump source would be equally effective.

7.   Reference No. 6, p. 262, Eq. (55).

8.   J. H. Birely and J. P. Lyman, J. of Photochemistry 4, 269 (1975).

9.   M. J. Kelley, R. E. Francke, and M. S. Feld, J. Chem. Phys. 53, 2979 (1970).

10. See, e.g., M. Benedict and T.H. Pigford, <u>Nuclear Chemical Engineering</u> (McGraw-Hill, 1957), p. 454.

11. This is a quantum-mechanical effect; classically $k(T) = 1$ for all T. See J. Bigeleisen and M.G. Mayer, <u>J. Chem. Phys.</u> <u>15</u>, 261 (1947).

12. The important exception is the ammonia/hydrogen exchange

$$NH_3 + HD \rightleftharpoons NH_2D + H_2$$

which occurs in the gas phase.

13. See, e.g., S.H. Bauer <u>et al.</u>, <u>Int. J. of Chem. Ken.</u> <u>5</u>, 93 (1973), and references cited therein.

14. Among which is the fact that H_2O is an effective V – T relaxer.

15. For a general discussion, see, e.g., P.B.D. de la Mare and R. Bolton, <u>Electrophilic Additions to Unsaturated Systems</u> (Elsevier, 1966), Chapter 5.

16. G.B. Kistakowsky and C.H. Stauffer, <u>J. Am. Chem. Soc.</u> <u>59</u>, 165 (1937).

17. See, e.g., D. Arnoldi, K. Kaufmann, and J. Wolfrum, <u>Phys. Rev. Letters</u> <u>26</u>, 1597 (1975), for a description of a diatomic molecule – atom isotopically selective reaction where it was possible to chose experimental conditions which satisfy this requirement.

18. See, e.g., S. Ruehlemann, <u>Z. Phys. Chem.</u> <u>242</u>, 353 (1969).

19. The dissociation products of NH_2D as a function of laser wavelength are not known. However, dissociation of NH_3 using a CO_2 TEA laser results in the production of NH_2 + H. See J.D. Campbell <u>et al.</u>, "Dissociation of NH_3 to Ground Electronic State Fragments by High Intensity CO_2 Radiation,"

preprint, Department of Physics, Bielefeld University, Bielefeld, Germany.

20. G. Koren et al., *Appl. Phys. Letters* 29, 40 (1976).

21. K. Woodall, private communication.