Applied Physics Letters

Deuterium separation with 1400-fold single-step isotopic enrichment and high yield by CO_2-laser multiple-photon dissociation of 2,2-dichloro-1,1,1-trifluoroethane

Cite as: Appl. Phys. Lett. **34**, 439 (1979); https://doi.org/10.1063/1.90819

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AIP Publishing

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The laser spectrum which was taken with the 5%-output mirror is shown in Fig. 3. It exhibits single axial-mode operation.

For the 5%-output mirror, we have calculated for $\lambda_p = 615$ nm from Eqs. (41), (43), (45), and (49) in Ref. 2 the cold-cavity lifetime $\tau_Q = 3.2$ nsec, the stimulated lifetime $\tau_s = 19\ \mu$sec, and the relaxation oscillation frequency $\omega_0 = 4.1 \times 10^6$ sec^{-1} for $P_{\text{out}} = 2.6$ mW or $2\pi/\omega_0 = 1.5\ \mu$sec, which is in quite good agreement with the experiment (Fig. 4).

In conclusion, within experimental error, pumping of the $Nd(Al,Cr)_3(BO_3)_4$ laser via Cr^{3+} up to Cr^{3+} concentrations of at least 10% is no less efficient than pumping via Nd^{3+}. Lowering the losses to a few percent would lead to thresholds in the mW range and to slope efficiencies exceeding 20%. We have estimated the material to be attractive for sun pumping because the emisssion spectrum of the sun and the Cr^{3+} absorption spectrum are well matched.

We thank Professor H.G. Danielmeyer for useful discussions. The work was supported by the Deutsche Forschungsgemeinschaft.

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Deuterium separation with 1400-fold single-step isotopic enrichment and high yield by CO_2-laser multiple-photon dissociation of 2,2-dichloro-1,1,1-trifluoroethane

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(Received 23 October 1978; accepted for publication 27 November 1978)

The compound 2,2-dichloro-1,1,1-trifluoroethane, CF_3CHCl_2, has been selected in an exhaustive search as the most promising working material for potentially viable laser separation of deuterium. Highly isotopically selective absorption in CF_3CDCl_2 occurs near 10.2 and 10.6 μm, accessible with the normal CO_2 laser. The single-step deuterium isotopic enrichment factor attains a value of 1400 at a fluence of 10 J/cm^2 for the dominant photoproduct, trifluoroethene ($CF_2 = CFD$ and $CF_2 = CFH$). The probability for CF_3CDCl_2 dissociation into $CF_2 = CFD$ photoproduct occurs with a fluence threshold near 1.5 J/cm^2 and appears to saturate near 100% yield above 15 J/cm^2. Liquid-phase base-catalyzed H/D exchange occurs rapidly with water without hydrolysis to permit redeuteration of the CF_3CHCl_2 working material.

PACS numbers: 28.60. + s, 33.80.Kn, 82.50.Cr, 82.30.Lp

Techniques for practical laser separation of deuterium are conceded to pose a very great challenge,[1-5] due primarily to the present low cost of the deuterium isotope. Stringent chemical, photochemical, and laser requirements strongly restrict what chemicals and processes can even be considered for large-scale photochemical deuterium separation.[6] These criteria include: (a) H/D exchange tied to a virtually inexhaustible hydrogeneous source; (b) greater than 1000 : 1 D/H selectivity in multiple-photon absorption for acceptable photon utilization, accessible by efficient high-power ir lasers, e.g., CO_2 laser at 9.2–10.8 μm; (c) deuterium-bearing dissociation products stable to deuterium loss by exchange with the remaining protonated molecules, walls, or moisture; and finally, (d) low cost, low toxicity, chemical stability, and sufficient volatility. A systematic and quite extensive survey of over 200 haloalkanes, ketones, aldehydes, esters, alcohols, amines, alkynes, alkenes, haloalkenes, and other compounds has identified 2,2-dichloro-1,1,1-trifluoroethane, CF_3CHCl_2, as the compound that best satisfies all the stated requirements for (practical) large-scale laser deuterium separation by infrared multiple-photon dissociation.[6,7] This letter discusses some of the physical, spectroscopic, and photochemical factors suggesting that CF_3CHCl_2 be seriously considered for use in laser separation of deuterium.

The compound CF_3CHCl_2 (Freon 123) was obtained commercially.[8] The deuterated compound containing 98% CF_3CDCl_2 was prepared by aqueous exchange with $D_2O + NaOD$. For large-scale heavy-water production, deuterium-depleted Freon 123 would be redeuterated with natural water according to the steps:

$$CF_3CHCl_2 + OH^- \rightarrow CF_3CCl_2^- + H_2O, \qquad (1)$$

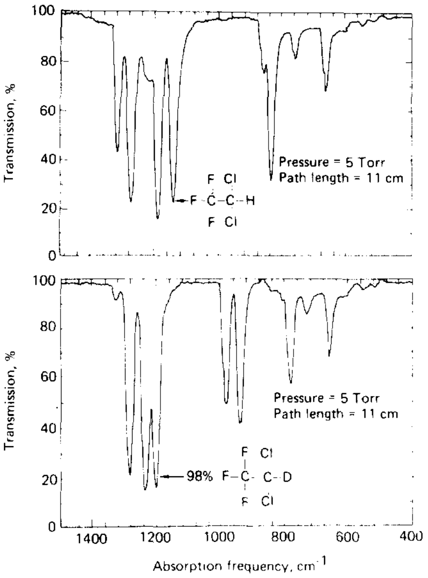

FIG. 1. Absorption spectra of gaseous 2,2-dichloro-1,1,1-trifluoroethane, CF_3CHCl_2 (upper trace), compared to absorption of 98% CF_3CDCl_2 (lower trace). Highly selective absorption in the deuterated species occurs for CO_2 laser excitation near 10.2 and 10.6 μm.

$$CF_3CCl_2^- + HDO \rightarrow CF_3CDCl_2 + OH^-. \qquad (2)$$

H/D exchange proceeds via base-catalyzed carbanion formation in Eq. (1), which is the rate-limiting step. The aqueous H/D exchange rate is about 0.07 sec^{-1}/mole liter at 20 °C, according to Hine.[9] Additonal advantages of Freon 123 are the slow hydrolysis rate which is estimated to be less than 10^{-6} of the H/D exchange rate,[10] and the deuterium enrichment factor of 1.26 which occurs during the aqueous exchange step.[9]

The infrared spectrum of CF_3CHCl_2 has been reported earlier,[11] but the infrared spectrum of CF_3CDCl_2 is reported here for the first time; both are shown in Fig. 1, which clearly indicates the two strong absorption features at 944 and 986 cm^{-1} in CF_3CDCl_2 (10.6 and 10.2 μm, C-D bands), in a spectral region in which CF_3CHCl_2 is highly transparent. The maximum absorption coefficient of CF_3CDCl_2 is about 2.0×10^{-2} $Torr^{-1}$ cm^{-1} at 944 cm^{-1}, corresponding to a room-temperature deuterium isotopic selectivity of about 100 : 1, based on linear absorption. The weak absorptions in CF_3CHCl_2 near 10.6 μm may be due to contributions of impurities, weak combination[11] or hot bands.

Room-temperature samples at 0.05–25 Torr were irradiated with 1–40 pulses from a mildly focused (focal length = 40–250 cm) commercial CO_2 TEA laser providing up to 5 J in 100-nsec FWHM pulses. Photolysis cells ranged in length from 30 to 120 cm, with a 3.5-cm diameter. The carbon-bearing photo-products were analyzed by gas chromatography (Chromosorb 102) using flame ionization detection. $CF_2 = CFD$ is the dominant deuterium-bearing photoproduct in multiple phototon dissociation of Freon 123 near 10.6 μm, and therefore deuterium enrichment was measured by mass spectrometric analysis of the deuterium content of the trifluoroethene product. Photolyzed gas samples were slowly admitted to the mass analyser through an *n*-pentane slush coolant at − 130 °C, which almost completely blocked unphotolyzed Freon 123 (boiling point = + 29 °C), while easily passing the trifluoroethene (boiling point = − 56 °C). The peak heights at mass 63 and 64, corresponding to the C_2F_2H and C_2F_2D fragments of trifluoroethene, permitted isotope analysis, after subtracting both a 2.2% contribution at mass 64 due to $^{13}C^{12}CF_2H$, and the slight residual interference from Freon 123 at mass 63 and 64 (5–20% of total height as determined from the Freon 123 mass-67 peak, $CF^{35}ClH$).

The thermal dissociation of Freon 123 in shock-tube studies[12] (1120–1260 °K) produces three main carbon-containing products—$CF_2 = CFH$, $CF_2 = CFCl$, and CF_3CCl_3—in addition to HCl. Collisionless dissociation of CF_3CDCl_2 in a reservoir of CF_3CHCl_2 by a pulsed CO_2 laser near 10.6 μm yileds $CF_2 = CFD$ as the dominant product, as well as the two fully halogenated hydrocarbons to a lesser extent. The major steps in the reaction mechanism are thought to be as follows:

$$CF_3CDCl_2 + nh\nu(10.6\,\mu m) \rightarrow CF_2 = CFCl + DCl, \qquad (3)$$

$$CF_3CDCl_2 + nh\nu(10.6\,\mu m) \rightarrow CF_3\dot{C}DCl^\dagger + Cl\cdot, \qquad (4)$$

$$CF_3\dot{C}DCl^\dagger + M \rightarrow CF_2 = CFD + Cl\cdot + M, \qquad (5)$$

$$Cl\cdot + CF_3CHCl_2 \rightarrow CF_3\dot{C}Cl_2 + HCl, \qquad (6)$$

$$CF_3CHCl_2 + CF_3\dot{C}Cl_2 \rightarrow CF_3CCl_3 + CF_3\dot{C}HCl. \qquad (7)$$

Evidently, the major dissociation channel is chlorine atom elimination [step (4)]; the resulting vibrationally excited CF_3CDCL radical many eliminate a second chlorine atom and rearrange to form the stable deuterium-bearing product $CF_2 = CFD$, either via collisions [step (5)] or perhaps by absorption of additional ir quanta. The Cl atom chain reaction implied in this mechanism is apparently very short.[12] Production of $CF_2 = CFH$, via step (7) followed by the H analog of step (5), may be detrimental to deuterium enrichment at high pressures.

The analysis of deuterium enrichment in the trifluor-

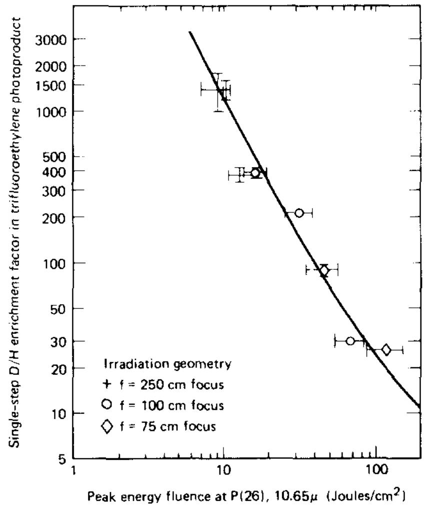

FIG. 2. The single-step D/H enrichment factor in trifluoreoethene produced from CO_2 laser photolysis at *P*(26), 10.65 μm of gaseous CF_3CHCl_2 at 0.5 Torr containing 0.5% CF_3CDCl_2 for various values of the laser energy fluence.

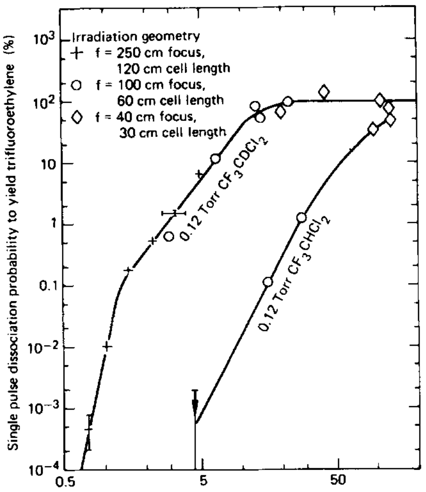

FIG. 3. The single-pulse probability that 2,2-dichloro-1,1,1-trifluoroethane will dissociate to yield trifluoroethene photoproduct as a function of peak CO_2 laser energy fluence using the $P(28)$ line, 10.67 μm. The upper curve gives the probability of $CF_2 = CFD$ yield from CF_3CDCl_2 photolysis at 0.12 Torr and the lower curve gives the probability of $CF_2 = CFH$ yield from CF_3CHCl_2 photolysis also at 0.12 Torr.

oethene photoproduct yields the single-step deuterium enrichment factor β, defined as follows:

$$\beta = \frac{[CF_2 = CFD]/[CF_2 = CFH]\ \text{(photoproduct)}}{[CF_3CDCl_2]/[CF_3CHCl_2]\ \text{(starting material)}}. \qquad (8)$$

A very strong improvement in the single-step deuterium enrichment factor resulted from photolysis at reduced energy fluence, as shown in Fig. 2. The data for Fig. 2 were all taken at a pressure of 0.5 Torr total Freon 123 containing 0.5% CF_3CDCl_2. Figure 2 shows that β increased from 27 at a fluence near 100 J/cm² to 1400 near 10 J/cm² fluence. At high fluence (100 J/cm²) β decreases rapidly above 1 Torr.

An explanation for the sensitivity of β to fluence is suggested by Fig. 3, which indicates the probability per single pulse that Freon 123 will dissociate to yield trifluoroethene as a function of energy fluence [$P(28)$, 10.67 μm at 0.12 Torr]. Figure 3 shows that CF_3CDCl_2 has an approximate dissociation threshold at about 1.5 J/cm² and saturates near 15 J/cm² at what appears to be 100% probability for dissociation to yield $CF_2 = CFD$. Figure 3 also shows the dissociation probability for production of $CF_2 = CFH$ from CF_3CHCl_2, which rises rapidly above about 20 J/cm² fluence. The absolute yields per pulse plotted in Fig. 3 were determined from the trifluoroethene yield per pulse (given by GC analysis) divided by the ratio of the irradiated cell volume V_f to the total cell volume. V_f enclosed the measured focal region where fluence exceeded the lesser of one-half the peak focal fluence or 7 J/cm²; this latter limit defines the regions of appreciable dissociation at higher fluence (Fig. 3).

The dissociation probability of both deuterated and protonated Freon 123 have also been measured as a function of CO_2 laser wavelength. As expected, at low fluences ($\le$ 5 J/cm²), the yield qualitatively varies with wavelength as does the linear absorption coefficient, while at higher fluences the yields saturates from 10.2 to 10.7 μm for CF_3CDCl_2. In addition, at high fluences, the probability of CF_3CHCl_2 dissociation increases rapidly with decreasing wavelength near the CO_2 laser short-wavelength limit (9.2 μm).

Examination of Figs. 2 and 3 suggests that the optimal operating fluence for deuterium isotope separation is about 10 J/cm², at which the dissociation probability to yield $CF_2 = CFD$ is about 40%. If the optical selectivity were equal to the isotopic enrichment factor, then the laser-related energy requirement per separated D atom, E_D, for deuterium separation by CO_2 laser multiple-photon dissociation of Freon 123 would be given by the expression

$$E_D = \frac{nhc}{\epsilon_l \phi \eta \lambda}\left(1 + \frac{N_H}{\beta N_D}\right). \qquad (9)$$

To provide a rough estimate of the effective energy efficiency of the process, we use the measured values of $\beta = 1400$, photolysis wavelength $\lambda = 10.65\,\mu$m, and dissociation probability $\phi = 0.4$, and assume the dissociation barrier $n = 25$ photons, the laser efficiency $\epsilon_1 = 14\%$, the molecular excitation efficiency $\eta = 0.5$, and the deuterium natural abundance $N_\delta / N_H = 150$ ppm; these values seem reasonably conservative, and some are likely to be substantially improved with more refined systems. Expression (9) then estimates a laser-related electrical energy of 0.60 keV (or ~ 1.5 keV of equivalent thermal energy) per separated D atom. This is encouraging, as it is substantially less than the primarily thermal energy value of 2.7 keV per separated D atom for the present GS process utilizing water/hydrogen sulfide exchange.[13] The recent demonstration of 1200-fold single-step deuterium enrichment at 100 Torr of natural isotopic abundance Freon 123 using 2-nsec duration CO_2 laser pulses [14] verifies the capability for high pressure operation of deuterium by large-scale CO_2 laser photolysis of Freon 123 are now quite promising, due to the unique properties of this molecule. Further research is under way to extend understanding of the photon, kinetic, and chemical dynamics of this dissociation process.

This study, as well as other ongoing analyses of advanced concepts for improved heavy-water production, has greatly benefited from the encouragement and support by Lowell Wood and Edward Teller. The authors also gratefully acknowledge the expert technical assistance of J.E. Bowman. This work was supported by U.S. Department of Energy Office of Advanced Isotope Separation Technology through the UCLLL under contract number W-7405-ENG-48.

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Current dependence of spontaneous emission and of junction resistance as a test of the internal dynamics of injection lasers[a]

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(Received 30 October 1978; accepted for publication 22 January 1979)

An expression is derived for the current dependence of spontaneous emission in the lasing state. It shows that the slope of the emission above threshold is controlled by a product of two terms, of which only one is affected by the dynamics of lasing. Since the other depends on subthreshold properties, the slope of the spontaneous characteristic is not a definitive test of laser models. While a rise in spontaneous emission above threshold is inconsistent with the linear rate equations describing the stimulated recombination, a strong saturation is not supportive of them. As an example, comparison of the properties of the laser of Paoli and Barnes, which exhibited a strong saturation, with data on other stripe units with various degrees of saturation shows that the unusually strong saturation they find is caused by an unusually low product of threshold current and external efficiency, not by a different form of the rate equation. As an aside it is shown that the slope ratio also measures the ratio of junction resistances above and below threshold.

PACS numbers: 42.55.Px, 42.80.Sa, 42.65.Cq

We examine the utility of the current dependence of the spontaneous emission above threshold as a test of the dynamical interaction in the coherent state of injection lasers. This characteristic is easy to measure, and studies of it have been offered as a support of a nonlinear model of lasing[1] (stimulated recombination rate nonlinear in stimulating power) and also of the linear rate equation.[2,3] Since a goal of laser development is control of the modal content of the beam, it is important to determine the form of the rate equations appropriate to actual devices, for they have a profound effect on modal powering.[4] Our present analysis shows that while the slope of the spontaneous emission characteristic can be inconsistent with the linear rate equations, it cannot by itself establish the proper form. It provides a necessary but not a sufficient test of a rate equation.

Our discussion concerns the change in slope of the spontaneous emission P_s on crossing threshold. Let Ψ be the ratio of the slopes above and below threshold current I_0,

$$\Psi \equiv \left(\frac{\partial P_s}{\partial I}\right)_{\text{above}} \left(\frac{\partial P_s}{\partial I}\right)^{-1}_{\text{below}}. \tag{1}$$

The task is to decompose Ψ into terms depending on the coherent power P, which explore the dynamics of the lasing state, and terms depending on spontaneous or passive properties.

Partition the current into I_c exciting the coherent radiation and I_s the spontaneous remainder.[5]

$$I = I_c + I_s. \tag{2}$$

Both P_s and I_s are exponential functions of the junction voltage V:

$$P_s = P_{so} \exp(V/n_1 V_T), \qquad I_s = I_{so} \exp(V/n_0 V_T), \tag{3}$$

and

$$P_s/P_{so} = (I_s/I_{so})^{n_0/n_1}. \tag{4}$$

V_T is the thermal voltage and n_0 and n_1 are constants. Since $I_c = 0$ below threshold,

$$\Psi = \left(\frac{\partial I_s}{\partial I}\right)_{\text{above}} = \left(1 + \frac{\partial I_c}{\partial I_s}\right)^{-1}_{\text{above}}. \tag{5}$$

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[a] Work supported in part by the U.S. Army Research Office.