DEUTERIUM ENRICHMENT VIA SELECTIVE DISSOCIATION OF FLUOROFORM-*d* WITH A PULSED CO₂ LASER

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Fluoroform-d undergoes multiphoton dissociation when irradiated with a pulsed CO₂ laser and yields DF by unimolecular elimination. Product analysis by infrared spectroscopy and gas chromatography shows that this process can be used to effect deuterium enrichment. A deuterium enrichment factor of greater than 5000 is obtained in natural fluoroform.

1. Introduction

Recognition of a limited supply of natural uranium for nuclear power reactors has given deuterium increased attention for its application in heavy water reactors (HWR) employing a thorium cycle and in deuterium--tritium fusion reactors (DTR). Canada is presently the major producer of deuterium in the form of heavy water, primarily for use in their CANDU reactors. Their projected production capacity of 3400 metric tons of D_2O per year by the early 1980's by use of the Girdler sulfide (GS) process is expected to be insufficient to meet demands for the mid-1990's [1]. The search for new means to separate deuterium is predicated on the high capital costs of the GS process and the toxicity of the large inventories of H_2S that the process requires.

A means of deuterium enrichment which has potential for large-scale application is reported here. The technique is based on the selective infrared multiphoton dissociation of fluoroform-d (CF₃D). The infrared spectra of CF₃H [2] and CF₃D [3] have been reported previously. The v_5 degenerate C-F stretching mode of CF₃D occurs at 975 cm⁻¹, a spectral region accessible with the output from a tunable CO₂ laser. In fig. 1 the Fourier transform infrared spectrum of this vibrational band is shown. In addition, the infrared spectrum of CF₃H in this spectral range is given, along with the CO₂ laser frequencies. The weak band in CF₃H, centered at 1015 cm⁻¹, is attributed to $2\nu_6$ (the ν_6 fundamental frequency is 507.6 cm⁻¹). At the peak of the P-branch (970 cm⁻¹), the CF₃D absorption cross section is approximately 3.0×10^{-19} cm². At this frequency, the absorption cross section of the $2\nu_6$ vibration in CF₃H is about 4.7×10^{-23} cm², which is smaller by a factor of 6300. Since Marling and Herman [4] have previously shown that in a multiphoton process the isotopic selectivity can considerably exceed the ratio of the linear absorption coefficients, the large ratio obtained for CF₃D/CF₃H makes fluoroform an extremely attractive system for deuterium enrichment.

The use of fluoroform for laser enrichment of deuterium has additional advantages over other systems previously studied. Thermal decomposition studies of CF_3H in shock tubes [5] indicate the dissociation and reaction channels to be

$$CF_3H \to : CF_2 + HF, \qquad (1)$$

followed by

$$2: CF_2 \to C_2 F_4 . \tag{2}$$

In the present study, direct unimolecular elimination of DF is also observed. In addition, this appears to be the only accessible dissociation channel. Other laser enrichment schemes of deuterium [4,6] employing hydro-

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Fig. 1. Infrared spectra of CF₃H showing the $2\nu_6$ band at 1015 cm⁻¹ and CF₃D showing the ν_5 fundamental at 970 cm⁻¹. The CO₂ laser lines are presented at the bottom for comparison.

carbons have reported more than one dissociation channel. Also, the DF generated upon CF_3D dissociation is easily removed from the feed material stream by, for instance, reaction with NaF. Heating of the resulting NaDF₂ would then yield the enriched DF.

2. Experimental

Due to the inherent experimental difficulty in collecting and analyzing small quantities of DF (or HF) gas because of its extremely high chemical reactivity, two indirect approaches were taken to evaluate reactions (1) and (2) and to determine the isotopic selectivity. The two approaches were to monitor infrared fluorescence from vibrationally hot DF or HF upon CO₂ laser irradiation of CF₃D or CF₃H, and to determine C_2F_4 formation by infrared spectroscopy and gas chromatography.

The CF₃D used in these experiments was obtained from Merck, Sharp, and Dohme of Canada, and had a specified isotopic purity of 98.9%. This purity was confirmed by mass spectrometric analysis. The CF₃H was obtained from Matheson Gas Company.

2.1. DF fluorescence

It is known that CO₂ laser irradiation of vinyl fluoride produces vibrationally excited HF even under collisionless conditions [7]. In the present study DF fluorescence is observed upon CO₂ laser-induced dissociation of CF3D. A line-tunable Lumonics model 203 CO₂ TEA laser tuned in all cases to the R(14), 10 6 μ m transition (971.9 cm^{-1}) was used to irradiate the samples. The laser output pulses, having a fwhm pulse width of 150 ns and a pulse energy of 900 mJ, were focused by a 17.5 cm focal length NaCl lens into a 30 cm long pyrex cell equipped with NaCl end windows. A liquid nitrogen cooled, photovoltaic InSb detector orthogonal to the laser beam was used to monitor infrared fluorescence. The detector was equipped with either a 3.04-3.99 µm bandpass filter to isolate DF emission, or a 2.09-2.73 µm filter to monitor HF fluorescence. The InSb detector signals were amplified and introduced into a Biomation 8100 transient recorder-Tracor-Northern 575A signal averager combination for averaging.

2.2. $C_2 F_4$ formation

A second approach for determining the degree of deuterium enrichment possible via selective dissociation of CF_3D was based on product analysis by infrared spectroscopy and gas chromatography. Infrared spectra of individual samples of CF_3H and CF_3D and mixtures of these two materials were recorded with a Nicolet model 7199 Fourier transform infrared spectrometer. A 15 cm long glass cell fitted with NaCl windows and containing samples at pressures ranging from approximately 0.1 kPa to 1.3 kPa was used. These samples were subsequently irradiated with 900 mJ pulses and the infrared spectrum was then re-recorded.

Quantitative analysis of irradiated samples was also made by gas chromatography. A Hewlett–Packard model 5840 A gas chromatograph equipped with a 10 ft Poropak Q column was employed. The column temperature was maintained at 40°C. A He carrier flow of 30 cm³/min was used. These conditions yielded retention times of 6.7 min for CF₃D and CF₃H and 9.1 min for C₂F₄. Relative GC sensitivity of C₂F₄ to CF₃H was 7.2/1. The detection limit for C₂F₄ was found to be equivalent to a C₂F₄ partial pressure of 10^{-3} Pa in the irradiation cell (cell volume = 288 cm³).

3. Results and discussion

Initial experiments involved irradiating individual samples of CF₃H and CF₃D. Infrared spectra were recorded prior to and following irradiation. Samples of CF₃D showed a significant decrease in CF₃D concentration after CO₂ laser irradiation. The band intensities dropped uniformly by 40% for 5000 laser pulses and 85% for 20000 pulses. Spectra of the irradiated CF₃D also revealed the appearance of a strong band at 1337 cm⁻¹ which is assigned to the CF₂ asymmetric stretching vibration (ν_9) of C_2F_4 [8]. By comparing these spectra with a reference spectrum of C_2F_4 , the ratio of the CF_3D decomposed to the C_2F_4 formed was found to be approximately 2:1, consistent with the prediction of reactions (1) and (2). As anticipated, no DF was observed in the irradiated sample spectra, due to its reaction with the glass cell. Samples of CF3H showed no apparent changes in the infrared spectrum after irradiation. Based on the C_2F_1 detection limits, via infrared spectroscopy, the laser decomposition of CF₂H, if any, was less than 1/1000.

Mixtures of CF₃H and CF₃D, ranging in ratio from 1:1 to 20:1, were also irradiated. Sample pressures were from 0.1 to 1.3 kPa. In all cases no detectable change in CF₃H band intensities was observed, while the CF₃D band intensities were reduced considerably. The presence of C₂F₄ was noted by the appearance of the band at 1337 cm⁻¹. Typical spectra of a mixture before and after irradiation are shown in fig. 2.

Since the activation energy for the elimination of HF from CF_3H is 290 ± 6.7 kJ/mole [9] and the dissociation energy is 235 ± 10 kJ/mole [10], approximately 55 kJ/mole is available for partitioning among the degrees of freedom of the products. Hence, the product

tion of vibrationally excited DF or HF might be expected. Indeed, when samples of CF_3D in the pressure range from 0.003 kPa to 1.3 kPa were irradiated, fluorescence in the 3.04–3.99 μ m region was observed. This DF fluorescence was characterized by an instantaneous risetime (within the detection limit of 3 μ s) and a decay time which was dependent on the CF_3D pressure. A fluorescence curve obtained from a 3.3 Pa sample of CF_3D is shown in fig. 3. Since approximately 0.5 collision occurs at this pressure, the presence of a risetime which follows the detector response suggests that vibrationally excited DF is produced in a direct, unimolecular elimination.

Irradiation of CF₃H showed HF fluorescence in the spectral region of 2.17–2.83 μ m. For a 1.3 kPa sample of CF₃H, the normalized, relative HF intensity was lower by a factor of 1/19000 compared with DF fluorescence from a 1.3 kPa sample of CF₃D. F fluorescence from lower sample pressures were difficult to measure due to detector limitations. Since the relative branching ratios for DF(v = 1) and HF(v = 1) are not known, the DF/HF fluorescence intensity ratio of 19000 can only be construed as an upper bound to the dissociation selectivity.

In further pursuit of ascertaining CF₃H decomposition, a gas chromatographic investigation was undertaken. Samples of CF3D at 0.53 kPa contained in a cell of 288 cm³ volume were irradiated and analyzed by gas chromatography. A C_2F_4 yield commensurate with reaction channels (1) and (2) was found. No other products were detected. An identical experiment performed with CF_3H showed no C_2F_4 formation. With a $C_2 F_4$ detection limit of 10^{-3} Pa, an enrichment factor of >80000 would be predicted from these two studies. However, a discrepancy arises when note is made of the fact that naturally occurring CF3D in a 0.53 kPa sample of CF₃H (0.015% or 8×10^{-2} Pa) should have decomposed to yield $1.6 \times 10^{-2} Pa C_2 F_A$ which is well within the GC detection limit. It was postulated that CF2 radicals were being lost by mechanisms other than recombination to form vapor phase C_2F_4 . These mechanisms may include loss of CF_2 to cell walls or formation of nonvolatile polymers. Indeed, C₂F₄ itself undergoes efficient polymerization. This postulate was checked by irradiating mixtures of CF3D and CF₃H at a constant total pressure of 0.53 kPa. The ratio of C_2F_4 formed to the initial CF_3D concentration dropped from 0.22 at 0.53 kPa of CF₃D, to 0.06 at 0.1



Fig. 2. Infrared spectra of a 4 : 1 mixture of CF_3H : CF_3D before (left spectrum) and after (right spectrum) CO_2 laser irradiation. No change in the CF_3H band intensities is detectable following irradiation, while a substantial decrease in the CF_3D band intensities occurs. Also, following irradiation C_2F_4 formation is indicated by the appearance of the band at 1337 cm⁻¹.



Fig. 3. Infrared fluorescence signal obtained upon CO_2 laser irradiation of 3.3 Pa of CF_3D . The fluorescence is from vibrationally excited DF and exhibits an instantaneous risetime within the detector response time.

Pa CF_3D (all CF_3D pressures take into account the natural abundance in CF_3H). In addition, this ratio did not drop monotonically, but showed evidence of leveling-off at the lower CF_3D pressures. These data are shown in fig. 4. A model which includes formation of CF_2 via dissociation of both CF_3D and CF_3H , as well as recombination to form C_2F_4 and loss via other mechanisms has been developed. This model fits the dissociation data obtained and allows an enrichment factor to be determined.

A mixture containing initial concentrations $[CF_3D]_0$ and $[CF_3H]_0$ is irradiated with N laser pulses. Each laser pulse causes a fraction β of the CF₃D to be decomposed and a corresponding fraction γ of the CF₃H to be decomposed. The concentration of CF₂ radicals produced with the *n*th laser pulse is then

$$[CF_{2}]_{n} = \beta (1 - \beta)^{n-1} [CF_{3}D]_{0}$$

+ $\gamma (1 - \gamma)^{n-1} [CF_{3}H]_{0}$. (3)

237



Fig. 4. C_2F_4 formation as a function of initial CF ₃D pressure in mixtures with CF₃H at a constant total pressure of 0.53 kPa. \approx are experimental data points, the solid curve is a least squares fit of the data to eq. (6), the lower dotted curve is obtained if no CF₃H decomposition is assumed, and the upper dotted curve is obtained if both CF₃H decomposition and CF₂ loss mechanisms are omitted.

After each pulse, the CF_2 radicals combine at a rate k_1 to form C_2F_4 and are lost by other mechanisms at a total rate k_2 . Accordingly,

$$d[CF_2]_n/dt = -k_1[CF_2]_n^2 - k_2[CF_2]_n$$
(4)

and

$$d[C_2F_4]_n/dt = \frac{1}{2}k_1[CF_2]_n^2.$$
 (5)

By solving eqs. (4) and (5) and summing over N laser pulses, the total concentration of C_2F_4 is given by

$$\begin{bmatrix} C_{2}F_{4} \end{bmatrix}_{T} = \frac{1}{2} \begin{bmatrix} 1 - (1 - \beta)^{V} \end{bmatrix} \begin{bmatrix} CF_{3}D \end{bmatrix}_{0}$$

+ $\frac{1}{2} \begin{bmatrix} 1 - (1 - \gamma)^{V} \end{bmatrix} \begin{bmatrix} CF_{3}H \end{bmatrix}_{0}$
- $\frac{1}{2}k \sum_{n=1}^{N} \log \{1 + (1/k) [\beta(1 - \beta)^{n-1} [CF_{3}D]_{0} \}$
+ $\gamma(1 - \gamma)^{n-1} [CF_{3}H]_{0} \}, \qquad (6)$

where $k = k_2/k_1$. Eq. (6) was fit by a least-squares procedure to the data and is shown by the solid curve in fig. 4. The calculated values for the parameters were $\beta = (1.14 \pm 0.38) \times 10^{-4}$, $\gamma = (2.19 \pm 0.73) \times 10^{-8}$, and $k = (7.27 \pm 0.92) \times 10^{-6}$ Pa. The lower dashed curve is obtained if no CF₃H decomposition is assumed and the upper dashed curve is obtained if both CF₂ losses and CF₃H decomposition are omitted. An estimate of 5200 for the deuterium enrichment factor is, therefore, obtained from the ratio β/γ .

Other possible reaction mechanisms not explicitly covered by the model include the reaction of CF_2 radicals with CF_3H ,

$$: CF_2 + CF_3 H \to C_2 HF_5^* \to C_2 F_4 + HF.$$
(7)

Politanskii [9], however, showed that reaction (7) does not occur in vapor, bulk reactions. He detected pentafluoroethane, not as a result of reaction (7), but from further conversions of C_2F_4 and HF on his reactor walls.

Another possible reaction which may effect the formation of HF is energy transfer between excited CF_3D and ground-state CF_3H , followed by additional photon absorption of the CF_3H , leading to decomposition,

$$CF_{3}D^{\frac{1}{2}} + CF_{3}H \rightarrow CF_{3}D + CF_{3}H^{\frac{1}{2}} ,$$

$$CF_{3}H^{\frac{1}{2}} + nh\nu \rightarrow : CF_{2} + HF .$$
(8)

Although eq. (3) does not distinguish CF_3H decomposition by MPD from the above bi-molecular process, the parameter γ represents a net effect of both processes averaged over the given operating conditions. This is easily seen by noting that the inclusion of reaction (8) necessitates the addition of a product term to equation (3). For simplicity, we drop the pulse number notation, *n*, and write

$$[CF_{2}] = \beta[CF_{3}D] + \gamma[CF_{3}H] + \phi[CF_{3}D] [CF_{3}H].$$
(9)

Since CF_3H decomposition is considerably less than that of CF_3D , the determination of γ and ϕ is influenced only at low CF_3D concentrations. Denoting $[CF_3D]/$ $[CF_2H] = R \ll 1$, eq. (9) can be written

$$[CF_{2}] = \beta[CF_{3}D] + \gamma'(1 + \phi'R)[CF_{3}H].$$
(10)

Averaging $\gamma'(1 + \phi'R)$ over the approximate region $10^{-4} < R < 10^{-2}$, then γ from eq. (3) $\approx \gamma'(1 + 10^{-2}\phi')$; and the enrichment factor $\beta/\gamma \approx \beta/\gamma'(1 + 10^{-2}\phi')$. Hence, at lower CF₃D concentrations, such as in natural fluoroform, the true enrichment factor, $\beta/\gamma'(1 + R\phi')$, may be somewhat higher than 5200; and, at high CF₃D concentrations, it may be somewhat lower. Volume 65, number 2

4. Conclusions

We have demonstrated the enrichment of deuterium via selective CO₂ laser dissociation of the CF₃D constituent in CF₃H with a CO₂ laser [‡]. Time resolved infrared fluorescence studies of the DF product molecule indicate direct elimination of vibrationally excited DF from the parent species. A comparison of DF and HF fluorescence intensities vield an upper bound of 19000 for the dissociation selectivity of CF₃D over CF₃H at a pressure of 1.3 kPa. Furthermore, an evaluation of $C_2 F_4$ production in mixed samples of $CF_3 D$ and CF₃H lead to a minimum enrichment factor of approximately 5000 in natural fluoroform. This value for the enrichment factor is substantially larger than that (≈1400) reported for deuterium enrichment via multiphoton dissociation of 2,2-dichloro-1,1,1trifluoroethane [4]. The enrichment in this letter system has been reported to drop dramatically at pressures greater than 0.1 kPa whereas in the present work the enrichment factor using fluoroform was derived at 0.53 kPa total pressure. Hence, selective laser dissociation of fluoroform-d may provide the basis for an im-

* Note added in proof: After the completion of this work, it was brought to our attention that the authors of ref. [4] have initiated laser studies on CF₃H and will publish their results in Chemical Physics Letters. proved deuterium enrichment scheme which could be scaled to commercial size.

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