Appl. Phys. B 51, 454–457 (1990)

Applied Physics B Photophysics and Laser Chemistry

# $^{18}$O-Selective IR MPD of Perfluorodimethyl Ether

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Received 20 April 1990/Accepted 11 July 1990

**Abstract.** The $^{18}$O-selective IR MPD of perfluorodimethyl ether $(CF_3)_2O$ has been studied. The dissociation yields of $(CF_3)_2{}^{18}O$ ($\beta_{18}$) and $(CF_3)_2{}^{16}O$ ($\beta_{16}$) and the isotope selectivity $\alpha(18/16)$ have been measured as functions of TEA $CO_2$-laser frequency, laser fluence and ether parent pressure. The $(CF_3)_2O$ molecule has been found to provide highly efficient $^{18}$O separation. The MPD yield of the desired isotope $^{18}$O varies in the range 3–13%; the selectivity $\alpha(18/16)$ achieves a value of 95 at the laser line 10P22, at moderate fluence $\phi = 4$ J/cm$^2$ and at $P_{(CF_3)_2O} = 0.5$ Torr.

**PACS:** 82.50, 33.00, 35.00

Isotope-selective infrared multiphoton dissociation (IR MPD) of polyatomic molecules has been successfully used to separate isotopes of a number of elements, e.g. carbon, hydrogen, and sulphur [1, 2]. The application of a pulsed TEA $CO_2$ laser as a source of excitation, and freons as initial substances made it possible to reach a high isotopic selectivity of the elementary separation act of $^{13}C$ $\alpha(13/12) = 10^2$–$10^3$ [3, 4]. As a result, the process of laser separation of $^{13}$C isotopes can now be realized on a large scale [5, 6]. At the same time, $^{18}$O separation by IR MPD was not so successful and a search is still continuing for an appropriate initial oxygen-containing molecule. For example, the $^{18}$O enrichment factors in the MP dissociation products of $(CF_3)_2CO$ and $CF_3COF$ molecules were 2.4 and 2.6, respectively [7, 8].

Aliphatic alcohols and ethers and their halogen derivatives are the most promising organic compounds for oxygen isotope separation since the stretching vibration of the ordinary C–O bond for these molecules falls within the $CO_2$ laser tuning range. Recently, we have studied isotope selective MPD of tetrahydrofuran $C_4H_8O$ [9] and $CF_3CH_2OH$ (2,2,2-trifluoroethanol) [10] molecules, where a selectivity $\alpha(18/16) \simeq 7.2$ in the dissociation product CO for $CF_3CH_2OH$ was obtained. Apparently, oxygen-selective IR MPD was first observed for $(CH_3)_2O$ molecules in [11], where the measured selectivity for $^{18}$O isotopes was 1.7. The selectivity value $\alpha = 90$ was reported for this molecule in [12]. But in our work [13] the maximum value of $\alpha(18/16)$ did not exceed 16. It was concluded in [13] that the value of $\alpha(18/16)$ in [12] had probably been overestimated. Results of $^{18}$O-selective IR MPD for a number of saturated ethers, starting from $(CH_3)_2O$, have recently been presented in [14]. In this work the value $\alpha$ for $(CH_3)_2O$ varied in the range 1.9–6.6 and a rather high selectivity, 350, was observed for diisopropyl ether, $(C_3H_7)_2O$.

In the present work we continue our search for a molecule suitable for $^{18}$O-selective IR MPD by investigating the $(CF_3)_2O$ molecule – a fully fluorinated analog of $(CH_3)_2O$. The $(CF_3)_2O$ molecule has an intense IR absorption band $\nu_{17}$ (970 cm$^{-1}$) assigned to the antisymmetric stretching vibration of the C–O bond ($\nu^a_{C-O}$) [15, 16]. This band is sufficiently isolated in the spectrum and its width is much narrower than that of $(CH_3)_2O$. This fact leads us to expect a higher selectivity.

## 1. Experimental

The experimental setup and measurement procedure used in this work are similar to those described in [10, 13]. The dissociation of $(CF_3)_2O$ was performed with the pulsed radiation of a tunable TEA $CO_2$ laser. The pulse duration was 80 ns (FWHM), its "tail" was ~1 μs duration and contained less than one third of the total energy. The $(CF_3)_2O$ used in these experiments had a natural abundance of oxygen isotopes ($^{18}O = 0.204\%$) and after additional purification it contained no less than 98% of the parent substance. The percentage of the detected impurity $CF_3H$ was about 1%.

The main final products of $(CF_3)_2O$ MPD in our experiments were $COF_2$, $CF_4$, and $C_2F_6$. A comparison of the consumption of $(CF_3)_2O$ with the amount of the various MPD products allowed us to conclude that under the conditions of our experiments (see below) almost the whole oxygen from the dissociated $(CF_3)_2O$ molecules is converted to $COF_2$. Since the mass peaks of $^{18}O$-enriched $COF_2$ coincide with those of the fragmentary ions of the parent ether, the MPD selectivity and yield were measured from the consumption of $(CF_3)_2O$ with a mass spectrometer. The dissociation yields of $(CF_3)_2{}^{18}O$-$\beta_{18}$ and $(CF_3)_2{}^{16}O$-$\beta_{16}$ were determined from the mass spectra of irradiated and unirradiated ether. For this purpose, argon was added as a marker in the ratio $(CF_3)_2O:Ar=100:1$. The consumption of both isotopic components was determined as the ratio $A_{16}=\frac{(I_{135}/I_{40})_N}{(I_{135}/I_{40})_0}$ or $A_{18}=\frac{(I_{137}/I_{40})_N}{(I_{137}/I_{40})_0}$ for the $^{16}O$- and $^{18}O$-containing components, where $I_{135}$, $I_{137}$, and $I_{40}$ are the peak intensities with $m/e=135, 137, 40$ corresponding to the molecular ions $CF_3$–$^{16}O$–$CF_2^+$, $CF_3$–$^{18}O$–$CF_2^+$, and $Ar^+$. The indices "$N$" and "0" correspond to the irradiated and unirradiated samples, respectively. The values $\beta_{16}$, $\beta_{18}$, and $\alpha$ were found from the following expressions

$$\beta_{16}=\frac{1}{\Gamma}[1-\sqrt[N]{A_{16}}],$$
$$\beta_{18}=\frac{1}{\Gamma}[1-\sqrt[N]{A_{18}}], \qquad (1)$$
$$\alpha=\beta_{18}/\beta_{16},$$

where $N$ is the number of laser pulses and $\Gamma$ the ratio of the irradiated volume to the cell volume.

## 2. Results

Figure 1 presents the spectral dependences of the MPD yields of $(CF_3)_2{}^{16}O$ ($\beta_{16}$) and $(CF_3)_2{}^{18}O$ ($\beta_{18}$) as well as the selectivity $\alpha=\beta_{18}/\beta_{16}$ on the laser radiation frequency $\Omega_{las}$. The dependences were measured with a gas pressure in the cell of 0.5 Torr and a fluence $\phi=4.0\ J/cm^2$. The MPD yield $\beta_{16}$ reaches 30% at the excitation in the center of the linear absorption band $\nu_{17}$ and remains practically constant in the case of the "blue" shift ($\sim 8\ cm^{-1}$, Fig. 1). In contrast, $\beta_{16}$ begins to fall rapidly as the laser frequency decreases (long-wave "red" shift). The measurements have shown that the MPD yield of the desired isotope $\beta_{18}$ may be rather high, $\beta_{18}=13\%$ at the frequency $\Omega_{las}=947.8\ cm^{-1}$ (10$P$16 line).

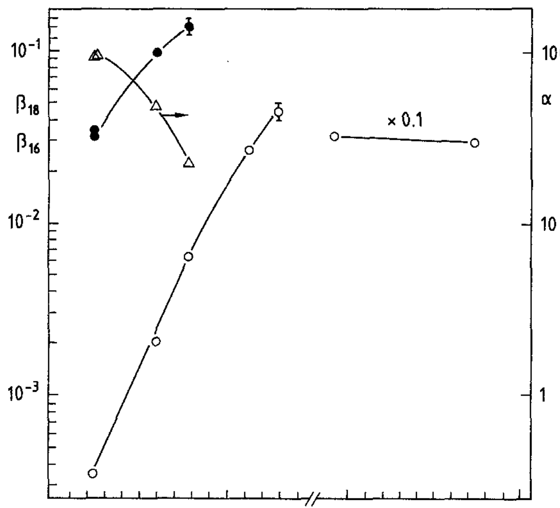

**Fig. 1.** Dependence of the dissociation yields of $(CF_3)_2{}^{18}O$ ($\beta_{18}$) and $(CF_3)_2{}^{16}O$ ($\beta_{16}$) and selectivity ($\alpha$) on laser radiation frequency $\Omega_{las}$ with $P=0.5$ Torr and $\phi=4\ J/cm^2$: (—●—) $\beta_{18}$; (—○—) $\beta_{16}$; (△) $\alpha$

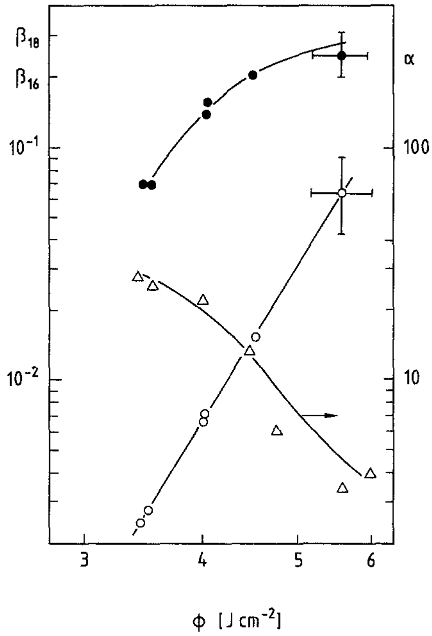

**Fig. 2.** Dependence of the dissociation yields $\beta_{18}$, $\beta_{16}$, and selectivity $\alpha$ on laser radiation fluence $\phi$, $\Omega_{las}=947.78\ cm^{-1}$ with $P_{(CF_3)_2O}=0.5$ Torr

The values of MPD yield measured for each component allowed a determination of the isotopic selectivity $\alpha=\beta_{18}/\beta_{16}$ and its dependence on the frequency $\Omega_{las}$. The dissociation yields $\beta_{16}$ and $\beta_{18}$ drop with different rates as the frequency is shifted to the long-wavelength region from the center of the $\nu_{17}$ band. As a result, the selectivity is enhanced and achieves $\alpha=95\pm5$ at $942.42\ cm^{-1}$ (10$P$22 line of $CO_2$ laser).

Figure 2 shows the yields $\beta_{16}$, $\beta_{18}$, and the selectivity $\alpha$ versus laser radiation fluence $\phi$ for the 10$P$16 line at a gas pressure of 0.5 Torr. As $\phi$ increases, the MPD yields for both components grow monotonically. With $\phi=5\ J/cm^2$, for example, $\beta_{18}$ may reach 30%. Since the MPD yield of the undesired component increases faster than that of the desired one, the selectivity decreases monotonically with increasing $\phi$.

In Fig. 3 the MPD yields and selectivity are given as functions of $(CF_3)_2O$ pressure. An increase in pressure (0.5–5 Torr) decreases the yield $\beta_{18}$ of the desired component $(CF_3)_2{}^{18}O$. The $\beta_{16}$ yield of the undesired component drops more slowly. Resulting in the selectivity decrease in the pressure range $P=0.5$–$3$ Torr. For $P\geq 3$, the value of $\beta_{16}$ begins to grow, leading to a rapid drop of the selectivity.

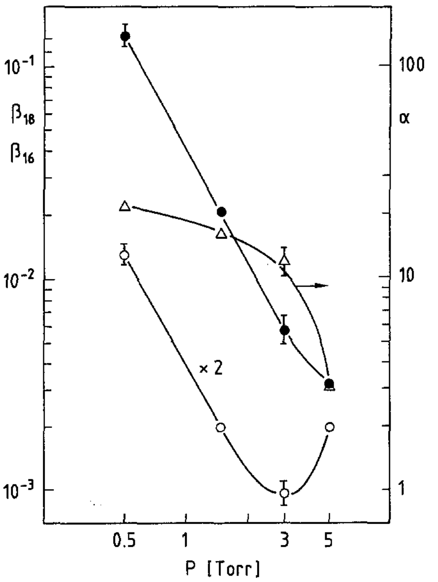

**Fig. 3.** Dependence of $\beta_{18}$, $\beta_{16}$, and $\alpha$ on $P_{(CF_3)_2O}$, $\Omega_{las} = 947.78\ cm^{-1}$ and $\phi = 4\ J/cm^2$. The values of $\beta_{16}$ are multiplied by a factor of 2

## 3. Discussion

The experiments show that the $(CF_3)_2O$ molecule provides sufficiently high separation parameters. The MPD yield of the desired isotope, for instance, lies in the range 3–13% and the selectivity achieves $\alpha(18/16) = 95$, which is one of the highest values for oxygen-containing molecules. It should be noted that rather high MPD yields can be attained with moderate laser radiation fluences, $\phi \simeq 4\ J/cm^2$. The dependences of the MPD yield and selectivity on the experimental conditions – laser frequency and fluence, ether pressure – are rather typical and similar to those obtained for other molecules and isotopes (see, e.g. [1, 2]).

Indeed, the selectivity drops with increasing fluence for practically all molecules studied earlier. This fluence effect is often explained by the power broadening. In the case of $(CF_3)_2O$, the selectivity decrease is obviously caused by the fact that for the desired isotope molecules the dissociation yield saturates at lower fluence than for the undesired ones. The pressure effect of $(CF_3)_2O$ is evidently determined by vibrational *V–V* energy exchange. As was shown for other molecules [17], the decrease in the yields of the two components $\beta_{16}$ and $\beta_{18}$ with increasing pressure at the initial stage is due to the vibrational deactivation of excited molecules by the bath of vibrationally "cooled" molecules of the rich isotope $(CF_3)_2{}^{16}O$. The drastic growth of $\beta_{16}$ above a certain pressure (3 Torr, Fig. 3) is determined by self-accelerating vibrational "heating" of $(CF_3)_2{}^{16}O$ molecules which causes a drop of selectivity.

The $^{18}O$-selective IR MPD of $(CF_3)_2O$ was reported in [14, 18]. The maximum selectivity $\alpha(18/16)$ was 2.5, which is much lower than the value obtained in our work.

The main difference between our experiments and the work performed by the Japanese group is that the latter worked with high fluences. Besides, the selectivity was measured in the dissociation product CO. We believe that the low selectivity in [18] is mainly caused by a high fluence; the value $\alpha = 2.5$ was measured in CO with $\phi = 15\ J/cm^2$. As is evident from Fig. 2, the value of $\alpha$ rapidly drops as $\phi$ increases. By extrapolating the experimental dependence $\alpha(\phi)$ to the region $\phi > 10\ J/cm^2$ we can obtain selectivity values close to those in [14, 18]. A high fluence is evidently also responsible for the formation of large amounts of CO in [18] as one of the final products of $(CF_3)_2O$ MPD. In the authors' opinion [14, 18], after the initial step: $(CF_3)_2O + nh\nu \rightarrow CF_3O^{\cdot} + CF_3^{\cdot}$, the "hot" radicals decompose sequentially or via secondary IR MPD forming, in part, CO.

In our experiments, the laser fluence ($\phi = 4\ J/cm^2$) was significantly smaller, therefore, the probability of "hot" radical formation and secondary IR MPD is much lower. Consequently, the relative CO yield has to drop. That is why in our experiments $COF_2$ was the main oxygen-containing dissociation product.

In conclusion, we wish to discuss some results of isotope-selective IR MPD of ethers. Table 1 presents some of these results obtained by us for $C_4H_8O$, $(CH_3)_2O$, and $(CF_3)_2O$. One of the most important parameters in laser separation of isotopes is IR MPD selectivity. The

**Table 1.** Characteristics of IR MPD of ethers

| Molecule and mode excited | Vibrational bandwidth (fwhm) | Laser line frequency [$cm^{-1}$] | Fluence [$J/cm^2$] | Pressure [Torr] | Yield of $^{18}O$-containing component (%) | Selectivity $\alpha(18/16)$ |
|---|---|---|---|---|---|---|
| Tetrahydrofuran<br>$C_4H_8O$ [9]<br>$\nu_7 = 1080\ cm^{-1}$ | 38 | 1048.66<br>9*P*18 | 6.1 | 0.3 | 1 | 1.03 |
| Dimethyl ether<br>$(CH_3)_2O$ [13]<br>$\nu_{17} = 1102\ cm^{-1}$ | 43 | 1050.42<br>9*P*16 | 3.8<br>3.8 | 5<br>0.5 | 0.05<br>0.6 | 16<br>7 |
| Perfluorodimethyl ether<br>$(CF_3)_2O$<br>$\nu_{17} = 970\ cm^{-1}$ | 15 | 942.42<br>10*P*22 | 4.0 | 0.5 | 3 | 95 |

highest selectivity has been achieved for $(CF_3)_2O$, and the lowest one for $C_4H_8O$. What does the selectivity depend on? The effect of secondary chemical reactions which may decrease the primary selectivity of IR MPD can be neglected for the ethers under study. This conclusion follows from an analysis of the rates of reactions in which the radicals formed by MPD participate. The contribution of collisional $V-V$ energy exchange can be neglected too, at least at low gas pressure (0.5 Torr). Therefore, we believe that the values of $\alpha$ given in Table 1 depend mainly on the spectral properties of the molecules. In the case of $C_4H_8O$, for example, the contribution of the stretching vibration of C–O bonds, $\nu_{C-O}$, to the excited mode $\nu_7$ is very small ($\sim 1\%$ [9, 19]). This must result in a low value of the oxygen isotopic shift for this mode and, hence, in a low selectivity. This conclusion is supported by the results of work [14] where a higher selectivity was obtained, $\alpha = 5$. In this work another mode ($\nu_8$) was excited in $C_4H_8O$. It is less intense in the IR spectrum but its component due to the $\nu_{C-O}$ is much larger ($\sim 20\%$ [19]).

In the case of $(CH_3)_2O$ the molecules were excited through the $\nu_{17}$ mode. The $\nu_{17}$ is a mixed stretching-deformation vibration of C–O and $CH_3$ bonds where the estimated contribution of the $\nu^a_{C-O}$ is no less than 50% [20]. This brings about a considerable oxygen-isotope shift $\Delta\nu_{C-^{18}O} = 12\ \text{cm}^{-1}$ to the longer wavelength side [11]. A comparatively low value of selectivity, $\alpha = 7$, in this molecule is obviously conditioned by a large width of the vibrational band ($\sim 43\ \text{cm}^{-1}$) that considerably exceeds the $\Delta\nu_{C-^{18}O}$.

In the case of $(CF_3)_2O$ the isotope shift is probably as large as in the case of $(CH_3)_2O$. At the same time, the band width is much narrower ($\sim 15\ \text{cm}^{-1}$, see Table 1). It is this factor that is evidently responsible for such a large increase in the IR MPD selectivity for this molecule.

In conclusion we would like to mention the availability of $(CF_3)_2O$ as a working substance for a large-scale LIS process. As far as we are informed $(CF_3)_2O$ is a by-product of some industrial fluoro-organic syntheses. This fact and the high values of MPD selectivity and yield are favourable for the realization of a large-scale LIS process using this molecule.

*Acknowledgement.* The authors would like to express their gratitude to Dr. K. N. Makarov for providing samples of perfluorodimethyl ether.

## References

1. V.N. Bagratashvili, V.S. Letokhov, A.A. Makarov, E.A. Ryabov: *Multiple Photon Infrared Laser Photophysics and Photochemistry* (Harwood, Chur 1985)
2. J.L. Lyman: "Laser-Induced Molecular Dissociation Application in Isotope Separation and Related Processes" in *Laser Spectroscopy and Its Applications*, ed. by L.J. Radziemski, R.W. Solarz, J.A. Paisner (Dekker, New York 1987)
3. M. Gauthier, C.G. Cureton, P.A. Hackett, C. Willis: Appl. Phys. B **28**, 43 (1982)
4. A.V. Evseev, V.B. Laptev, A.A. Puretzky, E.A. Ryabov, N.P. Furzikov: Kvant. Electron. **15**, 606 (1988) (in Russian)
5. G.I. Abdushelishvili, O.N. Avatkov, V.N. Bagratashvili et al.: Kvant. Electron. **9**, 743 (1982) (in Russian)
6. S. Arai, K. Sugita, P. Ma, Y. Ishikawa, H. Kaetsu, S. Isomura: Chem. Phys. Lett. **151**, 516 (1988)
7. P.A. Hackett, M. Gauthier, C.W. Willis, R. Pilon: J. Chem. Phys. **71**, 546 (1979)
8. E.B. Aslanidi, V.T. Zarubin, Yu.A. Turishchev: Laser Chem. **6**, 373 (1986)
9. V.B. Laptev, E.A. Ryabov, L.M. Tumanova: Zh. Fiz. Khim. **63**, 1898 (1989) (in Russian)
10. V.B. Laptev, E.A. Ryabov, L.M. Tumanova: Kvant. Electron. **16**, 1279 (1989) (in Russian)
11. V.V. Vizhin, Y.N. Molin, A.K. Petrov, A.R. Sorokinà: Appl. Phys. **17**, 385 (1978)
12. K.O. Kutschke, C. Willis, P.A. Hackett: J. Photochem. **21**, 207 (1983)
13. V.B. Laptev, E.A. Ryabov, L.M. Tumanova: Appl. Phys. B **49**, 77 (1989)
14. T. Majima, K. Sugita, S. Arai: Chem. Phys. Lett. **163**, 19 (1989)
15. J.D. Witt, J.R. Durig, D. DesMarteau, R.M. Hammaker: Inorg. Chem. **12**, 807 (1973)
16. H. Bürger, G. Pawelke: Spectrochim. Acta **31** A, 1965 (1975)
17. V.B. Laptev, N.P. Furzikov: Kvant. Electron. **14**, 2467 (1987) (in Russian)
18. T. Majima, T. Igarashi, S. Arai: Nippon Kagaku Kaishi N10, 1490 (1984)
19. L.A. Evseeva, L.M. Sverdlov: Izv. Vuzov, Fiz. **4**, 132 (1968) (in Russian)
20. P. Labarbe, M.T. Forel, Y. Bessis: Spectrochim. Acta **24** A, 2165 (1968)