Brief Communications

^{15}N Isotope-selective infrared multiphoton dissociation of nitromethane by a free electron laser

A. K. Petrov,[a]* *E. N. Chesnokov,*[a] *S. R. Gorelik,*[a] *K. D. Straub,*[b] *E. B. Szarmes,*[b] *and J. M. J. Madey*[b]

[a]*Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences,*
3 ul. Institutskaya, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 35 2350. E-mail: petrov@kinetics.nsk.su
[b]*Free Electron Laser Laboratory, Duke University, Durham, N.C., USA*

Successful experiments on the isotope-selective infrared multiphoton dissociation (IR MPD) of nitromethane molecules in the region of stretching vibrations of the NO_2 group have been performed for the first time under IR free electron laser (FEL) irradiation in a mixture with the natural content of the ^{15}N isotope of 0.4%. The content of the ^{15}N isotope in the products of NO dissociation varies within 0.1—1.6% as a function of the laser radiation frequency.

Key words: multiphoton dissociation, isotopic selectivity, free electron laser.

We have previously reported[1] on the first successful attempt at using IR free electron laser (FEL) radiation for isotope-selective multiphoton dissociation (MPD) of formic acid. Varying the wavelength of FEL radiation in the region of stretching vibrations of C=O, we were able to increase the contents of ^{13}C and ^{18}O from 1.1 to 22% and from 0.2 to 1%, respectively, in the CO formed due to the dissociation. In this work, we performed nitrogen isotope-selective IR MPD of nitromethane molecules by resonance excitation of the stretching vibrations of the NO_2 group. The absorption bands of these vibrations appear in the region of 6.3 μm and have high intensities and sufficiently great spectral shifts for nitrogen isotopes ^{14}N and ^{15}N (~25 cm^{-1}).

Experimental

Experiments were carried out on a Marc III free electron laser (Duke University, N. C., USA). The radiation was varied within 6.0—7.1 μm and consisted of macropulses with frequency 10 Hz, energy 4—8 mJ, and duration 1—1.5 μs. Each macropulse was a sequence of micropulses with duration 1—2 ps separated by an interval of 350 ps. The radiation was focused by a BaF_2 lens with a 90-cm focus distance to the center of a glass cylindrical cell with diameter 1.2 cm and length 12 cm. The cell was directly attached to a quadrupole mass spectrometer for analysis of the dissociation products. The $MeNO_2$ pressure in the cell was varied from 0.25 to 6 Torr in different experiments. The irradiation time was varied from 10 to 30 min, and conversion was within 2—6%. The compo-

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nents of the gas mixture were separated using a low-temperature trap before mass spectral analysis.

Results and Discussion

In early works on the study of the mechanisms of thermal[2,3] and photochemical[4] decomposition of nitromethane, the authors suggested that the following reaction with a dissociation barrier of 60 kcal mol^{-1} is the primary elementary act:

$$\mathrm{MeNO_2} \rightarrow \mathrm{Me} + \mathrm{NO_2} \qquad (1)$$

The complexity and variety of secondary chemical processes in this system were mentioned. In the later works,[5–7] the authors considered the isomerization of excited molecules

$$\mathrm{MeNO_2}^* \rightarrow \mathrm{MeONO}^* \qquad (2)$$

with a barrier of 47 kcal mol^{-1} [5] followed by the dissociation

$$\mathrm{MeONO}^* \rightarrow \mathrm{MeO} + \mathrm{NO}. \qquad (3)$$

In our experiments, NO and MeONO are the main products (Fig. 1). C_2H_6, CH_4, and C_2H_4 are also formed in minor (an order of magnitude lower) amounts. The absence of NO_2 means that no dissociation of the excited nitromethane molecules (1) occurs under the MPD conditions, and isomerization (2) with the formation of excited MeONO molecules, which are then decomposed partially to NO and the MeO$^\cdot$ radical and partially stabilized upon collisions with nitromethane molecules, is the main primary process. When the nitromethane pressure increases, the collision frequency increases and, hence, the fraction of MeONO molecules increases (Fig. 2). This scheme is confirmed by the calculations (performed according to the RRCM theory) of the lifetime of the excited MeONO molecules.

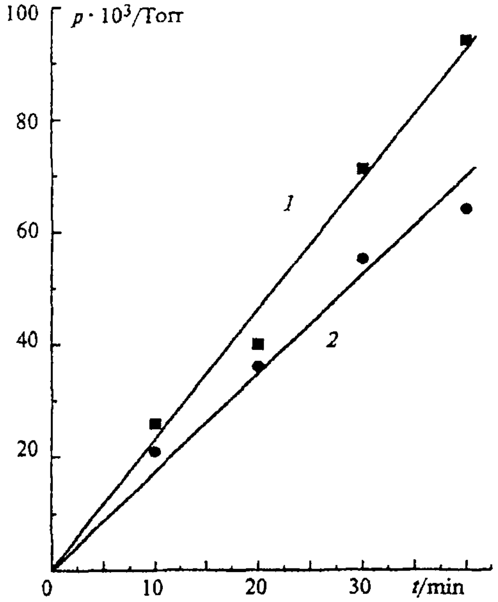

Fig. 1. Dependences of the partial pressure (p) of NO (*1*) and MeONO (*2*) on the irradiation time (pressure of $MeNO_2$ 1 Torr, laser radiation frequency 1580 cm^{-1}, and macropulse energy 8 mJ).

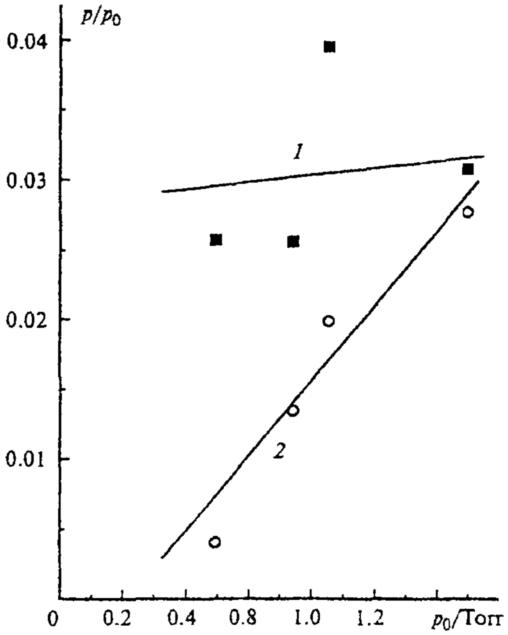

Fig. 2. Dependences of the yields of NO (*1*) and MeONO (*2*) on the initial pressure (p_0) (irradiation time 20 min, laser radiation frequency 1580 cm^{-1}, and macropulse energy 8 mJ).

Estimates of the radical concentration show that the gas-phase reactions between the dissociation products can be neglected under the conditions of our experiments. Therefore, the MeO$^\cdot$ radicals have time to diffuse to the cell wall, where C_2H_6 and other by-products can be formed due to reactions of particles adsorbed on the surface.

The isotope selectivity of MPD of nitromethane was studied by measurement of the $^{15}NO/^{14}NO$ ratios in the decomposition products using the mass spectral lines with $m/z = 31$ and $m/z = 30$, respectively. All experiments were carried out with samples with the natural content of ^{15}N (0.365%).

The IR absorption spectrum of nitromethane $Me^{14}NO_2$ contains the bands of symmetrical and (1384 cm^{-1}) and antisymmetrical (1582 cm^{-1}) stretching vibrations of the NO_2 group (Fig. 3). The corresponding absorption bands of $Me^{15}NO_2$ are not seen in the spectrum due to the low concentration. The position of the band of the antisymmetrical vibration of the $Me^{15}NO_2$ molecule (1557 cm^{-1}), whose isotope shift was calculated from the published[8] data, is shown by the dotted line in Fig. 3. Both a

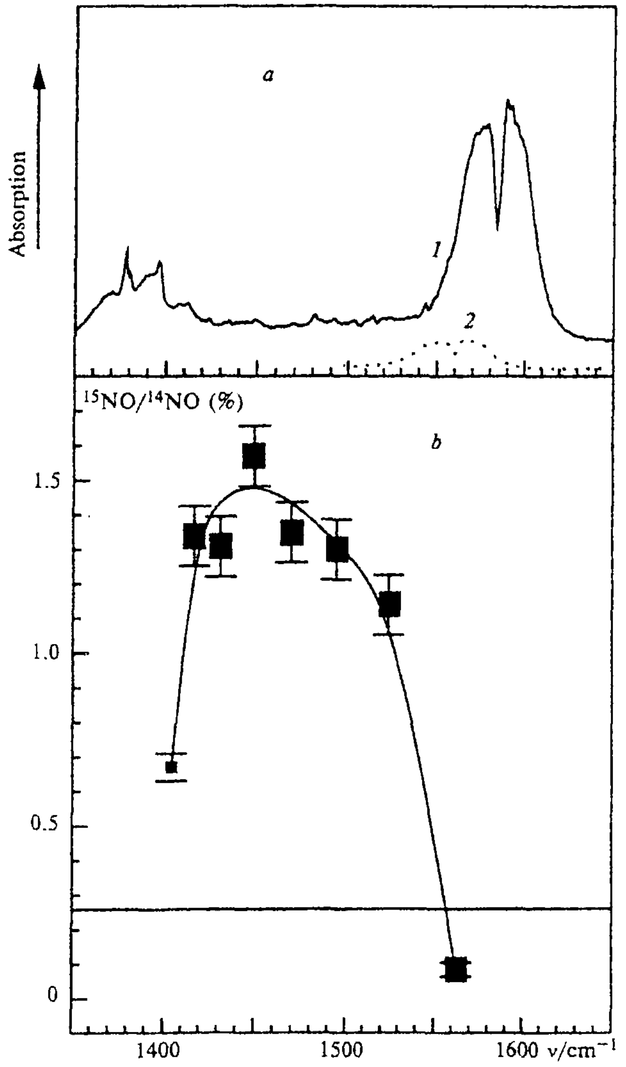

Fig. 3. *a*. Region of the absorption spectrum of $Me^{14}NO_2$ containing bands of stretching vibrations of the NO_2 group (*1*) and the band of the antisymmetrical vibration of the $Me^{15}NO_2$ molecule (*2*). *b*. Dependence of the ^{15}N isotope content in NO formed during dissociation on the laser radiation frequency. Solid line indicates the natural content of the ^{15}N isotope. The total pressure is 1 Torr.

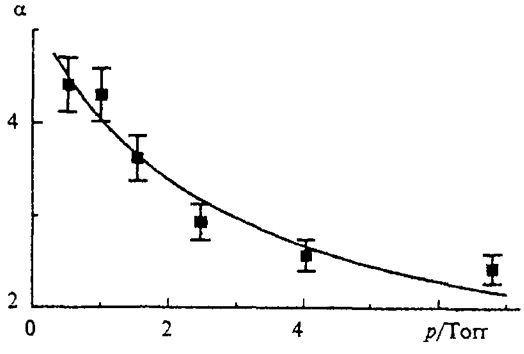

Fig. 4. Dependence of the enrichment coefficient of NO in the ^{15}N isotope (α) on the pressure of nitromethane vapor (*p*) at the laser radiation frequency of 1460 cm^{-1}.

decrease and an increase in the content of the ^{15}N isotope as compared to the natural content is observed when the frequency of the laser radiation changes. The maximum enrichment coefficient α that was achieved (determined as the ratio of ^{15}NO/^{14}NO to the natural content of ^{15}N) was a little higher than 4. The transition point, *i.e.*, the laser radiation frequency for which the probabilities of MPD of the both isotopic varieties were equal, was at 1550 cm^{-1}. $Me^{15}NO_2$ molecules dissociate predominantly when the radiation frequency is lower than the transition point, and $Me^{14}NO_2$ dissociate at a higher frequency. If the MPD probability is proportional to the absorption coefficient in the IR spectrum, the transition point would be in the middle between the vibration frequencies of $Me^{14}NO_2$ and $Me^{15}NO_2$, *i.e.*, at 1570 cm^{-1}. Since the maximum MPD yield is usually observed at frequencies lower than the absorption maximum in the normal spectrum (bathochromic shift), the transition point is also shifted to lower frequencies. The shift is 20 cm^{-1}, which is a typical value.[9,10] IR MPD is also characterized by the dependence of the enrichment coefficient on the initial pressure of nitromethane: the selectivity increases as the pressure decreases (Fig. 4).

The comparatively low IR MPD selectivity with respect to nitrogen isotopes in methane is explained, first, by the considerable spectral width ($\Delta\lambda/\lambda = 10^{-2}$) of the FEL radiation, which is ~20 cm^{-1}, being a little lower than the isotope spectral shift (25 cm^{-1}), and second, by the fact that the same region contains deformational vibrations of C—H of the methyl group (ν_3 = 1488 cm^{-1}, ν_4 = 1449 cm^{-1}, and ν_{12} = 1413 cm^{-1}),[11] which can contribute to the processes of IR multiphoton absorption and dissociation despite their low intensity. Since the frequency of the C—H vibrations only slightly changes on going from one nitrogen isotope to another, this contribution of the C—H vibrations to MPD is not selective. Preliminary experiments on IR MPD of nitromethane with tuning of the FEL radiation to the region of stretching vibrations of C—H (~3 μm) showed that multiphoton dissociation with the formation of the same products takes place, but its yield is not higher than 1% because of the low intensity of the absorption bands of these vibrations.

Thus, selectivity of the IR MPD dissociation with respect to nitrogen isotopes was observed for the first time for a nitromethane molecule.

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References

1. A. K. Petrov, E. N. Chesnokov, S. R. Gorelik, Yu. N. Molin, K. D. Shtraub, D. M. D. Meidi, and E. B. Sharmes, *Dokl. Akad. Nauk*, 1997, **332**, 774 [*Dokl. Chem.*, 1997 (Engl. Transl.)].
2. K. Glanzer and J. Troe, *Helv. Chim. Acta*, 1972, **55**, 2884.
3. C. G. Crawforth and D. J. Waddington, *J. Phys. Chem.*, 1970, **74**, 1425.
4. K. Honda, H. Mikuni, and M. Takahasi, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 3534.
5. M. J. S. Dewar, J. P. Ritchie, and J. Alster, *J. Org. Chem.*, 1985, **50**, 1031.
6. A. M. Wodtke, E. J. Hintsa, and Y. T. Lee, *J. Chem. Phys.*, 1986, **84**, 1044.
7. A. M. Wodtke, E. J. Hintsa, and Y. T. Lee, *J. Phys. Chem.*, 1986, **90**, 3549.
8. E. M. Popov and V. M. Shlyapochnikov, *Optika i spektr.* [*Optics and Spectroscopy*], Vol. 2. *Molekulyarnaya spektroskopiya* [*Molecular Spectroscopy*], 1963, 115 (in Russian).
9. E. P. Velikhov, V. Yu. Baranov, V. S. Letokhov, E. A. Ryabov, and A. N. Starostin, *Impul'snye CO_2 lazery i ikh primenenie dlya razdeleniya izotopov* [*Pulse CO_2 Lasers and Their Application in Isotope Separation*], Nauka, Moscow, 1983, 303 pp. (in Russian).
10. Yu. N. Molin, V. N. Panfilov, and A. K. Petrov, *Infrakrasnaya fotokhimiya* [*Infrared Photochemistry*], Nauka, Novosibirsk, 1985, 255 pp. (in Russian).
11. L. M. Sverdlov, M. A. Kovner, and E. P. Krainov, *Kolebatel'nye spektry mnogoatomnykh molekul* [*Vibrational Spectra of Polyatomic Molecules*], Nauka, Moscow, 1970, 559 pp. (in Russian).

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Phenyltetrafluorotelluromethoxide — a new fluorinating reagent for olefins

S. A. Lermontov and I. V. Bahtin*

*Institute of Physiologically Active Substances, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
E-mail: lermon@ipac.ac.ru*

Phenyltetrafluorotelluromethoxide fluorinates olefins to form 1,2-difluorides. The reaction with styrene afforded 1-fluoro-4-phenyl-1,2-dihydronaphthalene as the main product.

Key words: electrophilic addition, fluorination, olefins.

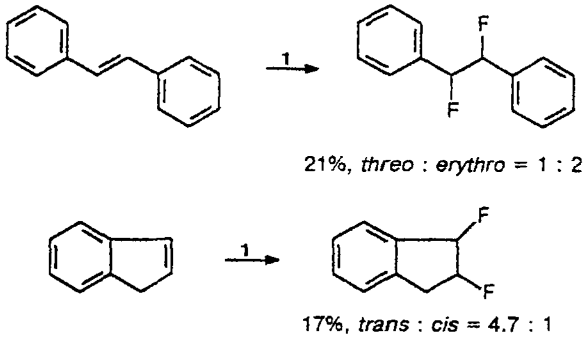
Phenylchalcogenopentafluorides are soft difluorinating reagents for olefins.[1] We found that, like the above-mentioned pentafluorides, *trans*-phenyltetrafluorotelluromethoxide (**1**) (which has been synthesized previously[2] by the reaction of an equimolar amount of trimethylsilyl methoxide with phenyltelluropentafluoride (Scheme 1)) is an electrophilic fluorinating reagent.

Scheme 1

1

The reactions of compound **1** with *trans*-stilbene and indene afforded the usual products of difluorination (Scheme 2).

Scheme 2



21%, *threo* : *erythro* = 1 : 2

17%, *trans* : *cis* = 4.7 : 1

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