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ISOTOPICALLY SELECTIVE INFRARED MULTIPLE-PHOTON DISSOCIATION OF MoF_6 BY A H_2-RAMAN LASER

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Abstract Infrared multiple-photon dissociation (IRMPD) of MoF_6 has been investigated with a parallel beam of a para-H_2 Raman laser newly developed by our group. MoF_6 gas (2 Torr, natural abundance) was put into in a static cell cooled to -58°C and was irradiated with the laser line at 728 cm^{-1}. The critical fluence of 0.11 Jcm^{-2} for complete dissociation was determined by analysis with a Gaussian beam model. Irradiation at the lower frequency side (728 cm^{-1}) of the MoF_6 ν_3 band enriched the lighter isotopes in the residue. A maximum value for selectivity of 1.1 was obtained.

INTRODUCTION

The laser method of isotope separation has many of advantages compared with existing methods for separating isotopes of heavy elements. Only a few papers have been published on the laser isotope separation of heavy metals other than uranium. Isotopic enrichment of osmium was investigated by Ambartzumian et al.[1], by IRMPD of OsO_4 with OCS as a scavenger. Tiee and Wittig[2] photolyzed SeF_6 with an NH_3 laser and CO_2 laser and observed that lighter isotopes were dissociated more efficiently than the heavier ones. Freund and Lyman[3] carried out isotopically selective dissociation of MoF_6 by irradiation of weak combination

bands with CO_2 laser radiation.

Recently many heavy metal isotopes have attracted much interest as useful materials in the field of atomic energy engineering and nuclear medicine. Molybdenum isotope is an example. Use of ^{97}Mo in the steel of a fusion-reactor first wall is desirable because it can reduce induced long-term radioactivity[4]. Molybdenum-98 is used as a starting material for the mother element ^{99}Mo producing ^{99m}Tc in nuclear medicine. Isotope shifts for heavy metals are small due to their high mass number. Furthermore, the hot band problem in heavy molecules is much more severe than in lighter molecules. Only 1.0% of the MoF_6 is in the vibrational ground state at 300K[5] and a large number of thermally populated vibrational states tend to shift and spread spectral features. The isotope shift is obscured by such spectral interference due to hot bands. However, isotope separation can be achieved on the isotope-shifted slope of the Q-branch envelopes by lowering the gas temperature to some extent. In this paper IRMPD of MoF_6 using a para-H_2 Raman laser was carried out and the results were analyzed on the basis of Gaussian beam model. It was observed that molybdenum isotope was enriched in the residual MoF_6.

EXPERIMENTAL

Figure 1 shows the infrared absorption spectrum for the ν_3 band of MoF_6. The CO_2 laser pulses at 9R(26) 1082.3 cm^{-1} were amplified and converted to 728 cm^{-1} by passing through a Raman cell filled with para-hydrogen[6]. Unconverted CO_2 laser radiation was eliminated by passing through a

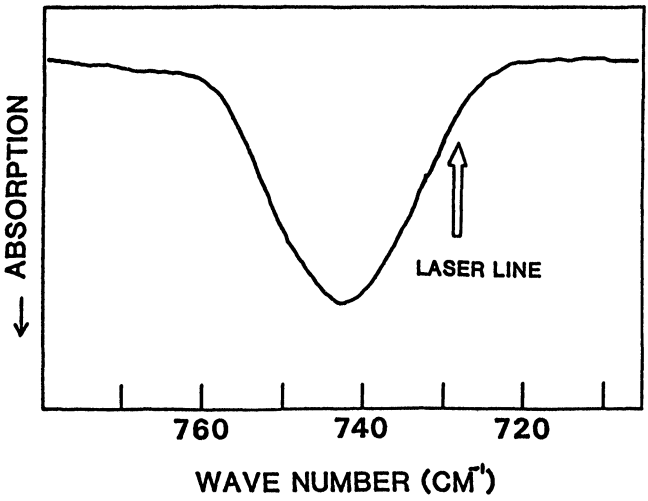

FIGURE 1. Infrared absorption spectrum for the ν_3 band of MoF_6.

absorption cell (20 mm in diameter, 5 cm in length) which contained 300 Torr of C_2H_5F, and the residual radiation at 728 cm^{-1} was used for irradiation of MoF_6 in a reaction cell (80 cm in length, 400 ml in volume). The maximum output energy at 728 cm^{-1} was 300mJ with a 50 ns pulse duration at 3 Hz repetition rate. The pulse energy was measured by a pyroelectric detector before and after passing through the reaction cell. The reaction cell had KBr side windows for measurement of infrared absorption. Perflon O-rings were used for vacuum sealing of the windows. Prior to irradiation, the cell wall was passivated with 600 Torr of 5 % F_2 in He for 15 min at 100° C. It was confirmed that there was negligible decomposition of MoF_6 by corrosive action. MoF_6 was purchased from Kantodenka Co. Ltd. and subjected to freeze-pump-thaw cycles before use. The cell

was kept at -58°C by immersing it in a n-octane slush bath. The fraction of dissociated MoF_6 was monitored during the irradiation by the measurement of the ν_3 band absorption at 741 cm^{-1} with an infrared spectrometer. After irradiation, undissociated MoF_6 was recovered from the cell and transferred into a sample bottle immersed in a liquid nitrogen dewer and introduced into a mass spectrometer. The isotope ratios of both irradiated and natural MoF_6 were then determined from the mass spectrum of the MoF_5^+ isotopic ions.

RESULTS AND DISCUSSION

Infrared mutiple-photon dissociation

The radial intensity distribution of the laser beam in multi-mode radiation of a TEA-CO_2 laser is relatively homogeneous. However, the Raman laser beam after conversion of single-mode TEA-CO_2 laser radiation is not homogeneous and has a Gaussian transverse profile. Therefore it is necessary to consider the inhomogeneity of the beam in deriving the relation between IRMPD dissociation yield and fluence. According to the analytical model for the reaction yield vs. fluence with an unfocused Gaussian beam under the optically thick condition[7], the critical fluence, Φ_c, for complete dissociation of a molecule is obtained experimentally from measurement of $\Phi(0,0)$, ω , λ , V_R, and n. Here $\Phi(0,0)$ is the Gaussian peak fluence at the cell entrance, ω is the Gaussian peak width at $1/e^2$, λ is the overall absorption coefficient in infrared multiple-photon absorption, V_R is the reaction volume, and n is the value for the power dependence of dissociation probability upon

fluence.

$$q(r,x)=[\Phi(r,x)/\Phi_c]^n \qquad \Phi(r,x)<\Phi_c$$
$$q(r,x)=1 \qquad \Phi(r,x)\geq\Phi_c \qquad (1)$$

In the IRMPD of 2 Torr of MoF_6, $\Phi(0,0)$, ω , and λ were determined from the energy measurement to be 1.60×10^{-2} J cm^{-2}, 3.19 cm, 2.29×10^{-2} cm^{-1}, respectively. The reaction volume, V_R, was determined to be 1.02×10^{-2} cm^3 by using the following relation

$$b=V_R/V_{cell} \qquad (2)$$

where V_{cell} is the cell volume and b is the specific dissociabtion rate constant obtained from the conversion, X, after irradiation by t pulses.

$$b=-(1/t)\ln(1-X) \qquad (3)$$

The value of n was assumed to be 4, which is typical in most IRMPD experiments[8]. The critical fluence, Φ_c, was thus estimated as $0.11 Jcm^{-2}$ for 2 Torr of MoF_6 cooled at -58°C.

Isotope selectivity

The enrichment factor, β_{res}, after irradiaton is defined in the case of a multicomponent isotopic system.

β_{res}=percent of isotope i after irradiation/percent of isotope i before irradiation (4)

Plots of β_{res} vs. molybdenum mass are shown in Fig.2.The enrichment factors were obtained by measuring the isotopic abundance of natural MoF_6 and of irradiated samples. In this experiment, light isotopes of 92, 94, 95, and 96 were enriched while heavy isotopes of 97, 98, and 100 were depleted in undissociated MoF_6.

The enrichment factor, β_{res}, depends on the conversion, X. The conversion-independent selectivity, S, is obtained from β_{res} and X as follows.

$$S=1+\ln \beta_{res}/\ln(1-X) \qquad (5)$$

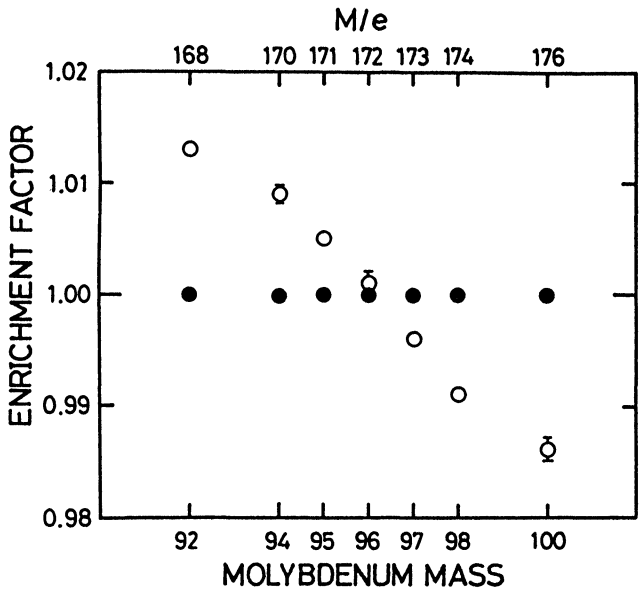

FIGURE 2. Enrichment factor in the residue vs. molybdenum mass after irradiation of 2 Torr of MoF_6 with a 728 cm^{-1} Raman laser beam at -58°C. The conversion was X=0.16. •, natural MoF_6; o, irradiated MoF_6.

The selectivity, S, of each of the Mo isotope is shown in Fig.3. The value of selectivity for isotopes of mass number 92, 94, 95, 96, are less than unity , while those for isotopes of mass number 97, 98, and 100 are more than unity. This indicates that irradiation on the lower frequency side (728 cm^{-1}) of the ν_3 band (Fig.1) enriched the heavier isotopes on the product. The results are explained on the basis that the isotope shift of the ν_3 band of MoF_6 is about 1.0 cm^{-1}/mass unit[9] and a red shift in an IRMPD spectrum. A maximum value for selectivity of 1.1 was obtained for ^{100}Mo.

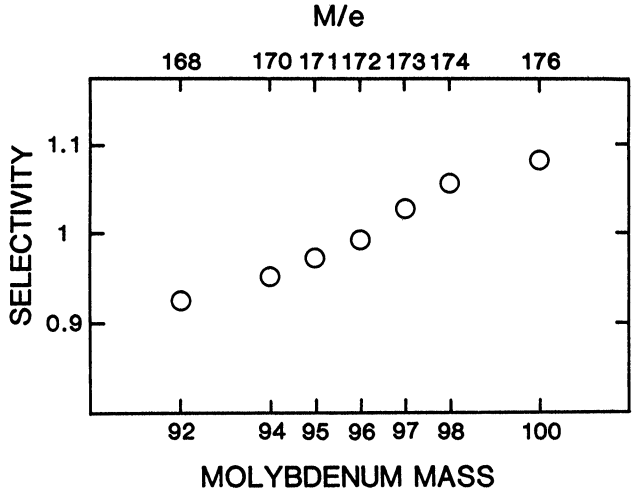

FIGURE 3. Selectivity vs. molybdenum mass obtained by irradiation of 2 Torr of MoF_6 cooled at $-58^{\circ}C$ with a 728 cm^{-1} Raman laser beam.

CONCLUSION

From the isotopic measurement of the unreacted MoF_6 remaining in the cell after irradiation, it was demonstrated that MoF_6 was dissociated, isotope selectively, by the irradiation of the para-H_2 Raman laser at $-58^{\circ}C$. The value for critical fluence was estimated to be as low as 0.11 Jcm^{-2} according to the analytical model. This appreciably low critical fluence strongly suggests that MoF_6 is one of the most promising working substance for the laser isotope separation of molybdenum.

REFERENCES

1. R. V. Ambartzumian, N. P. Furzikov, Y. A. Gorokhov, V. S. Letokhov, G. N. Makarov, and A. A. Puretzky, Optics Lett. 1, 22 (1977).
2. J. J. Tiee and C. Wittig, J. Chem. Phys. 69, 4756 (1978).
3. S. M. Freund and J. L. Lyman, Chem. Phys. Lett. 55, 435 (1978).
4. R. W. Conn, K. Okula, and A. W. Johnson, Nucl. Technol. 41, 389 (1978).
5. D. Jackson, Statistical Thermodynamic Properties of Hexafluoride Molecules, Los Alamos Informal Report, La-6025-MS, August 1975.
6. K. Midorikawa, H. Tashiro, Y. Aoki, K. Ohashi, K. Nagasaka, K. Toyoda, and S. Namba, J. Appl. Phys. 57, 1504 (1985).
7. S. Kato, J. Ichikawa, T. Ishii, and K. Takeuchi, to be submitted.
8. K. Takeuchi, I. Inoue, R. Nakane, Y. Makide, S. Kato, and T. Tominaga, J. Chem. Phys. 76, 398 (1982).
9. R. S. McDowell, R. J. Sherman, L. B. Asprey, and R. C. Kennedy, J. Chem. Phys. 62, 3974 (1975).