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ISOTOPICALLY SELECTIVE INFRARED MULTIPLE-PHOTON
DISSOCIATION OF MoF₆ BY A H₂-RAMAN LASER

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Abstract Infrared multiple-photon dissociation (IRMPD) of MoF₆ has been investigated with a parallel beam of a para-H₂ Raman laser newly developed by our group. MoF₆ 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 MoF₆ ν₃ 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 OsO₄ with OCS as a scavenger. Tiee and Wittig² photolyzed SeF₆ with an NH₃ laser and CO₂ laser and observed that lighter isotopes were dissociated more efficiently than the heavier ones. Freund and Lyman³ carried out isotopically selective dissociation of MoF₆ by irradiation of weak combination

bands with CO₂ 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 ⁹⁷Mo in the steel of a fusion-reactor first wall is desirable because it can reduce induced long-term radioactivity⁴. Molybdenum-98 is used as a starting material for the mother element ⁹⁹Mo 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 MoF₆ is in the vibrational ground state at 300K⁵ 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 MoF₆ using a para-H₂ 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 MoF₆.

EXPERIMENTAL

Figure 1 shows the infrared absorption spectrum for the ν_3 band of MoF₆. The CO₂ 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-hydrogen⁶. Unconverted CO₂ laser radiation was eliminated by passing through a

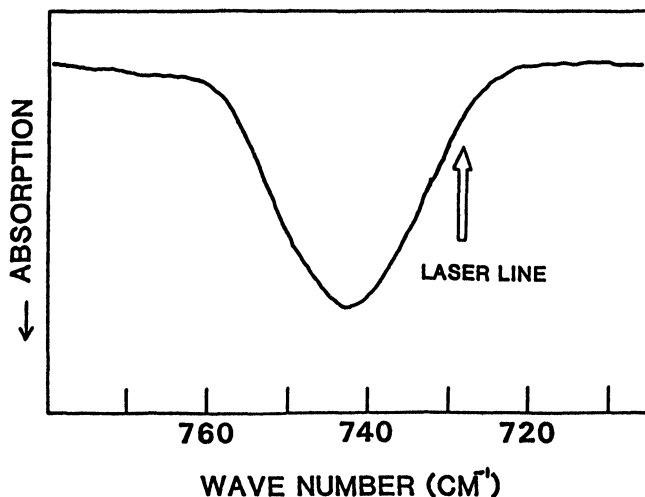


FIGURE 1. Infrared absorption spectrum for the ν_3 band of MoF₆.

absorption cell (20 mm in diameter, 5 cm in length) which contained 300 Torr of C₂H₅F, and the residual radiation at 728 cm⁻¹ was used for irradiation of MoF₆ 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 % F₂ in He for 15 min at 100° C. It was confirmed that there was negligible decomposition of MoF₆ by corrosive action. MoF₆ 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 multiple-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 condition⁷, 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.

$$q(r,x) = \left[\frac{\Phi(r,x)}{\Phi_c} \right]^n \quad \begin{array}{l} \Phi(r,x) < \Phi_c \\ \Phi(r,x) \geq \Phi_c \end{array} \quad (1)$$

In the IRMPD of 2 Torr of MoF₆, $\Phi(0,0)$, 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} cm³ by using the following relation

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

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

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

The value of n was assumed to be 4, which is typical in most IRMPD experiments⁸. The critical fluence, Φ_c , was thus estimated as 0.11 J cm⁻² for 2 Torr of MoF₆ cooled at -58°C.

Isotope selectivity

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

$$\beta_{\text{res}} = \frac{\text{percent of isotope } i \text{ after irradiation}}{\text{percent of isotope } i \text{ before irradiation}} \quad (4)$$

Plots of β_{res} vs. molybdenum mass are shown in Fig.2. The enrichment factors were obtained by measuring the isotopic abundance of natural MoF₆ 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 MoF₆.

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

$$\beta_{\text{res}} \text{ and } X \text{ as follows.} \\ S = 1 + \ln \beta_{\text{res}} / \ln(1-X) \quad (5)$$

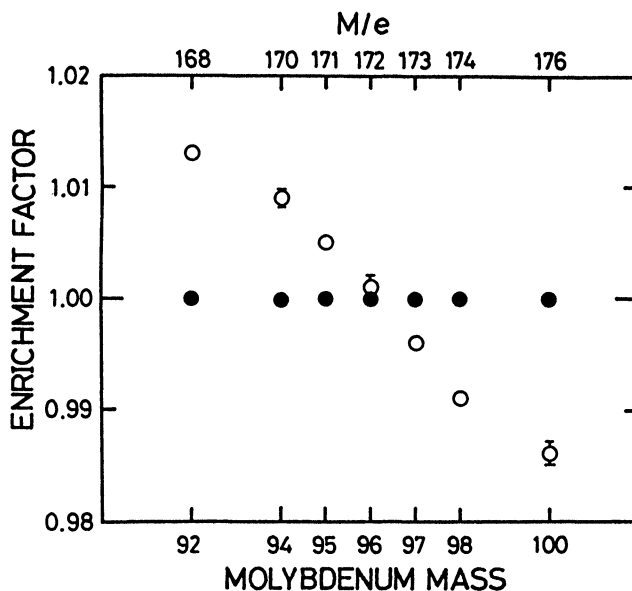


FIGURE 2. Enrichment factor in the residue vs. molybdenum mass after irradiation of 2 Torr of MoF₆ with a 728 cm⁻¹ Raman laser beam at -58°C. The conversion was X=0.16. ●, natural MoF₆; ○, irradiated MoF₆.

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 MoF₆ is about 1.0 cm⁻¹/mass unit⁹ and a red shift in an IRMPD spectrum. A maximum value for selectivity of 1.1 was obtained for ¹⁰⁰Mo.

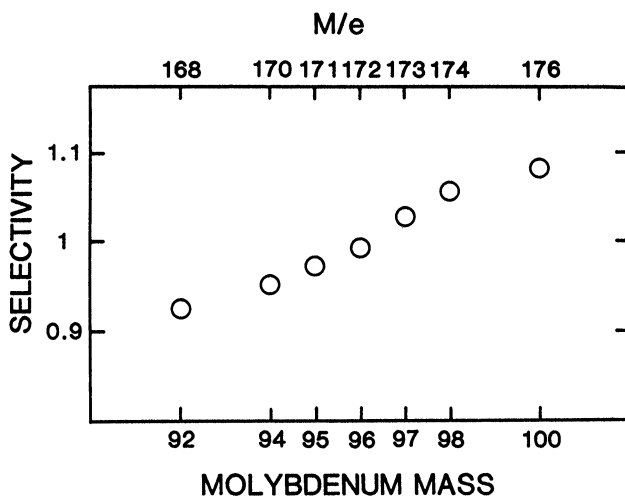


FIGURE 3. Selectivity vs. molybdenum mass obtained by irradiation of 2 Torr of MoF₆ cooled at -58°C with a 728 cm⁻¹ Raman laser beam.

CONCLUSION

From the isotopic measurement of the unreacted MoF₆ remaining in the cell after irradiation, it was demonstrated that MoF₆ was dissociated, isotope selectively, by the irradiation of the para-H₂ Raman laser at -58°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 MoF₆ is one of the most promising working substance for the laser isotope separation of molybdenum.

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