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Rapid Communication

Cross section of supercooled $^{238}UF_6$ in multiphoton absorption induced by 16 micrometer Raman-laser radiation

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Abstract. Measurements of multiphoton absorption of 16 μm Raman-laser radiation in supercooled $^{238}UF_6$ at 90 K were performed by using a pulsed Laval nozzle with an optical path length of 50 cm. The laser fluence was varied between 50 and 500 mJ/cm^2 for four frequencies in the range from 625 to 629 cm^{-1}. The energy absorbed by $^{238}UF_6$ molecules was investigated as a function of laser frequency or fluence, and highly accurate results were obtained with the use of the nozzle whose optical path length is much greater than that of nozzles used before. The results indicated that the absorption cross section at the peak absorption frequency (627.8cm^{-1}) was proportional to the -1/3 power of the fluence.

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In isotope separation by infrared lasers, a gaseous working molecule is dissociated isotope-selectively by laser radiation which is resonant with the vibrational frequencies of the molecule. Measurements of the cross section of the molecule in MultiPhoton Absorption (MPA) which occurs prior to dissociation are necessary for evaluation of the photon energy in laser isotope separation.

Gilbert et al. [1] reported the results of an experimental investigation on MPA of 16 μm radiation in UF_6, a working molecule for uranium enrichment, cooled at 90 K in a supersonic Laval nozzle. The optical path length of the nozzle used was 7.5 cm. The absorbance observed in their experiments was extremely small ($\leq 1\%$), which was almost comparable to the uncertainties of any currently available pyroelectric joulemeters (linearity of response $\approx$ 1%) used for recording infrared-laser beams. The small values of absorbance obtained in the case of short optical path length inevitably cause large experimental errors in the data of absorption cross sections.

When we, for instance, consider the case of UF_6 where the number density is approximately $5 \cdot 10^{15}$ cm^{-3} and the absorption cross section is assumed to be $1 \cdot 10^{-18}$ cm^2, the absorbance calculated using the Lambert-Beer law is 0.10 for an optical path length of 20 cm, or 0.22 for 50 cm. We believe that an optical path length of 20 cm or more is necessary to obtain absorbance signals about one order of magnitude larger than the measurement uncertainties and, therefore, guarantee accurate measurements on the cross section of UF_6.

We have developed a pulsed Laval nozzle with an optical path length of 50 cm [2] which is about seven times as long as that used by *Gilbert* et al. In this report, we present the results of our investigation on the cross section of supercooled UF_6 in MPA with this long-optical-path nozzle. We have taken full advantage of this long path length to investigate the cross section in the high-fluence range, which, to our knowledge, has not been studied yet because the absorbance was too small to be experimentally measured as a result of nonlinear absorption showing that the cross section decreases with increasing fluence. Extensive MPA investigations on polyatomic molecules (SF_6, CF_3I, C_2H_4 C_2H_3Cl, S_2F_{10} and UF_6) [3-7] have shown an intriguing experimental finding that the data for the absorption cross sections obtained at the peak absorption frequencies in the high-fluence region are proportional to the -1/3 power of the fluence. In this work, we investigate the fluence dependence of the cross section in supercooled UF_6 at 90 K and discuss the question whether or not the -1/3 power dependence would hold also for supercooled UF_6.

1. Experimental

A schematic diagram of the present experimental setup is shown in Fig.1. A para-H_2 Raman laser pumped by the TEA CO_2 laser operating in a single longitudinal mode was used as a source of 16 μm radiation [8,9]. The pulse duration of the Raman-laser beam was 50 ns (FWHM). The linewidth was about 0.007 cm^{-1}. The collimated laser beam passed through a pulsed Laval nozzle with KCl windows (optical path length: 50cm). The spatial profile of the beam was Gaussian with a $1/e^2$ radius of $\omega \approx 2$ mm.

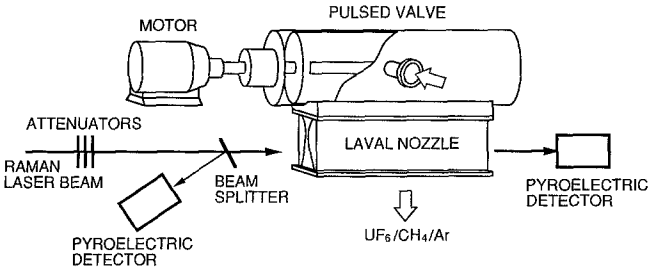

Fig. 1. Schematic diagram of experimental apparatus for multiphoton absorption of 16 μm Raman laser radiation in supercooled UF_6. The gas is a mixture of UF_6 (0.5% in mole%), CH_4 (2.5mole%) and Ar (97.0mole%). In the irradiation region, the total pressure is 9.0 Torr and gas temperature is 90 K. The radius at $1/e^2$ intensity of the 16 μm laser beam is about 0.2 cm

The gas mixture of 0.5 mole% UF_6, 2.5 mole% CH_4 and 97.0 mole% Ar was cooled in the pulsed Laval nozzle. Argon was used as a carrier gas. We added CH_4 gas to reproduce exactly the same gas conditions as in the dissociation experiments where it was used as a scavenger gas. Presumably, the CH_4 gas has no significant influence on MPA except that it acts as a collision partner, because it does not absorb 16 μm radiation. Details of the pulsed Laval nozzle have been described in [2]. Briefly, this nozzle consists of a double-drum-type valve and a 500-mm long Laval nozzle with a 3-mm wide throat. When the slit (30mm wide) of the rotating inner drum overlaps that (15mm wide) of the outer drum, the gas flows out from the inner drum to the Laval nozzle. The gas expansion in the nozzle generated a quasi-steady-state flow with a duration of about 10 ms. In the irradiation region, the UF_6 partial pressure and the gas temperature calculated from the values of gas pressure in the period of quasi-steady-state flow were 0.045 Torr and 90 K, respectively.

The incident and transmitted energies of individual laser pulses at the nozzle were measured by pyroelectric detectors (Gentec ED-200). To change the beam fluence, several NaCl flat crystals (5, 10, 25 and 35mm in thickness) were used as attenuators. The MPA data for single-frequency irradiation were taken at four different frequencies in the 625 ÷ 629 cm^{-1} range.

2. Results and discussion

For a collimated Gaussian-profile beam, the energy absorbed per mole of UF_6 present in the irradiated region (E_{abs}) at the input fluence Φ_{in} is given by

$$E_{abs} = \Phi_{in} \frac{1 - E_{out}/E_{in}}{2cL}, \quad (1)$$

where E_{in} and E_{out} are the input and output energies of the laser pulse, respectively, c is the UF_6 molarity and L the optical path length.

Figure 2 shows the data of E_{abs} (normalized to Φ_{in} of 0.2J/cm^2) obtained at four frequencies. The maximum of the absorbed energy was observed at 627.8 cm^{-1}. This

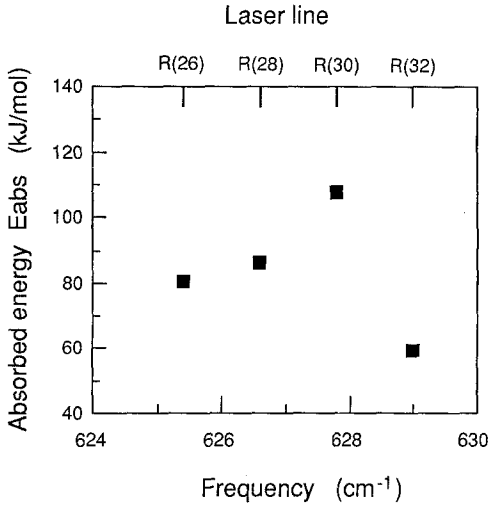

Fig. 2. Absorbed energy per mole of UF_6 as a function of laser frequency. The input fluence Φ_{in} is 0.2 J/cm^2

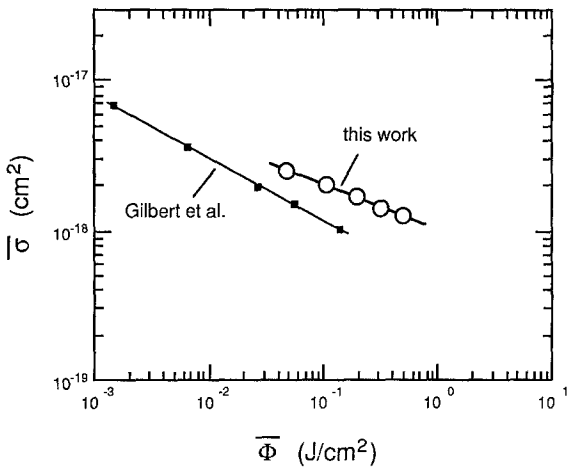

Fig. 3. Average absorption cross section as a function of average fluence at 627.8 cm^{-1}

frequency is close to the ground-state Q branch of the $^{238}UF_6$ ν_3 band measured by high-resolution spectroscopy [10].

Let us consider the fluence dependence of the absorption cross section at the peak frequency of the MPA spectrum in a manner similar to that of numerous polyatomic molecules in earlier MPA investigations [3-7]. The spatially averaged absorption cross section $\bar{\sigma}$, number of photons absorbed per molecule (η) and mean fluence $\bar{\Phi}$ are obtained by the following equations for a collimated Gaussian beam at the frequency ν:

$$\bar{\sigma} = -(nL)^{-1} \ln\left[E_{out}/E_{in}\right], \quad (2)$$

$$\eta = \frac{E_{in} - E_{out}}{\pi\omega^2 nLh\nu}, \quad (3)$$

$$\bar{\Phi} = \eta h\nu/\bar{\sigma}, \quad (4)$$

where n is the UF_6 number density, and h is Planck's constant. Figure 3 shows the fluence dependence of $\bar{\sigma}$, com-

pared with data obtained by *Gilbert* et al. [1] at the same frequency, observed at 627.8 cm^{-1}. Our data was found to satisfy $\bar{\sigma} \propto \bar{\Phi}^{-0.29}$ in the fluence region which overlapped with, and was higher than, that of *Gilbert* et al.

It is known from MPA in polyatomic molecules that linear absorption, where $\bar{\sigma}$ is constant and independence of $\Phi\zeta$ ($\bar{\sigma} \propto \bar{\Phi}^0$), is exhibited in the quite low-fluence region, and nonlinearity of absorption appears at high fluence. In several earlier MPA investigations, it has been observed that with increasing fluence, the nonlinearity of absorption leads to a rise of the parameter α in $\bar{\sigma} \propto \bar{\Phi}^{-\alpha}$ from the initial value of zero, which finally converges to about 1/3. In the papers by *Lyman* and co-workers [3,4], the relation $\bar{\sigma} \propto \bar{\Phi}^{-1/3}$ was shown in SF_6 for the fluence range $1mJ/cm^2 < \bar{\Phi} < 100mJ/cm^2$ at the 10P(16) CO_2 laser line ($947.7cm^{-1}$), which coincides with the peak absorption observed in the main isotope compound $^{32}SF_6$. *Judd* and co-workers [5,6] reported that in a number of polyatomic molecules such as CF_3I, C_2H_4, C_2H_3Cl and S_2F_{10}, the change in the fluence dependence of the cross section from $\bar{\sigma} \propto \bar{\Phi}^0$ to $\bar{\sigma} \propto \bar{\Phi}^{-1/3}$ was observed with increasing $\bar{\Phi}$. In addition, in UF_6 at 300 K, our previous experimental results [7] indicated a dependence of $\bar{\sigma} \propto \bar{\Phi}^{-1/3}$ at the peak absorption frequency for the fluence range ($10mJ/cm^2 < \bar{\Phi} < 300mJ/cm^2$), while for a lower fluence ($0.03mJ/cm^2 < \Phi < 5mJ/cm^2$) *Lucht* et al. [11] observed a different relationship ($\bar{\sigma} \propto \bar{\Phi}^{-0.14}$) which we interpreted as the evidence of transition from the linear absorption to the nonlinear absorption with the dependence of $\bar{\sigma} \propto \bar{\Phi}^{-1/3}$. From our data (shown in Fig.3) obtained with quite high accuracy, we found that the relationship $\bar{\sigma} \propto \bar{\Phi}^{-1/3}$ also holds for supercooled UF_6 at 90 K at the peak absorption frequency in the high-fluence range from 50 to 500 mJ/cm^2.

We did not describe in this paper in what range of fluence the transition from the $\bar{\Phi}^0$ to $\bar{\Phi}^{-1/3}$ in the functional dependence takes place since measurements at an even lower fluence result in large experimental errors caused by the decrease of the signal intensity. We note that the fluence range required for actually performing the laser isotope separation of uranium corresponds to that observed in this work and consequently the MPA data reported here will be very useful for the photon-energy evaluation in the uranium enrichment process and the design of the photochemical reactor.

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