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CO₂ Laser Absorption Measurement of CH₃CH₂Br using Photoacoustic Method

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The CO₂ laser absorption measurement of CH₃CH₂Br utilizing photoacoustic (PA) technique was performed using a cw and a pulsed CO₂ lasers. The absorption profile in the CO₂ laser wavelength region (9-10 μm) and the macroscopic small signal absorption cross section at 10P(20) (10.59 μm, 944 cm⁻¹) laser line were measured using a cw CO₂ laser. The laser fluence dependence on infrared multiphoton absorption (IRMPA) was also studied with a pulsed TEA CO₂ laser at 10P(20) laser line. In view of monotonic increase of PA signal with the rise of laser fluence, it was suggested that the anharmonicity in pumped vibration mode did not restrict ir multiphoton absorption in CH₃CH₂Br system as found in large molecular system.

Introduction

Number of reports on the infrared multiphoton absorption/dissociation (IRMPA/D) of molecules have been continuously increased recent years in accordance with the development of high power infrared lasers. These studies have been focused not only to develop an effective laser isotope separation technique¹⁻⁴ but also to investigate pure scientific features, such as mechanisms or dynamics of multiphoton absorption and dissociation.⁵⁻⁹

The vibrational bottleneck due to anharmonicity in pumped vibration mode or the rotational hole-filling phenomena has been found to exert significant effects on IRMPA processes.⁷⁻⁹ These effects are dependent on the molecular size of substrate, the kinds of buffer gases and the pressure of reaction system. An example of such effects has been reported on a small size molecule system, CDF₃.³ In the system it has shown several variation points of PA signal intensity with laser fluence change. These variation have been interpreted in terms of energy barriers caused by anharmonicities of the vibrational ladders.¹⁰ On the other hand, the MPA signal has shown monotonic increase with the rise of laser fluence for larger molecule system than CF₃CH₂Cl.^{11,12} This phenomenon in the larger molecule system has suggested that the quasicontinuum state is started at very low molecular energy levels, so an anharmonicity in pumped vibrational mode does not restrict energy randomization. Therefore, the mismatch of laser frequency due to anharmonicity in pumped mode at high energy levels or the rotational hole-filling effect plays insignificant roles in IRMPA process.

In this study we measured the ir absorption profile of CH₃CH₂Br in the CO₂ laser wavelength region and the macroscopic small signal absorption cross section at 10P(20) (10.59 μm, 944 cm⁻¹) laser line. The laser fluence dependence on IRMPA was also studied at the line using a pulsed TEA CO₂ laser. The present system was chosen for the study with two objectives in mind: First, CH₃CH₂Br, a prototype molecule of BHC (bromohydrocarbon), is a suitable molecule for the comparative study of photochemical behaviors between BHC and HFC (hydrofluorocarbon) groups, and easy to handle due to its strong absorption around 10 μm CO₂ laser wavelength region. Secondly, the PA technique was adopted for the measurement of photoabsorption because of its broad dynamic range.

Experimentals

Laser Systems

A home-made cw CO₂ laser was used to measure the ir absorption profile and the small signal absorption cross section of CH₃CH₂Br. The details of construction scheme have been described elsewhere.¹⁰ In brief, the laser gas mixed with CO₂:N₂:He=1:1.2:8 was flown fast into the laser cavity using a pump and maintaining ca. 10 Torr in the cavity. The output coupler mount was used as a cathode and the brewster window mount as an anode. The applied voltage between two electrodes was 20 kVDC. Laser cavity was constructed using a 1" dia ZnSe output coupler (80% reflection at 9-11 μm) and a ML-501 grating (PTR Co., 150 lines/mm, blazed at 10.6 μm). The laser was able to operate through 9R to 10P laser lines. The measured output power at 10P(20) laser line was ca. 5 W.

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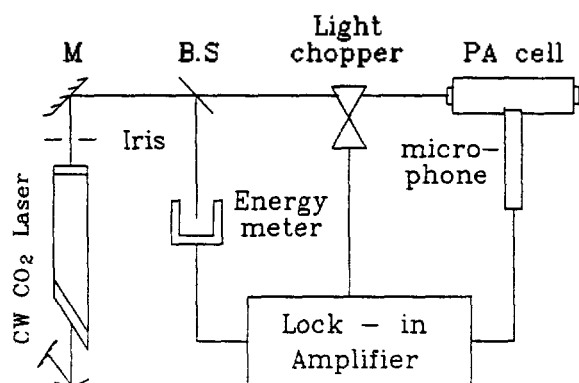


Figure 1. Experimental set-up for measuring absorption profile of $\text{CH}_3\text{CH}_2\text{Br}$ by a cw CO_2 laser.

A home-made pulsed TEA CO_2 laser was used for IRMPA experiment. The details of construction scheme are also described elsewhere.¹⁰ In brief, the laser cavity was constructed by using a 2" dia ZnSe output coupler and a ML-304 grating (PTR Co., 135 lines/mm, blazed at 10.6 μm). Two cham profile brass electrodes (width 80 mm, length 400 mm) were used as main electrodes. The operation power for the laser was supplied using a switching regulated power supply and 2-stage Marx bank circuitry with two 40 nF/100 kV capacitors (Maxwell). The laser was able to operate within $\pm 5\%$ output power fluctuations. The output features at charging voltage of 20 kV and at gas mixing ratio of $\text{CO}_2 : \text{N}_2 : \text{He} = 1 : 1.2 : 8$ were the pulse width of <100 ns with ca. 1 μs tail, divergence of ca. 15 mrad., and output energy of 1.5 J/pulse at 10P(20) laser line.

Apparatus and Procedure

IR Absorption Measurement. The ir absorption profile and the small signal absorption cross section of $\text{CH}_3\text{CH}_2\text{Br}$ were measured utilizing a cw CO_2 laser. The substrate, $\text{CH}_3\text{CH}_2\text{Br}$ (Aldrich), was used after several bulb-to-bulb distillations at ethanol slush bath temperature (ca. -100°C) for purification. The schematic diagram of the experimental set-up is displayed in Figure 1. A cylindrical PA cell (60 mm dia, 100 mm length) was made of stainless steel with a 1" dia KCl window attached to each end of the cylinder. Sample was introduced to the cell through a standard vacuum line while monitoring the sample pressure with a Barocel pressure sensor. The PA signal was obtained with a highly sensitive condenser microphone (B&K 4165) located near center of the cell, a preamplifier (B&K 2639) and a lock-in amplifier (EG&G 5209).

The small signal absorption cell was made of pyrex glass (20 mm dia, 500 mm length) attached both ends with KCl windows. The laser energy was measured at out side of the cell through the window using a power energy meter (Scientech 362).

IRMPA Measurement. The PA signal with variation of laser fluence of pulsed TEA CO_2 laser was monitored utilizing a digital oscilloscope (LeCroy 9400, bandwidth 125 MHz). The experimental set-up is displayed in Figure 2. An attenuation cell filled with SF_6 as an attenuator was placed in front of the PA cell for controlling the laser input energy. The input fluence was controlled by varying the pressure

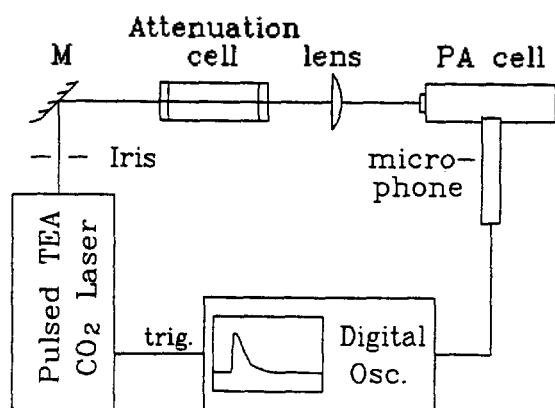


Figure 2. Experimental set-up for measuring IRMPA of $\text{CH}_3\text{CH}_2\text{Br}$ by a pulsed TEA CO_2 laser.

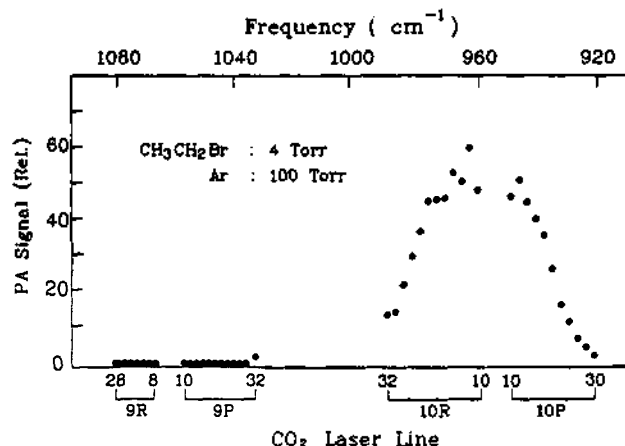


Figure 3. CW CO_2 laser absorption profile of $\text{CH}_3\text{CH}_2\text{Br}$ obtained by PA technique.

of SF_6 attenuator.

Laser beam was focused at a center of the PA cell using a ZnSe plano-convex lens ($f=150$ mm). Beam diameter was kept constant with a 14 mm dia iris. The focal waist was measured with a knife-edge and was ca. 0.6 mm. The signal was averaged over 20 laser pulses to compensate the pulse-to-pulse laser power fluctuations.

The sample was prepared by mixing 0.1 Torr of $\text{CH}_3\text{CH}_2\text{Br}$ with 20 Torr of Ar buffer gas.

Results and Discussion

IR Absorption Measurement with a cw CO_2 Laser

The PA signal profile of $\text{CH}_3\text{CH}_2\text{Br}$ is displayed in Figure 3. A broad ir absorption was observed at 10 μm wavelength region indicating either C-C stretching vibration (964 cm^{-1}) or CH_3 rocking vibration (964 cm^{-1}) of $\text{CH}_3\text{CH}_2\text{Br}$.¹³

The macroscopic small signal absorption cross section was calculated utilizing Beer-Lambert law, i.e., $I_t = I_0 \exp(-\alpha Nl)$, from the absorbance data at 10P(20) laser line obtained in the pressure range of 0-70 Torr, and listed in Table 1. Where I_t and I_0 denote transmitted and input laser intensities, α the absorption cross section, N the number of molecules per cm^3 , and l the cell length, respectively. The obtained absorption cross section was $(1.67 \pm 0.05) \times 10^{-20}$ cm^2 .

Table 1. Absorbance of CH₃CH₂Br at 10P(20) Laser Line of cw CO₂ Laser as a Function of Substrate Pressure

Pressure of CH ₃ CH ₂ Br (Torr)	Absorbance ($-\ln(I/I_0)$)
5.25	0.231
10.11	0.405
14.03	0.519
16.70	0.588
19.60	0.709
31.45	0.944
42.73	1.371
44.99	1.340
66.33	1.892

Table 2. PA Signal Intensities from IRMPA of CH₃CH₂Br (Using 0.1 Torr CH₃CH₂Br Mixed with 20 Torr Ar Buffer Gas, Averaged Over 10 Laser Pulses)

Fluence at Focus (ϕ ; J/cm ²)	PA Signal Intensity (S; mV)
9.62	1.09
12.40	1.28
14.94	1.25
26.72	2.34
33.79	2.67
51.34	4.28
59.88	4.81
65.20	4.75
72.73	5.87
84.50	6.56
93.05	7.25
99.45	7.65
111.22	7.96
124.07	8.46

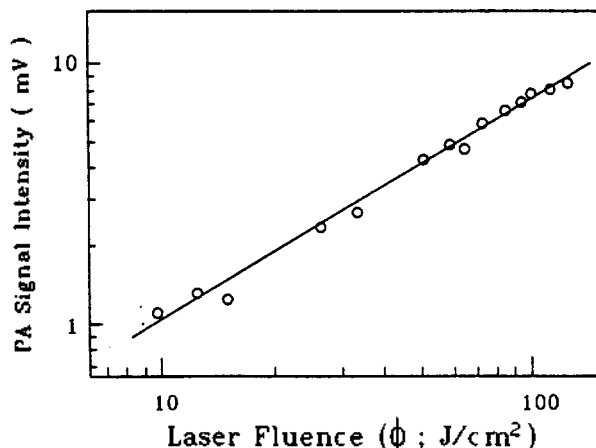
IRMPA Measurement with a pulsed TEA CO₂ Laser

The IRMPA results are listed in Table 2 and displayed in Figure 4. Any fluctuation due to dissociation reaction for measurements could be neglected because of negligible dissociation of the substrate within the fluence range and the number of pulses.

As shown in Figure 4, the PA signal intensity was shown monotonic increase with the laser fluence indicating that the vibrational anharmonicity in the pumped vibration mode of CH₃CH₂Br did not restrict the multiphoton absorption of *n* photons in the fluence range.

In IRMPA process, the induced pressure change via $V \rightarrow T$ energy transfer of absorbed laser energy is given by $\delta P \approx nh\nu \times P_s \times (P_s + P_b)$.¹¹ Where *n* denotes the average number of photons absorbed, *P_s* the partial pressure of substrate, and *P_b* the partial pressure of buffer gas, respectively. Since δP is dependent on *n* and *P_s* for $P_b \geq P_s$, the PA signal intensity, the pressure difference, at constant *P_s* is linearly dependent on *n*. The relationship between the average photons absorbed and the laser fluence is given by the equation.¹¹

$$n = C\phi^b$$

**Figure 4.** Photoacoustic signal from IRMPA of CH₃CH₂Br by a pulsed TEA CO₂ laser.

Where *C* and *b* denote the constants and ϕ denotes the laser fluence, respectively. The constant *b* reveals a degree of saturation against the laser fluence in IRMPA process. In our experimental fluence region, *b* is found to be 0.86 ± 0.03 and very close to 0.85 for 3,4-dichlorocyclobutene.¹¹

The absorbed energy by selective excitation of vibrational mode through MPA is randomized rapidly into whole internal degrees of freedom of the molecule, especially, for the larger molecule than CF₃CH₂Cl¹² of HCFC group. Since the quasicontinuum state of CH₃CH₂Br starts at very low molecular energy level,¹⁴ the anharmonicity in the pumped vibrational mode does not seriously restrict energy randomization. Therefore, the mismatch of laser frequency due to anharmonicity is expected to play insignificant roles in MPA process above this energy state. These findings suggest that the anharmonic energy barrier in pumped vibration mode of CH₃CH₂Br in BHC group can be overcome easily in MPA process by the intramolecular energy transfer to quasicontinuum states.

Conclusions

The ir absorption cross section of CH₃CH₂Br obtained in the pressure range of 0-70 Torr at 10P(20) cw CO₂ laser line was determined to be $(1.67 \pm 0.05) \times 10^{-20}$ cm². The IRMPA signal of CH₃CH₂Br using a pulsed TEA CO₂ laser was revealed to increase monotonically with laser fluence. From these observations, it was suggested that the anharmonicity in pumped vibration mode plays minor roles on IRMPA of CH₃CH₂Br system.

Acknowledgement. This work was done with financial assistance from the Korea Science & Engineering Foundation, which is gratefully acknowledged.

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Preparation and Characterization of Dinuclear Metal Complexes, $[(\text{PPh}_3)_2(\text{CO})\text{M}(\mu\text{-E})\text{M}(\text{CO})(\text{PPh}_3)_2](\text{SO}_3\text{CF}_3)_2$ (M=Rh, Ir; E=1,4-Dicyanobenzene and 1,4-Dicyano-2-butene)

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Received May 28, 1992

Hydrocarbon solution of $(\text{PPh}_3)_2(\text{CO})\text{MOSO}_2\text{CF}_3$ (M=Rh, Ir) reacts rapidly with 1,4-dicyanobenzene or 1,4-dicyano-2-butene to yield dinuclear metal complexes $[(\text{PPh}_3)_2(\text{CO})\text{M}(\mu\text{-dicyanobenzene})\text{M}(\text{CO})(\text{PPh}_3)_2](\text{SO}_3\text{CF}_3)_2$ (I: M=Rh; II: M=Ir) or $[(\text{PPh}_3)_2(\text{CO})\text{M}(\mu\text{-dicyano-2-benzene})\text{M}(\text{CO})(\text{PPh}_3)_2](\text{SO}_3\text{CF}_3)_2$ (III: M=Rh; IV: M=Ir), respectively. Compounds I, II, III, and IV were characterized by $^1\text{H-NMR}$, $^{31}\text{P-NMR}$, and infrared spectrum. Dichloromethane solution of II and IV reacts with H_2 and I_2 to yield oxidative addition complexes $[(\text{PPh}_3)_2(\text{CO})\text{IrX}_2(\mu\text{-E})\text{Ir}(\text{CO})(\text{PPh}_3)_2](\text{SO}_3\text{CF}_3)_2$ (V; E=1,4-dicyanobenzene, $\text{X}_2=\text{H}_2$; VI: E=1,4-dicyano-2-butene, $\text{X}_2=\text{H}_2$; VII: E=1,4-dicyanobenzene, $\text{X}_2=\text{I}_2$). All metal complexes are bridged by the cyanide groups. Compounds V, VI, and VII are characterized by conventional methods.

Introduction

The preparation of three-dimensional metal complex hosts able to accommodate aromatic molecules is of great importance in both organic and inorganic chemistry.¹ Recently, Robson and coworker² reported the design and construction of a new class of scaffolding-like materials comprising infinite polymer frameworks of 3D-linked molecular rods. Iwamoto and coworker³ have developed novel three-dimensional host structure from the Hofman-type $\text{Cd}(\text{NH}_3)_2\text{Ni}(\text{CN})_4$. Although scaffolding-like materials and Hofman-type clathrate are shape specific, the flexible structural modification is quite difficult. Ogura and coworkers⁴ prepared a macrocyclic polynuclear complex $[(\text{en})\text{Pd}(4,4'\text{-bpy})_4](\text{NO}_3)_6$ by constructing the inorganic host as a molecule. Such approach is important because the structural design is easily controlled. Recently, we⁵ prepared dinuclear and trinuclear metal complexes $[(\text{PPh}_3)_2(\text{CO})\text{M}(\mu\text{-E})\text{M}(\text{CO})(\text{PPh}_3)_2]\text{X}_2$ (M=Rh, Ir; E=pyrazine, 4,4'-dipyridyl, $\text{X}=\text{SO}_3\text{CF}_3$; E= $\text{Pd}(\text{CN})_4$, $\text{Pt}(\text{CN})_4$, $\text{X}=\text{none}$). The syntheses of trinuclear metal complexes prompted us to prepare dinuclear metal complexes bridged by the cyanide groups. Therefore, we chose 1,4-dicyanobenzene and 1,4-dicyano-2-butene as a bridging ligand. The four bridged compounds show interesting features because they are able

to control the size and they are possible models of 1-D polymer.

In this article, we wish to report the formation of dinuclear metal complexes bridged by 1,4-dicyanobenzene or 1,4-dicyano-2-butene and oxidative addition reaction.

Experimental Section

All manipulations of air-sensitive materials were carried out under an argon atmosphere with use of standard Schlenk or vacuum line technique or a Mebraun MB150 glovebox. $^1\text{H-NMR}$, and $^{31}\text{P-NMR}$ spectra were recorded on a Bruker WM-250 spectrometer in CDCl_3 . Chemical shifts are given in parts per million relative to tetramethylsilane for $^1\text{H-NMR}$ spectra and 85% H_3PO_4 for $^{31}\text{P-NMR}$ spectra. IR spectra were obtained by using a Perkin-Elmer 1310 instrument. Conductivity measurement was conducted with an Industrial Instrument Model RC216B2. Elemental analyses were carried out at the Basic Science Research Center. Reagent grade ether and benzene were distilled under argon from sodium-benzophenone ketyl. Dichloromethane was distilled under Ar from calcium hydride. $(\text{PPh}_3)_2(\text{CO})\text{MCl}^6$ (M=Rh, Ir) and $(\text{PPh}_3)_2(\text{CO})\text{MOSO}_2\text{CF}_3$ ⁷ (M=Rh, Ir) were prepared according to literature methods. 1,4-Dicyanobenzene and 1,4-Dicyano-2-bu-