

Production of Highly Concentrated ^{13}C by Continuous Two-Stage IRMPD. $\text{CBr}_2\text{F}_2/\text{HI}$, $\text{CCl}_2\text{F}_2/\text{HI}$, and $\text{CBrClF}_2/\text{HI}$ Mixtures

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Abstract. Difluoromethane CH_2F_2 containing 90–98% ^{13}C was obtained in the selective IRMPD of mixtures of $\text{CBr}_2\text{F}_2/\text{HI}$, $\text{CCl}_2\text{F}_2/\text{HI}$, and $\text{CBrClF}_2/\text{HI}$. In $\text{CBr}_2\text{F}_2/\text{HI}$ mixtures, the intermediate product CHBrF_2 resulting from the reaction between the initial decomposition fragment CBrF_2 and HI underwent secondary selective IRMPD to form highly ^{13}C -enriched CH_2F_2 in continuous laser irradiation. The intermediate product in the mixtures of $\text{CCl}_2\text{F}_2/\text{HI}$ and $\text{CBrClF}_2/\text{HI}$ was found to be CHClF_2 , but no significant secondary photodecomposition in $\text{CBrClF}_2/\text{HI}$ mixtures occurred owing to the low absorption cross section of CHClF_2 at the adopted laser frequencies and fluences. The observed decomposition probabilities and selectivities under different conditions with respect to laser frequency, fluence, and partial pressures of halogenated difluoromethanes and HI suggest that CBr_2F_2 is one of the better candidates for practical ^{13}C separation by IRMPD.

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Since the initial observation that polyatomic molecules undergo isotopically selective decomposition in an intense IR laser field, extensive efforts to utilize the fundamental principle for isotope separation have been made over the last decade. Although remarkably high isotope selectivities are attained in infrared multiple-photon decomposition (IRMPD) of several isotopic molecules, it is not easy to produce enriched compounds at sufficiently large yields. There have been some examples of practical separation basing on IRMPD [1, 2].

^{13}C is a very important isotope which has been widely employed as a tracer in areas ranging through chemistry, life science, medicine, environmental science, and biochemical synthesis. Investigation of the laser separation of ^{13}C has progressed actively in the last ten years. Now, it is believed that the field is approaching the stage of practical production [2]. An exhaustive survey of the progress up to 1985 was presented by Outhouse et al. [3]. In order to form a

connecting link between previous work and recent developments the present paper lays stress on an exposition of the substantial progress in ^{13}C separation using a TEA CO_2 laser.

At present, the TEA CO_2 laser is chosen for most schemes because of its relatively high conversion efficiency of electric energy to laser photon energy (10–20%) and its high output power with a low cost. Coincidentally, the stretching vibration of a C–F bond in various organic compounds is resonant with the oscillation of the 9.6- or 10.6- μm band of the CO_2 laser. In addition, there is a clear ^{13}C isotope shift in the vibration mode. Therefore, small Freon molecules have frequently been used as working substances in separating ^{13}C . Among them, halogenated trifluoromethanes (CF_3X , $\text{X}=\text{Cl}$, Br , or I) and difluorochloromethane (CHClF_2) have proved to be typical and fruitful. The nascent fragment in the IRMPD of halogenated trifluoromethanes [4–9] is trifluoromethyl CF_3 , and the ultimate product with enriched ^{13}C

is hexafluoroethane, if there is no scavenger in the system. With proper control of the reaction conditions, one can obtain a very high selectivity, for instance, C_2F_6 with a ^{13}C content of 80% has been obtained by the IRMPD of $CBrF_3$, when the compound was cooled to $-80^\circ C$ [5]. Another promising starting material is $CHClF_2$ [3, 10]. The IRMPD consists of the elimination of HCl from vibrationally excited $CHClF_2$ and the subsequent dimerization of CF_2 to form C_2F_4 . Using $CHClF_2$, Hackett et al. have shown that the production rate of 220 mg h^{-1} for ^{13}C at 50% atom fraction is beneficial in energy expenditure. However, the ^{13}C at a concentration as high as 90% can be obtained only at an extremely low yield, which is not useful in actual ^{13}C separation. Hence they proposed the two-stage enrichment method, that is, the C_2F_4 containing 50% ^{13}C formed in the first stage IRMPD was converted via some chemical process into $CHClF_2$, which could be used for the second stage enrichment to produce ^{13}C at a high concentration of over 90%. However, the conversion from C_2F_4 into $CHClF_2$ is not simple and undoubtedly causes a rise in cost.

On the other hand, Abdushelishvili et al. have proposed a cyclic system based on using NO as a scavenger in the IRMPD of CF_3Br or CF_3I [2]. The CF_3NO molecules produced in the first-stage photolysis are converted into CF_3Br or CF_3I by heating the molecules in the presence of Br_2 or I_2 . Our previous process consists of the ^{13}C -selective first-stage IRMPD of C_2F_6 and Br_2 mixtures, followed by the second-stage IRMPD of the resulting CF_3Br [5, 11].

There seems to be a general agreement that the two-stage enrichment process is necessary for practical ^{13}C separation and the product from the first-stage photodecomposition ought to be transformed chemically into the reactant to be used in the second-stage enrichment. It is better to directly produce the second-stage reactant in the first-stage photodecomposition. On the basis of this concept, we designed some reaction systems and obtained highly concentrated ^{13}C of over 90% through the two-stage enrichment [12].

The present paper covers a series of selective two-stage IRMPD processes using CBr_2F_2/HI , CCl_2F_2/HI , and $CBrClF_2/HI$. In CBr_2F_2/HI and CCl_2F_2/HI , the primary products $CHBrF_2$ and $CHClF_2$ from the first-stage photolysis were found to decompose in the continuous laser irradiation at the same frequency and fluence. The secondary decomposition resulted in the formation of CH_2F_2 at 98% ^{13}C concentration under optimum conditions.

1. Experimental

The details of the experimental apparatus and procedures were described in the previous papers [5, 11, 12].

CBr_2F_2 , CCl_2F_2 , $CBrClF_2$, and $CHClF_2$ were kindly supplied from Daikin Kogyo Company. The analytical results by gas chromatography (GC) showed that the purities of $CHClF_2$, CCl_2F_2 , and $CBrClF_2$ were 99.9, 99.9, and 99.7% respectively. The reagents were used directly without further purification in this experiment. The purity of CBr_2F_2 was found to be 97%, so we removed impurities such as $CHBrF_2$ and $CBrClF_2$ by low-temperature distillation at $-10^\circ C$. The final purity was 99.7%. $CHBrF_2$ was formed as a primary product in the first stage IRMPD of CBr_2F_2/HI mixtures. For the calibration of the response factor in GC, we synthesized $CHBrF_2$ according to the method proposed by Henne [13]. The $CHBrF_2$ prepared was purified by low-temperature distillation, and its purity finally exceeded 99% in GC. HI purchased from Matheson Company was firstly degassed at the temperature of liquid nitrogen and further purified by trap-to-trap distillation. The HI treated by this procedure did not show any impurity in IR analysis or in GC.

The laser employed was a TEA CO_2 laser from Ushio Denki Company, and was operated at a repetition rate of 3 Hz. The lasing medium consisted of $He(82.2\%)$, $CO_2(7.9\%)$, $N_2(7.9\%)$, and $CO(2\%)$. The main spike with a 100-ns FWHM contained 60–70% of the total pulse energy and the following tail lasted for about 2 μs . A Scientech 362 power meter with a Scientech 36001 detector was used to monitor the output of laser pulses. The fluctuation in output from pulse to pulse was less than $\pm 4\%$ under constant operational conditions. The attenuation of laser fluence was simply achieved by inserting one or more KBr or CaF_2 plates into the laser beam. The beam, after the truncation with an aperture (2.5 cm in diameter), was focused at a center of a reaction cell by a BaF_2 lens with a focal length of 120 cm. The fluence distribution at the focal point was measured using a 0.15-mm pinprick and the transverse profile was found to be flat rather than Gaussian. The two reaction cells were cylindrical Pyrex tubes with the same diameter (2.1 cm) and different lengths (10 and 62 cm). The windows at both ends were KBr disks. In addition, they had the KBr windows for IR measurements at the sides. The volumes were 55 cm^3 for the short, and 230 cm^3 for the long tube. The fluence distribution along the axial direction was almost homogeneous inside the short cell. However, the distribution was unavoidably inhomogeneous inside the long cell; the fluence at the front window was smaller than that at the focus by a factor of 0.58.

The qualitative and quantitative analyses of the samples were carried out using the GC-MS system which combined a Shimadzu GC-9A gas chromatograph with a NEVA TE-150 quadrupole mass spec-

trometer. After irradiation, the samples were introduced into the GC-MS system with the 6-m Porapak Q column connected in series with a 6-m Porapak N. The isotopic ratios in fresh reactants, unconsumed reactants, and products were determined in terms of a standard method for isotopic analysis in mass spectrometry. In CH_2F_2 , for example, the intensities of ion currents at $m/e=31, 32, 33,$ and 34 were integrated over the entire effluent time of CH_2F_2 in GC and the following equation interrelating $^{12}\text{CF}^+, ^{13}\text{CF}^+, ^{12}\text{CHF}^+, ^{13}\text{CHF}^+, ^{12}\text{CH}_2\text{F}^+,$ and $^{13}\text{CH}_2\text{F}^+$ ions was solved to find the ratio A between ^{12}C and ^{13}C

$$I_{31}A^3 - I_{32}A^2 + I_{33}A - I_{34} = 0,$$

where I_{31} denotes the integrated intensity at $m/e=31$ and the other I 's are by analogy.

The conversion of the ^{13}C component in each irradiation was controlled to within 40% by changing the laser pulse number. To evaluate enrichment processes, we defined a decomposition probability per pulse and selectivity on the assumption that the overall decomposition rate per pulse fits the so-called first-order kinetics. The decomposition probability per pulse iP_d of $^i\text{CF}_2\text{XY}$ is

$$^iP_d = \frac{V_{\text{cell}}}{V_{\text{ill}}n} \ln \frac{[^i\text{CF}_2\text{XY}]_0}{[^i\text{CF}_2\text{XY}]_n},$$

where i represents a mass number of carbon, and V_{cell} and V_{ill} represent the volumes of a cell and an illuminated zone, respectively. $[\text{CF}_2\text{XY}]_0$ and $[\text{CF}_2\text{XY}]_n$ are the concentrations of a halogenated difluoromethane CF_2XY before and after n pulse irradiation, respectively. The ratio of the decomposition probabilities $^{13}P_d/^{12}P_d$ corresponds to the selectivity S in the process examined. The decomposed fraction of $^i\text{CF}_2\text{XY}$ divided by the number of laser pulses was defined as the decomposition yield iY .

$$^iY = \frac{V_{\text{cell}}}{V_{\text{ill}}n} \frac{([\text{CF}_2\text{XY}]_0 - [\text{CF}_2\text{XY}]_n)}{[\text{CF}_2\text{XY}]_0}.$$

2. Results and Discussion

2.1. Mixtures of CBr_2F_2 and HI

Although several detailed examinations on the IRMPD of CBr_2F_2 were carried out [14–16], its application to separating ^{13}C has not yet been pursued earnestly. The IR spectrum of CBr_2F_2 suggests that the compound is suitable for separating ^{13}C in the TEA CO_2 laser-induced IRMPD. As shown in Fig. 1, the strong absorption corresponding to the ν_1 vibrational mode of $^{12}\text{CBr}_2\text{F}_2$ occurs at 1090 cm^{-1} and the isotope shift due to ^{13}C is 23 cm^{-1} . The CBr_2F_2 at 65% ^{13}C concentration in the figure was obtained by irradiating a mixture of 100-Torr CHClF_2 and 20-Torr

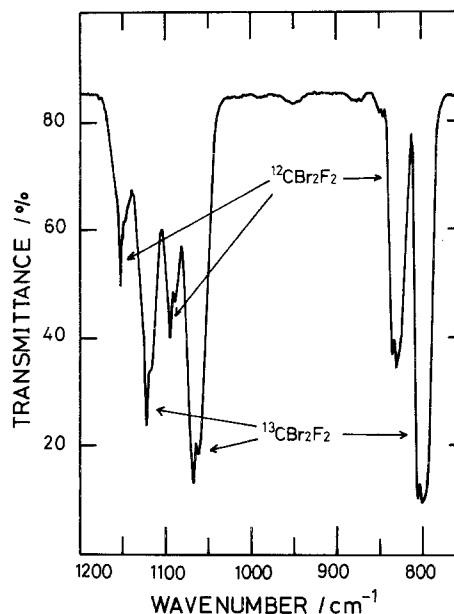
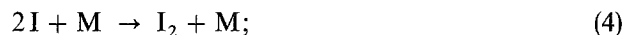
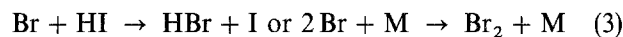
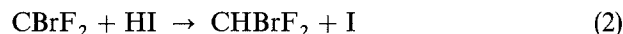
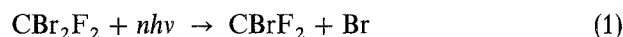


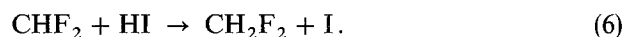
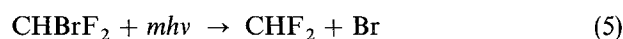
Fig. 1. Infrared absorption spectrum of CBr_2F_2 at 65% ^{13}C concentration obtained by irradiating a mixture of 100 Torr CHClF_2 and 20 Torr Br_2 with the 9P(24) laser line at a fluence of 4 J cm^{-2} . The ^{13}C -enriched product CBr_2F_2 was isolated from the irradiated mixture by a preparative gas chromatograph

Br_2 with the 9P(24) laser line at a fluence of 4 J cm^{-2} , and then separating CBr_2F_2 from the irradiated mixture by a preparative GC. In the IRMPD of CBr_2F_2 , the rupture of a C-Br bond occurs mainly in the fluence region examined here, as shown in the previous studies [14, 16]. The resulting nascent CBrF_2 radical reacts with HI to form a CHBrF_2 molecule. Coincidentally, the band due to the ν_8 vibrational mode of CHBrF_2 is located at 1108 cm^{-1} [17], so that the $^{13}\text{CHBrF}_2$ produced from the selective photodecomposition of CBr_2F_2 could absorb photons from the same laser line and undergo multiple-photon decomposition to form a CHF_2 radical. The mechanism for this two-stage ^{13}C enrichment process can be expressed as follows:

First stage:



Second stage:



The overall IRMPD results in an extremely high enrichment of ^{13}C in the final product CH_2F_2 . For

example, CH_2F_2 at 98% ^{13}C concentration was obtained by choosing the proper experimental conditions regarding laser frequency, laser fluence, and pressures of CBr_2F_2 and HI.

The above-mentioned mechanism can be further verified by the pulse number dependences of the ^{13}C fractions in CBr_2F_2 , CHBrF_2 , and CH_2F_2 , where the ^{13}C fraction corresponds to $100\% \times (\text{amount of } ^{13}\text{C} \text{ in each compound})/(\text{total amount of } ^{13}\text{C} \text{ in the system})$. Considering that the IRMPD of halogenated difluoromethanes is usually completed within a few dozen microseconds and the concentrations of HI are sufficiently high in the present systems, the two photolytic processes (1) and (5) are regarded as a set of consecutive reactions with respect to pulse repetition [18]. Assuming first-order depletion for $^{13}\text{CHBrF}_2$ as well as $^{13}\text{CBr}_2\text{F}_2$, we obtain the following differential equation,

$$\frac{d[^{13}\text{CHBrF}_2]_n}{dn} = \frac{V_{\text{ill}}}{V_{\text{cell}}} \times (^{13}P_{1d}[^{13}\text{CBr}_2\text{F}_2]_n - ^{13}P_{5d}[^{13}\text{CHBrF}_2]_n),$$

where $[^{13}\text{CHBrF}_2]_n$ represents the concentration of $^{13}\text{CHBrF}_2$ after irradiation with n pulses. $^{13}P_{1d}$ and $^{13}P_{5d}$ are the decomposition probabilities in processes (1) and (5), respectively. We can derive the following relation from the mathematical treatment of the differential equation:

$$\ln\left(\frac{[^{13}\text{CHBrF}_2]_{\text{max}}}{[^{13}\text{CBr}_2\text{F}_2]_0}\right) = \left\{ \frac{P_{1d}}{P_{5d} - P_{1d}} \right\} \ln\left(\frac{P_{1d}}{P_{5d}}\right),$$

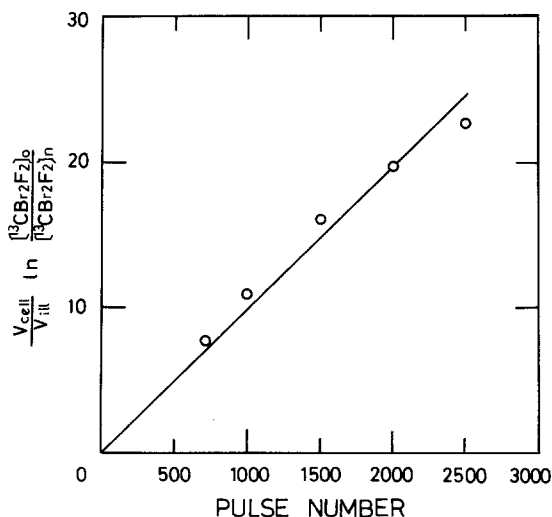


Fig. 2. Logarithmic plots of $(V_{\text{cell}}/V_{\text{ill}})\ln([^{13}\text{CBr}_2\text{F}_2]_0/[^{13}\text{CBr}_2\text{F}_2]_n)$ versus pulse number. Mixtures of 30 Torr CBr_2F_2 and 15 Torr HI were irradiated with the 9P(28) line at a fluence of 3.5 J cm^{-2} using a short cell. $[^{13}\text{CBr}_2\text{F}_2]_0$ is the concentration of $^{13}\text{CBr}_2\text{F}_2$ before irradiation; $[^{13}\text{CBr}_2\text{F}_2]_n$ is the concentration of $^{13}\text{CBr}_2\text{F}_2$ after n pulses; V_{cell} , volume of a cell; V_{ill} , volume of illuminated zone. $V_{\text{cell}}/V_{\text{ill}} = 14.3$

where $[^{13}\text{CHBrF}_2]_{\text{max}}$ is the maximum concentration of $^{13}\text{CHBrF}_2$ and $[^{13}\text{CBr}_2\text{F}_2]_0$ is the initial concentration of $^{13}\text{CBr}_2\text{F}_2$. Figure 2 demonstrates the first-order depletion of $^{13}\text{CBr}_2\text{F}_2$ and the decomposition probability $^{13}P_{1d}$ is acquired from the slope of the straight line in the figure. The ratio $^{13}P_{1d}/^{13}P_{5d}$ can be estimated to be 2.1 from the experimental results in Fig. 3. Using $^{13}P_{1d}$ and $^{13}P_{5d}$, we have calculated the evolution of the reactant and the products as a function of laser pulse number, as drawn in the dashed curves of Fig. 3. The calculated evolutions are in good agreement with the observed results. The decomposition probabilities $^{13}P_{1d}$ and $^{13}P_{5d}$ depend on the behavior of ground-state and excited state molecules in photon absorption as well as on the decomposition rates of highly vibrationally excited molecules beyond a threshold energy.

The decomposition of CHBrF_2 is considered to have two channels: three-center elimination of HBr and rupture of a C-Br bond. The threshold energies for the HBr elimination and the C-Br bond rupture are 56 and 62 kcal mol^{-1} , respectively [19], and they are close to each other. In the present IRMPD of mixtures of CBr_2F_2 and HI, we detected only CHBrF_2 and CH_2F_2 as the stable carbon-containing products without any evidence for the formation of CHF_2I . This fact suggests that CHBrF_2 , which is the product of the first IRMPD

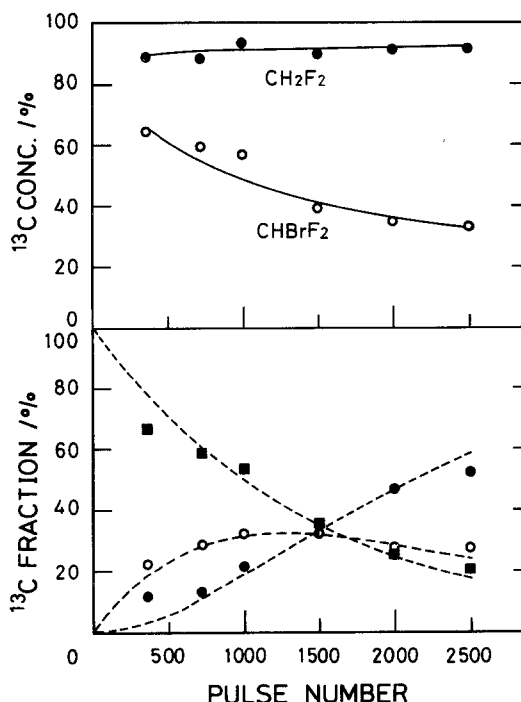


Fig. 3. ^{13}C fractions and ^{13}C concentrations of products as a function of pulse number. The experimental conditions are the same as Fig. 2. ■, CBr_2F_2 ; ○, CHBrF_2 ; ●, CH_2F_2 . Dashed curves, see text

of CBr_2F_2 in the presence of HI, undergoes the C–Br bond rupture to form a CHF_2 radical rather than the three-center elimination in the secondary IRMPD. CH_2F_2 originates from the subsequent reaction of the CHF_2 radical with HI. If the decomposition were the three-center elimination, CHF_2I should be formed by the insertion of a nascent CF_2 radical into a HI molecule. It has been well established that the IRMPD of CHClF_2 yields a CF_2 radical and a HCl molecule via three-center elimination of HCl [3, 10]. In fact, we observed the formation of CHF_2I in the IRMPD of mixtures of CHClF_2 and HI.

Polyatomic molecules in an intense IR laser field are frequently pumped to higher excited states beyond their dissociation thresholds. Stephenson and King have determined the translational, rotational, and vibrational energy contents of the nascent CF_2 radical using a laser-induced fluorescence technique, in which CHClF_2 was irradiated with the $9P(26)$ laser line at a peak intensity of $220 \times 10^6 \text{ W cm}^{-2}$ [15]. On the basis of the determination, they estimated that the total amount of energy in the CF_2 and HCl system is greater than $26.0 \text{ kcal mol}^{-1}$. Therefore, the average energy of the reactant molecules which dissociate should be ΔH_0 plus $26.0 \text{ kcal mol}^{-1}$, where ΔH_0 is the enthalpy change at $T=0 \text{ K}$ for the process $\text{CHClF}_2 \rightarrow \text{CF}_2 + \text{HCl}$. If ΔH_0 is not much different from $\Delta H = 50 \text{ kcal mol}^{-1}$ at room temperature, the average energy amounts to 76 kcal mol^{-1} .

On the other hand, the RRKM calculation on the rate constants for the two unimolecular decomposition channels of CHBrF_2 shows that C–Br bond rupture dominates over the three-center elimination in excited molecules with internal energies above about 66 kcal mol^{-1} , as presented in Fig. 4. The following parameters were used in the calculation: *Bond rupture*. (a) Vibrational frequencies of the molecule in cm^{-1} : 3003, 1276, 1130, 708, 579, 244, 1344, 1107, and 323 [17]; (b) vibrational frequencies of the activated complex in cm^{-1} : 3003, 1050, 1130, 300, 240, 1100, 1107, and 303; (c) critical energy, 62 kcal mol^{-1} . *Three-center elimination*. (a) Vibrational frequencies of the molecule in cm^{-1} , the same as bond rupture; (b) vibrational frequencies of the activated complex in cm^{-1} : 3003, 1500, 1130, 1100, 579, 400, 1600, and 1000; (c) critical energy, 56 kcal mol^{-1} .

The dependences of the decomposition probabilities of $^{12}\text{CBr}_2\text{F}_2$ and $^{13}\text{CBr}_2\text{F}_2$ on laser line are presented in Fig. 5. In the determination of the probabilities, $[^{12}\text{CBr}_2\text{F}_2]_n$ and $[^{13}\text{CBr}_2\text{F}_2]_n$ were obtained from $[^{12}\text{CBr}_2\text{F}_2]_0 - [^{12}\text{CHBrF}_2]_n - [^{12}\text{CH}_2\text{F}_2]_n$, and $[^{13}\text{CBr}_2\text{F}_2]_0 - [^{13}\text{CHBrF}_2]_n - [^{13}\text{CH}_2\text{F}_2]_n$, respectively, on the basis of material balance. The absorption cross sections of $^{12}\text{CBr}_2\text{F}_2$ and $^{13}\text{CBr}_2\text{F}_2$ become smaller upon shifting the laser line from $9P(26)$ to

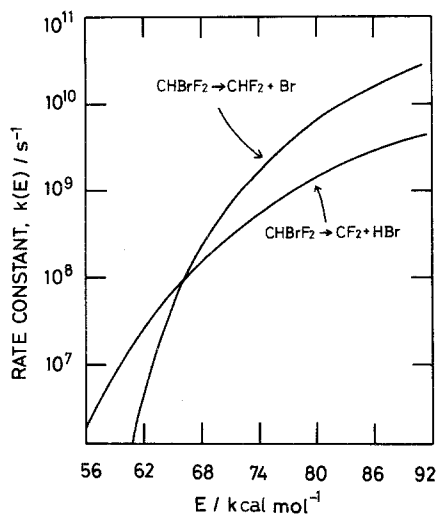


Fig. 4. RRKM rate constants $k(E)$ for unimolecular decomposition of CHBrF_2 as a function of internal energy E of molecule

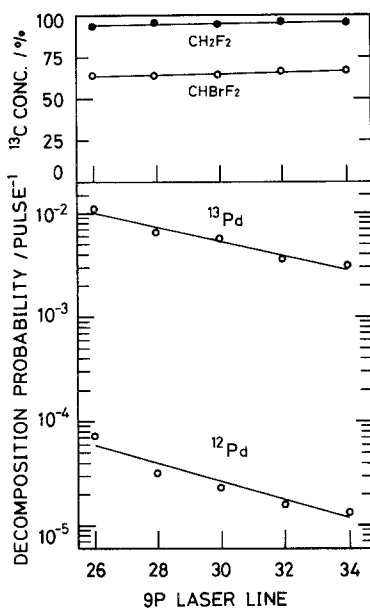


Fig. 5. Laser line effects on decomposition probabilities iP_d of $^i\text{CBr}_2\text{F}_2$ and ^{13}C concentrations of products. Mixtures of 30 Torr CBr_2F_2 and 15 Torr HI were irradiated with laser pulses using a long cell. Focus fluence, about 3.6 J cm^{-2}

$9P(34)$, and their reduction causes the systematic decreases in both decomposition probabilities. However, the ^{13}C concentration in CHBrF_2 or CH_2F_2 did not differ appreciably in the IRMPD for different lines. Therefore, it is evident that for ^{13}C separation the $9P(26)$ line is the most favorable among the laser lines examined because of the high decomposition probability of $^{13}\text{CBr}_2\text{F}_2$.

The marked enrichment can be attained by increasing the pressure of CBr_2F_2 , as shown clearly in Fig. 6,

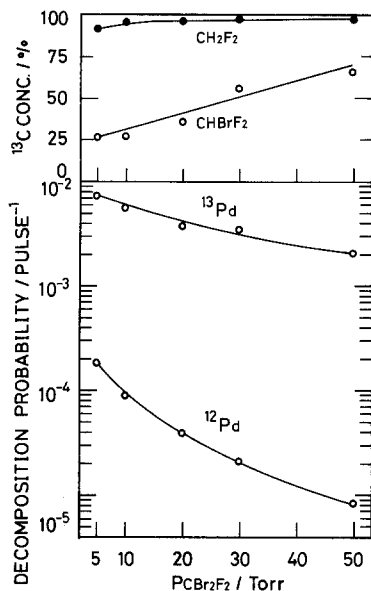


Fig. 6. Decomposition probabilities of $^{12}\text{CBr}_2\text{F}_2$ and ^{13}C concentrations of products as a function of CBr_2F_2 pressure $P_{\text{CBr}_2\text{F}_2}$, $P_{\text{HI}}:P_{\text{CBr}_2\text{F}_2}=1:2$; laser line, $9P(28)$; focus fluence, 3.0 J cm^{-2} ; long cell

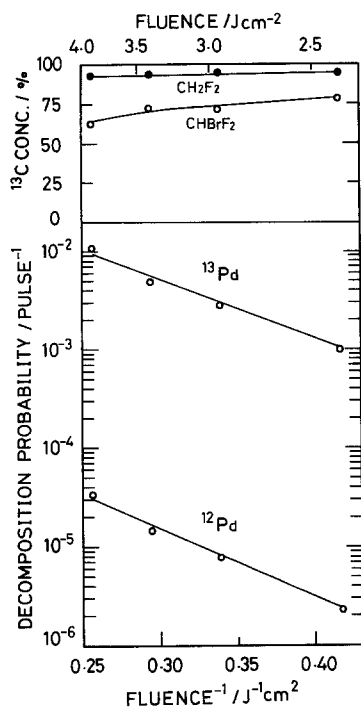


Fig. 7. Decomposition probabilities of $^{12}\text{CBr}_2\text{F}_2$ and ^{13}C concentrations of products as a function of incident fluence. Mixtures of 30 Torr CBr_2F_2 and 15 Torr HI were irradiated with the $9P(28)$ line using a short cell

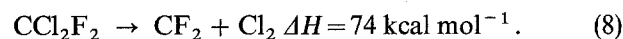
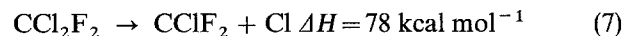
where $[\text{CBr}_2\text{F}_2]:[\text{HI}]$ is always 2:1. The ^{13}C concentrations in both products increase with increasing pressure. In particular, the concentration in CHBrF_2 grew from 27% at 5 Torr to 65% at 50 Torr, while the decomposition probabilities of $^{12}\text{CBr}_2\text{F}_2$ and

$^{13}\text{CBr}_2\text{F}_2$ decreased smoothly with increasing pressure. The final product CH_2F_2 showed the ^{13}C concentration as high as 98%, when the mixture of 50-Torr CBr_2F_2 and 25-Torr HI was irradiated with the $9P(28)$ laser line at a fluence of 3 J cm^{-2} . In Fig. 6, $^{12}\text{P}_d$ apparently decreases more rapidly than $^{13}\text{P}_d$ does. The pressure effects depend on the complicated balance between optical pumping and collisional deactivation of each excited isotopic species. Energy transfer should occur to a significant extent at such high pressures. Therefore, it is not easy to explain the pressure effects of $^{12}\text{P}_d$ and $^{13}\text{P}_d$ in terms of a reasonable kinetic model.

The effects of laser fluence on $^{12}\text{P}_d$ and $^{13}\text{P}_d$ of CBr_2F_2 as well as the ^{13}C concentrations in CHBrF_2 and CH_2F_2 are shown in Fig. 7. The relation between a decomposition probability and laser fluence is usually expressed by an Arrhenius-type equation. The equation is $P_d(\phi) = A \exp(-\phi_c/\phi)$, where A and ϕ_c are parameters, and ϕ is a fluence. The logarithmic plots of $^{12}\text{P}_d$ and $^{13}\text{P}_d$ against ϕ^{-1} give straight lines, as shown in Fig. 7. Both probabilities decrease by nearly one order on decreasing the fluence from 3.9 to 2.4 J cm^{-2} , while the ^{13}C concentrations in CHBrF_2 and CH_2F_2 increase slightly. This fact implies that the laser fluence is one of the important variables for enhancing the yield of ^{13}C in the selective IRMPD of CBr_2F_2 .

2.2. Mixtures of CCl_2F_2 and HI

CO_2 laser radiation can excite two vibrational modes of CCl_2F_2 : the ν_1 stretching and ν_6 rocking modes with absorption peaks at 1099 and 922 cm^{-1} , respectively [20]. The isotope shift for ^{13}C is 22 cm^{-1} for the ν_1 mode and the ^{13}C selective IRMPD occurs in the range of $1030\text{--}1080\text{ cm}^{-1}$ [21]. On the other hand, the ^{13}C selective multiple-photon excitation of the ν_6 mode seems to occur at wavenumbers out of the tunable region of a CO_2 laser [22]. Although CCl_2F_2 was the first molecule used in the ^{13}C separation by CO_2 -laser-induced IRMPD, the separation efficiencies were relatively low in the early studies [21–26]. The decomposition of CCl_2F_2 has two possible channels: molecular elimination of Cl_2 and rupture of a C–Cl bond [22, 27, 28]:

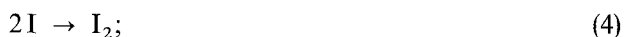
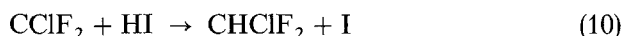
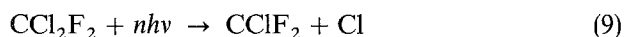


Grant and coworkers have shown that reaction (7) dominated over reaction (8) in the excitation of the ν_6 rocking mode with the $10P(38)$ line at 927.01 cm^{-1} [14, 28]. In our experiment, we detected only $\text{C}_2\text{Cl}_2\text{F}_4$ as a carbon containing product for the IRMPD of neat CCl_2F_2 , where the CO_2 laser lines of the $9P$ branch

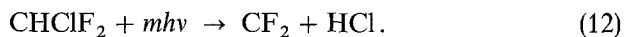
were used at a fluence of nearly 4 J cm^{-2} . We also observed considerable retardation of the decomposition of CCl_2F_2 as the photolysis proceeded deep in neat CCl_2F_2 . This fact suggests that the Cl_2 molecules accumulated in neat CCl_2F_2 react with CClF_2 radicals and the back reaction decreases the apparent decomposition yield of CCl_2F_2 .

Upon adding HI to CCl_2F_2 as a radical scavenger, $\text{C}_2\text{Cl}_2\text{F}_4$ was replaced by CHClF_2 and CH_2F_2 in the IRMPD. Figure 8 represents the plots of ^{13}C fractions and ^{13}C concentrations in both CHClF_2 and CH_2F_2 vs. pulse number. The ^{13}C fraction in CHClF_2 , after passing a maximum, apparently decreases, while its ^{13}C concentration gradually decreases with increasing pulse number over the entire region. On the other hand, the ^{13}C fraction in CH_2F_2 increases with increasing pulse number, while the ^{13}C concentration in CH_2F_2 shows a rapid increase at the beginning of the irradiation and thereafter retains a high value exceeding 90% until 2500 pulses. The CH_2F_2 at such a high ^{13}C concentration must result from the secondary ^{13}C -selective IRMPD of the enriched CHClF_2 produced initially as a primary product. This two-stage process can explain the markedly high enrichment of ^{13}C :

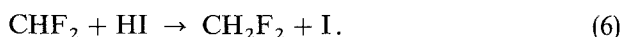
First stage:



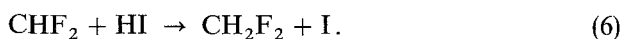
Second stage:



The reaction path from CF_2 to CH_2F_2 has not been elucidated clearly at this moment. The simple path is the consecutive hydrogen-atom abstraction of CF_2 from HI.



However, another path is the insertion of CF_2 into HI to form CHF_2I , which undergoes further IRMPD into CHF_2 and I:



$^{13}\text{CCl}_2\text{F}_2$ and $^{13}\text{CHClF}_2$ have their absorption peaks at almost the same wavenumbers: 1076 cm^{-1} for CHClF_2 [29] and 1077 cm^{-1} for CCl_2F_2 [21].

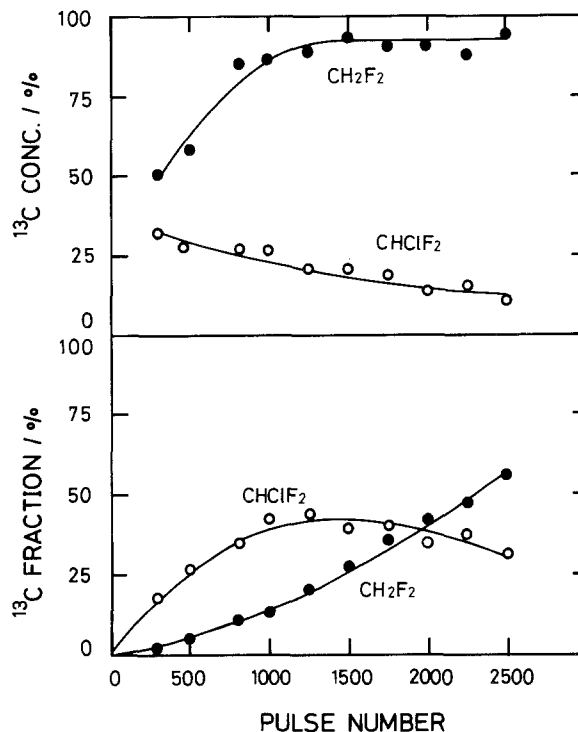


Fig. 8. ^{13}C fractions and ^{13}C concentrations of products as a function of pulse number. Mixtures of 5 Torr CCl_2F_2 and 5 Torr HI were irradiated with the 9P(22) line at a focus fluence of 4 J cm^{-2} using a long cell

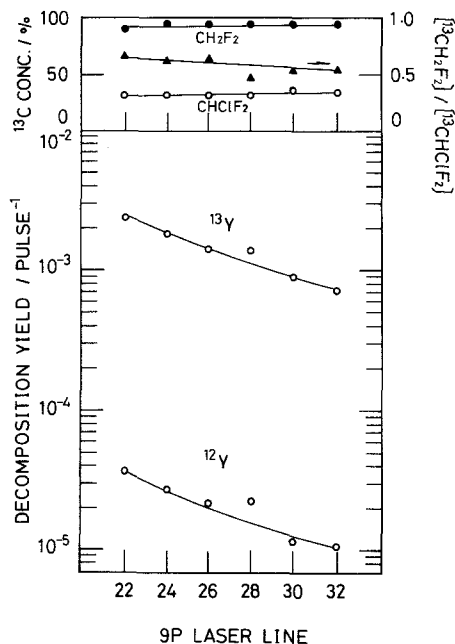


Fig. 9. Laser line effects on decomposition yields of $^{13}\text{CCl}_2\text{F}_2$, ^{13}C concentrations of products, and ratio of $[\text{CH}_2\text{F}_2]$ to $[\text{CHClF}_2]$. Mixtures of 10 Torr CCl_2F_2 and 10 Torr HI were irradiated with laser pulses at a focus fluence of 4.1 J cm^{-2} using a long cell

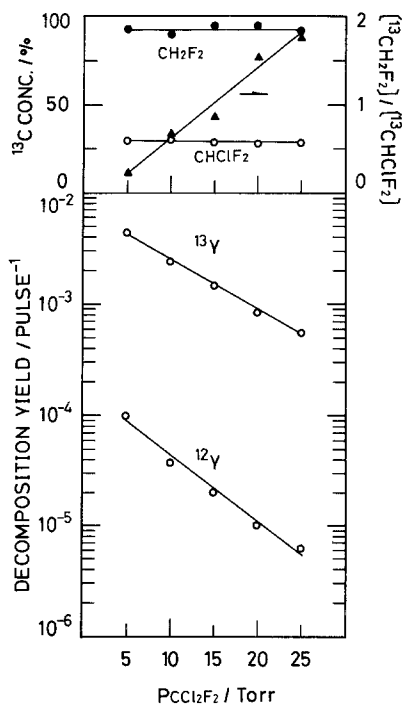


Fig. 10. Decomposition yields of ${}^i\text{CCl}_2\text{F}_2$, ${}^{13}\text{C}$ concentrations of products, and ratio of $[\text{}^{13}\text{CH}_2\text{F}_2]$ to $[\text{}^{13}\text{CHClF}_2]$ as a function of $P_{\text{CCl}_2\text{F}_2}$. $P_{\text{HI}}:P_{\text{CCl}_2\text{F}_2}=1:1$; focus fluence, 4.0 J cm^{-2} ; long cell

Moreover, CHClF_2 has a lower activation energy (56 kcal mol^{-1}) for molecular elimination of HCl [30], which is the exclusive channel in its IRMPD, as compared with that for C-Cl bond rupture in CCl_2F_2 (78 kcal mol^{-1}). These facts support the efficient occurrence of the second-stage IRMPD of ${}^{13}\text{CHClF}_2$ in the presence of ${}^{12}\text{CCl}_2\text{F}_2$ or ${}^{13}\text{CCl}_2\text{F}_2$.

Figure 9 shows decomposition yields ${}^{12}\text{Y}$ and ${}^{13}\text{Y}$ of CCl_2F_2 at different laser lines. The decreases of ${}^{12}\text{Y}$ and ${}^{13}\text{Y}$ with shifting the laser line toward a red side are attributed to the reduction of the absorption cross section in ${}^{12}\text{CCl}_2\text{F}_2$ or ${}^{13}\text{CCl}_2\text{F}_2$. The ${}^{13}\text{C}$ concentrations in both products are slightly enhanced with the change of the laser line in the same direction. The ratio of $[\text{}^{13}\text{CH}_2\text{F}_2]$ to $[\text{}^{13}\text{CHClF}_2]$ remains approximately constant.

The variations of ${}^{12}\text{Y}$ and ${}^{13}\text{Y}$ of CCl_2F_2 with the pressure of CCl_2F_2 are presented in Fig. 10. An increase in the pressure decreases both decomposition yields owing to collisional quenching of highly excited ${}^{12}\text{CCl}_2\text{F}_2$ and ${}^{13}\text{CHClF}_2$ molecules beyond their decomposition thresholds. Another interesting result is the rapid increase in the ratio of $[\text{}^{13}\text{CH}_2\text{F}_2]$ to $[\text{}^{13}\text{CHClF}_2]$ with increasing pressure. This means that the decomposition of ${}^{13}\text{CHClF}_2$ is not seriously quenched by increasing collisions as compared with that of ${}^{13}\text{CCl}_2\text{F}_2$. The mild pressure effect on the

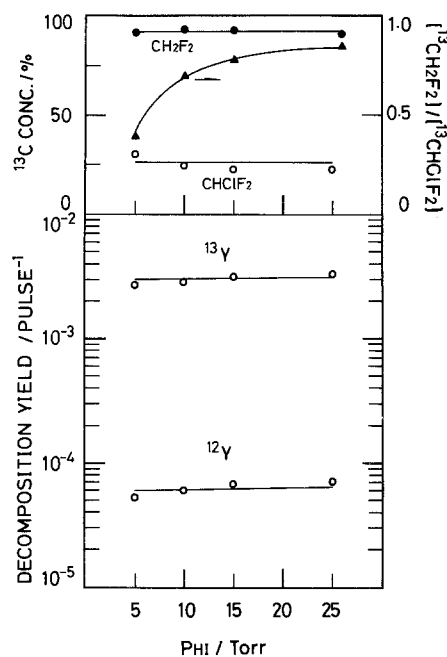


Fig. 11. Decomposition yields of ${}^i\text{CCl}_2\text{F}_2$, ${}^{13}\text{C}$ concentrations of products, and ratio of $[\text{}^{13}\text{CH}_2\text{F}_2]$ to $[\text{}^{13}\text{CHClF}_2]$ as a function of P_{HI} . $P_{\text{CCl}_2\text{F}_2}$, 10 Torr; laser line, $9P(22)$; focus fluence, 4.2 J cm^{-2} ; long cell

decomposition may be related to the relatively low decomposition threshold of CHClF_2 .

Figure 11 presents the relation between decomposition yields and HI pressure. The HI pressure has no significant effect on the decomposition of excited CCl_2F_2 . However, the ratio of ${}^{13}\text{CH}_2\text{F}_2$ to ${}^{13}\text{CHClF}_2$ increases with increasing HI. One possible explanation is the competition between the reactions of nascent CF_2 with HCl and HI , where the reaction of nascent CF_2 with HCl corresponds to the back reaction of the photolysis of CHClF_2 and that with HI leads to the formation of CH_2F_2 . The increase in HI pressure promotes the conversion of CHClF_2 into CH_2F_2 .

2.3. Mixtures of CBrClF_2 and HI

The deposition of IR photons on a CBrClF_2 molecule may lead to the rupture of a C-Br bond because of its low dissociation energy of 65 kcal mol^{-1} . The symmetric CF_2 stretching vibration mode can be utilized for the ${}^{13}\text{C}$ -selective excitation [31]. When HI is added to neat CBrClF_2 , the product containing ${}^{13}\text{C}$ is mainly CHClF_2 . However, the further IRMPD of CHClF_2 under the same conditions does not occur efficiently, because the laser radiation seems to be mostly absorbed by CBrClF_2 at these frequencies. Figure 12 shows the variations of decomposition probabilities of ${}^{12}\text{CBrClF}_2$ and ${}^{13}\text{CBrClF}_2$ as well as selectivity as

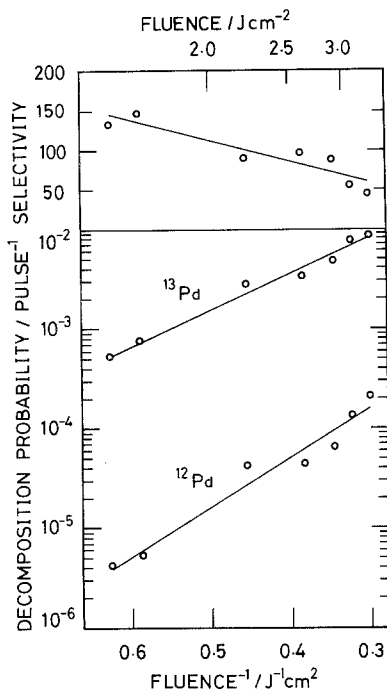


Fig. 12. Decomposition probabilities of $^i\text{CBrClF}_2$ and decomposition selectivity as a function of focus fluence. Mixtures of 15 Torr CBrClF_2 and 5 Torr HI were irradiated with the 9P(34) line using a long cell

a function of fluence. The observed $^{13}\text{P}_d$ is as high as about 1×10^{-3} pulse $^{-1}$ at a moderate fluence of 2.0 J cm^{-2} . Although an increase in fluence enhances the decomposition of both isotopic molecules, the selectivity is considerably lowered, as shown in the figure.

A pressure increase in CBrClF_2 resulted in a significant improvement of the selectivity accompanied with obvious decreases of $^{12}\text{P}_d$ and $^{13}\text{P}_d$. However, the increase in HI did not affect $^{12}\text{P}_d$ and $^{13}\text{P}_d$, or the selectivity, as seen in Fig. 13. The results imply that HI molecules do not contribute appreciably to the collisional quenching of highly vibrationally excited CBrClF_2 as compared to CBrClF_2 itself.

A higher selectivity could be attained either by shifting the laser line to the red side or by lowering the fluence. For example, the selectivity reached 220 at the 9P(38) laser line and at a fluence of 0.7 J cm^{-2} . Although the selectivity is high, the irradiation condition is not adequate for practical separation, because of the extremely low decomposition probability.

References

1. Silicon isotopes. M. Kamioka, S. Arai, Y. Ishikawa, S. Isomura, N. Takamiya: Chem. Phys. Lett. **119**, 357 (1985)
M. Kamioka, Y. Ishikawa, H. Kaetsu, S. Isomura, S. Arai: J. Phys. Chem. **90**, 5727 (1986)

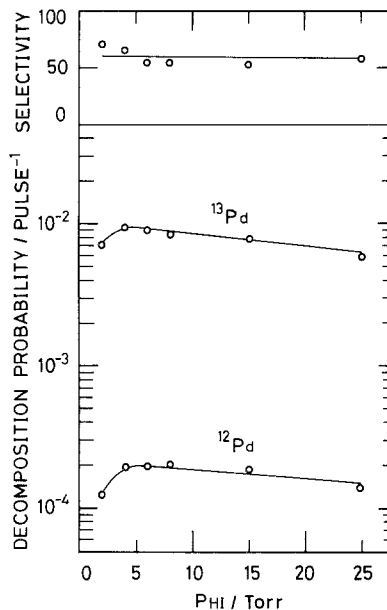


Fig. 13. Decomposition probabilities of $^i\text{CBrClF}_2$ and decomposition selectivity as a function of $P_{\text{HI}} - P_{\text{CBrClF}_2}$, 15 Torr; laser line, 9P(34); focus fluence, 3.3 J cm^{-2} ; long cell

2. G.I. Abdushelishvili, O.N. Avatkov, V.N. Bagratashvili, V.Yu. Baranov, A.B. Bakhtadze, E.P. Velikhov, V.M. Vetsko, I.G. Gverdsiteli, V.S. Dolzhikov, G.G. Esadze, S.A. Kazakov, Yu.R. Kolomiiskii, V.S. Letokhov, S.V. Pigul'skii, V.D. Pis'mennyi, E.A. Ryabov, G.I. Tkeshelashvili: Sov. J. Quant. Electron. **12**, 459 (1982)
3. A. Outhouse, P. Lawrence, M. Gauthier, P.A. Hackett: Appl. Phys. B **36**, 63 (1985)
4. M. Drouin, M. Gauthier, R. Pilon, P.A. Hackett, C. Willis: Chem. Phys. Lett. **60**, 16 (1978)
5. T. Watanabe, T. Oyama, O. Hayashi, Y. Ishikawa, T. Ishii, S. Arai: Nippon Kagaku Kaishi, 1517 (1984)
6. C.N. Plum, P.L. Houston: Appl. Phys. **24**, 143 (1981)
7. H. Kojima, T. Fukumi, S. Nakajima, Y. Maruyama, K. Kosasa: Chem. Phys. Lett. **95**, 614 (1983)
8. W. Fuss, W.E. Schmid: Ber. Bunsenges. Phys. Chem. **83**, 1148 (1979)
9. V.Yu. Baranov: IEEE J. Quant. Electron. QE-19, 1577 (1983)
10. M. Gauthier, C.G. Cureton, P.A. Hackett, C. Willis: Appl. Phys. B **28**, 43 (1982)
M. Gauthier, A. Outhouse, Y. Ishikawa, K.O. Kutschke, P.A. Hackett: Appl. Phys. B **35**, 173 (1984)
11. S. Arai, T. Watanabe, Y. Ishikawa, T. Oyama, O. Hayashi, T. Ishii: Chem. Phys. Lett. **112**, 224 (1984)
12. P.H. Ma, K. Sugita, S. Arai: Chem. Phys. Lett. **137**, 590 (1987)
13. A.L. Henne: J. Am. Chem. Soc. **59**, 1200 (1937)
14. R.J.S. Morrison, R.F. Loring, R.L. Farley, E.R. Grant: J. Chem. Phys. **75**, 148 (1981)

15. J.C. Stephenson, D.S. King: *J. Chem. Phys.* **69**, 1485 (1978)
16. Aa.S. Sudbø, P.A. Schulz, E.R. Grant, Y.R. Shen, Y.T. Lee: *J. Chem. Phys.* **70**, 912 (1979)
17. A. Palm, F.L. Voelz, A.G. Meister: *J. Chem. Phys.* **23**, 726 (1955)
18. J.J. Orlando, J. Reid, D.R. Smith: *Chem. Phys. Lett.* **141**, 423 (1987)
19. R.A. Cox, R.F. Simmons: *J. Chem. Soc. (B)* **19**, 1625 (1971)
20. H.H. Claassen: *J. Chem. Phys.* **22**, 50 (1954)
21. J.J. Ritter: *J. Am. Chem. Soc.* **100**, 2441 (1978)
22. D.S. King, J.C. Stephenson: *J. Am. Chem. Soc.* **100**, 7151 (1978)
23. J.L. Lyman, S.D. Rockwood: *J. Appl. Phys.* **47**, 595 (1976)
24. P. Fettweis, M. Neve de Mevergnies: *J. Appl. Phys.* **49**, 5699 (1978)
25. W.S. Nip, P.A. Hackett, C. Willis: *Can. J. Chem.* **59**, 2703 (1981)
26. J.J. Chou, E.R. Grant: *J. Chem. Phys.* **74**, 5679 (1981)
27. D.S. King, J.C. Stephenson: *Chem. Phys. Lett.* **51**, 48 (1977)
28. R.J.S. Morrison, E.R. Grant: *J. Chem. Phys.* **71**, 3537 (1979)
29. J.G. McLaughlin, M. Poliakoff, J.J. Turner: *J. Mol. Struct.* **82**, 51 (1982)
30. Aa.S. Sudbø, P.A. Schulz, Y.R. Shen, Y.T. Lee: *J. Chem. Phys.* **69**, 2312 (1978)
31. M.Z. El-Sabban, B.J. Zwolinski: *J. Molec. Spectrosc.* **22**, 23 (1967)