Kinetic Study of Infrared Multiphoton Dissociation. Two-Frequency Irradiation of CF₃¹³COCF₃ Molecules at Natural Abundance

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The characteristics of the infrared multiphoton excitation of hexafluoroacetone in region I and region II have been investigated by photolysis with two CO_2 laser pulses. The sequenced pulses were at different frequencies and had different fluences so that effects arising in the two regions could be clearly separated. We have studied the isotopically selective dissociation of $CF_3^{13}COCF_3$ molecules, present at their natural abundance, as a function of five parameters, the frequency of the dissociating second pulse, the fluence of both pulses, the substrate pressure, and the interpulse delay. The results give a picture of the kinetic behavior of vibrationally excited hexafluoroacetone molecules produced in the presence of strong infrared fields.

Introduction

Much effort has been devoted to demonstrating and understanding the use of two lasers to effect isotopically selective dissociation.¹⁻⁹ These experiments have been particularly instrumental in supporting the three-region model of multiphoton dissociation.¹⁰⁻¹⁴ In terms of this by now well-established model, a laser at a frequency ν_1 resonant with a molecular absorption band excites the system through region I (the region of discrete absorption bands) into region II (the region of quasi-continuum absorption). States in region II may then absorb energy from a second laser field, whose frequency, ν_2 , is far from resonance with any region I absorption transition, and be excited into region III (the region of a true dissociative continuum). In this manner the isotopically selective excitation (v_1) and the photochemical dissociation (v_2) are separated. This two-frequency approach confers obvious advantages whenever the power at frequency ν_1 is limited, as when using an optically pumped laser for example. However, it is not clear that it confers a significant advantage over single-frequency photolysis when v_1 may be varied, vide infra.

Many molecular systems have been studied by this technique. Sulfur hexafluoride has been dissociated by two CO_2 laser frequencies; ¹⁻³ selective dissociation of sulfur-32 was verified by analysis of the SOF_2 product.² Osmium tetroxide has been similarly dissociated;^{4,5} se-

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lective dissociation of light isotopes of osmium was verified by mass spectrometry of the residual substrate.⁴ Carbon tetrachloride has been dissociated by a combination of ammonia and carbon dioxide lasers⁶ ($\nu_1 = 780.5 \text{ cm}^{-1}, \nu_2$ = 1076 cm^{-1} ; selective dissociation of carbon-12 was verified by isotopic analysis of both the products and the depleted substrate. The same combination of lasers has been employed to selectively dissociate light isotopes of selenium in selenium hexafluoride; ⁷ depletion of the substrate was observed. CO₂ laser radiation has been combined with excimer laser radiation to selectively dissociate trifluoromethyl iodide; carbon-12 selective dissociation was confirmed by isotopic analysis of the hexafluoroethane produced.⁸ Finally, enhancement of dissociation yield was observed when a CO₂ laser ($\nu_2 = 1077 \text{ cm}^{-1}$) was used in concert with a CF₄ laser ($\nu_1 = 615 \text{ cm}^{-1}$) to dissociate uranium hexafluoride; no isotopic selectivity was reported.9

The experiments referred to above have not been confined to studies of the selectivity of the process. They have also addressed the question of the kinetic^{2,4,6} and the spectroscopic^{1-4,6,7,9} behavior of molecules in region II. In this regard these studies are complementary to the many IR-UV and IR-IR double-resonance studies of multiphoton-induced absorption. The results of these latter studies on the ubiquitous ${\rm SF}_6$ molecule have been summarized recently by Deutsch and Brueck,¹⁵ who intimate that intramolecular vibrational relaxation out of the ν_3 manifold in SF_6 occurs unimolecularly on a microsecond time scale in disagreement with the picosecond relaxation claimed by Kwok and Yablonovitch.¹⁶ Thus, it is clear that this field of study is by no means closed.

A more recent study on SF_6 by Jensen, Anderson, Reiser, and Steinfeld¹⁷ using a Q-switched CO₂ laser pump and a tunable diode laser probe has demonstrated the wealth of information to be gleaned from a high-resolution analysis of induced absorption at relatively low levels of vibrational excitation.

In the present work, we have attempted to probe the general features of excitation in region I and in region II by using the molecule hexafluoroacetone. This molecule is well studied for single-frequency excitation and decom-

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position.¹⁸⁻²¹ Two infrared frequencies were used so that predominantly one isotopic species $(CF_3^{13}COCF_3)$ is excited in resonance in region I and a delayed pulse at a second, nonresonant frequency excites the selectively activated molecules to the dissociation limit. The second frequency was chosen so that only molecules excited by the first pulse absorb and unexcited molecules are transparent. Thus, by measuring the yield of product and its isotopic selectivity, we are able to gain information on the spectroscopy and relaxation processes of molecules in the vibrational quasi-continuum. Furthermore, by investigating the effect of variation of the fluence and the frequency of each laser, the pressure of substrate, and the interpulse delay, we are able to compare the effectiveness of two-frequency excitation in promoting selective dissociation with previous results obtained by using one-frequency excitation.¹⁹⁻²¹ At this point we would like to reemphasize the general advantages conferred by (kinetic) studies of isotopically selective infrared multiphoton dissociation. Whenever high enrichment factors are observed in products, one is assured that secondary collisional effects, chain reactions, wall reactions, and thermal decomposition do not play significant roles. In this regard the present study of two-frequency, isotopically selective, infrared multiphoton dissociation of $CF_3^{13}COCF_3$ at natural-abundance isotope ratio provides a reliable body of chemical data with which to discuss the kinetics of infrared multiphoton absorption and dissociation.

Experimental Section

The v_{15} vibration of CF₃¹²COCF₃ (970 cm⁻¹, fwhm 20 cm⁻¹) corresponds to an asymmetric carbon–carbon stretch; in $CF_3^{13}COCF_3$, the transition occurs at 955 cm⁻¹.²² In a previous study,²⁰ it was shown that high selectivities are obtained following irradiation by a parallel beam of laser radiation on the red side of this band.

In the present study, samples were irradiated by sequential pulses of parallel beams from two Lumonics series 100 TEA-CO₂ lasers. The two beams were concentrated with 2-m lenses and passed almost colinearly through a 5-cm diameter, 18-cm long Pyrex cell equipped with NaCl windows and connected directly to a Hitachi Perkin-Elmer RMU-6D mass spectrometer. The fluence of the first pulse, at a frequency ν_1 , close to the ¹³C band center, was chosen to cause virtually no decomposition; the focal area of this laser beam was 0.64 cm^2 . The subsequent pulse arrived after a fixed time delay (0.2–10 μ s), monitored with a photon drag detector, and its frequency was varied over the regions 1080-1020 and 940-920 cm⁻¹; the focal area of this beam was 0.30 cm^2 . Both lasers emitted high-order spatial modes of uniform intensity distribution. Both beams were apertured after the laser to give a "top-hat" intensity profile. The beam areas were determined from burn patterns of suitably attenuated beams. The resultant intensities were constant across the beam profile and throughout the irradiation cell. Low-jitter, midplane spark gaps were used to fire both lasers with a resulting interpulse timing uncertainty of ± 30 ns. Both lasers were operated in conventional gain-switched fashion resulting in typical temporal profiles. These profiles varied from shot to shot, but each consisted of a typical gain-switched,



Figure 1. Reaction probabilities for CF3¹³COCF3 as a function of the fluence F_2 of the second laser pulse (lower curve). The upper curve shows product isotopic selectivities (α = reaction probability (CF₃¹³COCF₃)/reaction probability (CF₃¹²COCF₃)). Experimental conditions are listed in Table I.

self-mode-locked spike (fwhm, 80 ns), followed by a $5-\mu s$ tail. Delays shorter than $0.2 \ \mu s$ were not used to avoid overlapping of the two pulses.

When both lasers were fired, copious decomposition was observed. As shown previously,¹⁸⁻²⁰ the multiphoton decomposition of CF_3COCF_3 produces CO and C_2F_6 , and most of the selectivity is reflected in formation of enriched CO product. Dissociation probabilities and isotopic selectivities were obtained directly from the ¹³C-enriched carbon monoxide produced, by measuring both its pressure with an MKS capacitance manometer (accuracy, 10⁻⁴ torr) or a Consolidated Electrodynamics electrostatic manometer (accuracy, 10^{-5} torr) and its mass spectrum with a Hitachi-Perkin-Elmer RMU-6D. The data were then reduced to give the probability that molecules irradiated by the second laser would dissociate.²⁰ These reaction prob-abilities were measured both for $CF_3^{13}COCF_3$ molecules present at their natural abundance and for $CF_3^{12}COCF_3$ molecules. Since the output energy of each laser was extremely stable $(\pm 0.5\%)$, multiple-pulse experiments could be performed. Therefore it was always possible to accumulate enough enriched CO to allow a precise determination of its pressure. The principle source of uncertainty in the measurement of total reaction probabilities was therefore the interpulse timing jitter which we assume to have been averaged out by multipulse irradiation. The principle source of error in the determination of the dissociation probabilities of individual isotopically substituted molecules lay in the determination of the isotopic selectivity due to interference between CO peaks and massspectrometer background peaks. These sources of experimental uncertainty lead to a total uncertainty of $\pm 10\%$ for the reaction probabilities.

Results

The parameters varied in the present study include the pressure of substrate (P), the fluence of the first laser (F_1) and its frequency (ν_1) , the fluence of the second laser (F_2) and its frequency (ν_2) , and the interpulse delay Δt . The frequency of the first laser was fixed at 937 or 944 cm⁻¹ because of the demonstrated high selectivity for CF₃¹³COCF₃ dissociation.¹⁹

The results are shown in Figures 1-6, and the pertinent experimental details are listed in Table I.

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Figure 2. Reaction probabilities as a function of the fluence of the first laser pulse. Open circles refer to $CF_3^{13}COCF_3$; filled circles refer to $CF_3^{12}COCF_3$; experimental conditions are listed in Table I.



Figure 3. Reaction probabilities as a function of hexafluoroacetone pressure. Open circles refer to $CF_3^{13}COCF_3$; filled circles refer to $CF_3^{12}COCF_3$; squares refer to α values and require the right-hand ordinate; experimental conditions are listed in Table I.

TABLE I: Parametric Studies of Two-Frequency Irradiation of $CF_3^{13}COCF_3$ at Natural Abundance

m^{ν_1}, m^{-1}	$m_2^{\nu_2}, m^{-1}$	$\Delta t, \mu s$	P, torr	F_1, J cm ⁻²	F_2 , J cm ⁻²	figure no.
937	1077	0.2	0.5	2.0	a	1
944	1047	0.2	0.5	а	4	2
937	1077	0.2	а	1.8	2	3
937	1077	a	0.5	1.8	2	4, 5
937	1077	а	1.0	1.8	2	5
937	1077	а	2.0	1.8	2	5
937	а	0.2	0.5	1.9	4	6

^a Denotes parameter varied; all experiments carried out at T = 20 °C.

Figure 1 demonstrates that increasing the fluence of the second laser increases the yield of the isotopically selective



Figure 4. Reaction probabilities as a function of interpulse delay. Open circles refer to $CF_3^{13}COCF_3$; filled circles refer to $CF_3^{12}COCF_3$; experimental conditions are listed in Table I. The arrows indicate the reaction probabilities observed when the second laser pulse was blocked before the reaction cell.



Figure 5. First-order relaxation rate constants for molecules accessible by the second laser field as a function of hexafluoroacetone pressure. The rates were obtained from the slopes of plots of in (enhanced reaction probability) vs. interpulse delay time. Open circles refer to $CF_3^{13}COCF_3$; filled circles refer to $CF_3^{12}COCF_3$; experimental conditions are listed in Table I.

dissociation without degrading the isotopic selectivity (in contrast with the one-frequency dissociation²⁰). Figure 2 demonstrates that increase in fluence of the first laser increases yield at the expense of isotopic selectivity. The frequency of the first laser was fixed at 944 cm⁻¹ and the second completely off-resonance to the blue at $v_2 = 1047$ cm⁻¹.

The decomposition probabilities for both ¹²C and ¹³C species decrease steadily with an increase in hexafluoroacetone pressure, as shown by the data in Figure 3. However, below 1 torr, the isotopic selectivity, α , increases with an increase in pressure.

Figure 4 shows the effect of increasing the interpulse delay for 0.5 torr of hexafluoroacetone. The exponential decrease in reaction yield with increasing delay can be



Figure 6. Reaction probabilities and product isotopic selectivities (α values) as a function of the frequency of the second laser pulse. Open circles refer to CF₃¹³COCF₃; filled circles refer to CF₃¹²COCF₃; squares refer to α values; experimental conditions are listed in Table I. Also shown is the low-intensity infrared absorption spectrum of hexa-fluoroacetone. The arrow marks the frequency of the first laser pulse, $\nu_1 = 937 \text{ cm}^{-1}$.

represented by a first-order rate constant for each isotopic species. Data obtained at other pressures indicate that this first-order rate is itself pressure dependent. Figure 5 details the pressure dependence of this relaxation rate for both CF₃¹³COCF₃ and CF₃¹²COCF₃. It appears that the pressure dependence of this rate constant is greater for CF₃¹³COCF₃ molecules than for CF₃¹²COCF₃ molecules. Further, the data do suggest that there is a true unimolecular contribution to the relaxation process since the data of Figure 5 extrapolate to a zero-pressure rate of $(4 \pm 2) \times 10^5$ s⁻¹ for both isotopically substituted molecules. As is reported in Figure 4, we note that, when the interpulse delay is 10 μ s, no yield enhancement is observed and a double-pulse yield equal to that obtained when only the first laser is fired is obtained.

The effect of varying the frequency of the second laser is shown in Figure 6, together with the low-intensity, one-photon absorption spectrum of hexafluoroacetone.

Discussion

The results may be interpreted in terms of a model which we have recently discussed with reference to single-frequency excitation of both trifluoromethyl bromide²³ and hexafluoroacetone.²⁰ The present work verifies several aspects of that model.

The results of Figures 1 and 2 confirm those features of the three-region model which first suggested the use of two infrared lasers to increase the yield of selective decomposition. However, the exponents themselves are interesting. We note from Figure 1 an increasing yield linearly proportional to the fluence (F_2) of the second laser, suggesting that the yield is only limited by the photon density available (at ν_2) to pump molecules through region II. The data are also consistent with nonresonant pumping since decomposition probabilities increase by the same degree for both ¹³C and ¹²C species. However the data of Figure 2 demonstrate a high-order dependence of dissociation probability upon the fluence of the first laser P_d $\propto F_1^4$. This supports the interpretation (a) that the first pulse is essential to excite molecules to a minimum level (in region II) from where facile absorption of v_2 photons

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is possible and (b) that the absorption of ν_1 photons in region I is the rate-controlling process giving high-order fluence dependence, the same as observed in single-frequency, parallel-beam experiments.^{18,19} The pressure increase in selectivity reported in Figure 3 has become a common observation in single-frequency studies^{20,23} and is attributed to collisional quenching accentuating the difference in up-pumping rates through region I between ¹²C and ¹³C species. Since the frequency $v_1 = 937$ cm⁻¹ is resonant with the CF313COCF3 manifold, these molecules will be less susceptible to collisional quenching of the up-pumping process through region I than the nonresonant $CF_3^{12}COCF_3$ molecules. Hence it is to be expected that for these conditions α increases with pressure. The observation reported above, that excitation with the second laser does not discriminate between these isotopic variants, provides very strong evidence that the collisional enhancement of selectivity is not associated with excitation through region II. Furthermore, the data of Figures 4 and 5 provide strong evidence that the effect is not associated with relaxation of molecules in region III as (i) the isotopic selectivity does not increase with time and (ii) C-13 species are more readily quenched than C-12 species.

We emphasize that the effect has its origin in kinetic processes occurring during the first pulse, i.e., at "zerotime". At subsequent times the relaxation of region II molecules has an influence on the observed results particularly since the results reported in Figure 3 were obtained at 0.2- μ s delay.

One can obtain similar dissociation probabilities for equivalent selectivities in single-frequency experiments by red shifting ν_1 . Thus at $\nu_1 = 929 \text{ cm}^{-1}$ and $F_1 = 6 \text{ J cm}^{-2}$, we obtained $\alpha = 200$ for ${}^{13}P_d = 5 \times 10^{-2}$ at 0.5 torr of hexafluoroacetone.¹⁹ Obviously the only significant advantage of the two-frequency method is realized when ν_1 cannot be varied. A full comparison of the efficiency of the two methods of approach requires that quantum yields (molecules dissociated/photon absorbed) rather than dissociation probabilities be reported. These measurements have yet to be made.

The nature of the relaxation process(es) deserves some discussion. The possible mechanisms for removing excited molecules from the influence of the second laser pulse are (1) diffusion of molecules out of the irradiated region, (2) vibrational quenching of excited molecules by cold molecules (energy transfer), and (3) redistribution of excess vibrational energy over the vibrational levels of the molecule.

The diffusional process has been analyzed by Stephenson and King.²⁴ They show that for cylindrical symmetry, in the low-pressure limit, the concentration of some intermediate species S(t) decays by the law

$$S(t) = S(0)(L^2 + R^2) / (L^2 + R^2 + C^2 t^2)$$
(1)

where t is the interpulse delay, R and L are approximately the radii of the two laser beams, and $C = (2kT/m)^{1/2}$ is the most probable molecular velocity. In the present case $R \approx 0.45$ cm, $L \approx 0.31$ cm, and $C = 1.7 \times 10^4$ cm s⁻¹; graphical fitting of eq 1 or a first-order approximation of the diffusional loss process gives a first-order diffusional rate constant of $k_p = C/(R^2 + L^2)^{1/2} = 3.2 \times 10^4$ s⁻¹ which applies for interpulse delays of less than 50 μ s. Thus it would appear that for the present irradiation geometry diffusional loss will be insignificant at all pressures studied. Therefore, it would seem that there is some real unimolecular relaxation process which removes vibrationally

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excited molecules from the influence of the second laser frequency. This process is hard to understand, but it would appear to be similar to that causing the gross spectral changes for induced absorption observed by Deutsch and Brueck¹⁵ for sulfur hexafluoride. These workers observed that the relaxation of induced absorption occurred over a period of $3 \pm 2 \mu s$ and that this relaxation time appeared to be pressure independent. A tentative suggestion that this was due to collisionless vibrational intramolecular energy transfer with rate constant of the order of 10⁶ s⁻¹ was made. Although we do not claim such an interpretation, the two results taken together do suggest that further studies of relaxation of molecules in the vibrational continuum would be most worthwhile. Several problems not addressed in the present study are relevant. Firstly, to what extent are changes in the induced absorption spectrum responsible for the observations? Obviously multiple probe frequencies as used by Deutsch and Brueck¹⁵ are more informative than the single probe frequency used in the present study. Secondly, to what extent is the extrapolation to zero pressure valid? This extrapolation is questionable when rotational relaxation or collision-induced dephasing effects with large cross sections are important; such effects are seen in the curved Stern-Volmer plots observed in formaldehyde photophysics, for example.²⁵ Finally, to what extent are coherent effects between the two laser fields important? In the present study, no effort was made to remove the 5- μ s tail from the output of the first laser, whereas Deutsch and Brueck¹⁵ ran their laser with a N2-lean gas mix which ensured no significant afterpulse; moreover their probe beam was a low-intensity CW CO₂ laser.

Bimolecular contributions to the relaxation rate are somewhat easier to understand. The data of Figure 5 can be analyzed to yield a bimolecular relaxation rate constant for $CF_3^{13}COCF_3$ of $(1.6 \pm 0.4) \times 10^{10} L m^{-1} s^{-1}$. This can be attributed to vibrational quenching of excited CF₃¹³COCF₃ by "colder" CF₃¹²COCF₃ molecules present in 90-fold excess. The quenching rate constant corresponds to unit efficiency for deactivation. The quenching rate constant for $CF_3^{12}COCF_3$ molecules is significantly less (<8 × 10⁸ L m⁻¹ s⁻¹). This may be explained by postulating that vibrationally excited molecules *CF₃¹²COCF₃ are much closer to thermal equilibrium within the irradiated volume than are $CF_3^{13}COCF_3$ molecules. This postulate is most reasonable since the first laser field is resonant with the $CF_3^{13}COCF_3$ manifold. The difference in bimolecular relaxation rates is seen to be significant in placing the overall degree of excitation of the intermediate molecules and in terms of an explanation of the collisionless relaxation process referred to above. Thus, one explanation for the data for $CF_3^{13}COCF_3$ molecules is that the intermediate molecules overlap region III so that the molecules probed by the second laser are those with RRKM unimolecular spontaneous dissociation rates of the order of 10⁵ s⁻¹ whose fate in the absence of the second laser field at high pressure would be bimolecular quenching and at low-pressure dissociation. However, the difference in bimolecular quenching rates does not allow a similar explanation for $CF_3^{12}COCF_3$ molecules. This explanation for thermally equilibrated CF₃¹²COCF₃ molecules is equivalent to postulating the decomposition by the second pulse being due to interaction with thermally developed hot bands.

The expected shape of the dissociation spectrum for states in the vibrational quasi-continuum is a slowly varying broad absorption band. The spectral dependence detailed in Figure 6 shows incipient structure, and the enhanced reaction probability appears to be increasing going to the blue at the frequency limit of the second laser $(\sim 1090 \text{ cm}^{-1})$. The most probable reason for this involves the presence of two weak combination bands located at 1080 and 1027 cm⁻¹.²² The continuum absorption bands appear to be sharper for $CF_3^{12}COCF_3$ molecules than for $CF_3^{13}COCF_3$. This is again indicative of the higher degree of excitation achieved by $CF_3^{13}COCF_3$ during the first laser pulse. This results in a marked spectral dependence for the selectivity of the two-laser dissociation, with maximum isotopic selectivity observed when the second laser is tuned between the two combination bands. We wish to emphasize that the range of frequencies reported in Figure 6 is almost exhaustive. The laser frequencies reported effectively cover the $00^{\circ}1-02^{\circ}0$ band of the ${}^{12}CO_2$ laser (R(26)-P(44)), whereas, when the second laser is tuned to the 00°1-10°0 band, the reaction yield is dominated solely by its interaction with the ground-state (thermal) distribution of molecules so that measurements of enhanced reaction yield are difficult to make; this effect may also contribute to α values at the lowest frequencies studied. We are considering extending the frequency range of the measurements by using lines from a laser using isotopically substituted CO_2 .

Conclusions

The experiments in which the irradiation fluences were varied support the proposition that excitation through region I depends strongly upon laser intensity, whereas excitation through region II depends only upon laser energy.

The experiments in which pressure and interpulse delay were varied support the model that we have recently proposed to explain the increase in isotopic selectivity with pressure observed when a minor isotope is excited to the red of its absorption band.²³ The most critical aspect of this model, that of a competition between up-pumping through region I and vibrational relaxation in this region, is confirmed by the present experiments which probe the number density of molecules in region II after the first laser pulse.

Experiments performed in the pressure range 0.5–2.0 torr extrapolate to yield a zero-pressure relaxation rate which is too large to be explained by diffusion. This result is unexplained and could result from an improper extrapolation. Similar data were obtained by Deutsch and Brueck for SF₆ in the pressure range 0.025–0.10 torr.¹⁵ More work is required in this area.

The difference in bimolecular relaxation rates observed for the two isotopically substituted species may be explained by assuming that $CF_3^{13}COCF_3$ molecules achieve a much higher degree of vibrational excitation during the first laser pulse than do $CF_3^{12}COCF_3$ molecules and that, on the time scale of these experiments, $CF_3^{12}COCF_3$ molecules within the irradiated zone are in thermal equilibrium. We see no evidence for energy-transfer processes by which energy transfer from $*CF_3^{13}COCF_3$ leads to $*CF_3^{12}COCF_3$ which may be rapidly pumped to dissociation.

Molecules in the vibrational quasi-continuum are seen to have broad absorption spectra which correlate with low-intensity spectra. The breadth of these spectral bands is seen to increase with the degree of vibrational excitation.

Although it is not always directly reported, the effect of varying ν_2 , F_2 , F_1 , Δt , and P on the isotopic selectivity can be calculated from these results. Highly selective two-frequency induced dissociation of $CF_3^{13}COCF_3$ mole-

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cules at their natural abundance (1.11%) has been demonstrated ($\alpha \rightarrow 500$). However, similar selectivities have been observed in single-frequency irradiations (cf. ref 20). Which method offers the most efficient route to the separation of carbon isotopes awaits the quantitative determination of the photon absorption rates during the two irradiation pulses. Such measurements are under investigation.

Intensity and Pressure Effects in Infrared Multiphoton Dissociation. Photolysis of Hexafluoroacetone and Trifluoromethyl Bromide with 2-ns Laser Pulses

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We have carried out a study of the effect pulse length on the infrared multiphoton dissociation of hexafluoroacetone. A constant fluence of 1.8 J cm⁻² was used, for both short-pulse (2-ns fwhm) and long-pulse (~120-ns fwhm, 5- μ s tail, gain-switched, self-mode-locked TEA CO₂ laser) irradiations. The dissociation yields are very significantly different both in their magnitude and in their dependence on pressure of substrate or of added hexafluoroethane. At moderate pressures (>0.2 torr) collisional effects dominate the long-pulse irradiation. Possible explanations of these effects are discussed. A study of the isotopically selective dissociation of trifluoromethyl bromide revealed that, although the intensity is high, isotopic selectivity ($\alpha \approx 20$) is retained.

Introduction

In single-photon-induced photochemical studies one may conveniently separate the excited-state preparation process from its subsequent decay processes. In multiphoton-induced photochemistry this division is harder to make. This is particularly true for multiphoton-induced infrared photochemistry. For example, under certain experimental conditions (high pressure, low intensity) no chemical reactions occur, whereas under other conditions (molecular beam, high intensity) extremely endoergic reactions are driven; we cite a study of the multiphoton dissociation reaction $CH_2CHCN \rightarrow C_3N \rightarrow C_2$.¹ At intermediate conditions, one may favor bimolecular² or bulk thermal reactions of the vibrationally excited gas.³ One may also design experiments in which up-pumping of molecules by the laser field competes with vibrational relaxation by unexcited molecules; this may lead to an increase in isotopic selectivity with pressure.⁴ Clearly, one must take great care in defining the photolysis conditions (laser fluence, flux, and frequency and substrate pressure, temperature, and composition) before one may fully realize the potential of photolysis in the infrared to drive molecularly specific photochemically induced reactions, e.g., selective excitation of isotopically substituted molecules, isomers, or chemically different components of mixtures.

It has recently been demonstrated that photolysis with CO_2 laser pulses of moderate energy (2 J) and short pulse length (2 ns) leads to isotopically selective dissociation of trifluoromethane and that shortening the laser pulse length decreases the effect of "detrimental energy-removing collisions during the laser pulse".⁵ In this paper we have studied the photolysis of hexafluoroacetone irradiated at a frequency close to the maximum of its ν_{15} dissociation spectrum as a function of substrate pressure and composition and of the length the laser pulse to ascertain whether other significant experimental advantages are conferred by photolysis with short-duration, high-intensity pulses. To conveniently assess the potential of short-pulse irradiation for inducing isotopically selective dissociaiton, we have also studied the selective dissociation of $^{13}CF_3Br$ at natural abundance, both in the presence and in the absence of inert gases.

Experimental Section

Short-pulse irradiations were performed with the output of a TEA CO₂ laser system designed to provide 2-ns pulses over a wide tuning range.⁶ The system used a grating tuned injection mode-locked oscillator to produce a train of 4-ns pulses.^{7,8} A single pulse was selected from the train by using (a) the characteristics of the module itself to obtain a large pulse-to-prepulse contrast ratio and (b) an air breakdown at a variable aperture to provide a high contrast ratio between the selected pulse and the post pulses. After amplification in the same gain module, a typical 2-ns (fwhm) pulse (Figure 1b,c) contained ~900 mJ and had a pulse-to-background energy contrast of ~ 50:1 when the laser was operated on the P(8) 10.6- μ m transition.

Before illuminating the sample the beam passed through a NaCl beam splitter where a portion of the laser output was used to monitor pulse duration and pulse-to-background contrast on a photon drag detector. The beam was then compressed with an R = 18-m concave radius of curvature mirror before entering the cell with a cross

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