Infrared Free-Electron-Laser Photolysis of $CFCl_3$ and CF_2Cl_2

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A tunable infrared free-electron laser comprised of a train of picosecond pulses was utilized to destroy the Freons $CFCl_3$ and CF_2Cl_2 by multiple-photon dissociation. The experiments explored the effects of laser frequency, laser fluence, spectral bandwidth, frequency chirping, reactant partial pressure, and oxygen (or air) partial pressure. We determined the optimum laser frequencies for dissociation of both of the Freons and also showed that a broader spectral bandwidth laser enhances reaction. A strong reduction of dissociation fraction with increasing pressure made infrared photodissociation of Freons at near atmospheric pressure difficult. Improvement of the high-pressure photolysis would require a laser macropulse much shorter than the 2 μs used in these experiments.

1. Introduction

The man-made chlorofluorocarbons (CFCs), especially Freon-11 ($CFCl_3$) and Freon-12 (CF_2Cl_2), have been implicated as causing most of the observed destruction of the stratospheric ozone layer resulting in increased surface exposure to UV-B radiation (294−320 nm). Freons released at the surface of the earth eventually reach the stratosphere where exposure to sunlight below 200 nm dissociates the Freons. Each free chlorine atom then catalytically removes an oxygen atom from up to 10^5 ozone molecules. This has prompted an international agreement known as the Montreal Protocol on Substances that Deplete the Ozone Layer-1987. It was later amended in London in 1990 to curtail further production by 1996.

Professor Thomas Stix of Princeton University has proposed[1] an atmospheric engineering solution to the CFC problem that would use over 1000 2−3 MW infrared lasers stationed around the globe to photodissociate the Freon molecules within the troposphere before they drift into the stratosphere. The reaction products would then react with water and other atmospheric species and be removed from the air in rain. This approach requires absorption of 30−40 laser photons per Freon molecule in the region of several absorption bands in the 8−12 μm spectral region. Laboratory experiments with microsecond[2−4] and nanosecond lasers[5] have shown that, at least at low pressures, this photochemistry may be feasible. Stix's[1] own analysis, which includes arguments for photolysis near atmospheric pressure and projections of the scope and cost of this solution, indicates that the present technology is too costly by a factor of 10−20. Bullock and co-workers[6] have also considered the possibility of this type of atmospheric treatment. They also were somewhat pessimistic about the economic viability of laser removal of atmospheric Freons. Both analyses[1,6] were constrained to the carbon dioxide laser, and both also lacked data on the efficiency of infrared multiple-photon dissociation (IRMPD) at high pressures.

The Free-electron laser (FEL) offers the versatility in spectral and temporal output that may enable, via the multiple-photon process, attainment of efficient photodissociation of Freons, possibly to the degree needed to reconsider Stix's proposal. The FEL laser offers easy wavelength tunability to strong molecular absorption resonances, adjustable spectral bandwidth by synchrotron sidebands or frequency chirping, high peak power in picosecond pulse trains, and potential scalability to high average power levels. Synchrotron sideband emission, a feature unique to FELs, is manifested as an irregular lasing spectrum on the long-wavelength side of the resonant wavelength. For example, the Los Alamos APEX FEL operated with sidebands extending out to 10% beyond the initial lasing wavelength.

Infrared photochemistry by multiple-photon dissociation has been the subject of extensive research since the mid 1970s. The process has been the subject of several book-length[7−10] and many shorter reviews.[11−17] The infrared excitation process, which eventually leads to molecular dissociation, occurs by successive absorption of many (~30) infrared photons at a frequency at or near a strong infrared resonance.

Virtually all the earlier experimental work on this process has been with the CO_2 laser. From these experiments we know that many factors influence the absorption and dissociation. Among these are the laser fluence, the gas pressure, the laser frequency, the laser pulse characteristics, and the molecular properties.

The laser fluence effect depends somewhat on the molecular size. For molecules near the size of the Freons we are considering in this paper the energy absorbed per molecule increases with about the 2/3 power of the fluence[13] over a fairly broad range. The dissociation probability increases with about the 4th power of the fluence up to near a dissociation probability of 1.0.

The effect of gas pressure is critical for the atmospheric cleaning application. Dissociation does occur under collisionless conditions. At low pressures collisions tend to enhance absorption, but as the total pressure of nonabsorbing gas increases, dissociation ceases.[7]

Because of molecular anharmonicity absorption resonances tend to shift to lower frequency with vibrational excitation. Consequently, the highest reaction probabilities tend to be at frequencies somewhat lower than the low-intensity absorption

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maximum. Absorption bands much higher than the laser frequency[18] may also have an influence on absorption and dissociation.

The frequency width and the total pulse length are two laser pulse characteristics that influence absorption and dissociation. Pulse length does not have much effect at low pressure, but at high pressure the shorter pulses induce more dissociation. This is because the shorter pulse competes better with collisional de-excitation. Even with the narrow range available with the CO_2 laser, increased frequency width enhances both the absorption[7,19] and dissociation.[7,20]

One molecular characteristic that has a strong influence on the absorption and dissociation is size.[12] The density of vibrational states increases more rapidly with internal energy for larger molecules. This increase favors absorption by increasing the energy at which the quasi-continuum[15] is reached and by statistically favoring absorption over emission. Other important molecular characteristics are the energy required for dissociation and the pathways available for reaction.

The initial reaction for Freon-11 is probably

$$CFCl_3 \rightarrow CFCl_2 + Cl \tag{1}$$

which requires[21] 305 ± 8 kJ/mol. The initial Freon-12 reaction is similar,

$$CF_2Cl_2 \rightarrow CF_2Cl + Cl \tag{2}$$

which requires[21] 318 ± 8 kJ/mol.

Most published experiment work on the infrared dissociation of polyatomic molecules has involved the pulsed carbon dioxide laser. The FEL differs in many respects. Some of these differences are advantages and some are not. The broad tuning range of the FEL is the biggest advantage over CO_2 lasers. Another is the broad and variable frequency width available. The main factor that most influences the frequency width is the presence or absence of synchrotron sidebands. Evaluating the effect of these two advantages is a major focus of this paper.

In an earlier publication[22] we reported the measurement of the effect of the presence or absence of sidebands in the infrared photolysis of Freon-11. This experiment with the Los Alamos APEX FEL showed photolysis with sidebands and none without them. Time restrictions prevented a more thorough evaluation. Results were sufficiently encouraging to arrange for additional experiments with an FEL with better beam control and availability. We reported an initial evaluation of these experiments in the FELIX annual report[23] and at two conferences.[24,25]

2. Experiment

We performed all experiments at the Dutch National Free-Electron Laser Facility “FELIX” located at the FOM Institute for Plasma Physics—Rijnhuisen, Nieuwegein, The Netherlands. FELIX[26] operates as a user facility for experiments such as the ones we performed. The laser pulse consists of a train of micropulses that comprise the macropulse. The computer-controlled gap spacing of the permanent magnet undulator determines the laser frequency, and the optical cavity tuning determines other characteristics of the pulses, such as the spectral line width and pulse energy. Chirping of the macropulse to longer wavelengths is an option employed for some experiments. The FELIX facility is capable of operating over a broad range of parameters. Table 1 lists the nominal characteristics of the laser at the time of the experiments. Some of these parameters have improved considerably since that time. The macropulse length used in the experiments was 2 μs.

We constructed six reaction cells for the infrared irradiation experiments. Each of these was of a stainless steel cylinder 5 cm diameter and 8 cm long equipped with a valve and fill tube entering from the side. The cells each had a 1 cm diameter hole along the center and NaCl or KCl windows at the ends. The optical path length was 7.5 cm and the volume of each cell was 6 cm^3.

TABLE 1: Nominal Output Characteristics of the FELIX Free-Electron Laser

spectral range	6−110 μm
micropulse energy	10 μJ
micropulse duration	1−10 ps
micropulse separation	1 ns
macropulse power	10 kW
macropulse duration:	8 s
macropulse repetition rate	5 Hz
macropulse energy	20−80 mJ
spectral width	0.5−7%
average power	0.4 W

The infrared pulse from the FEL was gently focused into the center of the cell being irradiated with a 1.0 m radius-of-curvature mirror. The beam radius at the focus was about 1 mm. This gave a fluence range at the focus of 1−10 J/cm^2. On several occasions we did a careful radial and longitudinal profile of the beam by using a variable aperture and a laser energy detector. These profiles varied imperceptibly during all the experiments. The measurements gave a value for the irradiated volume of

$$v_i = 7.17\ \mathrm{mm}^3 \tag{3}$$

which is the beam area ($1/e^2$) at the beam waist times the cell length. For all experiments we assumed that all reactions occurred in this volume for the purposes of reporting the fraction of molecules that dissociate per laser pulse (*f*/*p*). During the sample irradiation a computer and associated instrumentation were used to measure the pulse energy and to count the laser pulses.

The measurements of the amount of reaction and reaction product identification were done with a Fourier transform infrared spectrometer (FTIR). The instrument used was a Nicolet Magna-IR System 550. All measurements were made at a resolution of 0.5 cm^{-1}. The time to obtain a spectrum at this resolution was about 2 min. The change in the integrated absorbance of some prominent absorption band in the Freon was used to obtain the amount of reaction.

The gases we used in the experiments were $CFCl_3$ (Freon-11), CF_2Cl_2 (Freon-12), oxygen, and room air. The first three were reagent purity chemicals supplied by Matheson and were used without further purification. The Freon-11 used in the experiments was the vapor over the liquid reagent.

The parameters varied in the experiments were the laser pulse energy, laser wavelength, absorber and diluent partial pressures, spectral line width, and number of laser pulses.

A typical experiment involved the following steps: (1) evacuate the irradiation cell; (2) fill the cell with Freon gas (1 Torr in most experiments); (3) add diluent oxygen or air to the desired total pressure (5 Torr for most experiments); (4) take an infrared spectrum with the FTIR; (5) irradiate the sample with up to 2000 pulses; (6) take a final infrared spectrum. The changes in the integrated absorbance of the strong Freon absorption peaks determined the extent of reaction.

3. Experimental Results

Most of the experiments were performed with oxygen or air. Under these conditions the reaction products identified from the FTIR spectra for Freon-11 were COFCl, $COCl_2$, CO, and HCl. For Freon-12 the products were COF_2, COFCl, CO, HF, and HCl. The hydrogen-containing species were minor and

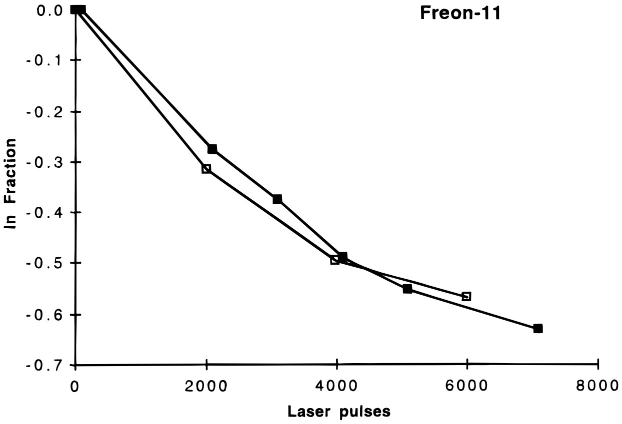

Figure 1. Fraction of Freon-11 remaining vs number of laser pulses for (1) 0.19 Torr initial Freon-11 and oxygen added to 4.98 Torr (open symbols) and (2) 1.00 Torr initial Freon-11 and oxygen added to 5.08 Torr (filled symbols). The values of *f*/*p* were, respectively, 0.021 and 0.019.

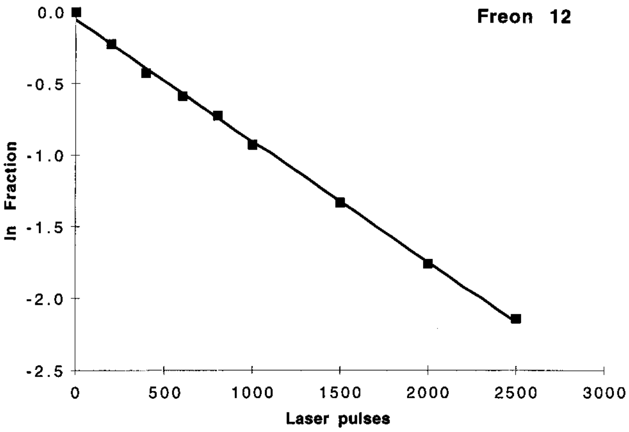

Figure 2. Fraction of Freon-12 remaining vs number of laser pulses for 1.01 Torr initial Freon-12 and oxygen added to 5.08 Torr. The solid line is a fit to the points that give $f/p = 0.117$.

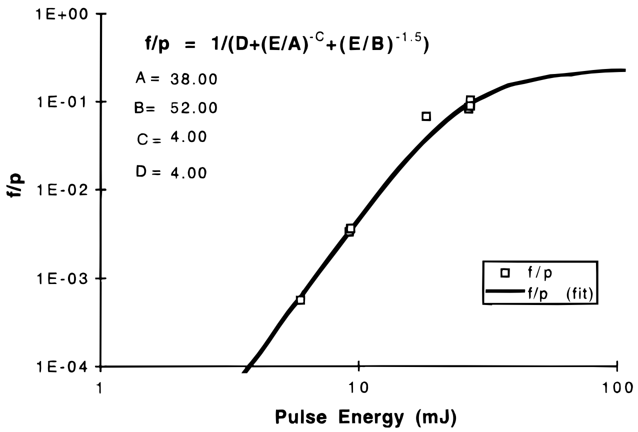

Figure 3. Points are the measured values of *f*/*p* for different pulse energies for Freon-11. The solid line is a fit to the points using the equation listed, where *E* is the pulse energy in millijoules and *A*, *B*, *C*, and *D* are the parameters of the equation.

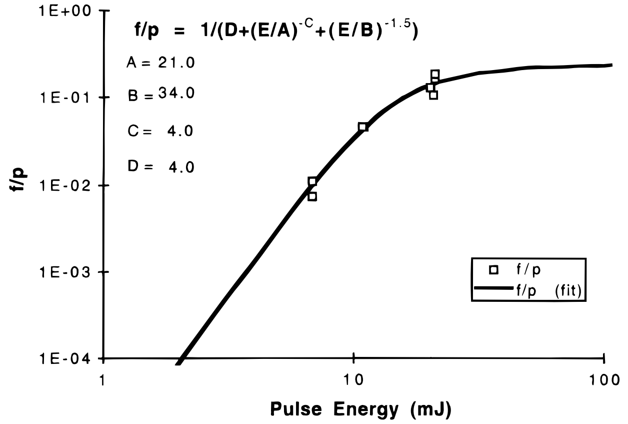

Figure 4. Points are the measured values of *f*/*p* for different pulse energies for Freon-12. The solid line is a fit to the points using the equation listed, where *E* is the pulse energy in millijoules and *A*, *B*, *C*, and *D* are the parameters of the equation.

probably resulted from adsorbed water in the gas lines. A likely unidentified species is Cl_2.

The first set of experiments for each of the two Freons was to determine the amount of reaction as a function of the number of laser pulses . Figure 1 shows how the fraction of Freon-11 changes with the number of laser pulses for two different gas mixtures. The mixture with less Freon reacts slightly more rapidly. If a constant fraction of the mixture reacted per pulse and if no back reaction occurred to the original Freon, the points from each experiment would lie on a straight line. We see some curvature, which may be due to back reaction. The laser wavelength (11.8 μm) was near the peak of the FTIR spectrum (see below). For these (and all other) experiments the fraction reacted per pulse in the irradiated volume is

$$f/p = -\frac{\text{slope}}{v_i} \qquad (4)$$

where "slope" is the initial slope from Figure 1. The curvature in Figure 1 may actually have resulted in a steeper initial slope and, hence, a higher value of *f*/*p* if more measurements had been made between 0 and 2000 pulses as was done in Figure 2.

Figure 2 shows a similar result for Freon-12 for irradiation near the center of the absorption band at 11.3 μm. In this case, however, the slope was constant over the entire range of number of pulses, which indicates no back reaction to the original Freon.

With one set of experiments for each of the two Freons we have determined the extent of reaction as a function of the laser pulse energy. Figures 3 and 4 show the results. The dependence of reaction (*f*/*p*) on laser pulse energy or on fluence has been the subject of a large amount of research[13,27,28] with CO_2 laser pulses. The pulse energy dependence in these figures is consistent with that previous work.

The values of *f*/*p* versus the pulse energy were fit to the equation in each of these figures. This equation is a fairly general expression that would represent the pulse energy dependence reported in many of the above-cited reviews. Later in the paper we discuss the significance of the equations in Figures 3 and 4. The data in the two figures are too sparse to correctly determine all parameters of the equations, but the data are sufficient to use the equations for making adjustments to f/p for variations in the pulse energy for some of the data we present later in the paper.

One of the major objectives of this set of experiments was to measure the reaction spectrum for the two Freons, that is, to measure the fraction of molecules reacted per laser pulse as functions of the laser frequency for some constant value of the laser pulse energy. Figures 5 and 6 show the results of these measurements. The solid line in each figure is the FTIR spectrum of 1.0 Torr of the Freon in oxygen at 5.0 Torr total pressure. The spectra were measured in the irradiation cells that have a 7.5 cm path length. The points connected by dashed lines are the measured fraction reacted per pulse at the indicated pulse energies. In each case the measurements were actually made at a pulse energy that differed somewhat from that indicated. These measurements were adjusted to the indicated pulse energies by using the solid lines and parameters in Figures

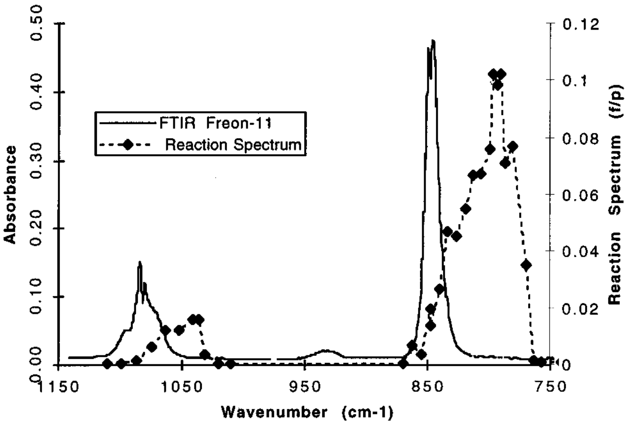

Figure 5. FTIR spectrum of Freon-11 (left axis) with the laser reaction points (*f*/*p*) (right axis). Measured points were adjusted to 27 mJ/pulse. Cell length was 7.5 cm, Freon pressure was 1.0 Torr in oxygen, and total pressure was 5 Torr.

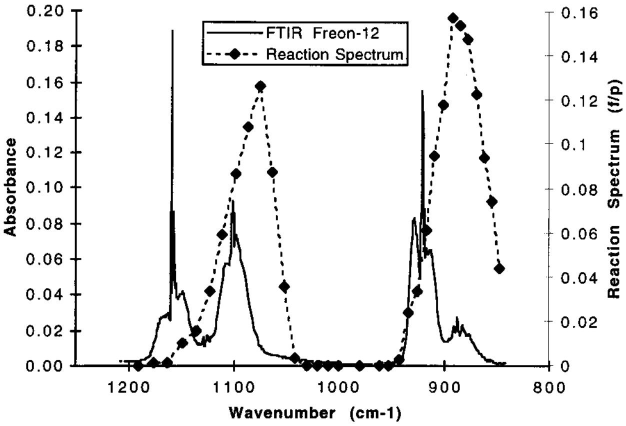

Figure 6. FTIR spectrum of Freon-12 (left axis) with the laser reaction points (*f*/*p*) (right axis). Measured points were adjusted to 20 mJ/pulse. Cell length was 7.5 cm, Freon pressure was 1.0 Torr in oxygen, and total pressure was 5 Torr.

3 and 4. As an example of this pulse energy correction, consider the high point in Figure 5 at 796.8 cm^{-1} (12.55 μm). The measured *f*/*p* for this point was 0.0708 at a pulse energy of 22.70 mJ. From the parameters in Figure 3 the value of *f*/*p* at 27 mJ was 1.445 times higher than at 22.70 mJ. We used this factor to increase the point we are considering to $f/p = 0.1024$. Similar corrections for pulse energy were made for all the points in Figures 5 and 6.

Several things are worth noting in these two figures. First, the reaction spectrum peaks are correlated with the small signal infrared resonances, but the reaction peaks occur at lower frequencies. Second, Freon-12 reacts more easily than Freon-11. Even though the infrared spectrum is weaker and the pulse energy is lower, the peak of the reaction spectrum is higher by more than 50%.

Both Freons show an exponential reduction of reaction fraction with increased pressure of oxygen. Figures 7 and 8 show the results of this measurement. For the narrowest frequency width pulse (0.5%) the fraction reacted per pulse decreases 7.2%/Torr for Freon-11 and 10.7%/Torr for Freon-12. The reduction of the reaction fraction with pressure was so great that any reaction was unobservable at 100 Torr or above for either molecule. The pressure dependency measurements were made near the peak of the reaction spectra for the two molecules (Figures 5 and 6).

Both Freons show an increase in fraction reacted as the frequency line width was increased from 0.5% to 3.0% (Figures 7 and 8). That increase was virtually the same for both Freons, 36% for Freon-11 and 34% for Freon-12.

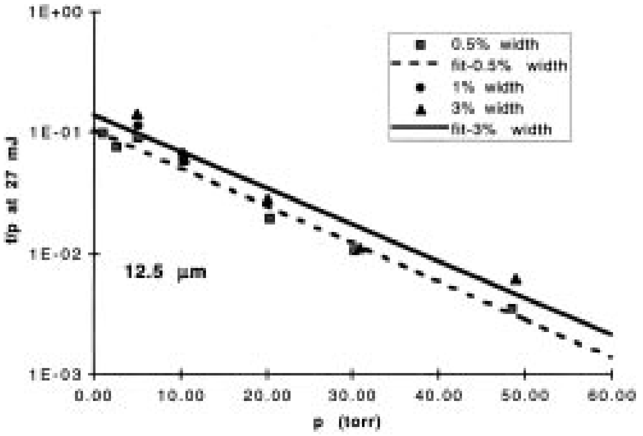

Figure 7. Fraction of Freon-11 reacting per pulse corrected to 27 mJ at 12.5 μm vs gas pressure. Gas was 1 Torr Freon-11 plus oxygen. Some points are averages of several measurements at the indicated pressure. Legend indicates frequency width. Lines are least-squares fits to points.

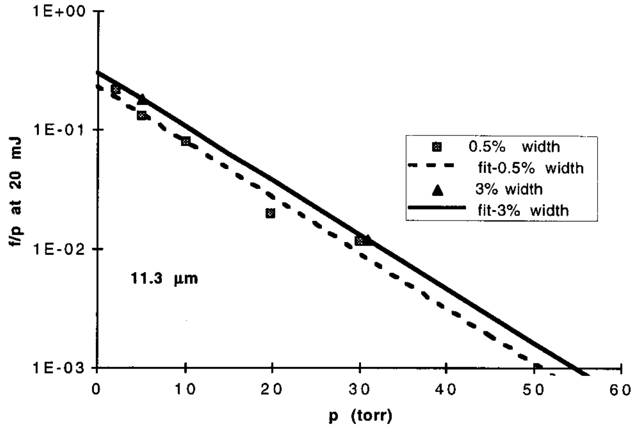

Figure 8. Fraction of Freon-12 reacting per pulse corrected to 20 mJ at 11.3 μm vs gas pressure. Gas was 1 Torr Freon-12 plus oxygen. Some points are averages of several measurements at the indicated pressure. Legend indicates frequency width. Lines are least-squares fits to points.

In the earlier publication[22] we reported the measurement of a dissociation fraction of 1.2% with another FEL. The bandwidth for that experiment was 3%, and the pulse length was 25 μs. Several experiments we performed with the FELIX laser were similar to that experiment in all aspects but the pulse length (2 μs for the FELIX laser). The dissociation fraction for the FELIX laser was 5.5%. Reducing the pulse length to 2 μs (to 8%) increased the dissociation fraction 4.5 times.

The FELIX has the capability to chirp the laser frequency, that is, to increase the laser wavelength during the laser pulse. The reason for attempting a dissociation experiment with a chirped pulse was to keep the laser frequency in resonance with the molecular oscillation as the absorbing molecules become more vibrationally excited. Generally, molecular anharmonicity tends to shift the oscillation frequency to lower values with increased vibrational frequency. We did several experiments with Freon-11 to test the effect of chirping to longer wavelengths. Other experimental conditions were the same as in Figure 5. The chirping was about 3% during the 2 μs pulse. Figure 9 shows the fraction reacted in two experiments with a part of the reaction spectrum of Figure 5. It shows that chirping does enhance the reaction fraction. The horizontal lines are the fraction reacted in the chirping experiments. The length of the lines cover the frequency range of the chirped laser pulse. The pulses were chirped from left to right in this figure. The chirp from 844 to 820 cm^{-1} gave a result that was 91% above that of the average of the narrow-pulse experiments in that range,

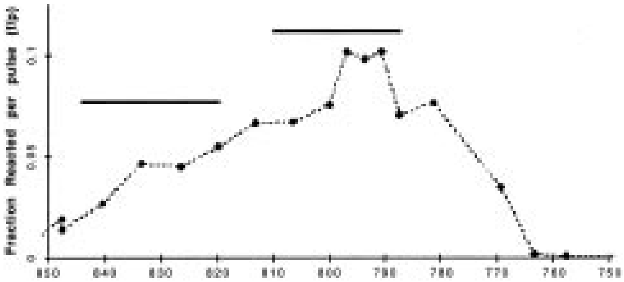

Figure 9. Fraction reacted per pulse in chirped experiments (horizontal lines). Chirping was to lower wavenumber. Also shown is a portion of the reaction spectrum with narrow pulse from Figure 5. All results were scaled to 27 mJ/pulse, and all were with 1 Torr Freon-11 in oxygen at 5 Torr.

and the 810−787 cm^{-1} result was 37% above the narrow-pulse results. However, in the region of comparison with the measurements with the broadened (3%) laser pulses (Figure 7), the chirped pulses enhanced the reaction fraction to almost the same extent as the broad pulse. We conclude that chirping and a broad laser pulse have the same effect.

4. Discussion of Results

The reaction of Freon-11 under the action of infrared laser radiation probably begins with reaction 1. The $CFCl_2$ radical, however, is apparently sufficiently stable that it can either re-form the $CFCl_3$ molecule by the reverse of reaction 1,

$$CFCl_2 + Cl \rightarrow CFCl_3 \tag{5}$$

or by abstraction of a chlorine atom from the chlorine molecule,

$$CFCl_2 + Cl_2 \rightarrow CFCl_3 + Cl \tag{6}$$

The radical may also lose another chlorine molecule,

$$CFCl_2 \rightarrow CFCl + Cl \tag{7}$$

and then be scavenged by oxygen,

$$CFCl + O_2 \rightarrow COFCl + O \tag{8}$$

In the case of Freon-12, a similar mechanism probably applies. However, the reaction equivalent to reaction 7 is apparently sufficiently rapid that reactions similar to reactions 5 and 6 do not occur. The $CFCl_2$ molecule has a considerably stronger carbon−chlorine bond[21,29,30] (234 kJ/mol) than does the CF_2Cl molecule[21,29,30] (202 kJ/mol). The measured dependence on number of laser pulses, Figures 1 and 2, supports these conclusions. The curvature of Figure 1 indicates re-formation of the original Freon-11 as products accumulate (Cl_2). The pure exponential decay of Freon-12 (Figure 2) indicates that once the molecule dissociates, it does not re-form from the reaction products.

The intensity and frequency of the absorption resonances, the vibrational anharmonicity of the vibrational modes, and collisional and noncollisional energy transfer processes all influence the absorption and dissociation. The temporal and frequency profiles of the FEL laser pulse also influence the absorption process. The net effect of these processes is the results shown in Figures 3−9. The pulse energy dependence of the dissociation (Figures 3 and 4) is precisely what one would expect from successive absorption of laser photons for the geometry of the irradiated region. The slope of 4 at lower energies is similar to what was measured for many similar species with carbon dioxide lasers (see, for example, ref 27 and cited references therein). The $E^{1.5}$ terms follow from the slight focusing of the laser and are due to the geometry[28] of the irradiation. If the local reaction fraction increases with a high power (2 or greater) of the laser fluence, then the observed fraction of molecules reacting in a cell will scale with the 1.5 power of the laser pulse energy.

In both Figures 5 and 6 the reaction spectrum peaks are slightly below the peaks of the FTIR spectra. At those frequencies the initial absorption cross section was large enough for absorption of an initial photon. After that initial absorption the anharmonic shift enhances absorption of additional photons. Eventually, the molecule absorbs sufficient energy for dissociation. The peaks occur where the least restriction exists for absorption of sufficient laser energy. For Freon-12, absorption of laser energy associated with FTIR bands at higher frequencies also contributes to the energy of reaction, particularly after the molecule becomes more highly excited.

We do not know all the anharmonicity constants for the Freons that would be necessary to reconstruct the absorption spectra of the absorbing molecules as the molecule becomes more highly excited. However, for some other species, the complete set of anharmonicity constants has been measured. In SF_6,[31] for example, the average anharmonic shift in the 10.6 μm region is 2.5 cm^{-1} per 1000 cm^{-1} of vibrational excitation. Because of the variation of the anharmonic shift with molecular state, the shift will also involve a broadening of the shifted spectrum for a given amount of internal excitation. This broadening, again for SF_6,[31] is about 2/3 the anharmonic shift. If we consider the laser absorption near the 1075 cm^{-1} peak of the Freon-12 reaction spectrum and assume that the anharmonic shift and broadening for that molecule are the same as for SF_6, we see that the transition centered at 1105 cm^{-1} will remain in resonance with the laser frequency up to about 15 000 cm^{-1}. Above that energy, which is about half the energy necessary for dissociation, the transition centered at 1160 cm^{-1} will come into resonance and will remain in resonance until the molecule has absorbed the energy necessary for dissociation. The anharmonic coupling among the various states of the vibrationally excited molecules not only shifts the frequencies of absorption but also, by mixing of states of similar energy, tends to make more transitions available for absorption. This quasi-continuum thus created enables the molecule to absorb sufficient energy for dissociation.

Because of the collisions occurring during the laser pulse, the rotational states of the molecule change rapidly enough for a large fraction of the molecules to absorb the laser radiation. This collisional redistribution of rotational energy apparently has the effect of increasing the shift of the peaks of the reaction spectrum. We can compare the shift we measured for Freon-11 with that measured by Lupo and Quack[5] with a shorter (CO_2) laser pulse at lower pressure. They also determined that the peak of the reaction spectrum was shifted to lower frequency. The shift they measured was just 4 cm^{-1}, while the shift we measured for the same absorption band (Figure 5) was 44 cm^{-1}. More collisions during the laser pulse is the likely explanation for this difference. The pressure in our experiments was 5 times greater than those of Lupo and Quack,[5] and the FEL macropulse was as much as 20 times longer than the CO_2 laser pulse. The number of collisions experienced by the absorbing molecules during the laser pulse was as much as 100 times greater for our experiments than in the experiments of Lupo and Quack.[5] The larger number of collisions during the FEL laser pulse tended to allow access to a greater number of rotational (and vibrational) states and thus prevented what has been called the "rotational bottleneck" (see reviews in refs 7−17). With the restriction of the rotational bottleneck reduced by a greater number of molecular collisions, the molecular anharmonicity becomes a more important restriction to absorption and dissociation. This effect of having the collisions shift the absorption resonance to lower frequencies has also been observed[32] in SF_6.

Collisional de-excitation of the vibrationally excited molecules prior to dissociation results in the exponential decrease of reaction fraction with pressure (Figures 7 and 8). Collisions can either increase or decrease the internal energy of the molecule, the decrease being more likely. The rates of both these processes are proportional to the pressure. The rate of laser excitation is to first order independent of pressure. The increased pressure also adds to the heat capacity of the system, which tends to keep the temperature down. At higher pressures, collisional de-excitation dominates, making it more unlikely for absorption of sufficient energy to dissociate the molecule.

Our experiments resulted in very little molecular dissociation at pressures above 50 Torr. Consequently, the current FEL laser was not sufficiently intense for dissociation at pressures approaching atmospheric pressure. At such pressure, a possible way to induce molecular reactions with infrared radiation would be to use shorter laser pulses. The shorter pulse would reduce the number of molecular collisions during the pulse. As noted earlier in the paper, molecular collisions during the laser pulse affect other aspects of the absorption and dissociation processes, such as the shift of the reaction spectrum to lower frequencies. However, restricting dissociation at high pressure by collisional deactivation is the most important. The slope of the curves in Figures 7 and 8 should decrease as the laser pulse is shortened. As noted above, we have one experimental comparison that indicates that this is so. The experiment with the Los Alamos APEX FEL,[22] which had a macropulse 12.5 times longer than the FELIX macropulse, was compared with a similar experiment with the FELIX laser. For comparable parameters, the dissociation fraction was 4.5 times greater for the FELIX laser.

We can make a rough estimate of the pulse length necessary to have significant reaction at atmospheric pressure. The pulse length necessary to have the fraction reacted reduced at atmospheric pressure to only 25% of that in the low-pressure limit would be 1/50 of 2 μs, or 40 ns. Such FELs are not available currently.

5. Conclusions

The experiments reported in this paper give a good characterization of the infrared photochemistry of the two Freon species. The molecules behave similarly to molecules irradiated with CO_2 lasers. Frequencies somewhat lower than the frequencies of the infrared absorption peaks show the highest reaction fraction. With 2 μs pulses the pressure decreases the reaction fraction at about 10% and 7% per Torr for Freon-11 and Freon-12, respectively.

As the length of the laser pulse decreases, absorption competes more favorably with collisional de-excitation. As demonstrated in the comparison of dissociation of Freon-11 with the two different laser pulsewidths, a much shorter laser pulse would make infrared photolysis of Freons possible near atmospheric pressure. Our estimate is that about a factor of 50 shorter pulse (40 ns) would be necessary to have photolysis occur near atmospheric pressure.

For application to chemical photolysis in low pressure, we have determined that rf-linac-based free-electron lasers have significant advantages over fixed frequency lasers such as CO_2 lasers. However, the relatively long macropulse train was a drawback for circumstances when the pressure was a significant fraction of atmospheric pressure. General application of FELs for photochemistry at moderate to high pressure will require devising some means of compressing the macropulse to ≤ 100 ns.

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