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Infrared FEL photochemistry: Multiple-photon dissociation of Freon gas *

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Abstract

Wavelength tunability, synchrotron sidebands, and picosecond pulse structure are inherent FEL characteristics that should be advantageous for photochemistry involving infrared multiple-photon photodissociation. Tuned to an absorption resonance, the FEL sideband structure will overlap the broad, excited-state spectral absorption and should lead to enhanced dissociation. The Los Alamos APEX FEL was operated with and without sidebands to test this hypothesis on CFCI_3 (Freon 11), an inert chlorofluorocarbon widely used in refrigeration systems and one of the gases implicated as depleting the ozone in the Earth's stratospheric layer. The FEL wavelength was set at the C-Cl stretch absorption resonance at 11.8- μm , the oscillator cavity length was detuned first to minimize and then to maximize the spectral bandwidth, and the beam was focused through a pair of test cells (1.0 Torr Freon+1.7 Torr air). Comparison of final and initial absorbance spectra indicated the CFCI_3 photodissociation yield was 1.2% for the cell exposed with sideband spectra (3% FWHM) and 9-ns micropulse separation. Negligible effect was seen without sidebands, albeit at lower total beam fluence. Although the result of this single experiment is not large enough to be conclusive, it does provide a basis for optimizing the FEL temporal and spectral parameters to attain higher photodissociation yield in future tests.

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1. Introduction

The man-made chlorofluorocarbons (CFC), especially Freon 11 (CFCl_3) and Freon 12 (CF_2Cl_2), have attracted public attention because they have been linked to depletion of the ozone layer in the Earth's stratosphere, resulting in increased surface exposure to UV-B radiation (294-320 nm) [1-4]. Freons released at the surface of the Earth eventually reach the stratosphere where exposure to sunlight below 200 nm dissociates the chlorine atoms. Each free chlorine atom then catalytically removes an oxygen atom from up to 100,000 ozone molecules before leaving its itinerant cycle. The 60 to 140 year life of Freons as they diffuse through the troposphere, as well as the continuing new releases by human processes, have prompted an international agreement known as the Montreal Protocol on Substances that Deplete the Ozone Layer-1987 [1-3], amended in London in 1990 [2], to curtail further production by 1996.

Thomas Stix [5] of Princeton University has proposed an atmospheric engineering solution to the CFC problem that would use over one-thousand, 2 to 3-MW infrared lasers stationed around the globe to photodissociate the Freon molecules within the troposphere, before they drift into the stratosphere. The freed chlorine atoms would then combine with water or oxygen and fall to the Earth in rain. This approach is based on multiple-photon absorption of 30 to 40 infrared photons at the C-Cl (or C-F) stretch resonant wavelengths between 8 to 12 μm (specific to the type of Freon). Laboratory demonstrations with nanosecond-pulse infrared lasers have shown that 30 to 40 absorbed photons can release the Cl atom with sufficient efficiency to be of potential interest [6]. Even so, Stix' projections for the scope and cost of such a laser solution are not considered feasible with present technology, perhaps by a factor of 10 to 20 [7]. Bullock, et al. [8] have suggested that an optimization of the laser pulselength and spectrum could significantly reduce the size of Stix' proposal.

Free-electron lasers offer the versatility in spectral and temporal output that may enable, via the multiple-photon absorption process, attainment of efficient

photodissociation of Freons, as well as other classes of large molecules. FELs offer easy wavelength tunability to 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, manifests as an irregular lasing spectrum on the long wavelength side of the resonant wavelength. For example, the Los Alamos APEX FEL has operated with sidebands extending out to 10% beyond the initial lasing line.

We briefly describe the salient features of the multiple-photon absorption (MPA) processes: Initially, radiation within a specific, narrow-band infrared wavelength is required to excite a molecule up the ladder of discrete energy levels into the quasi-continuum of states. The absorption spectrum of these excited molecules is shifted to wavelengths longer than the initial resonance by up to 10%. Subsequent exposure within this broad wavelength range can further excite the molecule past the dissociation level. This is made possible by the monotonically increasing density of available states within the quasi-continuum with increasing energy level [9]. Generally, MPA depends primarily on laser fluence with a weak dependence on intensity of laser excitation (incoherent addition of laser photons is sufficient) [10]. However, for CF_2HCl (a molecule similar to the Freons), high-intensity mode-locked CO_2 laser pulses have produced 5-10 faster dissociation rates than non-mode-locked pulses of the same fluence [11].

We envisioned that the FEL sideband structure could match the broad, excited-state spectral absorption and lead to greater dissociation efficiency than with single, narrow-band wavelength. Supporting this expectation are previous ir multiple-photon dissociation experiments with other heavy molecules, e.g. CF_2HCl [12] and OsO_4 [13] in which exposure with two wavelengths produced 10 to 300 more dissociated products than with a single, resonant wavelength. To test this hypothesis, we tuned

the Los Alamos APEX FEL to the 11.8- μm absorption resonance (C-Cl stretch) of Freon 11 and exposed a pair of test cells, with and without sidebands. The following sections (2-5) present the experimental procedures, the experimental results, a discussion of the results, and a summary including suggestions for future tests.

2. Experimental procedures

Two identical test cells (76 mm length, 35 mm diameter) with NaCl windows were filled with 1.0 Torr of CFCl_3 plus 1.7 Torr of air to provide H_2O and O_2 known to be effective scavengers for photodissociated Cl atoms [6]. The infrared transmission of the gas-filled cells was measured with a Mattson Instruments FTIR spectrometer set for 0.5 cm^{-1} resolution and equipped with computer data processing capability for storing and processing successive measurements.

The FEL beam was focused at the center of the cells to a spot-size radius of 0.35 mm as measured with a Spiricon linear pyroelectric array. Laser energy was monitored at the entrance and exit of the cells with Laser Precision pyroelectric energy meters. The FEL was operated at 1 Hz with parameters listed in Table 1, and the temporal dependence of the macropulse and integrated spectrum were monitored on each shot. The degree of sideband generation was obtained by adjusting the resonator length, attaining bandwidths of 1% (full-width at $1/e$) when detuned and 3% with zero detuning (see Fig. 1).

We conducted tests at the strongest absorption resonance of CFCl_3 at 11.8 μm , corresponding to a C-Cl stretch vibration. Figure 2 shows a comparison of the initial cw transmittance measured with the FTIR spectrometer and the pulsed transmittance using the FEL tuned for narrow bandwidth ($\sim 1\%$) and attenuated by a factor of 100 to $\sim 1 \text{ MW/cm}^2$ peak intensity. Even at this relatively low intensity, the absorption resonance is significantly saturated. Subsequently, the cells were exposed to 2000

macropulses of the unattenuated FEL beam tuned to 11.8 μm . Visual observation verified the absence of optical breakdown within the cells. At the end of the FEL exposures, the absorbance spectra were remeasured and compared to the initial absorbance to determine the fractional dissociation.

Regrettably, the very limited availability of the FEL beam forced us to severely abbreviate the scope of our tests planned for a wide range of FEL and Freon gas parameters. Thus, only two exposures were accomplished, with and without sidebands, but with different micropulse separations and pulse fluences.

3. Experimental results

Figure 3 shows the final absorbance and net change in absorbance of a cell of Freon 11 measured after exposure to 2100 FEL macropulses with 3% (FW-1/e) sideband spectra and 9-ns micropulse separation (see Table 1). Since absorbance is proportional to molecular number density, fractional photodissociation is derived directly from the ratio of the absorbance change and absorbance spectrum measured just prior to exposure. The most accurate measure of fractional absorbance change at each of the two resonances (9.26 μm and 11.78 μm) is obtained from the ratio of the absorbance change-wave number product integrated over the shaded regions divided by the initial absorbance integrated over the same spectral ranges. A small, but definite photodissociation yield of 1.2% was so derived (see Table 2). Previous photodissociation studies by Hudgens [14] identify this photodissociation process as $\text{CFCl}_3 \rightarrow \text{CFCl}_2 + \text{Cl}$. The test without sidebands (1% FW-1/e) and lower intensity produced negligible photodissociation product.

The resonant wavelength of the FEL exhibited significant instability ($\pm 0.07 \mu\text{m}$), comparable to the 0.2 μm FWHM bandwidth of the 11.8- μm resonance. Likewise, the pulse-to-pulse variation of the laser output energy was large, with $\pm 30 - 40\%$ standard deviation. The output power level was $\sim 10\%$ of that normally produced by this FEL,

due primarily to the high diffraction losses of the particular resonator in place at the time of these tests.

4. Discussion

The low dissociation yield obtained in these tests probably involved the following parameters:

1. Laser wavelength: The $\pm 0.07 \mu\text{m}$ pulse-to-pulse variation of the FEL resonant wavelength may have been too large. With greater stability, a more optimal initial wavelength would have been on the long side of the resonance [6], perhaps between 11.9 and 12.0 μm .
2. Laser fluence and micropulse separation: Efficient use of sidebands requires sufficient fluence at the initial molecular resonance to excite molecules into the quasi-continuum. Our 0.6 J/cm^2 axial fluence at the resonant wavelength, distributed over 25 μs , was probably insufficient. To offset collisional de-excitation (decay time estimated at 1 to 10 $\mu\text{s/Torr}$) of the molecules during the macropulse, a more compressed pulse structure would be advantageous.
3. Scavenger gas: The number of scavenger molecules (O_2 and H_2O) available per dissociated CFCI_3 molecule was probably insufficient, allowing excessive recombination to occur. A much larger ratio (10:1) of scavenger molecules per CFC molecule were effective in photodissociation experiments by Lupo and Quack [6].

Our initial plans had been to investigate most of the above parameter variations during these experiments. With more FEL beam time and adjustment of parameters, larger dissociation yields would probably be obtained.

As an alternative to the use of sidebands, negative frequency chirping during the macropulse may be an effective way to excite molecules up the vibrational levels to dissociation. Such capability has recently been reported by A. van der Meer, et al. [15] using the Dutch FEL at the FOM Institute for Plasma Physics at Nieuwegein.

5. Summary

When operated with spectral sidebands extending 3% beyond the resonant wavelength and 25- μ s macropulselength, the Los Alamos APEX FEL photodissociated a small fraction (1.2%) of the irradiated volume of a cell of Freon 11 (1.0 Torr + 1.7 Torr air). Negligible effect was seen without sidebands, albeit at lower total beam fluence. With the influence of a wide range of parameters (FEL temporal and spectral structure, scavenger gas, cell pressure) yet remaining to be explored, the potential advantages of FEL sidebands on multiple-photon dissociation remains an open question. Although the result of the single experiment reported here is not large enough to be conclusive, it does provide a basis for optimizing the FEL temporal and spectral parameters to attain higher photodissociation yield in future tests.

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Table 1

FEL experimental parameters

	Without sidebands	With sidebands	Units
Wavelength, resonant	11.8	11.8	μm
Spectral bandwidth, FW-1/e	1	3	%
Stability of resonant wavelength	± 0.07	± 0.07	μm
Macropulse energy	1.7 ± 0.7	13 ± 4	mJ
Beam $1/e^2$ radius at focus	0.35	0.35	mm
Macropulse fluence thru cell	0.6 ± 0.3	4.7 ± 1.6	J/cm^2
Number of FEL macropulses	2000	2100	
Macropulse length	25	25	μs
Micropulse separation	46.2	9.2	ns
Micropulse energy	3.2 ± 1.3	4.8 ± 1.6	μJ
Micropulse length	10	10	ps
Micropulse peak power	320 ± 130	480 ± 160	kW
Peak intensity	115 ± 50	175 ± 60	MW/cm^2

Table 2

Experimental results

	Without sidebands	With sidebands
Macropulse fluence at $11.8 \pm 0.1 \mu\text{m}$	$0.6 \text{ J}/\text{cm}^2$	$0.6 \text{ J}/\text{cm}^2$
Macropulse fluence in sidebands	~ 0	$4 \text{ J}/\text{cm}^2$
Fraction of gas cell volume exposed	58%	61%
Per cent dissociation of exposed gas	$< 0.5\%$	1.2%

Figure captions

Fig. 1. FEL spectrum with sidebands near 11.8 μm integrated over one macropulse.

Scale: 0.13 $\mu\text{m}/\text{cm}$ with wavelength increasing to the left.

Fig. 2. Transmission at the 11.8- μm resonance of CFCl_3 as measured with an FTIR spectrometer (line) and the pulsed FEL (circles). FEL beam was attenuated to an intensity of $\sim 1 \text{ MW}/\text{cm}^2$ with 1% bandwidth (FW at $1/e$). CFCl_3 partial pressure: 1.0 Torr partial pressure; path length: 76 mm.

Fig. 3. FTIR absorbance spectrum of CFCl_3 (1.0 Torr, 76 mm path length):

a) before exposure, and b) net decrease after FEL exposure with 3% sidebands. The scale of b) is magnified by a factor of 70x. (Exposure conditions are given in Tables 1 and 2.)

12.12 11.86 11.73

Wavelength, μm

Fig. 2.

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