

Vibron-mediated electronic relaxation in crystalline chlorine

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Abstract

Luminescence decay of thin solid films of molecular chlorine exhibit distinctly non-exponential temporal behavior following pulsed ultraviolet laser excitation. The temporal characteristics are dependent on sample temperature and laser fluence in the range 11–80 K. This behavior is attributed to internal conversion from the first excited $A'(^3\Pi_{2u})$ electronic state to the ground state, which is accelerated by phonons and localized vibrational excitons (vibrons). This unusual mechanism of electronic relaxation is consistent with a recent theoretical model for the mechanism of explosive desorption of cryogenic films.

1. Introduction

Laser vaporization of solid targets is an effective technique for generating gas phase atoms and molecules having translational energies in the range of several electron volts. This can be a useful method for depositing thin films of refractory materials [1,2], embedding reactive atoms into an inert host material for synthesizing energetic solids [3,4], or for vaporizing biomolecules and other polymers by matrix assisted laser desorption for mass spectrometric studies [5].

In a recent series of papers, the translational energy distributions of small molecules and fragment atoms have been measured following laser vaporization of the corresponding cryogenic solids [6–10]. Weaver and Leone have summarized much of the experimental data by noting that the overall vapor-

ization process is essentially photothermal in nature [11]. However, the principal mechanism of energy absorption is via electronic excitation, and extensive fragmentation may occur when the laser photon energy exceeds the bond dissociation energy of the molecule.

Fain and Lin have proposed a model of explosive laser-induced desorption [12]. Briefly, the laser energy is initially stored as electronic excitation, some of which decays by non-radiative relaxation into phonon modes of the solid. Population of excited phonon modes increases the rate of non-radiative relaxation, thereby introducing a mechanism of positive feedback. If the initial amount of energy deposited by the laser exceeds a threshold value predicted by the theory, then the cascade can become explosive. The result is a catastrophic rate of energy deposition into phonon modes, resulting in vaporization of the sample.

In this paper, we present measurements of laser-

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induced electronic luminescence of crystalline chlorine samples which exhibit distinctly non-exponential temporal decays depending on temperature and laser fluence (energy per unit area). The results are consistent with the type of phonon and vibron-mediated electronic relaxation required by the theory of Fain and Lin.

2. Experimental details

Two sets of experiments were conducted; the first was at the University of California-Irvine, and the second was at the University of Utah. In the Irvine experiments, thin films of chlorine were deposited from the vapor onto a sapphire plate held at 11 K on the cold tip of a closed-cycle helium refrigerator (Air Products Model DE-202) in a high vacuum apparatus. In most experiments the chlorine vapor was introduced in a pulsed mode using a molecular beam valve (General Valve Series 9). The vacuum shroud was equipped with fused silica windows for transmitting the excitation laser beam and for collecting the luminescence from the chlorine films. The luminescence was collected with a 4 inch focal length quartz lens, passed through a 1 cm path length cell filled with acetone (to block the 308 nm scattered light), focused onto the entrance slit of a 0.15 m monochromator, and detected with a Hamamatsu IP28 photomultiplier tube. The output of the photomultiplier was terminated in a 1 k Ω resistor at a Tektronics Model 2430 digitizing oscilloscope. Waveforms were averaged in the scope and subsequently transferred to a personal computer for analysis.

The excitation laser used in most experiments was a Lambda-Physik Model EMG101MSC excimer laser operating at 308 nm. In some experiments, the frequency-doubled output of an excimer-pumped dye laser was used at 337 nm, but there was no significant difference in the results obtained. The laser beam was passed through a variable attenuator (Newport Model 935-5) and the beam energy was measured with a pyroelectric joulemeter (Molelectron Model J50). A schematic drawing of the apparatus is shown in Fig. 1.

The Utah experiments were conducted using a similar apparatus except that the excitation laser was

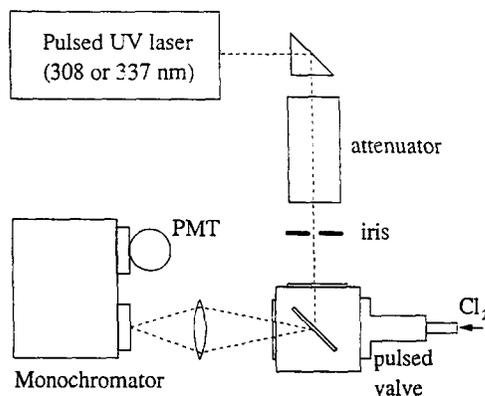


Fig. 1. Schematic diagram of the experimental apparatus.

a Molelectron nitrogen laser (337 nm), the ultra-high vacuum chamber was pumped to 10^{-8} Torr using a turbomolecular pump, the sample deposition was continuous rather than pulsed, and the detection system included a SPEX triple monochromator (0.6 m) and a Hamamatsu R928 photomultiplier tube. Similar results were obtained in both sets of experiments, though the light collection and transmission efficiency was better in the Irvine apparatus, allowing data to be collected at lower excitation laser fluence.

In both sets of experiments, chlorine was purified by vacuum distillation and stored in glass bulbs equipped with greaseless stopcocks prior to deposition.

3. Results

Pulsed UV laser excitation of thin films of crystalline chlorine results in a bright red luminescence that is visible to the naked eye. The emission spectrum, recorded with a setup identical to the one used in the present, has already been published [13]. The apparent maximum intensity of this luminescence occurs near 840 nm. However, this is determined by the red wavelength cutoff of our detection, and the true maximum of the emission occurs at somewhat longer wavelengths. The emission is broad and almost completely unstructured, exhibiting only a hint of a vibrational progression near 500 cm^{-1} , consistent with the ground state vibrational frequency of molecular chlorine. Emission spectra were recorded

with a boxcar integrator using a gate width of 100 μs . Spectra obtained using gate delays of 0 and 1000 μs were essentially identical, apart from the lower overall intensity of the latter.

The temporal dependence of the luminescence decay at low excitation fluence ($1.3 \mu\text{J}/\text{cm}^2$) is shown in Fig. 2. A least-squares fit of the data to a single exponential decay:

$$I(t) = I_0 \exp(-k_1 t), \quad (1)$$

shows that at 11 K, the luminescence decay constant, k_1 , is $500 \pm 5 \text{ s}^{-1}$. Similar data were obtained using the same sample at temperatures up to 80 K. The value of k_1 increases with sample temperature, as shown in the inset to Fig. 2.

The dependence of the temporal behavior on irradiation fluence is illustrated in Fig. 3. In this experiment, two decay curves were recorded from the same sample using the same total laser pulse energy ($0.6 \mu\text{J}$). However, the spot size at the sample was reduced from 1.5 mm diameter (low fluence) to 0.2 mm diameter (high fluence) by inserting a lens into the beam just before the vacuum chamber. The two sets of data show nearly the same initial intensity, but the high fluence data exhibits a faster initial decay during the first 100 μs . At long times, the

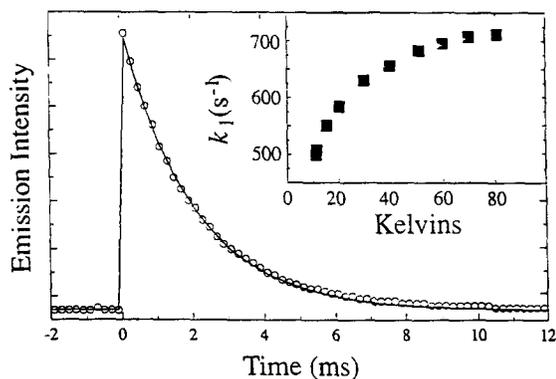


Fig. 2. Temporal dependence of solid Cl_2 luminescence intensity at 835 nm following pulsed laser excitation at 308 nm. The incident laser fluence at the sample is $1.3 \mu\text{J}/\text{cm}^2$ and the sample temperature is 11 K. The experimental data (open circles) were averaged over 256 laser pulses. The solid curve is a least-squares fit to a single exponential decay, resulting in a decay constant $k_1 = 500 \pm 5 \text{ s}^{-1}$. The inset shows the measured dependence of k_1 on the sample temperature.

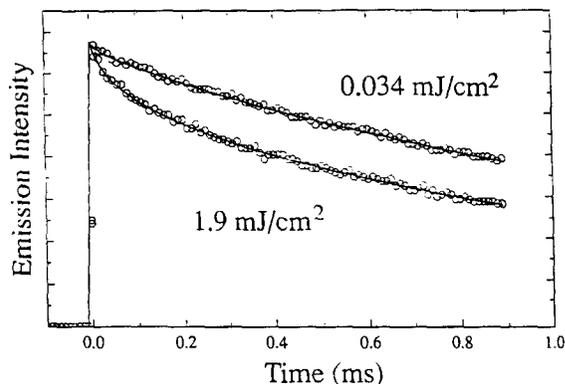


Fig. 3. Laser-induced luminescence from crystalline Cl_2 illustrating the effect of increased 308 nm laser fluence on the temporal behavior. Both luminescence decay curves were obtained from the same sample at 11 K using a total laser pulse energy of $0.6 \mu\text{J}$. A lens was inserted in the beam to reduce the diameter of the laser spot size at the sample from 1.5 mm (low fluence, upper trace) to 0.2 mm (high fluence, lower trace). Note that the initial intensity is the nearly the same (i.e., the data have not been scaled).

decay constants are the same within experimental uncertainty. The rate and magnitude of the fast component of the decay at short times was found to be independent of sample thickness.

It is apparent from the data presented in Fig. 3 that increasing the irradiation fluence at constant laser energy results in a luminescence decay that has the same initial intensity but smaller integrated intensity. This is consistent with a process in which the higher concentration of absorbed laser energy increases the rate of non-radiative relaxation. An alternative mechanism might involve an increase in the radiative rate. However, if such were the case then raising the fluence at constant laser energy would result in an increase in the initial luminescence intensity, I_0 , as well as an increase in the luminescence quantum yield (integrated intensity); this is inconsistent with our observations (Fig. 3).

A series of experiments was carried out to confirm that increasing the fluence affects only the non-radiative contribution to the relaxation rate. In these measurements the total laser energy was varied while keeping the area of the irradiated spot constant (0.6 cm^2). This allowed a change in fluence over almost two orders of magnitude while maintaining a constant collection efficiency of the luminescence.

The data were subjected to a non-linear least-squares fit to the functional form

$$\frac{I(t)}{I_0} = \exp[-k_1 t - C_1 \ln(C_2 t + 1)] \quad (2)$$

which will be justified in the discussion below. Here, I_0 is the measured initial luminescence intensity at $t=0$. The parameters k_1 , C_1 and C_2 are extracted from the fitting procedure, and are presented in Table 1. The value of I_0 , divided by the measured laser fluence for each of the seven experiments, is plotted as a function of laser fluence in Fig. 4. The results show that the initial luminescence yield decreases slightly with increasing laser fluence. Also shown in Fig. 4 is the fluence dependence of the integrated luminescence intensity (also scaled by the measured laser fluence). It was not possible to record the entire decay curve with sufficient accuracy to determine the integrated intensity by direct numerical integration of the data. Instead, the integrated intensity was computed numerically using the functional form of Eq. 2 along with the least-squares parameters listed in Table 1. The results shown in Fig. 4 show that the initial luminescence intensity decreases slightly with increasing laser fluence, whereas the integrated intensity exhibits a more pro-

Table 1

Least-squares parameters from fits of luminescence data (11 K) to Eq. 2

Fluence (mJ cm ⁻²)	I_0 (arb.)	k_1 (s ⁻¹)	k_3/k_2 (C_1)	$V_0 k_2$ (C_2 , s ⁻¹)
0.012	49.0	552 ± 9	0.0084 ± 0.0022	(1.7 ± 2.1) × 10 ⁶
0.030	120.0	521 ± 13	0.027 ± 0.005	(6.5 ± 2.7) × 10 ⁴
0.063	265.0	516 ± 23	0.062 ± 0.011	(2.1 ± 0.6) × 10 ⁴
0.121	534.0	519 ± 14	0.059 ± 0.005	(6.7 ± 1.3) × 10 ⁴
0.36	1370.0	497 ± 21	0.157 ± 0.009	(3.6 ± 0.4) × 10 ⁴
0.63	2130.0	475 ± 22	0.206 ± 0.009	(3.3 ± 0.3) × 10 ⁴
0.89	2960.0	509 ± 22	0.212 ± 0.008	(4.9 ± 0.4) × 10 ⁴

nounced decrease with increasing fluence. This observation is consistent with the results shown in Fig. 3, and implies that increasing laser fluence results in an increase in the rate of non-radiative relaxation rather than an increase in luminescence rate.

4. Discussion

Although the luminescence observed in solid Cl₂ is broad with a barely discernible vibronic structure, it is consistent with an assignment to the $A'(^3\Pi_{2u}) \rightarrow X(^1\Sigma_{g+})$ transition of molecular chlorine. This strongly forbidden molecular transition is activated in condensed media. It was first observed in matrix isolated Cl₂ [14], and subsequently assigned by Bondybey and Fletcher [15]. The transition most likely borrows intensity through matrix induced mixing between $A'(^3\Pi_{2u})$ and the nearby $^1\Pi_{1u}$ state. The observed radiative lifetimes of Cl₂(A') are 76 ms, and 48 ms, in solid Ar and Kr, respectively [15]. A comparison of the emission spectra of UV excited Cl₂ in solid Ar, Kr, Xe and neat Cl₂ convincingly shows that they all originate from the same transition, namely $A' \rightarrow X$ [13]. These spectra are sharp in Ar and Kr, and show the characteristic triplet pattern of isotopic splitting. The vibronic bands are already broadened in Xe, such that the isotopic splitting is completely masked, and further broadened in neat Cl₂, such that the progression is barely discernible [13]. The same transition has also been studied in Cl₂ dimers and small clusters isolated in solid Kr [16]. The vibronic line widths broaden in the progression from monomer to dimer to cluster to neat solid Cl₂. The fluorescence decay time is the same in the

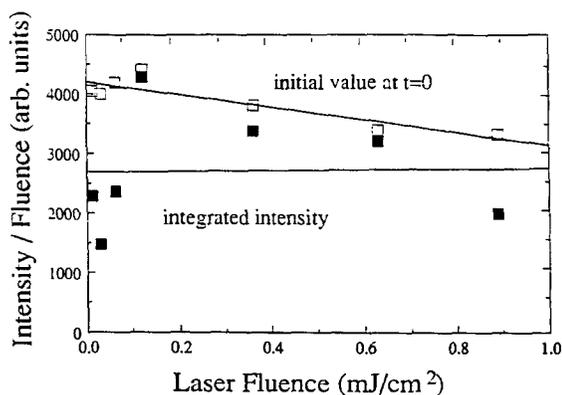
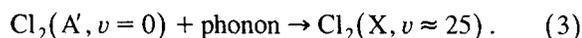


Fig. 4. Plot of Cl₂ luminescence intensity (divided by measured laser fluence) as a function of laser fluence. Initial intensity at $t=0$ (squares) exhibits a slight decrease with increasing fluence, whereas the total integrated intensity (circles) exhibits a much more pronounced decrease. The luminescence data were obtained at 11 K using 308 nm excitation. Fluence was varied by changing the laser pulse energy while maintaining a constant area of the beam at the sample (0.6 cm²).

isolated monomer and dimer, shortens to 13 ms in the small clusters [16], and, according to the data shown in Fig. 2, further shortens in solid chlorine to 2 ms. Based on the temperature dependence of this observed relaxation rate, the fact that at 10 K the dependence has a finite slope, and only reaches a constant value at high temperature, it is clear that this decay is not purely radiative, but rather the result of phonon-assisted internal conversion,



In the present studies, as established in matrix isolated Cl_2 , the A' state is reached through dissociative pumping. At the excitation wavelengths used, 308 nm and 337 nm, the dominant absorption from the ground state of Cl_2 is to the dissociative ${}^1\Pi_{1u}$ state. The population in the A' state is therefore the result of efficient cage induced recombination and relaxation in the states that correlate with the $\text{Cl}({}^2P_{3/2}) + \text{Cl}({}^2P_{3/2})$ asymptote, as first noted by Bondybey and Fletcher [15]. The cage effect is complete – no permanent dissociation is observed in matrix isolated monomers, dimers or clusters [16]. The same seems to hold in the neat solid. We had expected that in the neat solid a new channel for reactive dissociation might open up, through $\text{Cl} + \text{Cl}_2$ exchange reactions. This would have been observable as a rise time in the $A' \rightarrow X$ emission, due to the delayed recombination of separated atoms. However, the observed luminescence is prompt, indicating that recombination is complete well within the pulse widths of the lasers used (10^{-8} s). Moreover, we do not observe any thermoluminescence which would be characteristic of diffusion controlled recombination of permanently dissociated molecules. We conclude that the cage effect is complete in neat Cl_2 as well.

It is relevant to note that in this dissociative pumping scheme, a significant amount of the initial excitation energy is dumped into the lattice. The excitation is promoted with 4 eV photons, and the vibrationally relaxed A' state has an energy of 2.1 eV. Thus, the balance of this energy, nearly 2 eV, is dissipated into the lattice. Because the initial preparation is to a strictly repulsive molecular potential, the excess energy is impulsively transferred to the lattice. In atomic solids, this excess energy is dissipated via shock waves [17,18], and through phonons [19].

These two mechanisms should also be active in the molecular solids, i.e., there will be extensive center of mass excitation of the host molecules; however, now we also expect significant internal excitation of the nearest neighbor molecules, and the creation of vibrational phonons (vibrons). Due to the anharmonicity of the molecule, we expect highly vibrationally excited states to be localized, and to decay via energy transfer from molecular vibrations to phonons and librations. Independent of the details of these dissipation processes, the picture to bear in mind is that $\text{Cl}_2(A')$ excitations are created suddenly, surrounded by significant vibronic activity locally. The effect of such vibrational excitations on the electronic excitation center is what we consider in the rest of this paper.

The results of our experiments show that in the limit of low-fluence excitation, the luminescence intensity follows a first-order exponential decay described by Eq. 1. As the laser fluence increases, the non-radiative portion of the decay rate increases significantly during the first ≈ 100 μs following excitation. Because the increase in the non-radiative decay rate is associated with increases in the fluence, it was quickly established that some form of local excitation by the laser is responsible for increasing the rate of internal conversion from the A' state to the ground electronic manifold. The obvious choices for the nature of this excitation are lattice phonon modes involving molecular center of mass motion, vibrational phonon modes involving molecular internal excitations (vibrons), or nearby electronically excited chlorine molecules.

Enhanced relaxation by interaction of neighboring electronically excited molecules can be ruled out easily. The absorption coefficient of chlorine at 308 nm is 2×10^{-19} cm^2 (base e). Therefore, at a fluence of 1.9 mJ/cm^2 (corresponding to the high fluence conditions illustrated in Fig. 3), the fraction of chlorine molecules excited in an optically thin sample is 6×10^{-4} . On average, each electronically excited molecule is separated from the next nearest excited molecule by 11 ground state molecules. Because the optical transition is forbidden by electric dipole selection rules, the probability of even one excitation transfer by dipole–dipole interactions is completely negligible; we estimate the exciton hopping rate for this process to be about 10^{-7} s^{-1} . This

makes it extremely unlikely that relaxation is caused by interaction of excited molecules with each other.

Thermal excitation of lattice phonons can also be ruled out. In this model, the non-radiative relaxation rate of electronically excited $\text{Cl}_2(A')$ molecules is a function of the lattice temperature. Deposition of energy by the laser excitation raises the local temperature of the film, thereby increasing the relaxation rate until the excess temperature can be conducted into the supporting substrate. At an incident laser fluence of 1.9 mJ/cm^2 , the total amount of energy deposited into an optically thin sample is 460 J/mol of chlorine molecules. If the Debye temperature of the chlorine lattice is 140 K (a rough estimate), then each laser pulse could heat the sample from 11 K to a maximum of 60 K (assuming the quantum yield for forming the A' state is much less than unity). We have measured the relaxation rate between 11 and 80 K (Fig. 2) and found a modest temperature dependence, but the rate would have to increase more than one order of magnitude in order to account for the fluence effect illustrated in Fig. 3. Noting that the temperature dependence of the relaxation rate appears to saturate at 800 s^{-1} , heating simply cannot account for the observed magnitude of the transient increase in relaxation rate. We stress that the electronic relaxation is indeed assisted by excitation of low-frequency phonons. The temperature-dependence of k_1 shown in Fig. 2 is ample evidence of this. However, this type of interaction cannot account for the fluence-dependent changes in relaxation rate, which occur on a much faster time scale ($\approx 100 \mu\text{s}$) than the overall decay ($> 1 \text{ ms}$).

By process of elimination, we may conclude that vibrational excitons, or vibrons, are responsible for the quenching. After considering numerous kinetic schemes for modeling the experimental data, we concluded that the most reasonable model involves creation of a localized 'hot spot' in the immediate vicinity of each electronically excited molecule. This localized excitation can enhance the rate of non-radiative intersystem crossing to the ground state. However, the effect is limited to the first $\approx 100 \mu\text{s}$ due to diffusion of the energy away from the neighborhood of the electronically excited molecule.

In principle, the 'hot spot' could be caused by excitation of acoustic lattice modes. However, this ordinary heat energy should be dissipated throughout

the lattice on a time scale of a few picoseconds, i.e., many orders of magnitude faster than the observed effect. A simple estimate of this time is obtained by dividing 5 nm (the approximate distance between excited molecules) by the ordinary speed of sound ($\approx 2 \text{ nm/ps}$). On this basis, we conclude that the excitation that is mainly responsible for the enhanced non-radiative decay must be localized vibrons. Decay of the vibrational energy away from the 'hot spot' may proceed by one of two channels: energy transfer to neighboring molecules by a resonant vibration–vibration process, which in the case of homonuclear diatomics is governed by the rather inefficient coupling through transition quadrupoles [20]; or via decay of the vibrational energy to relatively low-frequency acoustic phonon modes. Thus, the decay of vibronic hot spots, especially where high lying overtones are populated, is expected to be many orders of magnitude slower than transport of acoustic excitations.

The fluence dependence of the localized vibronic energy has a simple explanation. The A' state molecules created during the initial part of each laser pulse may be re-excited within the laser pulse to a high-lying charge transfer state, namely the D' state, with relatively high efficiency. Unlike the ${}^1\Pi_{1u} \leftarrow X$ transition, the $D' \leftarrow A'$ excitation has an oscillator strength near unity. Therefore, when the fraction of molecules excited to the A' state reaches 10^{-3} , the probability of excitation up to the ion-pair state becomes comparable to that of exciting ground state molecules. The ion-pair states do not emit in solid Cl_2 ; they are quenched by non-radiative energy transfer, as evidenced by the absence of any UV emission in these solids. The quenching must proceed via electronic–vibrational energy transfer. Now, the 8 eV of the two-photon energy is converted to the 2.1 eV electronic excitation of the A' molecule, with the $\approx 6 \text{ eV}$ balance being deposited as vibrational and acoustic phonons in neighboring molecules. Contrary to the impulsive dissociative excitation mechanism, now we expect a gentler cascade, and therefore a smaller partition of the excess energy into center of mass motion. Thus, this sequential two-photon excitation scheme provides for the creation of $\text{Cl}_2(A')$ surrounded by highly vibrationally excited neighbors, which may in turn couple to the electronically excited state or dissipate into the

lattice. With this physical picture in mind, we proceed with kinetic treatments of the data.

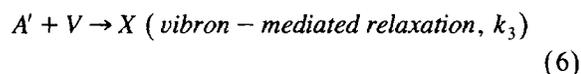
We considered several kinetic schemes for modeling the luminescence decay data. The various models differed in their assumptions regarding the mechanism of relaxation of the localized, vibrationally highly excited neighbors of the A' excited molecule. The models considered:

(1) A first-order decay of localized vibrational phonons, characteristic of direct energy transfer to lattice phonons.

(2) A second-order decay, characteristic of vibron–vibron scattering (analogous to the enhanced rate of electronic relaxation that is the main observation in this work).

(3) Energy migration by resonant vibration–vibration energy transfer, characteristic of diffusive flow of vibrons away from the electronically excited A' state molecule.

Each of these schemes gave a predicted functional form for the luminescence decay that contained three parameters to be determined from the fits. Each functional form was sufficiently flexible that satisfactory fits could be obtained and plausible values of the fitting parameters extracted. Therefore, we are unable to distinguish unambiguously between these different models for the hot spot decay on the basis of the luminescence decay kinetics. The quality of the fits for the second-order decay model were slightly better than the others, so we chose to interpret the data in terms of this kinetic model:



Analytic solution of this kinetic scheme requires that we make the assumption that decay of the vibrons is dominated by step (5). The temporal dependence of the luminescence decay (which is proportional to the A' excited state population) is then given by

$$I(t) = I_0 \exp \left[-k_1 t - \frac{k_3}{k_2} \ln(V_0 k_2 t + 1) \right] \quad (7)$$

where V_0 is the initial population of vibrons deposited by the laser pulse. Note that Eq. 7 is the

same as Eq. 2 used to fit the data, except that the terms k_3/k_2 and $V_0 k_2$ were represented by the parameters C_1 and C_2 , respectively. The values are given in Table 1 as a function of laser fluence.

Whereas this study was initially motivated by different considerations, we recognized the significance of our finding in view of the work of Fain and Lin [12]. In their theory of laser-induced explosive desorption, they propose that laser excitation initially creates a reservoir of vibronically excited molecules. Interaction between the vibron and phonon modes allows the phonons to be amplified in a process that is somewhat like stimulated emission in a laser gain medium. The principal result of the theory was to predict the existence of a threshold fluence for explosive desorption and the dependence of that threshold on surface coverage of adsorbate molecules on an inert substrate. The predictions are consistent with a previously reported experimental study of laser-induced desorption of CH_2I_2 from a sapphire substrate [21–23].

Our study of vibron-mediated electronic relaxation in crystalline chlorine provides support for the role of such a mechanism in crystalline chlorine, for which experimental studies of laser-induced desorption have been previously reported [6–8]. The only significant difference between our model and the one advanced by Fain and Lin is that the interaction they considered was between a reservoir of electronically excited states and the lattice phonons. Although population of lattice phonons has an observable effect on the electronic relaxation rate, the most important interaction in our experimental study appears to be between the reservoir of electronically excited states and the lattice vibrons. Otherwise, the formalism and the central thesis of the theory are directly supported by our experimental observations.

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