Peak-Power Dependence of Rovibronic Populations Below
the Quasicontinuum During IR Multiphoton Absorption*+

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Abstract:

Experimental studies on IR multiphoton absorption and dissociation have generally provided insight only into the relationship of IR laser characteristics such as power, wavelength, and mode structure to the observables dissociation yields, average number of photons absorbed, and product energy distribution. As a result, theoretical modeling of absorption at levels below the quasicontinuum has been based on facts somewhat removed from the actual phenomenon of interest. The experiments presented here provide information on the unperturbed rotational/vibrational populations of levels subsequent to IR excitation at levels below 4000 cm^{-1} of energy.

The experiment makes use of molecular beam techniques in conjunction with IR-visible double resonance. A CO_2 laser of known pulse duration prepares vibrationally excited thiophosgene, $\text{Cl}_2\text{C}=\text{S}$. The absorbing transition is $2\nu_4$ (see Table I). A tunable nitrogen-pumped dye laser scans the visible excitation spectrum to probe the perturbed rotational-vibrational populations of the pumped mode. Because the electronic transition is electric dipole forbidden, combination hot bands having the appropriate quantum numbers of the ground state are used in the analysis.

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Peak Power Dependence of Rovibronic Populations Below
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Experimental studies on IR multiphoton absorption and dissociation have generally provided insight only into the relationship of IR laser characteristics such as power, wavelength, and mode structure to the observables dissociation yields, average number of photons absorbed, and product energy distribution. As a result, theoretical modeling of absorption at levels below the quasicontinuum has been based on facts somewhat removed from the actual phenomenon of interest. The experiments presented here provide information on the unperturbed rotational/vibrational populations of levels subsequent to IR excitation at levels below 4000 cm^{-1} of energy.

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The salient results of these studies are listed below.

(1) As shown in Figure 1a for room temperature molecules and Figure 1b for rotationally cooled molecules, the CO₂ laser interacts with all rotational states of the vibrationless $[(v, v_2, \dots, v_6) = (000000)]$ level. This is quantitatively verified from rotational analysis of the $2_0^1 3_0^1 4_0^1$ band based on the work of Lombardi.¹ Similar results are obtained when the 4_0^1 transition is probed. These observations are not consistent with the present theoretical understanding.

(2) When the pulse duration t_p is 200ns, levels $v=0-4$ decrease in population, and levels $v=6,8$ remain unchanged (within the limit of detection) at all IR-laser energies. However, when t_p is 500ns, the populations of $v=2,3$ increase. These results indicate a marked dependence on peak power as predicted from theory. Table II summarizes the results.

(3) Whereas changes in populations produced by IR excitation are generally uniform with respect to the rotational levels for all transitions, the rotational populations of the 4_3 level show marked variation (Figure 2). This is attributed to Coriolis coupling of rotational states of b_1 symmetry to the combination band $1_1 + 3_1$. The latter has a larger anharmonicity than the v_4 mode and anharmonic bottleneck effects are expected to be more important for these levels at low peak power.

Additional studies are currently in progress to measure rotational populations of the vibrationless level with higher dye-laser resolution and to obtain vibrational populations of levels $v=6,8,10,12$ when the pulse duration is 500ns. (The frequencies of the $2_0^1 3_0^1 4_n^1$, where $n=6,8,10,12$, are known from fluorescence measurements.) These results should facilitate model calculations of the peak power dependence of IR multiphoton absorption below the quasicontinuum.

¹J. R. Lombardi, J. Chem. Phys. 52, 6126 (1970).

Figure Caption

Fig. 1 (a) Laser excitation spectrum of the $2_0^{13}3_0^{14}0^1$ band at room temperature showing the effect of IR pumping on rovibronic populations. The CO_2 laser frequency is 944 cm^{-1} ; the intensity 8 MW cm^{-2} ($t_p = 200\text{ns}$). Scan speed is $2 \text{ \AA min}^{-1}$; chart speed, 1 cm min^{-1} ; chart scale, 10 V full scale. The inserted frequency scale indicates the band origin (0.0) of the $^{35}\text{Cl}^{35}\text{Cl}$ isotope. Also noted are the RR and PP branches and the calculated positions of the rotational clusters $n=J-1/2$, $K=6.5$ and $24(19429.8 \text{ cm}^{-1})$. (b) Laser excitation spectrum of the $2_0^{13}3_0^{14}0^1$ band at a rotational temperature estimated to be $10^0\text{--}30^0 \text{ K}$ from the computer simulated spectrum of the $^{35}\text{Cl}^{35}\text{Cl}$ isotope. Comparison with (a) shows the effects of cooling and the reduced IR pumping efficiency under these conditions. Experimental conditions are the same as in (a), except the chart scale is 5V full scale in (b). Note that the three isotopic species are well separated under conditions of rotational cooling whereas at room temperature the $^{37}\text{Cl}^{37}\text{Cl}$ isotope is obscured by the rotational structure of the $^{35}\text{Cl}^{35}\text{Cl}$ isotope.

Fig. 2 (a) Laser excitation spectrum of the 4_3^0 band at room temperature. (b) Laser excitation spectrum of the 4_3^0 band perturbed by IR laser pumping ($\omega_{\text{CO}_2}=944 \text{ cm}^{-1}$; $I \sim 1.9 \text{ MW/cm}^2$, $t_p=500\text{ns}$). The dye-laser, scan drive and chart recorder conditions are the same as in Fig. 1, except the chart scale is 1V full scale. The peak labelled ($1_0^{13}3_0^{14}0^1$) is postulated as one explanation for the abnormally large IR laser-induced increase in the spectrum at $\sim 17297 \text{ cm}^{-1}$, 1419 cm^{-1} above the false origin 4_0^1 . The combination band 1_13_1 has an observed frequency of 1420 cm^{-1} .

Table I. Fundamental and overtone frequencies of the $\tilde{X}^1A_1$ state of thiophosgene taken from references 19 and 20

Mode			Frequency	Anharmonicity
a ₁	ν_1	CS stretch	1137.7	-4.0 $\pm$ 1.2
	ν_2	CCl stretch	497.0	
	ν_3	CCl ₂ bend	288.5	1.5 $\pm$ 1.1
b ₁	ν_4 : n=1	out-of-plane	471.0	-0.23 $\pm$ 0.02
	n=2		941.9	
	n=3		1412.7	
	n=4		1883.6	
b ₂	ν_5	CCl stretch	818	
	ν_6	CCl ₂ rock	288	

Table II. Changes in vibrational populations of levels of the pumped mode, $2\nu_4$. Room temperature populations are calculated from the Boltzmann relationship $n_i = \frac{N e^{-\epsilon_i/kT}}{q_v}$ where n_i is the population of molecules having energy ϵ_i , N the total number of molecules ($=1$) and $q_v = \prod_{i=1}^6 \frac{e^{-h\nu_i/2kT}}{1 - e^{-h\nu_i/kT}}$ the vibrational partition function. Populations n_i subsequent to laser pumping are calculated as $n_i' = n_i + (I/I_0 - 1)n_i = n_i + \Delta n_i$ where I is the integrated laser-induced fluorescence intensity subsequent to IR pumping, I_0 , the unperturbed intensity. For each laser intensity and level, Δ is indicated in parentheses. The experimental error, $\pm 2\sigma$, in Δ , not indicated in the table, is less than 15% determined from at least two independent measurements for each experiment.

Laser Intensity (MW/cm ²)/t _p (ns)	ωCO ₂ (cm ⁻¹)	populations						
		n ⁰ (Δ)	n ₁ (Δ) (x10 ²)	n ₂ (Δ) (x10 ³)	n ₃ (Δ) (x10 ⁴)	n ₄ (Δ) (x10 ⁵)	n ₆ (Δ) (x10 ⁷)	n ₈ (Δ) (x10 ⁹)
0		0.48	4.5	4.3	4.1	3.8	3.5	3.1
8/200	944	0.36(0.25)	3.7(0.17)	3.8(0.12)	3.4(0.18)	3.3(0.13)	3.5(<10 ⁻⁹)	3.1(<10 ⁻⁷)
4.6/200	944	0.40(0.17)	4.0(0.12)	4.0(0.08)	3.7(0.09)	3.5(0.08)	3.5(<10 ⁻⁹)	3.1(<10 ⁻⁷)
1.5/200	944	0.40(0.17)	4.5(<0.01)	4.1(0.04)	3.9(0.05)	3.7(0.03)	3.5(<10 ⁻⁹)	3.1(<10 ⁻⁷)
8/200	949	0.38(0.20)	4.3(0.05)	4.0(0.08)	3.7(0.10)	3.5(0.07)	3.5(<10 ⁻⁹)	(3.1(<10 ⁻⁷))
4.6/200	949	0.43(0.10)	4.5(0.0)	4.3(0.01)	4.1(0.0)	3.7(0.02)		
1.5/200	949	0.46(0.05)	4.5(0.0)	4.3(0.0)	4.1(0.0)	3.8(0.0)		
1.9/500	944	0.43(0.11)	4.1(0.10)	4.8(0.12)	5.1(0.25)

Fig 1a

Fig 1b

Fig 2