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COLLISIONLESS INFRARED MULTIPHOTON PRODUCTION OF ELECTRONICALLY EXCITED PARENT MOLECULES

Z. KARNY*, A. GUPTA, R.N. ZARE
Department of Chemistry, Stanford University, Stanford, California 94305, USA

and

S.T. LIN, J. NIEMAN and A.M. RONN
Chemistry Department of the City University of New York at Brooklyn College, Brooklyn, New York 11210, USA

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In the absence of collisions chromyl chloride (CrO_2Cl_2) shows orange fluorescence when the parent molecule is irradiated by the focused output (50 J/cm^2) of a pulsed TEA CO_2 laser tuned to coincide with ν_1 and/or ν_6 infrared absorption features. Time-resolved fluorescence is investigated over the pressure range 5×10^{-4} to 15 torr. As the pressure is increased, a secondary collision-induced emission component appears. We interpret the collisionless part of the emission to arise from infrared transitions between the high vibrational levels of the ground state and the low vibrational levels of an electronic state of chromyl chloride lying below the ground state dissociation limit.

1. Introduction

The first reports of infrared multiphoton dissociation of molecules also stated that this process is accompanied by visible emission [1–7]. Since then, there has been much interest in and speculation about the origin of this molecular luminescence. The early experiments [1–3] used cw CO_2 laser irradiation and are thought to have produced luminescence through simple heating of the absorbing gas. However, this mechanism cannot explain the visible emission observed in the field of a pulsed TEA CO_2 laser at a power level insufficient to cause optical breakdown [4–7]. Much of this molecular emission appears to be caused by radical recombination or by subsequent chemical reaction [8–10], although the first workers were led in many cases to believe that this emission was "instantaneous" with the laser pulse at the pressures they used.

However, in at least one instance the existence of collision-free production of an electronically excited product seems well documented. Haas and Yahav [11] studied the unimolecular decomposition of tetramethyldioxetane using a pulsed TEA CO_2 laser. On focusing the laser beam they observed a blue emission whose rise time follows very closely that of the laser pulse at pressures as low as 0.07 torr. They suggest that this luminescence is due to the formation of an acetone excimer.

We report here a study of the infrared multiphoton dissociation of chromyl chloride (CrO_2Cl_2) and the collisionless production of electronically excited CrO_2Cl_2. It appears that this is the first case in which the infrared multiphoton pumping process causes the parent molecule to be electronically excited in the absence of collisions. The rarity of electronic excitation in infrared multiphoton absorption seems to reflect the general rule that the ground state of a molecule correlates adiabatically with ground state products. However, the chromyl chloride molecule may be the first example of a class of exceptions in which a bound excited state is located below the ground state dissociation limit.

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* Present address: Nuclear Research Centre, Beer-Sheva, Israel.

Then the excited state becomes populated by infrared transitions from the high vibrational levels of the ground state.

2. Experimental

Studies of the behavior of CrO_2Cl_2 under intense irradiation by a CO_2 laser were carried out at both institutions. The Stanford CO_2 laser system (Lumonics model 801) was grating tuned. The energy of a pulse (measured by a Scientech 36-001 power meter) was 0.2 to 0.7 J depending on the line selected. The pulse shape, viewed by a pyroelectric detector (Molectron model P3.01), showed a long tail (3 μs) when the CO_2 laser operated with a $He/CO_2/N_2$ mixture but a rather sharp pulse (200 ns fwhm) without N_2.

The Brooklyn CO_2 laser was a home-built TEA laser that was also grating tuned. It provided a higher energy content per pulse. Depending upon the line selected pulse energies of 0.4 to 2.5 J were available. The pulse shape was similar to that described above having a 2 μs tail in N_2 rich mixtures and a 400 ns tail with no N_2, as measured by a HgTe–CdTe detector having a rise time of 5 ns.

Most experiments on the infrared multiphoton dissociation of chromyl chloride (Research Organic/Inorganic Chem. Corp., 99.5% purity) were carried out in static cells of various sizes (2" i.d. cylindrical cell at Stanford, 1" i.d. cylindrical cell or a 2 liter bulb at Brooklyn) having a pyrex body and salt windows. Dissociation products were detected using an infrared spectrophotometer (Perkin Elmer model 421). Some experiments were also performed using a flow system which enabled us to lower the pressure to the collision-free regime (5×10^{-4} torr). In both the static cell and the flowing system we recorded the molecular emission, its time development, its pressure dependence, and its dependence on laser power and fluence. Another cell, stainless steel body equipped with a capacitance microphone, provided opto-acoustic spectra of the CrO_2Cl_2 under intense infrared irradiation.

In the Stanford experiments the laser beam was focused by a 2" diameter, 12" focal length BaF_2 lens. The molecular emission was observed at right angles to the laser beam. A resolved spectrum of the emission was obtained with a 1 m monochromator (SPEX model 1704) using gated detection electronic (PAR model 162 boxcar integrator). In the Brooklyn experiments the laser beam was focused by a 1" diameter, 5" focal length ZnSe lens or a 2" diameter, 10" focal length Ge lens and the molecular emission was observed perpendicular to the laser axis by a 1/2 m spectrometer (Jarrell–Ash) equipped with an RCA C31034 photomultiplier. Infrared emission was also recorded at right angles to the laser axis, viewed through a silicon and sapphire window combination by an InSb (Spectronics) photovoltaic detector.

3. Results

Chromyl chloride has two strong absorption bands in the 10 μ region (fig. 1), one assigned to the $\nu_6(B_1)$ asymmetric Cr–O stretch at 1000 cm^{-1}, the other to the $\nu_1(A_1)$ symmetric Cr–O stretch at 990 cm^{-1} [12]. The high R-branch transitions of the CO_2 10.6 μ band coincide with both bands. Conventional absorption experiments at three different laser fluences yield an apparent absorption coefficient of about 0.0074 cm^{-1}

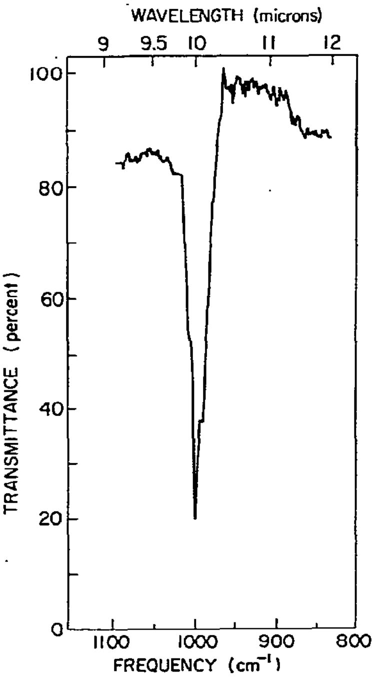

Fig. 1. The infrared absorption spectrum of CrO_2Cl_2 (5 torr).

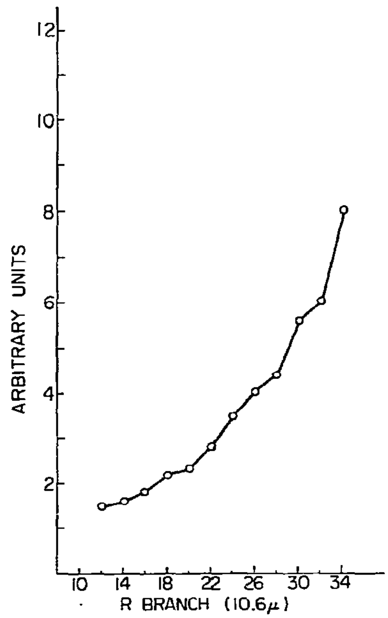

Fig. 2. The opto-acoustic signal from CrO_2Cl_2 when irradiated by various CO_2 laser R-branch lines (10.6 μ) using an unfocused beam.

torr^{-1} for the R(30) line. Opto-acoustic measurements show residual nonresonant absorption across the entire R branch of the CO_2 10.6 μ band (fig. 2). No signal could be detected when chromyl chloride is irradiated using P-branch transitions of the 10.6 μ band or the transitions of the 9.6 μ band.

The multiphoton absorption causes the appearance of both visible emission and the subsequent formation of "brown smoke" which was identified to be CrO_2. When H_2 was added to the irradiated mixture, the characteristic infrared absorption of HCl was observed. The hydrogen chloride was observed to emit in the infrared region as well.

We propose that the multiphoton dissociation process is the sequential removal of Cl atoms as depicted below:

$$\begin{tikzcd}
CrO_2Cl_2 + nh\nu \arrow[r] \arrow[dr] & CrO_2Cl_2^* \arrow[d, "nh\nu?"] \\
 & CrO_2Cl + Cl \arrow[d, "nh\nu"] \\
 & CrO_2 + Cl
\end{tikzcd}$$

3.1. The visible luminescence

Fig. 3 presents a spectrum of the molecular luminescence when chromyl chloride is irradiated by the focused output of the CO_2 laser; when the output is unfocused, no emission is observed. By comparing fig. 3 to previously published spectra of $CrO_2Cl_2^*$ in a matrix [13], we identify the emission as that of the electronically excited parent molecule. The nature of the electronic transition responsible for the CrO_2Cl_2 emission is not clear. Molecular orbital calculations show that there are at least three singlet–singlet transitions occurring in this general energy region [14,15] and this result is in agreement with photoelectron spectroscopy [15] and with absorption and fluorescence spectroscopy studies [13,16–18].

The CrO_2Cl_2 molecule has C_{2v} symmetry but it is nearly tetrahedral. This causes the t orbital to split into three nearly degenerate orbitals, $2a_2, 4b_2$, and $4b_1$. All three of these orbitals are nonbonding in character. The lowest-lying unfilled orbital is $7a_1^*$, which is mainly a chromium $d\pi^*$ orbital and is strongly Cr–Cl antibonding. The visible absorption and fluorescence spectrum of CrO_2Cl_2 is thought to result from the $(2a_2, 4b_1, 4b_2) \leftrightarrow 7a_1^*$ transitions. The origin of the first excited state is near 17200 cm^{-1}, which requires the absorption of about 18 infrared photons (975 cm^{-1}) to reach this level.

The energy required to rupture the CrO_2Cl–Cl bond is estimated to be 83 kcal/mole from mass spectrometric studies [19] and 68 kcal/mole from the appearance of photodecomposition products [20]. In either case, the dissociation limit exceeds the origin of the first excited electronic state by 19–34 kcal/mole, indicating that this electronically excited state of CrO_2Cl_2 is located substantially below the dissociation limit of the ground state.

In the past the CrO_2Cl_2 $7a_1^*$ excited state has been

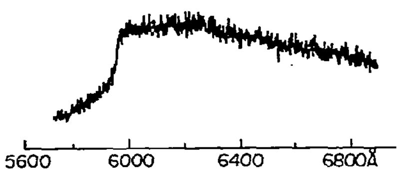

Fig. 3. Molecular luminescent spectrum following irradiation of CrO_2Cl_2 by a CO_2 laser.

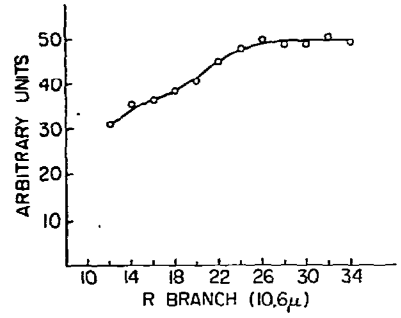

Fig. 4. Plot of the total luminescent intensity versus CO_2 laser R-branch lines (10.6 μ).

claimed to be predissociated [13,16–18] because the emission breaks off near the electronic origin, although Halonbrenner et al. [20] found that irradiation at these wavelengths caused no photodecomposition. However, the disappearance of the emission in itself does not show that dissociation is responsible. An alternative explanation would be that the excited molecule undergoes the radiationless process of internal conversion. Semiclassical calculations show that the density of ground state vibrational levels at the origin of the first excited state is about 3×10^6 per cm^{-1} [21]. We believed at first that cross over from the high vibrational levels of the CrO_2Cl_2 ground state to the low vibrational levels of $7a_1^*$ might have been responsible for populating this excited state by a process that might be called reverse internal conversion. However, because the energy level density of $7a_1^*$ compared to that of the ground state at the same energy is so sparse, we are forced to abandon this hypothesis in favor of direct infrared transitions.

We present in fig. 4 a plot of the luminescent intensity versus laser wavelength, normalized to constant laser power. Comparison of fig. 4 with fig. 2 shows that the opto-acoustic signal falls much more rapidly than the luminescent signal with increasing laser wavelength. The opto-acoustic signal measures energy deposition while the luminescent signal is a measure of only those molecules having enough energy to reach the luminescent state. There is no reason to expect that the wavelength dependence of these two signals is the same. As the laser output is focused more tightly, the opto-acoustic signal becomes smoother. We interpret this to mean that nonlinear absorption is only a small fraction of the total absorption when using an unfocussed beam.

The luminescent intensity appears to vary linearly with the laser power (0.2–1.1 J/p). At higher laser fluences, one might promote dissociation in CrO_2Cl_2. In the Brooklyn experiments it was observed that a tightly focused 1 to 1.5 J pulse will broaden the fluorescence spectrum shown in fig. 3 to 3400 Å. Based on the work of Halonbrenner et al. [20] it might be speculated that emission from CrO_2Cl and CrO_2 contribute to the observed spectra.

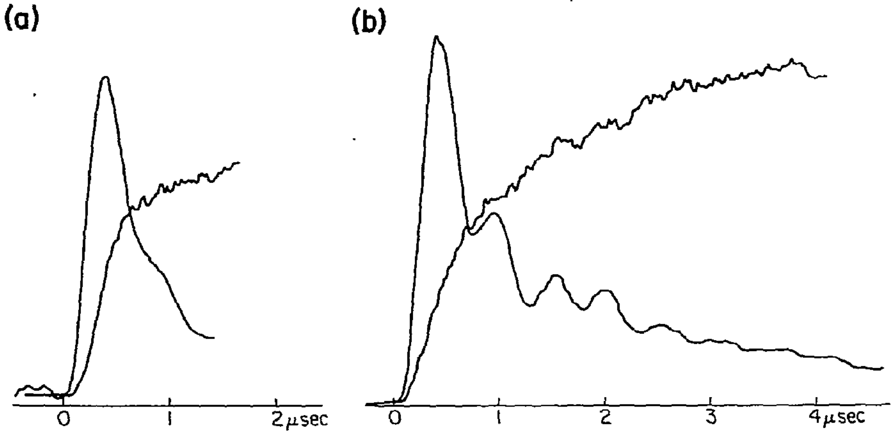

Fig. 5. The rise time of the luminescent signal versus the CO_2 laser pulse shape for (a) short and (b) long pulse durations. The CrO_2Cl_2 pressure is 1×10^{-3} torr.

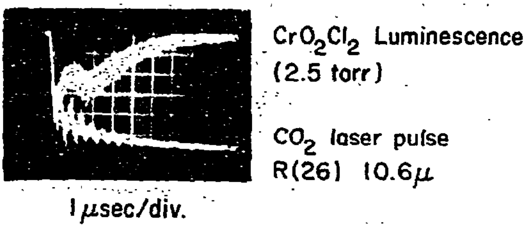

Fig. 6. The molecular luminescence showing collisionless as well as as collisional components. For comparison purposes the CO_2 laser pulse is also displayed.

3.2. Time behavior

The time evolution of the luminescent signal was studied at different pressures of CrO_2Cl_2 and for different laser pulse shapes. Fig. 5 shows the luminescent response plotted together with the laser pulse for short and long laser pulses, respectively. In both cases, there is a rapid rise of the molecular emission which ends after the initial laser spike. Thereafter a slower rise occurs followed by a decline in the signal intensity.

The initial rise time of the molecular luminescence is independent of pressure (5×10^{-4} to 1 torr) and shows no change when the laser power is attenuated by a factor of two. The fall time of the molecular luminescence is pressure dependent. At very low pressures the falloff stretches to 60 μs, while at pressures around 2 torr the falloff occurs at the end of the laser pulse. We conclude that the cross section for quenching $CrO_2Cl_2^*$ emission is quite large. Under certain pressure conditions it is possible to observe clearly both a collisional and a collisionless component to the molecular emission (fig. 6).

A study was made whether the molecular luminescence was delayed in time with respect to the laser pulse. However, when the different response times of the two types of detectors are taken into account, we conclude that the molecular luminescence is prompt within our experimental timing uncertainty (50 ns).

3.3. Infrared emission

No emission was expected nor observed with the InSb detector in pure CrO_2Cl_2 at 40–2000 mtorr over the wavelength range of 1–6 μ. Emission from the overtones of ν_1 and/or ν_6 are very weak. In chromyl chloride–hydrogen mixtures (2 torr CrO_2Cl_2, 2–6 torr H_2), however, an emission was observed. Unlike the visible emission the infrared signal has a longer rise time than the laser pulse. Its fall time is quite long and the wavelength is characterised to lie between 1 and 3.5 μ, using cutoff filters. The longer rise time indicates emission from the reaction products and the failure of a 100 torr HCl cold filter to attenuate the emission indicates little or no emission from HCl in the $v = 1$ state. However, a heated water vapor filter is found to attenuate the signal by 40%. The infrared emitters present in the reaction mixture are presently unknown, but may be vibrationally excited HCl [22], H_2O, as well as hydrated species.

3.4. Dielectric breakdown experiments

A tightly focused laser beam when impinging upon a 1 : 3 mixture of CrO_2Cl_2 and H_2 at a total pressure of 30 torr will initiate a chain, or branched chain reaction accompanied by an intense burst of light (fig. 7). A single laser pulse will induce a complete conversion of the red CrO_2Cl_2 gas into a green powder, identified as Cr_2O_3 which adheres to the cell walls. Irradiation of the same mixture but at lower pressure (1–2 torr) yields only CrO_2 and HCl.

This colorful chemical transformation corresponds to the chromium atom being reduced from a valence state of 6 to 3 via laser-induced dielectric breakdown (LIDB) [23]. The mechanism responsible for this collisionally controlled high pressure chain reaction is not fully understood presently but is thought to closely parallel other LIDB studies currently in progress [24].

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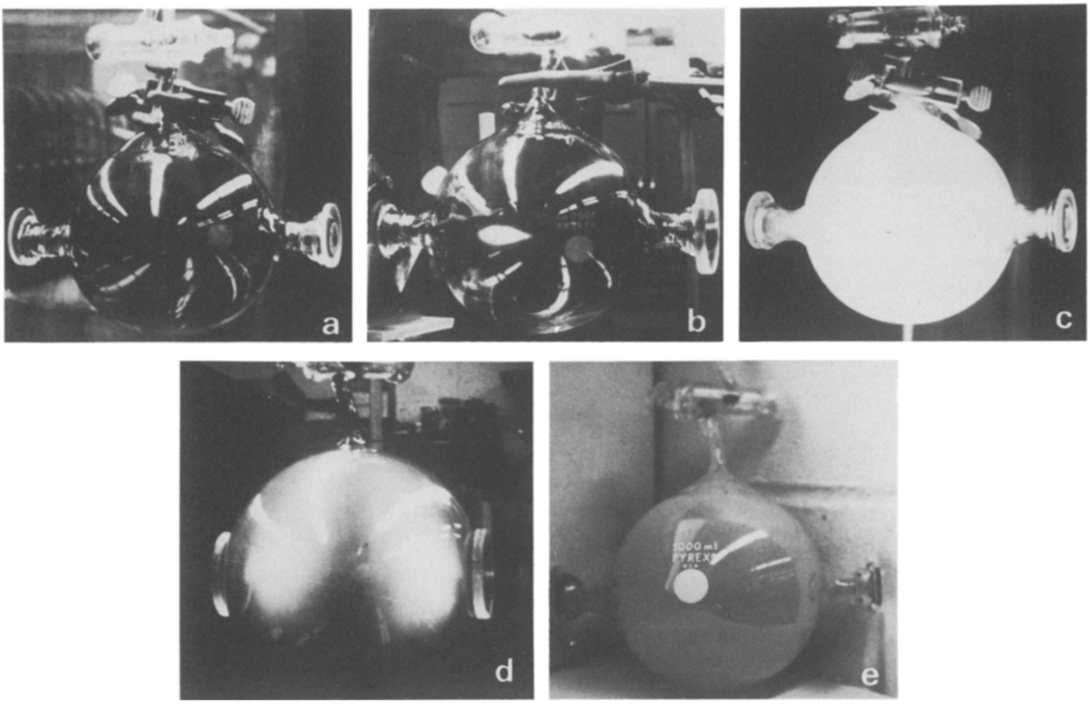

Fig. 7. Laser-induced dielectric breakdown in a 1 : 3 mixture of CrO_2Cl_2 to H_2 (30 torr total pressure). The sequence of snapshots (a) through (e) shows the development of this laser-initiated chain reaction causing CrO_2Cl_2 to be reduced to Cr_2O_3.

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