Collision-Induced Electronic Relaxation of Thiophosgene (S₁)

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Fluorescence from the electronically excited thiophosgene (Cl₂CS) in its first excited singlet state (S₁) is efficiently quenched by collision. Rates of the collision-induced electronic relaxation were obtained for various vibrational levels in the S₁ state by measuring the fluorescence lifetimes. We found that the relaxation process is strongly energy-dependent; the rate consistently increases by a factor of ~40 with the increase of vibrational energy from 0 to 1450 cm⁻¹. Collision-induced intersystem crossing from the S₁ to the first triplet state (T₁) is attributed to the major process responsible for the electronic relaxation.

Introduction

Collision-induced nonradiative relaxation of electronically excited molecules is unique of various collisional processes in the sense that the process transforms an electronic energy into vibrational energy. It plays an important role in combustion or photochemical reactions where significant amount of electronically excited species are formed and involved in the reactions.[1,2] Despite its importance it has been slow to understand the process since the final states reached through the nonradiative decay are highly vibrationally excited levels which are extremely difficult to characterize even with the state-of-the-art lasers and molecular beam technique. In order to better understand the process, more information on the dependence on nature of the initial vibronic states, collision partners, and the distribution of final states, should be accumulated.

Thiophosgene (Cl₂CS) is one of a few favorable molecules which allow such state-resolved investigation into the inter- and intramolecular nonradiative processes owing to its extraordinary photochemistry and well-established spectroscopy. Since fluorescence from both the S₁(Ã¹A₂) and S₂(B̃¹A₁) states observed two decades ago,[3,4] plenty of information on its gas- and liquid-phase photochemistry[5,6] and photophysics[7~10] has been stockpiled. The molecule has been characterized spectroscopically by electron diffraction and microwave studies of its S₀(X̃¹A₁) state.[11] Analyses of the optical absorption and laser-induced fluorescence spectra have provided the band assignments, location of electronic origins, geometries, and vibrational frequencies of the T₁(ã³A₂),[12,13] S₁,[14] and S₂ states.[4,7,8,15,16] Fluorescence from the singlet excited states renders laser-induced fluorescence (LIF) a sensitive diagnostic tool for the photophysical processes.

The first singlet excited state (S₁) of thiophosgene, which corresponds to the (nπ*) configuration, is located 18716 cm⁻¹ above the ground state zero-point level,[14] and the first triplet state (T₁) is at 1224 cm⁻¹ below the S₁ origin.[13]

In this work we have measured the collisional relaxation rate of thiophosgene molecules prepared in the single vibronic levels in its S₁ state. The decay rates show strong dependence upon the vibrational energy of the levels. The origin of the decay process is ascribed to collision-induced intersystem crossing comparing the observed vibrational energy dependence with the theoretical model for non-radiative decay proposed by Freed[17] and Bixon and Jortner.[18]

Experimental

The schematic of the experimental setup employed in this work is shown in Figure 1.

The laser source for excitation of thiophosgene consists of a pulsed dye laser (Lambda Physik SCANmate 2E) pumped with a Q-switched Nd : YAG laser (Spectra-Physics GCR-150-10). Two dyes, Coumarin 500 and Coumarin 540A, were used to cover the spectral region of 490-556 nm with a typical output energy of 1.0 mJ/pulse and bandwidth of 0.15 cm⁻¹. A linear Pyrex cell, 25 cm long and 1 inch in diameter, equipped with quartz windows on both sides, and painted black on the exterior, was used for the fluorescence excitation spectroscopy and fluorescence lifetime measurement. At the center of the cell a viewport with a quartz window was attached to detect the fluorescence from the excited thiophosgene.
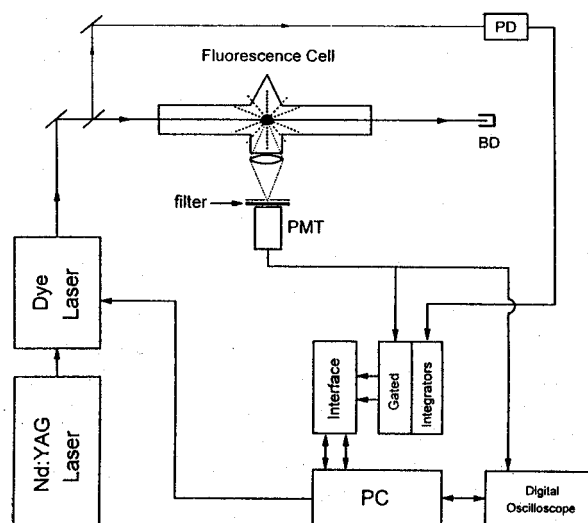

Figure 1. Schematic of the experimental apparatus. PD: photodiode, PMT: photomultiplier tube, PC: personal computer, BD: beam dump.

The unfocused output of the dye laser, tuned to excite vibronic bands of the $S_1(\tilde{A}^1A_2)\leftarrow S_0(\tilde{X}^1A_1)$ was sent through the cell at room temperature. The fluorescence was collected with a 2″ dia. quartz lens, filtered from the scattered excitation light with two glass filters (Schott RG 610 and OG 570) and a narrow slit, and then detected with a photomultiplier tube (PMT : Hammatsu R928). In the fluorescence excitation spectroscopy, the PMT output was integrated in a gated integrator (SR 250) and stored in a personal computer (PC) with the laser wavelength. A small portion of the excitation laser beam was split in front of the cell with a quartz plate and detected with a photodiode to monitor the laser intensity fluctuation. The PMT output signal was sent to a 300 MHz digital oscilloscope (LeCroy 9450A) to obtain the time evolution. Each decay curve was digitized and averaged for 500 decay profiles in the oscilloscope, and stored in a PC for further analyses. The fluorescence lifetimes were determined by fitting the decay profiles to a single exponential function with a commercial least-square regression routine. This detection system allows accurate measurement of lifetime as short as about 7-8ns with the time resolution being limited mostly by the 5-6ns duration of the excitation laser pulse.

The fluorescence excitation spectrum of thiophosgene in a collisionless condition was obtained with an unskimmed pulsed jet expansion system. A detailed description of the system is provided elsewhere.[19] In brief, the premixture of thiophosgene in He was expanded into a vacuum chamber through a pulsed valve with a 0.5 mm nozzle diameter and the laser beam crossed 25 mm downstream from the nozzle. The fluorescence from the excited molecules was detected and processed in the same manner as in the cell experiment at room temperature.

The thiophosgene sample was used as obtained from the Aldrich Chemical Co.

Results

Figure 2 shows a portion of two fluorescence excitation spectra for the $(\tilde{A}\leftarrow\tilde{X})$ transition of thiophosgene obtained in two different conditions, in a static cell at room temperature and in a supersonic jet expansion. It is easily noticeable that the band intensity of the spectrum in a collisional condition in a static cell significantly declines with increasing vibrational energy compared with that in a collisionless condition. This observation indicates that the Cl_2CS molecules excited to the higher vibrational levels of the S_1 are quenched by collision more efficiently than those in the lower levels, which invoked us to endeavor a more quantitative measurement on the energy dependence.

The fluorescence lifetimes of various vibrational levels of the S_1 state were measured at the sample pressure of 0.8 Torr up to 1500 cm^{-1} of vibrational energy. Although the fluorescence from the S_1 state decays biexponentially in the collisionless condition,[20] all of the decay curves obtained in this work were well fit to single exponential functions. (see Figure 3) The lifetimes obtained in the fitting are listed in Table 1 with the level assignments and corresponding vibrational energies. The fast component of the fluorescence decay of thiophosgene in the collisionless condition have lifetimes longer than 10 μsec for the levels investigated in this work.[20]
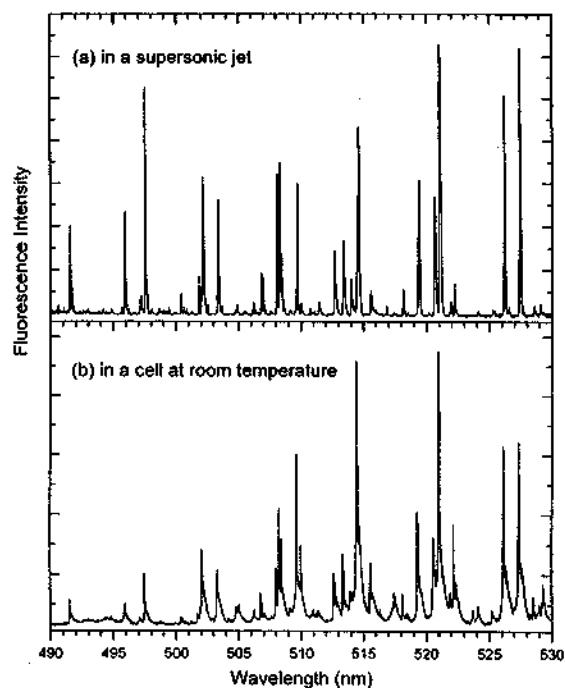

Figure 2. A portion of fluorescence excitation spectra of thiophosgene (Cl_2CS) obtained in (a) collisionless and (b) collisional conditions. It is easily noticeable that the band intensity of the spectrum in a cell at room temperature significantly decreases with increasing vibrational energy.
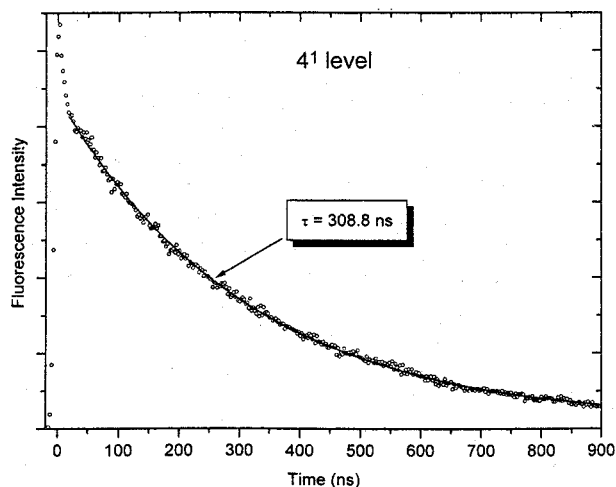

Figure 3. Fluorescence decay trace of the 4^1 level at 0.8 Torr. The trace was fit to a single exponential decay with a lifetime of 308.8ns. The spike around t=0 is from the scattered light of the excitation pulse.

Since the observed decay rates are >50 times more rapid than those in the zero-pressure limit, the contribution of intramolecular relaxation and radiative processes to the observed decay rate is negligible. Hence the inverse of the fluorescence lifetimes (τ) gives the collisional relaxation rates of those vibronic levels excited by the laser, from which the rate constants (k_{relax}) for the collision-induced relaxation process are deduced. The rate constants are also listed in

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Table 1. Fluorescence Lifetimes and Collisional Relaxation Rate Constant

Vibrational energy	Assignment	τ(ns)	k_{relax} $(1/\tau,$ cm^{3}s$^{-1})$
0.0	0^0	313.6	1.23×10^{-10}
0.4	4^1	308.9	1.25×10^{-10}
245.0	3^1	142.7	2.71×10^{-10}
245.4	3^14^{1a}	133.7	2.89×10^{-10}
245.4	3^14^{1b}	137.4	2.81×10^{-10}
279.6	4^2	139.2	2.77×10^{-10}
292.5	4^3	137.5	2.81×10^{-10}
447	4^4	101.7	3.79×10^{-10}
480.4	2^14^1	90.9	4.25×10^{-10}
490.4	3^24^1	69.0	5.60×10^{-10}
537.5	3^14^3	56.6	6.83×10^{-10}
725	4^36^{2b} $2^13^14^{1b}$	50.8	7.60×10^{-10}
907.9	1^14^1	45.0	8.57×10^{-10}
970.0	$2^13^24^1$	29.2	1.32×10^{-9}
1152.4	$1^13^14^1$	15.6	2.47×10^{-9}
1204.2	1^14^3	18.9	2.29×10^{-9}
1387.3	$1^12^14^1$	19.5	2.04×10^{-9}
1451.5	$1^13^14^3$	~7	~5.52×10^{-9}

$_a$The same level was reached via two different transitions. ^{b}The two bands are overlapped.

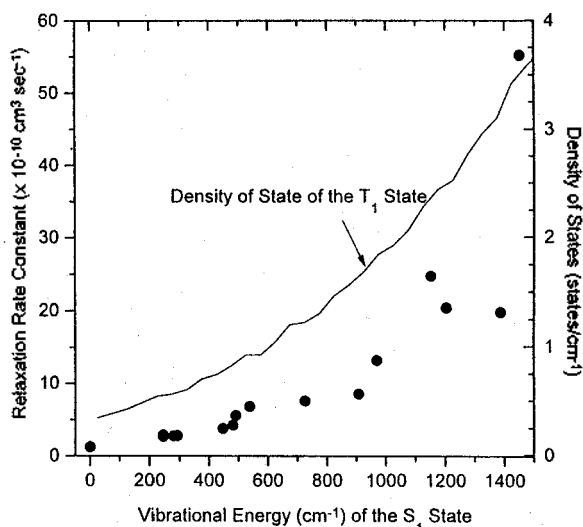**Figure 4.** Collisional relaxation rate constants and density of state of the T₁ state as a function of the vibrational energy of Cl₂CS(S₁). Note the pertinent ordinates to the rate constant and the density.
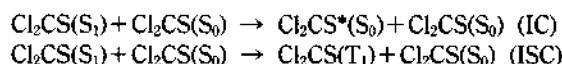
the last column of Table 1 and graphically shown in Figure 4. The rate constant consistently increases from 1.23×10^{-10} cm^3 sec^{-1} for the electronic origin and to 5.52×10^{-9} cm^3 sec^{-1} for the $1^13^14^3$ level even though there exists some fluctuation.

This observation is in sharp contrast to the previous report by McDonald and Brus,[3] which shows a slight decrease of the rate with energy. This discrepancy is supposed to arise from the 200-500ns long pulse duration of the laser that

McDonald and Brus utilized in their work.[3] With such a long pulse laser it might not be possible to accurately determine the lifetimes shorter than 1 μs. Furthermore the spectral bandwidth of their excitation laser was as wide as 2-6 Å which prevented from exciting a single vibronic level.

Discussion

The experimental results suggest that collision opens (an) additional nonradiative decay channel(s) to the excited Cl₂CS (S₁). The feasible candidates for the collision-induced processes are the internal conversion (IC) to the S₀ state and intersystem crossing (ISC) to the T₁ state as shown below.

$$Cl_2CS(S_1)+Cl_2CS(S_0) \rightarrow Cl_2CS^*(S_0)+Cl_2CS(S_0) \text{ (IC)}$$
$$Cl_2CS(S_1)+Cl_2CS(S_0) \rightarrow Cl_2CS(T_1)+Cl_2CS(S_0) \text{ (ISC)}$$

where * symbol represents that the molecule is vibrationally hot. Collisionally induced predissociation is excluded here since the threshold for predissociation is known to be located at ~3400 cm^{-1} above the origin of the S₁ state.

Bixon and Jortner[18] and Freed[17] have proposed that the rate constant for nonradiative relaxation processes is given by Eq. (1) in the statistical limit where the condition of $v\rho \gg 1$ is satisfied.
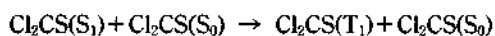
$$k_{nr}=\frac{4\pi^2}{h}\ v^2\ \rho \tag{1}$$

where ρ is the density of the state of the final state and v is the nonadiabatic coupling matrix element. The internal conversion of the Cl₂CS(S₁) to the S₀ state may be regarded as the limiting case since the state density[21] of the S₀ is ~2000/cm^{-1} in the energy range studied in the present work, and the rate is not enhanced by collisions. The density[21] of the triplet state is only 0.3-3/cm^{-1} in the same energy range, which may be regarded as an 'intermediate' case in the collisionless condition. In the cases where collisions exist, however, the collisional broadening of vibronic levels converts the intermediate case to the statistical limit as proposed by Freed. In such cases collisions significantly enhance the nonradiative decay rate.

According to Eq. (1), the rate constant of nonradiative decay is proportional to the density of state of the final state assuming the coupling matrix element v does not vary significantly in the statistical limit. The ρ of the S₀ state is ~1500 /cm^{-1} at the origin of the S₁ and slowly increases to ~2200 /cm^{-1} with vibrational energy up to 1450 cm^{-1} in the S₁. If internal conversion is the major channel for the collisional relaxation, the ratio of the rate constants for the lowest and highest energy levels would be ~1.5, which is much smaller than the observed value, ~40. Furthermore the observed decay rate is strongly collision-dependent in sharp contrast to the prediction that the rate should be independent of pressure since the internal conversion to the S₀ corresponds to the statistical limit even in collisionless environments. Hence the collision-induced IC drops off from the possible candidate.

Intersystem crossing is the only feasible process left. The ISC to the T₁ state may be enhanced by collisions as stated above, in agreement with our observation. A solid evidence supporting the ISC as the major decay channel comes from comparison of the energy dependence of the T₁ state density

with the measured rate constants, which is shown in Figure 4. The density of the triplet state shows an increase by a factor of ~10 for the same energy range, which is much closer to the observed value than the IC. More importantly the triplet state density keeps track of the overall trend of the rate constant variation with energy. These agreements lead us to the conclusion that the major channel for the collisional relaxation of the S_1 state is the intersystem crossing to the T_1 and the contribution of internal conversion is negligible or minor if any.

Now that the excited Cl_2CS in its S_1 state are confirmed to collisionally relax to the T_1 state, the fate of the Cl_2CS molecules in the T_1 state should be established to complete the electronic relaxation mechanism. A conceivable process is the radiative decay to the S_0 state, *i.e.*, phosphorescence. However, the lack of phosphorescence[13,22] following the excitation to the S_1 state in the gas phase eliminates the radiative decay of the thiophosgene molecules relaxed to the T_1 state. In addition, the molecules excited directly to the T_1 state exhibit no emission[23] even though the oscillator strength of the T_1-S_0 transition is as large as an 1/6 of that for the S_1-S_0 transition.[12] These results unambiguously support that the T_1 state decays through an intramolecular radiationless process which should be the intersystem crossing to the S_0. The decay path of Cl_2CS excited to the S_1 state in the collisional condition may be summarized as follows.

$Cl_2CS(S_1) + Cl_2CS(S_0) \rightarrow Cl_2CS(T_1) + Cl_2CS(S_0)$
(collision-induced ISC)
$Cl_2CS(T_1) \rightarrow Cl_2CS^*(S_0)$ (intramolecular ISC)

Although our attention has been paid only for the electronic relaxation, collision may also cause vibrational relaxation in the same electronic manifold when the vibrationally excited levels of $Cl_2CS(S_1)$ are accessed. If the vibrational relaxation occurs at a comparable or higher rate to the electronic decay, the time evolution of fluorescence would not follow the single-exponential function, and the measured lifetimes appear longer than the true values since the relaxation populates lower vibrational levels which have longer fluorescence lifetimes. In the present work, however, the vibrational relaxation turned out to be insignificant. Several fluorescence decay curves for levels with vibrational energies >1000 cm^{-1} have shown some deviation from the single-exponential function but the extent was trivial. This result is consistent with the previous observation that the emission spectrum of the $Cl_2CS(S_1)$ is insensitive to the pressure of the sample.[22,24] Thus it is obvious that collision mostly brings about the electronic relaxation to the $Cl_2CS(S_1)$ rather than the vibrational energy transfer.

Mode or state specificity has been a controversial topic in many aspects of chemical kinetics and dynamics.[25] The question lying in collisional relaxation processes is whether the rate constants are a simple function of energy or depend upon the identities of the initial states. Let us address the problem for the collision-induced relaxation rate constants of $Cl_2CS(S_1)$ here. The rates shown in Figure 4 and Table 1, do not increase smoothly with energy but exhibit some fluctuation. The most noticeable example is the $1^1 2^1 4^1$ and $1^1 3^1 4^3$ levels. Those are only 64.2 cm^{-1} apart but the rates differ by almost a factor of 3. Although it may not be possible

to offer a quantitative analysis, a qualitative explanation can be provided for the difference for these two levels; since both the S_1 and T_1 states have a non-planar geometry, excitation of the v_4 (out-of-plane bend) mode would increase the coupling between the initial S_1 level and the final T_1 ones, resulting in significant increase of the relaxation rate. Therefore the levels with higher excitation in the v_4 mode may decay more rapidly than others as one can see for the $1^1 2^1 4^1$ and $1^1 3^1 4^3$ levels. The $1^1 4^3$ level is also a good example for the argument. It has 183.1 cm^{-1} less energy than the $1^1 2^1 4^1$ level but show a comparable lifetime. In order to better understand the state specificity pertinent to the collisional relaxation of Cl_2CS, more extensive experimental data and theoretical calculations may be required.

It is worth of consideration that the collision-induced ISC is highly efficient for $Cl_2CS(S_1)$. For example, the quenching rate constant of the electronic origin is 1.23×10^{-10} cm^{3}s^{-1}. This value corresponds to the cross section of 37.5 Å^2, which is 1.3 times larger than the hard sphere cross section.[26] At higher energies the efficiency becomes even higher. Such a large cross section is common for self-quenching and originates from the resonant energy transfer between two equivalent molecules. Heavy atoms in the thiophosgene molecule may contribute further to the high efficiency through the external heavy atom effect. Nearly the same quenching efficiency has been observed for glyoxal in which the additional interaction is provided by hydrogen-bonding forces.[27]

Conclusion

Fluorescence from the $Cl_2CS(S_1)$ is efficiently quenched by collision. The collision-induced electronic relaxation rates have been measured for various vibrational levels from the fluorescence lifetimes. The relaxation process strongly depends on the energy and identity of the vibrational levels where the molecules are populated. The rate consistently increases by a factor of ~40 with the increase of vibrational energy from 0 to 1450 cm^{-1} and the levels with higher excitation in the v_4 (out-of-plane bend) mode decay more rapidly. Collision induces intersystem crossing from the S_1 to the first triplet state (T_1) and to consequently quench the fluorescence from the S_1 state. The observed vibrational energy dependence is likely from the increase of the density of vibrational levels in the triplet manifold. The Cl_2CS molecules relaxed to the T_1 state seem to decay to the ground state via intramolecular intersystem crossing.

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Analysis of Rotationally Cooled Vibronic Emission Spectra (1²A₂→1²B₂) of m-Xylyl Radical

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The rotationally cooled but electronically excited m-xylyl radical has been generated in a jet from the gas mixture of precursor m-xylene and buffer gas He by a technique of corona excited supersonic expansion. The visible vibronic emission spectra in the transition of $1^2A_2 \rightarrow 1^2B_2$ of m-xylyl radical in the gas phase have been recorded using a Fourier transform spectrometer. The spectra have been analyzed for the assignments of the vibrational frequencies in the electronic ground state with combination of the torsional frequencies reported previously.

Introduction

The vibronic structure and spectra of benzyl and three isomeric xylyl radicals have long been of interest to spectroscopists. They have been studied by a variety of techniques.[1] Substitution of a methyl group for a hydrogen in an aromatic compounds is supposed to have least perturbation on the aromatic ring. However, in the xylyl radicals, it is likely to have more significant effects. The small splitting between the A and B electronic states may be largely altered as well as the shift in the torsional and vibrational frequencies of the xylyl radicals. The information about the internal dyna-

mics of methyl groups may be provided by spectroscopic experiments at higher frequencies, in the visible and ultraviolet regions of the electromagnetic spectrum.[2,3] This is because the properties of the potential energy surface along the methyl group torsional coordinate often change upon electronic excitation. A vibrationally resolved electronic spectrum may provide information about the difference in the barrier shape, height, or even conformational preference.

The xylyl radicals have been studied by numerous experimental and theoretical works. Most of earlier works on the xylyl radicals were limited to low resolution vibronic studies in either the gas phase[4] or the solid phase.[5,6] The earlier