THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 107, NUMBER 48, DECEMBER 4, 2003

LETTERS

Thiophosgene, A Molecule Tailor-Made for Testing Fundamental Theoretical Concepts of Radiationless Transitions: Intramolecular Dynamics of S_1 Cl_2CS

Takashige Fujiwara,[†] **David C. Moule,**[‡] **and Edward C. Lim***[,†,§]

Department of Chemistry and The Center for Laser and Optical Spectroscopy, The University of Akron,
Akron, Ohio 44325-3601, and Department of Chemistry, Brock University, St. Catharines,
Ontario L2S 3A1, Canada

Received: July 29, 2003; In Final Form: September 26, 2003

The collision-free $S_1[\tilde{A}^1A_2(n\pi^*)]$ thiophosgene, with small ($<$3484 cm^{-1}) and large ($>$9284 cm^{-1}) excess vibrational energies, does not exhibit radiationless transitions to bound electronic states (S_0 and T_1), as evidenced by intense $\tilde{A} \rightarrow \tilde{X}$ fluorescence with nearly constant lifetimes. The lack of radiationless transitions can be traced to the absence of the promoting mode for the $^1A_2 \rightarrow {}^1A_1$ internal conversion and the vanishingly small spin−orbit coupling and very small Franck−Condon factor for the $^1A_2(n\pi^*) \rightarrow {}^3A_2(n\pi^*)$ intersystem crossing. In the intermediate range of excess energies (3484−9284 cm^{-1}), fluorescence is not observed, consistent with the occurrence of predissociation. Quantum beat-modulated fluorescence decays, attributable to $^1A_2(n\pi^*)-{}^3A_1(\pi\pi^*)$ perturbations, have been observed for excitation of $1^12^13^14^1$ and nearby S_1 vibronic levels. This places the $\tilde{b}^3A_1(\pi\pi^*)$ state at about 20 350 cm^{-1} above the ground electronic state, in excellent agreement with the existing estimate. Interestingly, the S_1 radiative lifetime is about an order of magnitude shorter in a supersonic jet as compared to the vapor phase at room temperature, indicating that the probability of the vibronically induced $\tilde{A}^1A_2(n\pi^*)-\tilde{X}^1A_1$ radiative transition is significantly reduced at higher temperatures, due probably to Coriolis coupling.

Introduction

A central concept in the theory of electronic radiationless transitions[1] is the classification of molecular vibrations into “promoting” and “accepting” modes.[2] The promoting mode renders the electronic matrix elements finite, whereas the accepting mode provides the Franck−Condon factor for radiationless transitions. For internal conversion between the initial electronic state (ψ_i) and the final electronic state (ψ_f), the vibrational symmetry of the requisite promoting mode (Q_p) is determined by the condition that the direct product $\Gamma(\psi_f) \otimes \Gamma(Q_P) \otimes \Gamma(\psi)$ contains the totally symmetric irreducible representation of the point group.

A molecule tailor-made for testing the fundamental theoretical concepts of electronic radiationless transitions is thiophosgene, Cl_2CS, which is vibrationally deficient[3] due to the lack of a normal mode vibration of a_2 symmetry (the internal motion of a_2 symmetry is a rotation about the C═S bond axis). The first and second excited singlet states of thiophosgene are, respectively, an nπ^* state of A_2 symmetry and a $\pi\pi^*$ state of A_1 symmetry.[4] The $\tilde{A}^1A_2(n\pi^*)$ state, located at 18 716 cm^{-1} in the gas phase,[5] lies approximately halfway between the $\tilde{B}^1A_1(\pi\pi^*)$ state at 34 278 cm^{-1} and the $\tilde{X}^1A_1$ ground state (Figure 1). Consistent with the symmetry forbiddeness of the $\tilde{B}^1A_1 \rightarrow \tilde{A}^1A_2$

---

* Corresponding author. Fax: 330-972-6407. E-mail address: elim@uakron.edu.

[†] The University of Akron.

[‡] Brock University.

[§] Holder of the Goodyear Chair in Chemistry at The University of Akron.

10.1021/jp0309264 CCC: $25.00

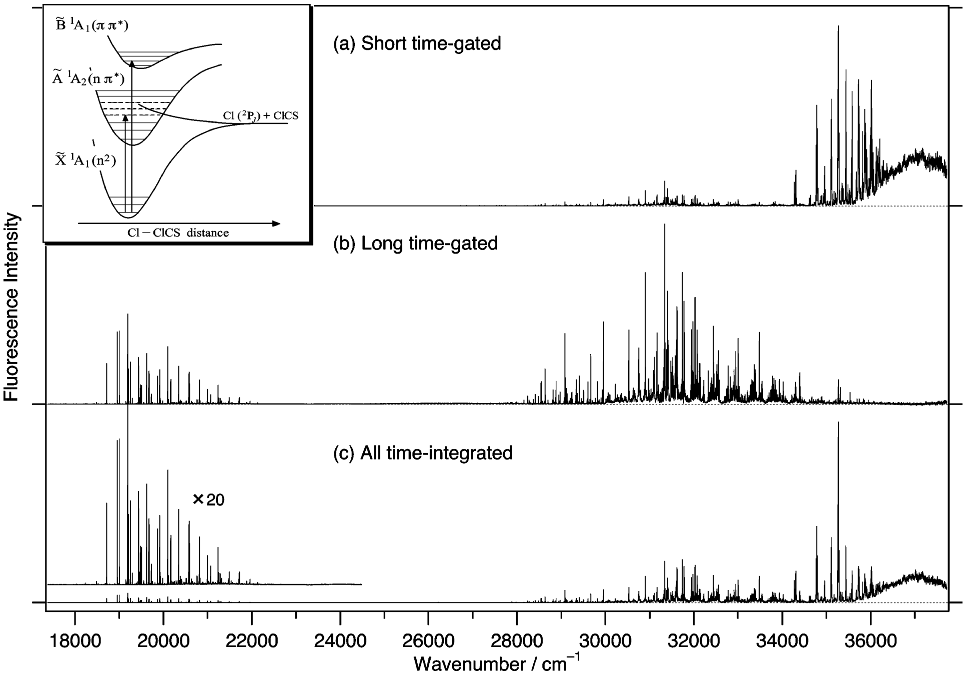

Figure 1. Time-resolved $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ fluorescence excitation spectra of jet-cooled thiophosgene in the energy range 17 700−37 700 cm^{-1}, recorded with different time-gate arrangements: (a) first 20 ns, (b) starting at 140 ns with a 300 ns width; (c) all time-integrated. Total emissions were monitored and normalized to input laser powers. The broad unstructured feature at about 37 000 cm^{-1} is believed to be the $\tilde{B} \leftarrow \tilde{X}$ (or $S_2 \leftarrow S_0$) transition of the thiophosgene dimer, as its intensity is much weaker in warmer supersonic beams. Inset: Schematic energy level diagram of thiophosgene.

and the $\tilde{A}^1A_2 \rightarrow \tilde{X}^1A_1$ internal conversions, resulting from the absence of the a_2 promoting mode,[6] the quantum yields of $\tilde{B} \rightarrow \tilde{X}$ and $\tilde{A} \rightarrow \tilde{X}$ fluorescence have been reported as unity.[7] The lack of a significant $S_1(\tilde{A}) \rightarrow T_1(\tilde{a})$ intersystem crossing, also evident from the high efficiency of the $\tilde{A} \rightarrow \tilde{X}$ fluorescence, can be traced[6] to the very small S_1-T_1 electronic gap (1224 cm^{-1})[8] and the lack of direct $S_1(n\pi^*)-T_1(n\pi^*)$ spin−orbit coupling.[9] The small electronic gap renders an irreversible S_1-T_1 intersystem crossing impossible in the absence of collisions, even if vibronic spin−orbit coupling[10] provides sufficient electronic matrix elements for the radiationless transition.

Strictly speaking, the symmetry forbiddeness of the internal conversion, arising from the lack of a promoting mode, applies to molecules with low degrees of vibrational excitation. For an S_1 or S_2 molecule with a high degree of vibrational excitation, an anharmonic coupling of the b_1 vibration (out-of-plane wag) with a b_2 vibration (antisymmetric C−Cl stretch or S−C−Cl bend) can provide a promoting mode of a_2 symmetry, as $b_1 \otimes b_2 = a_2$. Moreover, when the molecule is excited into the high-lying vibrational levels of S_1, the vibrational density in the T_1 state may become large enough to allow irreversible intersystem crossing to the triplet manifold. In addition, the Franck−Condon factor for the $S_1 \rightarrow S_0$ internal conversion would increase with increasing vibrational energy[11] in S_1 due to the nonplanar geometry of S_1, vis-à-vis the planar S_0 state.[6] Thus, even if the quantum yield of the internal conversion is negligibly small at low excess energies (accurate determination of fluorescence quantum yield is very difficult), it could be significant at high excess energies. These considerations suggest that the photophysical properties of vibrationally highly excited S_1 thiophosgene could be significantly different from those of S_1 molecules with low degrees of vibrational excitation.

In this Letter, we describe the excess vibrational energy dependence of the intensity and temporal characteristics of the $S_1 \rightarrow S_0$ fluorescence of jet-cooled thiophosgene. The result demonstrates the absence of electronic radiationless transitions from S_1, establishes the energy threshold for predissociation, locates the second triplet state of $\pi\pi^*$ character, and unveils a very unusual temperature dependence of the S_1 radiative decay.

Experimental Section

In the experiments described herein, a tunable dye laser (Lambda Physik ScanMate) pumped by an excimer laser (Lambda Physik COMpex 102) was used, with and without frequency doubling, to excite thiophosgene seeded in a supersonic beam of He carrier gas. Helium gas at a stagnation pressure of 3−4 atm was bubbled into the liquid sample of thiophosgene maintained at about 5 °C, and expanded through a solenoid-driven valve (General Valve) of diameter 0.5 mm operating at repetition rates of 10 Hz and a pulse duration of <300 μs. The cold supersonic beam of thiophosgene so generated was intersected by the laser beam 15 mm downstream. $S_2 \rightarrow S_0$ and $S_1 \rightarrow S_0$ fluorescence were observed at right angles to the molecular and laser beams, and detected by a photomultiplier through a variety of band-pass and sharp cutoff filters, to seamlessly record an entire range of the $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ excitation spectra. The dispersed fluorescence spectra were recorded using a CCD spectrograph (Oriel InstaSpec V) with a spectral resolution of ~1.6 nm. The temporal characteristics of the emission were measured by a time-correlated single photon counting technique.

Thiophosgene was used with and without fractional distillation. No significant difference in the fluorescence excitation spectra was found between samples distilled and not distilled.

Results and Discussion

Predissociation. Figure 1 presents the time-resolved fluorescence excitation spectra (total emission) in the energy range 18 700−37 700 cm^{-1}. The spectrum (a) recorded with a short gate (0−20 ns) is identical to the fluorescence excitation spectrum of the $S_2 \rightarrow S_0$ emission (not shown), and it can be

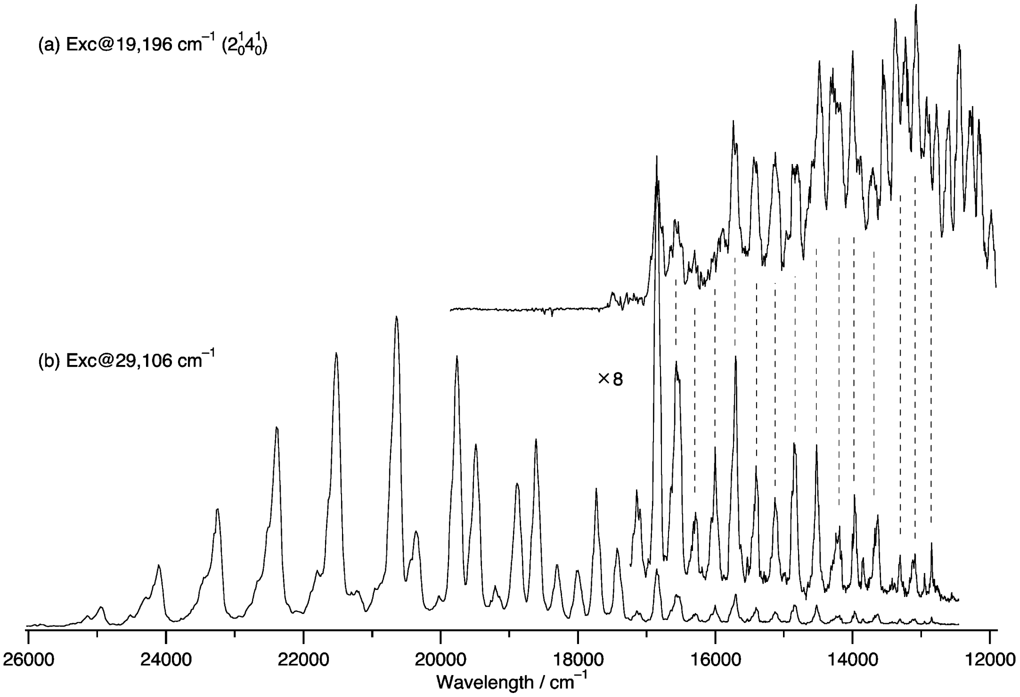

Figure 2. Comparison of the low-resolution dispersed fluorescence spectra of S_1 thiophosgene, obtained following excitation of the 2^14^1 vibronic level and a high-energy vibronic feature at 29 106 cm^{-1} (see Figure 1).

readily assigned to the features due to $S_2 \leftarrow S_0$ absorption. The spectrum (b) recorded with a long gate (140−440 ns), on the other hand, has its intensities at energies below the 0_0^0 band of the $S_2(\tilde{B}) \leftarrow S_0(\tilde{X})$ absorption. On the basis of the dispersed fluorescence and fluorescence lifetimes following excitation of these lower energy features (vide infra), we assign the latter spectrum to the $S_1 \leftarrow S_0$ absorption. The occurrence of the intensity maximum at about 12 800 cm^{-1} above the false origin (4_0^1) is consistent with this assignment for two reasons. First $^1B_2$−$^1A_2$ vibronic coupling (vide infra), which induces the $^1A_2$−$^1A_1$ transition, is expected to be more efficient for the higher lying vibronic levels of the $^1A_2(\tilde{A})$ state due to smaller $^1B_2$−$^1A_2$ vibronic energy gaps. Second, owing to the nonplanarity and the large C−S bond length of the $\tilde{A}(^1A_2)$ state relative to the planar ground state, a vertical transition from the ground state would most likely occur into the high-lying vibrational levels of the excited state, by the Franck−Condon principle.

The most striking feature of the excitation spectra in Figure 1 is the breaking-off of the $S_1 \rightarrow S_0$ fluorescence that occurs at 3484 cm^{-1} above the S_1 origin and the reappearance of the emission at about 9284 cm^{-1}. Thus, over a wide energy range of about 5800 cm^{-1}, there is no observable emission whatsoever from the S_1 thiophosgene. This behavior is consistent with the occurrence of predissociation[12] leading to the production of $Cl(^2P_{1/2})$ and $ClCS(\tilde{X})$[13] (see inset of Figure 1). The characteristic feature of the predissociation, as probed by the $S_1 \rightarrow S_0$ fluorescence of thiophosgene, would be that there is a region of E_{vib} in which the emission intensity (or lifetime) is extremely weak (or extremely short) due to a transition to the repulsive state. For E_{vib} far below and far above the intersection region, the fluorescence intensity (or lifetime) is expected to be normal due to very small nonadiabatic interactions between the bound and repulsive states (see inset of Figure 1). To state it differently, far below the crossing point the molecule has insufficient energy to dissociate, whereas far above the crossing point the molecule moves rapidly past the crossing point as it vibrates. On the basis of the observed onset of the fluorescence break-off, we place the curve crossing (leading to predissociation) at 3484 cm^{-1} above the electronic origin of S_1, in excellent agreement with the existing estimate[4] of 3454 ± 190 cm $^{-1}$.

Electronic Relaxation. The assignment of the higher energy fluorescence excitation spectrum, centered at about 31 500 cm^{-1} (see Figure 1b), to the $S_1 \leftarrow S_0$ absorption of thiophosgene is supported by dispersed fluorescence experiments. Figure 2 compares the dispersed fluorescence spectrum of a vibronic level at 29 106 cm^{-1} above the ground electronic state with that of a low-lying vibronic (2^14^1) level of S_1 thiophosgene. It should be noted that the long-wavelength tail of the former contains features that closely mimic the resonance fluorescence from the 2^14^1 level. This correspondence can be accounted for if the vibrationally highly excited S_1 level undergoes extensive intramolecular vibrational energy redistribution (IVR)[14] to produce levels that contain low degrees of excitation in the optically active modes (ν_4, in particular). The dispersed fluorescence from other high-lying vibronic levels also bears the spectral characteristics of levels that undergo extensive IVR.

Figure 3 compares the fluorescence decay from a low-lying S_2 vibronic level (0^0) and those from low- and high-lying S_1 vibronic levels. The S_1 lifetimes, which fluctuate between about 2 μs and about 5 μs, do not vary in any systematic manner over the excitation energies 18 176−34 000 cm^{-1}.

The essential identity of the fluorescence lifetime at very small and very large E_ν indicates[11] that the S_1 thiophosgene does not exhibit significant radiationless decay to bound electronic states, even when the molecule is endowed with very high degrees of vibrational excitation. The lack of $S_1(A_2) \rightarrow S_0(A_1)$ internal conversion from the vibrationally highly excited S_1 molecule implies that the higher order promoting mode $b_1 \otimes b_2$, with a_2 symmetry, is not efficient in inducing the radiationless transition. The near constancy of the fluorescence lifetime also indicates that $S_1 \rightarrow T_1$ intersystem crossing from the high-lying vibrational manifold of S_1 is also inefficient. This can be attributed to a small Franck−Condon factor for the radiationless transition that arises from the small S_1−T_1 electronic energy gap (1224 cm^{-1})[8] and very similar equilibrium geometries of the $^1A_2(n\pi^*)$ and $^3A_2(n\pi^*)$ states.[6] In combination with the forbidden nature of

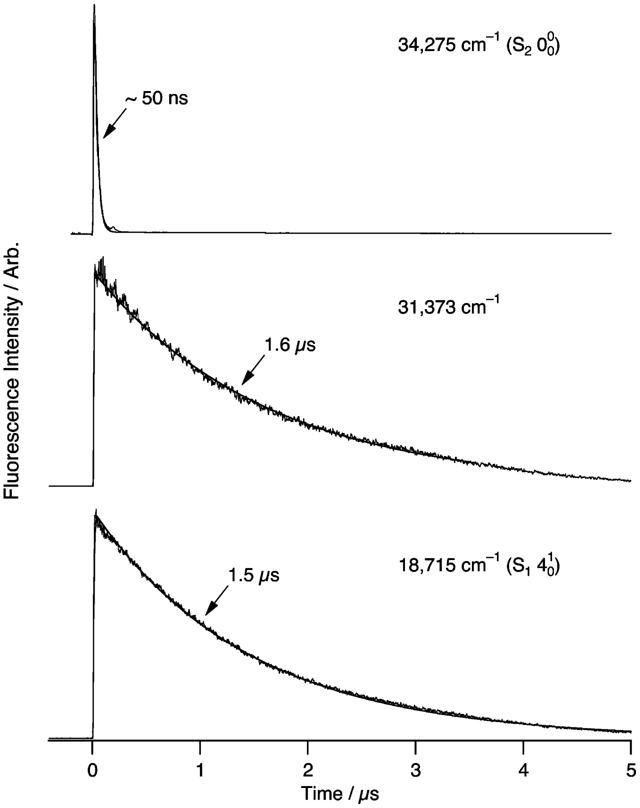

Figure 3. Fluorescence decay from a low-lying vibronic level (0°) of the $\tilde{B}$ (S_2) state and that from the 4^1 and high-lying vibronic levels of the $\tilde{A}$ (S_1) state.

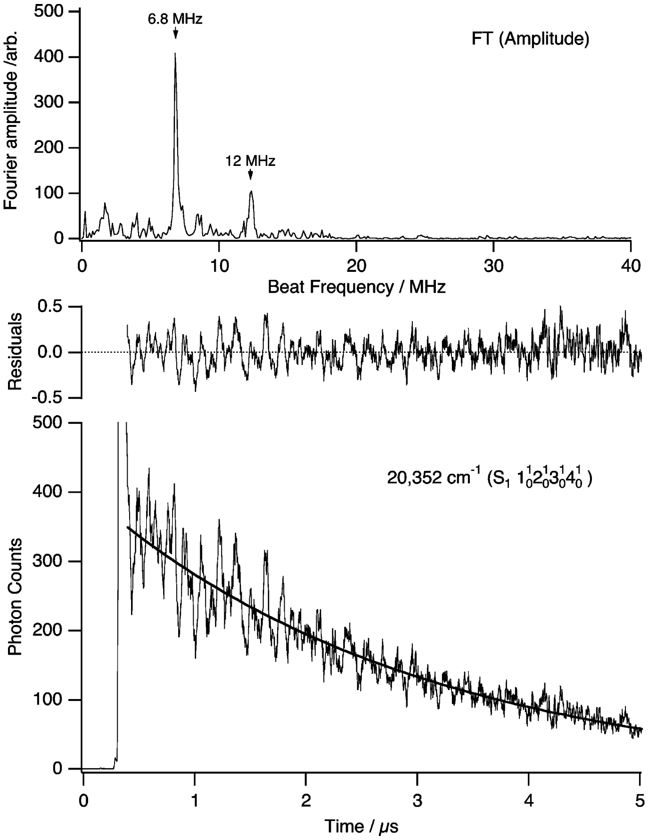

Figure 4. Quantum beat-modulated fluorescence decay, and its Fourier transform, for the $1^1 2^1 3^1 4^1$ level of S_1 thiophosgene.

direct S_1−T_1 spin−orbit coupling, they could render the $S_1 \rightarrow T_1$ intersystem crossing unimportant even at very large E_{vib}. As intersystem crossing from S_1 to the higher lying $\tilde{b}^3A_1$ ($\pi\pi^*$) state is not possible for collision-free thiophosgene, due to the much smaller vibrational density of the $\tilde{b}$ state relative to that of the $\tilde{A}$ state, the only available decay channel of the S_1 thiophosgene is the radiative transition to S_0.

Radiative Transition. Another interesting feature of the $S_1 \rightarrow S_0$ fluorescence of thiophosgene is its short lifetime in the supersonic jet (1−4 μs) as compared to the collision-free lifetimes of 25−35 μs, reported for the low-lying vibronic levels of thiophosgene vapor at room temperature.[12,15,16] Since the measured quantum yield of the emission is known to be unity in the vapor phase at room temperature,[7] the measured lifetimes must represent the radiative lifetime of the $\tilde{A}^1A_2$(nπ^*) state. Consistent with this conclusion, 35 μs is also the radiative lifetime (τ_r) expected from the approximate equation $\tau_r \cong 1.5/f\bar{\nu}^2$, using the observed oscillator strength ($f \cong 1.2 \times 10^{-4}$)[17] and transition frequency ($\bar{\nu} \cong 19\,000$ cm^{-1}). Thus, there is little doubt that the measured 35 μs lifetime of McDonald and Brus[12] represents the S_1 radiative lifetime of the thiophosgene vapor at room temperature. Since it is highly unlikely that nonradiative decay, unimportant at room temperature, would become important under the low-temperature conditions of supersonic free jet,[11] the much longer lifetime of the $S_1 \rightarrow S_0$ fluorescence at room temperature must have its origin in the smaller radiative decay rate of S_1 at elevated temperatures. This is possible if Coriolis coupling affects the $S_1 \rightarrow S_0$ radiative transition to a significant degree.

The $\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$ system of thiophosgene is electric dipole forbidden and gains its intensity by vibronic coupling.[5] The out-of-plane vibration (ν_4) of b_1 symmetry induces interaction between the $^1A_2$(nπ^*) state and the higher lying $^1B_2$(n4s) state, whereby the electric dipole-forbidden $^1A_2$(nπ^*) ← $^1A_1$ transition gains intensity from the allowed $^1B_2 \leftarrow {}^1A_1$ Rydberg transition. Consequently, the $S_1 \leftarrow S_0$ absorption spectrum exhibits a false origin 4_0^1 (and 4_1^0) and all intense bands contain one quantum, or odd quanta, of the ν_4 vibration.

The radiative transition probability between the $^1A_2$(nπ^*) state and the ground state would be sensitive to Coriolis interaction, which couples the vibronically active vibration (ν_4) with other vibrational modes of the molecule. To be more specific, the oscillator strength of the $S_1 \leftarrow S_0$ absorption, or the $S_1 \rightarrow S_0$ radiative decay rate, would decrease by the Coriolis coupling. Since the matrix elements of Coriolis coupling depend strongly on the rotational quantum numbers,[18] the decrease in the radiative decay rate (or the increase in the radiative lifetime) could be significant at high rotational temperatures. We therefore propose that the increased radiative lifetime of S_1 thiophosgene at high temperatures has its origin in a Coriolis coupling of the optically active ν_4 mode with optically inactive vibrational modes of the molecule. Consistent with this proposal, the measured $S_1 \rightarrow S_0$ fluorescence lifetime of jet-cooled thiophosgene was found to increase as the temperature of the supersonic beam is raised by reducing the backing pressure of the carrier gas.

Quantum Beats. Interestingly, thiophosgene exhibits quantum beats in emission when it is excited into S_1 vibronic levels lying in the vicinity of 20 340 cm^{-1} above the ground electronic state. Figure 4 displays the beat-modulated fluorescence decay of the $1^1 2^1 3^1 4^1$ level. Fourier analysis reveals two major frequency components at 6.8 and 12.0 MHz (Figure 4). Similar, but more complex, beat patterns were also observed for S_1 vibronic levels lying slightly above $1^1 2^1 3^1 4^1$.

We attribute the quantum beats to singlet (S_1)−triplet (T_2) interaction of the $\tilde{A}^1A_2$(nπ^*) state with the $\tilde{b}^3A_1$($\pi\pi^*$) state, which has been estimated[19] to lie at $20\,160 \pm 1\,500$ cm^{-1} above the ground state. As the $^3A_1(\pi\pi^*) \rightarrow {}^1A_1$ radiative transition is nearly forbidden due to the lack of $^3A_1-{}^1A_1$ spin−orbit coupling,[20] and since the $^3A_1 \rightarrow {}^3A_2$ internal conversion is symmetry forbidden owing to the absence of an a_2 promoting mode, the perturbation of the S_1 state by the T_2 state is expected to have negligible effects on the S_1 lifetime, as observed in experiments. On the basis of the threshold energy for the observation of beat-modulated fluorescence decay, we place the $\tilde{b}^3A_1(\pi\pi^*)$ state at about 20 340 cm^{-1}, in excellent agreement with the estimate[19] based on the electron-impact energy loss spectrum of Kuppermann and co-workers.[21]

Conclusion

From the lack of S_1 radiationless decay to the strongly temperature-dependent S_1 radiative decay, thiophosgene is a molecule tailor-made for demonstrating the fundamental aspects of molecular photophysics. The lack of nonradiative decays in the S_1 thiophosgene can be attributed to the extremely small electronic matrix elements for internal conversion and intersystem crossing, whereas the strong temperature dependence of the S_1 radiative decay rate has been proposed to arise from the Coriolis coupling that mixes the vibronically active mode (ν_4) with the inactive modes. The threshold energy for the break-off of the S_1 fluorescence and that for the appearance of quantum beats in fluorescence decay place the crossing point for predissociation and the $\tilde{b}^3A_1(\pi\pi^*)$ state at energies that are close to the predicted values.[4.19]

Acknowledgment. This work was supported in part by the Office of Basic Energy Sciences of the U.S. Department of Energy and, in part, by the National Science and Engineering Council of Canada. We are grateful to Dr. Willem Siebrand for helpful comments.

References and Notes

(1) See, for reviews: (a) Henry, B. R.; Siebrand, W. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley-Interscience: London, 1970; Vol. 1, p 153. (b) Freed, K. F. In *Topics in Applied Physics*; Fong, F. K., Ed.; Springer: Berlin, 1976; Vol. 15, p 23. (c) Avouris, P.; Gelbart, W. M.; El-Sayed, M. A. *Chem. Rev.* **1977**, *77*, 793.

(2) Lin, S. H.; Bersohn, R. *J. Chem. Phys.* **1968**, *48*, 2732.

(3) Gardner, P. J.; Kasha, M. *J. Chem. Phys* **1969**, *50*, 1543.

(4) Maciejewski, A.; Steer, R. P. *Chem. Rev.* **1993**, *93*, 977 and references therein.

(5) Brand, J. C. D.; Callomon, J. H.; Moule, D. C.; Tyrrell, J.; Goodwin, T. H. *Trans. Faraday. Soc.* **1965**, *61*, 2365.

(6) Moule, D. C.; Lim, E. C. *J. Chem. Phys.* **1999**, *110*, 9341.

(7) Steer, R. P. *Rev. Chem. Int.* **1981**, *4*, 1 and references therein.

(8) Clouthier, D. J.; Moule, D. C. *J. Mol. Spectrosc.* **1973**, *87*, 471.

(9) This is a specific (C_{2v}) case of El-Sayed's rule (El-Sayed, M. A. *J. Chem. Phys.* **1963**, *38*, 2834.), which states that the spin−orbit coupling between singlet and triplet states of the same orbital character is generally small.

(10) Lim, E. C. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1977; Vol. 3, p 305.

(11) Lim, E. C. *Adv. Photochem.* **1997**, *23*, 165.

(12) McDonald, J. R.; Brus, L. E. *Chem. Phys. Lett.* **1972**, *16*, 587.

(13) Okabe, H. *J. Chem. Phys.* **1977**, *66*, 2058.

(14) See, for a recent review: Felker, P. M.; Zewail, A. H. *Adv. Chem. Phys.* **1988**, *70*, 265.

(15) Brenner, D. M. *J. Phys. Chem.* **1980**, *84*, 3341.

(16) Kawasaki, M.; Kasatani, K.; Sato, H. *Chem. Phys.* **1985**, *94*, 179.

(17) Burnell, L. *Acad. R. Belg., Bull. Cl. Sci., Mem.* **1958**, *30*, 1.

(18) Papousek, D.; Alieve, M. R. In *Molecular Vibrational−Rotational Spectra*; Elsevier: Amsterdam, 1982.

(19) Hachey, M.; Grein, F.; Steer, R. P. *Can. J. Chem.* **1993**, *71*, 112.

(20) The spin−orbit coupling of the $^3A_1(\pi\pi^*)$ state with the $^1A_2(n\pi^*)$ state would not induce the $^3A_1 \rightarrow {}^1A_1$ radiative transition due to the dipole forbidden character of the $^1A_2 \rightarrow {}^1A_1$ transition.

(21) Flicker, W. M.; Masher, O. A.; Kuppermann, A. *Chem. Phys. Lett.* **1978**, *57*, 183.A