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Highly Varying Photophysical Properties of Thiocarbonyls: Validation of Fundamental Theoretical Concepts of Electronic Radiationless Transitions

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A homologous series of gas-phase thiocarbonyl compounds displays highly variable photophysical properties. Thus, while thioformaldehyde, H_2CS, and thiocyclopentanone, H_8C_5S, exhibit fluorescence as well as phosphorescence, thiophosgene, Cl_2CS, displays fluorescence but not phosphorescence, and thiocyclobutanone, H_6C_4S, exhibits neither fluorescence nor phosphorescence. We show here that the very different emission characteristics of the four closely related thiocarbonyls can be rationalized on the basis of the presence or absence of the promoting mode for $S_1 \rightarrow S_0$ internal conversion and the extent of S_1 and T_1 nonplanarity at the thiocarbonyl center.

Introduction

Classifications of molecular vibrations into "promoting modes" and "accepting modes" are the central theoretical concepts of the electronic radiationless transitions that date back more than three decades.[1] Although the role of the accepting modes in radiationless transitions has been amply demonstrated experimentally, that of the promoting mode has not been so demonstrated. The primary reason for this lies with the fact that the past photophysical measurements have been concerned mostly with large molecules with relatively low symmetries, for which the promoting mode for internal conversion (radiationless transition between two electronic states of the same spin multiplicity) is always present. In the present study, the photophysical properties of thioformaldehyde and thiophosgene (which lack the requisite promoting mode) are compared with those of the closely related thiocyclobutanone and thiocyclopentanone (which possess the promoting mode) to illustrate the role of the promoting mode in the $S_1(n\pi^*) \rightarrow S_0$ internal conversion. The highly varying molecular nonplanarity of the excited states also allows for the demonstration of the role of the accepting mode in $S_1 \rightarrow S_0$ internal conversion and $T_1 \rightarrow S_0$ intersystem crossing (radiationless transition between two electronic states of different spin multiplicity).

In the statistical limit of radiationless transitions (in which the molecule undergoes an irreversible, exponential decay), the rate constant, k_{nr}, of nonradiative decay from the initial electronic state $|\mathrm{s}\rangle$ to the final electronic state $|\ell\rangle$ is given by[2]

$$k_{\mathrm{nr}} = \frac{2\pi}{\hbar}|\langle \mathrm{s}|\hat{v}|\ell\rangle|^2 \rho_\ell \quad (1)$$

where $\hat{v}$ represents the perturbation responsible for the radiationless decay, and ρ_ℓ is the density of states in $|\ell\rangle$. To the first order, $\hat{v}$ is the nuclear kinetic energy operator ($\hat{T}_{\mathrm{N}}$) for internal conversion and spin−orbit coupling ($\hat{H}_{\mathrm{SO}}$) for intersystem crossing.

When the Condon and normal mode approximations are adopted, the matrix elements for internal conversion $\langle \mathrm{s}|\hat{T}_{\mathrm{N}}|\ell\rangle$ between the Born−Oppenheimer states $|\mathrm{s}\rangle = |\phi_{\mathrm{s}}(q,Q)\rangle|\chi_{\mathrm{s}}(Q)\rangle$ and $|\ell\rangle = |\phi_\ell(q,Q)\rangle|\chi_\ell(Q)\rangle$ can be written in the form

$$V_{\mathrm{sl}} = -\hbar^2 \sum_i \left\langle \phi_{\mathrm{s}} \left| \frac{\partial}{\partial Q_i} \right| \phi_\ell \right\rangle \left\langle \chi_{\mathrm{s}u_{\mathrm{i}}} \left| \frac{\partial}{\partial Q_i} \right| \chi_{\ell v_{\mathrm{i}}} \right\rangle \prod_{j \neq i} \langle \chi_{\mathrm{s}u_{\mathrm{j}}} | \chi_{\ell v_{\mathrm{j}}} \rangle - \frac{\hbar^2}{2} \sum_i \left\langle \phi_{\mathrm{s}} \left| \frac{\partial^2}{\partial {Q_i}^2} \right| \phi_\ell \right\rangle \langle \chi_{\mathrm{s}u_{\mathrm{i}}} | \chi_{\ell v_{\mathrm{i}}} \rangle \prod_{j \neq i} \langle \chi_{\mathrm{s}u_{\mathrm{j}}} | \chi_{\ell v_{\mathrm{j}}} \rangle \quad (2)$$

where ϕ and χ represent the electronic and vibrational wave functions, respectively, u and v are vibrational quantum numbers for modes i and j, and Q_i represents the mass-weighted normal coordinate for mode i. The second term involving the second derivative of ϕ with respect to Q is very small[3] so that it is customary to neglect this term in the description of the matrix elements for internal conversion. Note from eq 2 that the matrix elements responsible for internal conversion are composed of two factors: an electronic integral $\langle \phi_{\mathrm{s}}|\partial/\partial Q_i|\phi_\ell\rangle$ representing nonadiabatic coupling between the two electronic states and the vibrational integrals containing a nuclear momentum integral $\langle \chi_{\mathrm{s}}|\partial/\partial Q_i|\chi_\ell\rangle$ and an overlap integral $\langle \chi_{\mathrm{s}}|\chi_\ell\rangle$. Lin and Bersohn[4] designated the vibration for which the electronic matrix elements are finite as the "promoting mode" and those for which the overlap integrals are nonvanishing as the "accepting modes". To the lowest order, the electronic matrix elements in eq 2 are determined by the vibronic coupling integral[4,5]

$$\left\langle \phi_{\mathrm{s}}(q,Q) \left| \frac{\partial}{\partial Q} \right| \phi_\ell(q,Q) \right\rangle = \frac{\left\langle \phi_{\mathrm{s}}(q,Q) \left| \dfrac{\partial U(q,Q)}{\partial Q} \right| \phi_\ell(q,Q) \right\rangle}{E_\ell(Q) - E_{\mathrm{s}}(Q)} \quad (3)$$

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where U is the potential energy of interaction between the electrons and nuclei and E represents the energy of the electronic state. Because the vibronic coupling operator $\partial U/\partial Q$ transforms as the nuclear coordinate Q, eq 3 forms the basis of selection rules for internal conversion: the matrix elements will be finite only for vibration Q that has the same representation of the molecular point group as the direct product $\phi_s \otimes \phi_\ell$. Stated another way, a vibrational mode capable of vibronically coupling the initial and the final electronic states of internal conversion is needed to promote the radiationless process.

For intersystem crossing between the $|s\rangle$ and $|\ell\rangle$ states that are directly coupled by spin−orbit interaction, the matrix elements $\langle s|\hat{H}_{SO}|\ell\rangle$ contain only the vibrational overlap integrals involving

$$V_{sl} \approx \langle s|\hat{H}_{SO}|\ell\rangle \prod_k \langle \chi_{su_k}|\chi_{\ell u_k}\rangle \tag{4}$$

accepting modes.[2] As in internal conversion, the Franck−Condon factors, which are the squared sum of the vibrational overlap integral involving accepting modes, control the efficiency of radiationless transitions.

From eqs 2−4, it is clear that the promoting mode and spin−orbit coupling contribute to the electronic factor for radiationless transitions, whereas the accepting modes determine the vibrational (or Franck−Condon) factor for radiationless transitions. Thus, the electronic and Franck−Condon factors for radiationless transitions, together with the radiative transition probabilities, determine the emission characteristics of polyatomic molecules.

The thiocarbonyl compounds chosen for comparison are thioformaldehyde, thiophosgene, thiocyclobutanone, and thiocyclopentanone. These compounds are tailor-made for testing the fundamental theoretical concepts of radiationless transitions for several reasons. First, they exhibit highly varying emission characteristics that require explanation. Because the nature and the energy level dispositions of low-lying excited states of these thiocarbonyl compounds are very similar, any variations in the photophysical properties must be due to the differences in the electronic or vibrational factor for radiationless transitions. Second, the molecules are small enough to allow accurate determination of the ground and excited-state potential energy surfaces from the fits to the observed energy levels as well as from high-level ab initio calculations. The geometries so obtained are highly variable, especially the extent of molecular nonplanarity at the thiocarbonyl carbon center. Third, two of the molecules are "vibrationally deficient"[6] in that the symmetry species for normal modes of the vibrations fail to span all of the irreducible representations of the point group to which the molecules belong. This missing mode just happens to be the vibration that promotes internal conversion from S_1 to S_0. It will be shown that the highly varying emission characteristics of the thiocarbonyl compounds confirm the important roles that promoting and accepting modes play in radiationless transitions.

Experimental Section

The experimental and theoretical data needed for correlating the photophysical properties with the electronic and vibrational factors for radiationless transitions are available for three of the four thiones. We present here only the experimental details concerning the spectroscopic and geometric characterization of the fourth molecule, thiocyclobutanone.

The precursor of thiocyclobutanone, cyclobutanone S-trithane $(C_4H_6S)_3$, was prepared by passing H_2S for 2 h into an ice-cold solution of 12 M hydrochloric acid and cyclobutanone (3:1 by volume). The resultant solid was washed with distilled water and was used without further purification. The trimer was cracked at 700 °C in a 20-cm long dimpled fused silica pyrolysis tube, and the products flowed directly into a 2 m White-type multiple reflection cell set to 28 traversals. The spectra were recorded on a Bausch and Lomb 1.5 m spectrograph at a dispersion of 1.5 nm/mm. A 450 W Xe arc provided the light continuum, and an Fe/Ne hollow-cathode lamp provided the lines for the reference spectrum. Calibration was made from the 10× enlarged photographic plates. The optical densities were converted into a digital scan with a recording microdensitometer.

Results and Analyses

Low-Lying Electronic States and Radiationless Transitions. The $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ absorption systems of the four thiocarbonyls represent electronic transitions to the first excited states of $n\pi^*$ character, which are of A_2 representation in C_{2v} or G_4 nonrigid symmetry.[7] The $S_1(n\pi^*)-T_1(n\pi^*)$ electronic energy gap is about 1200 cm^{-1} for all of the thiocarbonyls. Because of the very small S_1-T_1 electronic energy gap and the small spin−orbit coupling between the two $n\pi^*$ states,[8] the $S_1 \rightarrow T_1$ intersystem crossing is not expected to occur in the absence of collision.[9,10] Thus, the only radiationless transitions of concern here are the $S_1(n\pi^*) \rightarrow S_0$ internal conversion and the $T_1(n\pi^*) \rightarrow S_0$ intersystem crossing resulting from the direct $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ excitations of the molecule. The efficiency of these radiationless transitions is expected to depend on the magnitudes of the electronic integral $\langle \phi_s|\partial/\partial Q_i|\phi_\ell\rangle$ involving the promoting mode Q_i (for the internal conversion), the electronic integral $\langle \phi_s|\hat{H}_{SO}|\phi_\ell\rangle$ involving the spin−orbit coupling operator (for the intersystem crossing), and the vibrational overlap integral associated with accepting modes (for both cases). A theoretical analysis of the $T_1 \rightarrow S_0$ intersystem crossing for thiophosgene by Moule et al.[11] indicates that the matrix elements of spin−orbit coupling are expected to be similar (and large because of the high atomic number of the sulfur atom) for the four thiocarbonyls, so that any large variation in the efficiency of the $T_1 \rightarrow S_0$ intersystem crossing can be ascribed to the difference in the Franck−Condon factors (square of the vibrational overlap integrals). The theoretical study also demonstrated that the C═S out-of-plane bending mode (ν_4) is the dominant contributor to the Franck−Condon factor governing the $S_1 \rightarrow S_0$ internal conversion and the $T_1 \rightarrow S_0$ intersystem crossing. In what follows, we therefore consider only two factors: the presence or absence of the vibrational mode of a_2 symmetry, and the C═S out-of-plane distortion in the upper electronic state.

Promoting Mode for $S_1 \rightarrow S_0$ Internal Conversion. Thioformaldehyde, H_2CS, and thiophosgene, Cl_2CS, do not have a normal mode of a_2 symmetry (the internal motion of a_2 symmetry in these molecules corresponds to rotation about the C_2, or C═S, axis), whereas thiocyclobutanone, H_6C_4S, and thiocyclopentanone, H_8C_5S, have true a_2 normal modes, Figure 1. The electronic factor for the $^1A_2(S_1) \rightarrow {}^1A_1(S_0)$ internal conversion is therefore expected to be much greater for H_6C_4S and H_8C_5S than for H_2CS and Cl_2CS.

Out-of-Plane Bending Potentials. The major conformational difference among the four thiocarbonyls considered here is the nonplanarity of the $S_1(n\pi^*)$ and $T_1(n\pi^*)$ excited states relative to the planar ground state. The vibrational potentials for the C═S out-of-plane mode have been previously described for thioformaldehyde, thiophosgene, and thiocyclopentanone but not for thiocyclobutanone.

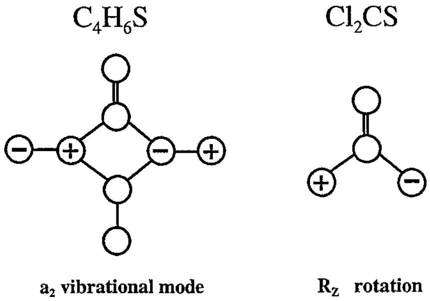

Figure 1. Internal motion of a_2 symmetry, showing that it is a genuine normal mode for thiocyclobutanone or thiocyclopentanone and a rotation about the C_2 axis for thiophosgene or thioformaldehyde.

H_2CS. The experimental studies of Clouthier and co-workers[12,13] as well as the ab initio CI calculations of Hatchey and Grein[14,15] clearly demonstrate that the $S_1(n\pi^*)$ and $T_1(n\pi^*)$ states of thioformaldehyde adopt planar equilibrium geometry. The out-of-plane C=S wagging potential is very flat for both the S_1 and T_1 states.

Cl_2CS. The $S_1 \leftarrow S_0$ absorption system of thiophosgene has been analyzed by Brand and co-workers,[16] who showed that the $S_1(n\pi^*)$ state is nonplanar, with the C=S bond bent from the ClCCl plane by an out-of-plane angle, θ, of about 32°. The vibronic analysis of the $T_1 \leftarrow S_0$ absorption system, by Moule and Subramanian,[17] showed that the T_1 state of thiophosgene also adopts a pyramidal conformation. A barrier height of 726 cm^{-1} and angle θ of 32° have been obtained for the triplet state from a fit of the energy levels of a quadratic-Lorentzian double-minimum function to the observed levels in ν_4. These conclusions are supported by the MP4/6-31G(d,p) calculations of Moule et al.,[11] which yield for the triplet state barrier heights of 770−845 cm^{-1} and θ of 32.07°−32.69°. By contrast, the same computational methodology shows the ground state of thiophosgene to be planar.[11]

H_8C_5S. The visible spectrum of thiocyclopentanone, H_8C_5S, has been recorded by Judge and Moule[18] in the vapor phase at long path lengths. The low-energy part of the spectrum was attributed to the spin-forbidden $T_1 \leftarrow S_0$ transition. This system has an open vibrational structure and is characterized by a strong 0_0^0 band. The strength of this band and the absence of progressions in the C=S out-of-plane mode are a clear indication that the T_1 state does not undergo a molecular distortion at the thiocarbonyl carbon.

The remaining absorption bands at higher wavenumbers were observed to form a dense structure that was assigned to the spin-allowed $S_1 \leftarrow S_0$ system. These bands displayed a complex pattern that was based on a weak 0_0^0 origin band. The similarity of the ring-mode frequencies in the S_0 and S_1 states is an indication that the out-of-plane conformations do not change on electronic excitation. The above analyses for thiocyclopentanone, based on Franck−Condon considerations, suggest that the CCCS frame of the molecule is planar in S_0, T_1, and S_1 states.

H_6C_4S. The microdensitometer tracing of the $S_1(n\pi^*) \leftarrow S_0$ absorption spectrum of thiocyclobutanone obtained with a 2 m White-type multiple reflection cell (see Experimental Section) is shown in Figure 2. As in the related cyclobutanone system,[19] the Franck−Condon activity in the spectrum is dominated by transitions to the odd quanta of C=S out-of-plane wag (ν_{19}) with the 19_0^1 pseudo-origin at 18 575 cm^{-1}. The progression members are labeled in the figure. The first member of this progression at 0 + 272 cm^{-1} is given the assignment 19_0^3 on the basis of its intensity and the vibrational interval. A hot band attached to the pseudo-origin at 0 − 356 cm^{-1} is assigned to 19_1^0. The locations of these three bands establish that the ν_{19} mode has a frequency of 356 cm^{-1} in S_0 and 272 cm^{-1} in S_1. The appearance of a band progression in the antisymmetric (b_1 in C_{2v} symmetry) C=S wagging vibration requires that the $S_1(^1A_2)$ $n\pi^*$ state adopts a nonplanar equilibrium structure at the thiocarbonyl center. Because the S_1-T_1 interval is very small, the equilibrium structures of these T_1 and S_1 companion states are expected to be very similar.

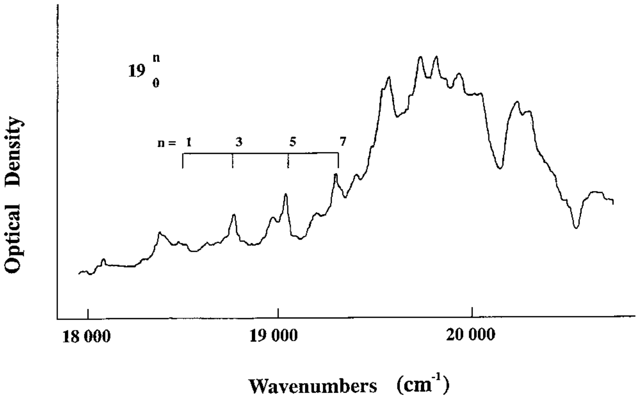

Figure 2. Visible $S_1 \leftarrow S_0$ absorption spectrum of thiocyclobutanone in the vapor phase at room temperature.

Emission Characteristics. *H_2CS.* The $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ laser excitations of the gas-phase molecule to the low-lying vibronic levels lead to the appearance of fluorescence[20] and phosphorescence.[21] The high quantum yields of the emissions[22] suggest that the $S_1 \rightarrow S_0$ internal conversion (competing with the $S_1 \rightarrow S_0$ fluorescence) and the $T_1 \rightarrow S_0$ intersystem crossing (competing with the $T_1 \rightarrow S_0$ phosphorescence) are not efficient in H_2CS.

Cl_2CS. Strong fluorescence is observed from the gas-phase thiophosgene upon $S_1 \leftarrow S_0$ excitation of the molecule.[23] The quantum yield of the $S_1 \rightarrow S_0$ emission is reported to be of unity,[22] indicating that the $S_1 \rightarrow S_0$ internal conversion is very inefficient. On the other hand, no phosphorescence is observed in the gas-phase Cl_2CS following the $T_1 \leftarrow S_0$ excitation.[9,11,24]

H_6C_4S. Neither fluorescence nor phosphorescence is observed in thiocyclobutanone upon direct excitation of the molecule into S_1 or T_1, indicating that the $S_1 \rightarrow S_0$ internal conversion and $T_1 \rightarrow S_0$ intersystem crossing are highly efficient.

H_8C_5S. Strong fluorescence and phosphorescence are observed in gas-phase thiocyclopentanone. As in thioformaldehyde, the $S_1 \rightarrow S_0$ internal conversion and the $T_1 \rightarrow S_0$ intersystem crossing appear to be very inefficient.

Schematic representations of the emission characteristics and the out-of-plane bending potential curves for the excited (S_1 or T_1) and ground states are given in Figure 3.

Discussion

The nonplanar distortion of the tetraatomic ketones and thiones, which lead to a double-minimum potential, does not affect the vibrational selection rules for internal conversion for the following reasons. While planar to nonplanar distortions can be viewed as an abrupt change from C_{2v} to C_s symmetry, the correlation of a smooth increase in barrier height from the rigidly planar to rigidly nonplanar conformation can be described by the G_4 nonrigid point group. The G_4 group allows the $v = 0(+)$ and $v = 1(-)$ vibrational levels of the planar molecule to corelate with the $v = 0(+)$ and $v = 0(-)$ of the nonplanar molecule. Thus, for the nonplanar rigid molecule, the $v = 0$

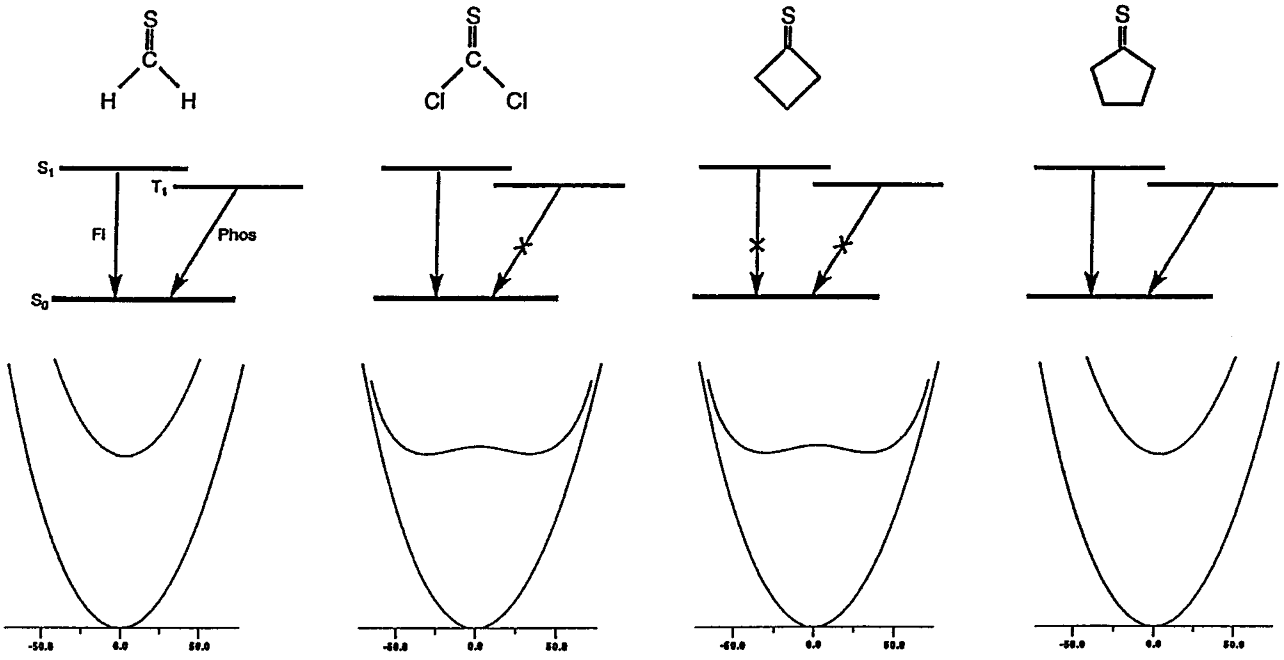

Figure 3. Schematic representations of the emission characteristics and the C=S out-of-plane bending potential curves for the excited (S_1 or T_1) and S_0 ground states of the four thiones.

zero-point level is characterized by two levels (+) and (−). For both planar and nonplanar cases, the (+) and (−) levels are labeled by the representations a_1 and b_1. The promoting mode that transforms as a rotation about the R_z axis retains its symmetry labeling in both low- and high-barrier cases as the a_2 representation of the G_4 group. Thus thiophosgene, which lacks the promoting mode of a_2 symmetry in planar conformation, remains vibrationally deficient even after the out-of-plane deformation.

The very different emission characteristics of the four thiocarbonyls, illustrated in Figure 3, can be rationalized on the basis of the presence or absence of the promoting mode for $S_1 \rightarrow S_0$ internal conversion and the extent of S_1 and T_1 nonplanarity at the thiocarbonyl center. Consider first the emission characteristics of thioformaldehyde and thiophosgene. The observation of fluorescence is expected from both of these compounds because they lack the promoting mode of a_2 symmetry needed for $S_1(A_2) \rightarrow S_0(A_1)$ internal conversion. The presence of phosphorescence in thioformaldehyde and its absence in thiophosgene can be attributed to the difference in their T_1 geometries. The Franck−Condon factors for the $T_1 \rightarrow S_0$ intersystem crossing to the planar S_0 state would be small for the case of planar T_1 thioformaldehyde and much larger for the strongly nonplanar T_1 thiophosgene. A subnanosecond $T_1 \rightarrow S_0$ nonradiative lifetime of thiophosgene has been obtained on the basis of computed S_0 density of states and ab initio matrix elements of T_1−S_0 spin−orbit coupling.[11] The same pyramidal deformation of S_1 thiophosgene should also lead to an ultrafast $S_1 \rightarrow S_0$ internal conversion (via Franck−Condon factor), if it were not for the lack of the promoting mode. Apparently, the favorable Franck−Condon factors for the internal conversion are more than compensated for by the very small electronic matrix elements caused by the lack of the promoting mode of a_2 symmetry. Consistent with this interpretation, thiocarbonyl chlorofluoride, ClFCS, which lacks symmetry, does not fluoresce or phosphoresce.[25]

The fully emissive (fluorescence and phosphorescence) behavior of the planar S_1 and T_1 states of thiocyclopentanone can be rationalized if it is assumed that the favorable electronic factors for the internal conversion (due to the presence of the promoting mode) and the intersystem crossing are compensated by the small Franck−Condon factors for the radiationless transitions. In the case of the S_1 and T_1 states of thiocyclobutanone, the strong pyramidal distortion would lead to very efficient nonradiative decays, consistent with the absence of fluorescence and phosphorescence.

The above criteria, based on the electronic and vibrational factors for radiationless transitions, can also be used in principle to predict the photophysical properties of the analogous carbonyl compounds, albeit with caveats. The oscillator strength of the $S_1 \leftarrow S_0$ absorption system is typically about 1 order of magnitude greater in the carbonyl compounds than in the corresponding thiocarbonyl systems.[13] As a consequence of the greatly enhanced $S_1 \rightarrow S_0$ radiative transition probability, the fluorescence from the S_1 carbonyl center is expected to be more readily observed than from the corresponding S_1 thiocarbonyl moiety. On the contrary, because of the greatly reduced $^1A_1(\pi\pi^*)$−$^3A_2(n\pi^*)$ spin−orbit coupling (relative to that of the thiocarbonyls), which is the main source of the $T_1 \rightarrow S_0$ radiative transition probability, the observation of phosphorescence is much more difficult in carbonyl compounds. Moreover, formaldehyde, cyclobutanone, and cyclopentanone are all nonplanar along the C=O out-of-plane wagging coordinate. The photophysical properties of the carbonyls are therefore expected to be not as highly variable as they are in the corresponding thiocarbonyl compounds. Consistent with this expectation, the aforementioned carbonyl compounds all exhibit fluorescence but not phosphorescence.[26] Even so, the $S_1(A_2) \rightarrow S_0(A_1)$ fluorescence is the strongest in formaldehyde, which lacks the a_2 promoting mode for the $S_1 \rightarrow S_0$ internal conversion, and stronger in the less nonplanar cyclopentanone than in the strongly nonplanar cyclobutanone.

We would like to briefly comment on the applicability of the Condon approximation in radiationless transitions. In the derivation of eq 2, the vibrational coordinate dependence of the electronic wave function is neglected by invoking the Condon approximation by evaluating the integrals at the equilibrium position. The vibrational symmetry selection rules based on this approach are only approximately valid because the matrix elements of internal conversion do not factorize into products of promoting and accepting modes. Nevertheless, the results and analyses presented herein suggest that this physically insightful formulation, based on the Condon approximation, provides a qualitatively accurate description of electronic radiationless transitions.

From the above discussion, it should be noted that the efficiency of fluorescence is determined by the balance between the electronic factor, which depends on the presence or absence of the promoting mode for $S_1 \rightarrow S_0$ internal conversion, and the Franck−Condon vibrational factor, which is determined by the degree of the out-of-plane deformation of S_1. If the S_1 state is strongly nonplanar, the molecule lacking the promoting mode may not fluoresce. Conversely, the molecule with a promoting mode may fluoresce if the out-of-plane deformation is small. An example of the former case may be difluorothiocarbonyl,[25] whereas the latter is represented by thiocyclopentanone.

Conclusion

The principal finding of this paper is that highly varying photophysical properties of the homologous series of thiones can be rationalized on the basis of two factors: the presence or absence of the promoting mode for internal conversion and the extent of the excited-state nonplanarity.

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