

STRUCTURAL STABILITY AND SUBSTITUENT EFFECTS ON THE PHOTOPHYSICAL PROPERTIES OF THIOANISOLE EXPLORED BY EXCITED-STATE DYNAMIC SIMULATIONS

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Abstract

The photophysical properties of thioanisole (SCH₃) and its derivatives as a representative system for investigating aryl sulfides were explored by TD-DFT using the B3LYP functional. Thioanisole appears in a variety of chemical applications due to its structural and reactive properties such as in dyes, drugs, and materials. Our investigations focus on the structural, photophysical, and dynamic properties influenced by substituents (F and Cl) on absorption and emission spectra. The electronic transition mainly corresponds to S₀→S₂ ($\pi\rightarrow\sigma^*$) with excitation energies of 5.11 eV and 5.02 eV for SCH₃F and SCH₃Cl, respectively. The dynamic simulations on the first-excited state provide additional insights that complement those obtained from static calculations. The fluorescence spectrum of SCH₃F typically shows a blue shift, while the fluorescence spectrum of SCH₃Cl displays a red shift compared to SCH₃. These findings indicate that the inductive effect plays a crucial role in structural stability, particularly influencing internal conversion during the dynamics, which may lead to a reduced fluorescence intensity.

Keywords: On-the-fly dynamic simulations; Thioanisole; B3LYP; TD-B3LYP; Substituent effects

Introduction

Fluorescence is a fascinating phenomenon in which certain substances absorb light at one wavelength and emit it at another, typically a longer wavelength. This emission of light is what sets fluorescence apart from other forms of luminescence, such as phosphorescence or chemiluminescence (Valeur and Berberan-Santos,

2013). The emitted light usually falls within the visible spectrum, although it can also extend into the ultraviolet or infrared regions. The fluorescence process begins with the absorption of photons by fluorescent molecules or materials. The applications of fluorescence span across numerous fields, owing to its sensitivity, specificity, and

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versatility (Shahzad *et al.*, 2009). Several factors can decrease or enhance the intensity of fluorescence in a material, and researchers and technicians must consider these factors when designing experiments or selecting appropriate fluorophores and experimental conditions (Dragan *et al.*, 2012).

The fluorescence properties of a molecule are intimately tied to its molecular structure and electronic configuration by tailoring specific structural features, such as conjugation, functional groups, and molecular geometries (Ibnaouf *et al.*, 2018; Jun *et al.*, 2024). These parameters are taken into account to modulate and enhance fluorescence in a molecule. Through careful design and optimization, researchers can generate fluorescent compounds with improved quantum yields, extended emission wavelengths, and enhanced photostability (Fu *et al.*, 2008).

To gain more understanding of structural stability reflecting the fluorescence intensity, the thioanisole (SCH₃) molecule, consisting of a benzene ring and a thiomethyl (-SCH₃) group, is one of the fundamental benzene derivatives (Manoharan *et al.*, 2000). The methylthio group's electron-donating nature enables studies of substituent effects on photoinduced reactivity and energy transfer, while thioanisole's well-known photochemical pathways - like bond cleavage and oxidation - make it ideal for mechanistic analysis. The molecular structure of thioanisole has been extensively studied with several experimental methods (Gellini *et al.*, 2002; Yamakita *et al.*, 2006) and theoretical calculations (Bossa *et al.*, 2002; Bzhezovskii and Kapustin, 2002; Bzhezovskii *et al.*, 2004). Thioanisole is a representative system for investigating the photophysics of aryl sulfides, which appear in dyes, drugs, and materials. It is frequently employed as a scavenger in peptide synthesis, where it serves to neutralize nucleophilic byproducts generated during the global deprotection of side chains (Yang, 2016). These reports suggested that thioanisole would be a planar or perpendicular conformer concerning the rotation of the thiomethyl group (Nagasaka-Hoshino *et al.*, 2008; Lee *et al.*, 2011; Zhang *et al.*, 2015; Kim *et al.*, 2016). The molecule's stability depends on whether it is in a planar or perpendicular form which influence its energy, and absorption and emission characteristics (Andrusenko *et al.*, 2023). Additionally, Zhang *et al.* (Zhang *et al.*, 2022) performed theoretical calculations to predict a stable structure of fluorothioanisole (SCH₃F) and compared with Cl-substituted SCH₃ derivatives

(SCH₃Cl). They showed strong activation of the vibrational modes involving the motion of the -SCH₃ group indicating that steric effects between the substituents play a role in determining the stabilities of the molecules. It is noteworthy that this spectroscopic work is useful for the further dynamic studies of the thioanisole molecule and its derivatives.

While static calculations alone are valuable for providing initial insights and are computationally less demanding, dynamic simulations provide a more comprehensive and realistic understanding of the structural stability and photophysical properties (Hospital *et al.*, 2015) by accounting for temporal, thermal, and environmental factors (Hillers-Bendtsen *et al.*, 2022). This leads to more accurate and detailed predictions, which are essential for advancing the design and application of new materials in photophysics and related fields. Dynamic simulations can capture the time-dependent behavior of molecules, providing a more realistic picture of how structures fluctuate over time. To further understand the substitution effects (e.g., the steric and inductive effects) on the stable structures of thioanisole (SCH₃) derivatives, we investigated the structural properties of SCH₃F and SCH₃Cl by dynamic simulations. In this work, we aim to simulate UV/Vis absorption, emission spectra, and detailed pictures of all systems through the quantum dynamic simulations on the excited state.

Computational details

Ground-state optimization for all geometries of thioanisole (SCH₃) and its derivatives, as shown in Figure 1, was performed using density functional theory (DFT) at Becke's three parameters hybrid functional and the Lee-Yang-Parr correlation function (B3LYP) (Stephens *et al.*, 1994) in the gas phase. The basis set chosen for all atom types was the triple- ζ valence quality with one set of polarization functions (TZVP) (Schäfer *et al.*, 1992) basis set. All local minima were confirmed by the absence of an imaginary mode in vibrational analysis calculations. Important parameters including bond lengths, bond angles, and dihedral angles were collected and determined. The simulated infrared (IR) spectra of all compounds both in the ground (S₀) and first excited (S₁) states were computed to analyze their structural and electronic properties.

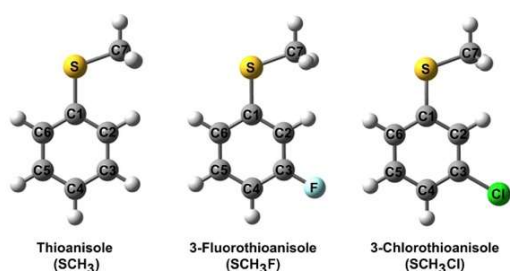


Figure 1. Ground-state (S_0) optimized geometries of SCH_3 , SCH_3F , and SCH_3Cl computed at B3LYP/TZVP level of theory

For vertical excitations, time-dependent DFT (TD-DFT) at TD-B3LYP with the same basis set was employed to explore excitation energies. These calculations were carried out using the TURBOMOLE 5.10 program package (Ahlich *et al.*, 1989; Sheldon *et al.*, 2024). Then, the optimized geometries for each system were used as initial geometries in photoexcitation dynamics. On-the-fly dynamic simulations of all systems were performed with the NEWTON-X program package (Barbatti *et al.*, 2007) interfaced with TURBOMOLE. The initial conditions for the dynamics were generated using a harmonic oscillator Wigner distribution for each normal mode. Twenty-five trajectories as a representative set for each system were simulated at TD-B3LYP/TZVP level of theory with a time step of 1 fs with a maximal duration of 500 fs. Our previous studies for the case of TD-B3LYP/TZVP level of theory for excited dynamics were discussed in the following references (Kungwan *et al.*, 2012; Daengngern *et al.*, 2016). The dynamics simulation details such as energy differences between S_1 and S_0 states ($S_1 - S_0$), emission spectra, average bond lengths, and bond angles were analyzed by statistical analysis and described in the next section.

Results and Discussion

Geometry optimizations

The geometries of SCH_3 and its derivatives optimized using DFT and TD-DFT at the B3LYP/TZVP level for the S_0 and S_1 states, respectively, were obtained as shown in Figure 1. Important parameters from the optimized geometries such as bond lengths and dihedral angles of SCH_3 , SCH_3F , and SCH_3Cl for the S_0 and S_1 states are listed in Table 1. The calculated bond lengths of the S-C7 bond in the S_0 state are 1.825, 1.825, and 1.825 Å for SCH_3 , SCH_3F , and SCH_3Cl , respectively. In the S_1 state, these distances are slightly shorter than those in their ground state, especially in the SCH_3 system. The S-C1 bond length in the S_0 (S_1) state for SCH_3 , SCH_3F , and SCH_3Cl are 1.788 (1.780), 1.785 (1.771), and 1.785 (1.771) Å, respectively, and shorter in the S_1 states, mirroring the S-C7 bond length. The C-F and the C-Cl bond lengths in the S_0 (S_1) state of SCH_3F and SCH_3Cl are 1.355 (1.363) and 1.767 (1.760) Å, respectively, suggesting enhanced conjugation in these systems. This agrees well with the previous study by Zang *et al.* (Zhang *et al.*, 2022). Bond lengths between C and F are shorter than that of C and Cl by ~ 0.400 Å. From Table 1, all compounds are planar with the CCCC dihedral angle at the benzene ring of ~ 0.0 degrees for all structures in the S_0 and S_1 states. Similarly, the C1C2SC7 torsion is $\sim 0^\circ$ which is planar in both states. For the SCH_3F and SCH_3Cl substituent the C1C2C3X (where X is H, F, and Cl) angle is 180.0° in S_0 and S_1 for both structures indicating that the steric effect between the two substituents is not involved in the relative orientation of the -SCH₃ group in both states where the planarity of this benzene ring may affect the delocalization.

Table 1. Summary of the important bond distances (Å) and dihedral angles ($^\circ$) in the S_0 and S_1 states computed at the B3LYP/TZVP level of theory

	State	Distance (Å)			Dihedral angle ($^\circ$)		
		S-C7	S-C1	C-X (F, Cl)	C1C2C3C4	C1C2SC7	C1C2C3X (X is H, F, Cl)
SCH_3	S_0	1.825	1.788	-	0.0	0.0	180.0
	S_1	1.780	1.780	-	0.2	0.7	180.0
SCH_3F	S_0	1.825	1.785	1.355	0.0	0.0	180.0
	S_1	1.817	1.771	1.363	0.0	0.0	180.0
SCH_3Cl	S_0	1.825	1.785	1.767	0.0	0.0	180.0
	S_1	1.815	1.771	1.760	0.0	0.2	180.0

Table 2. Vertical excitation energies of SCH₃, SCH₃F, and SCH₃Cl at TD-B3LYP/TZVP level of theory. H and L represent HOMO and LUMO, respectively

	State	Excitation Energy (eV, nm)	Oscillator Strength (f)	Transition
SCH ₃	S ₀ →S ₁	4.63, 268	0.0161	H → L (88%)
	S ₀ →S ₂	5.10, 243	0.2341	H → L+I (90%)
SCH ₃ F	S ₀ →S ₁	4.72, 263	0.0322	H → L (54%)
	S ₀ →S ₂	5.11, 242	0.2320	H → L+I (55%)
SCH ₃ Cl	S ₀ →S ₁	4.57, 271	0.0166	H → L (88%)
	S ₀ →S ₂	5.02, 247	0.2246	H → L+I (94%)

Calculated absorption spectra and frontier molecular orbitals

Excitation energies are vital for predicting fluorescence, phosphorescence, lifetimes, and quantum yields. They aid in estimating band gaps in semiconductors, assessing visible light absorption in photocatalysts, tuning sensor responses, validating computational models, and guiding experiments when data is lacking.

The calculated maximum wavelength of absorption spectra (λ_{max}), excitation energies, oscillator strengths (f), and major contributions of SCH₃, SCH₃F, and SCH₃Cl are listed in Table 2. The electronic transition of SCH₃ to the first-excited state (S₁) requires 4.63 eV with a low oscillator strength. This transition occurs from the HOMO to LUMO and is attributed to the π - π^* state. The electronic transition energy required for the π - σ^* state is 5.10 eV (HOMO to LUMO+1). Moreover, the electronic transition for SCH₃F is S₀→S₁ occurs at 4.72 eV while the S₀→S₂ transition is at 5.11 eV. The energies of the π - π^* and π - σ^* states of SCH₃Cl are 4.57 and 5.02 eV, respectively. From the maximum absorption wavelengths, Cl substitution in the SCH₃Cl at the meta position in the benzene ring results in a red shift (λ_{max} 271 nm) compared to SCH₃. In SCH₃F, the least affected by the heteroatom substitution, the substitution of F at the meta position resulted in a slight difference in the absorption spectra compared with non-substituted thioanisole (SCH₃). A slight blue shift can be observed in SCH₃F with a λ_{max} of 263 nm. However, the maximum absorption wavelengths from static calculations of SCH₃ (λ_{max} 268 nm) are lower than those found experimentally at 334 nm at low temperatures (Malongwe *et al.*, 2016). Nevertheless, the excitation energies at TD-B3LYP and RI-post HF methods are adequate for the description of the energy surface for the excited state process as discussed in ref (Daengngern *et al.*, 2016).

In the region of the conical intersection (CI) between excited states, the excitation energies of coupled cluster are also reliable. It is important to

acknowledge that neither TD-B3LYP nor coupled-cluster methods are well-suited for accurately describing regions near conical intersections (CIs), which typically require multi-reference approaches for reliable treatment. In this study, the molecular geometry of thioanisole exhibits reduced symmetry due to the fluctuating planarity between the aromatic ring and the rotating -SCH₃ group. Consequently, its photophysical behavior is relatively conventional, with fluorescence observed from the S₁→S₀ transition in accordance with Kasha's rule. We emphasize that such fluctuations in structural planarity may contribute to a decrease in fluorescence intensity - an effect not captured by static, rigid geometry optimizations. Dynamic simulations are therefore essential to account for this time-dependent structural variation and its impact on emission behavior. Thus, we explore this with on-the-fly dynamic simulations which will be discussed in the next section.

Excited state dynamics simulations

On-the-fly dynamic simulations in the excited state of 25 trajectories were performed to provide information such as probability and dynamic properties of SCH₃, SCH₃F, and SCH₃Cl observed by the movement over time of the molecule from 0 fs to 500 fs at TD-B3LYP/TZVP level of theory. This TD-B3LYP method is suitable and can be used to explore the behavior in the first excited state of the systems.

Excited state dynamics molecular structures

For all trajectories of SCH₃ (25 trajectories), there are 13 trajectories that achieve dynamic simulations up to 500 fs. But, another 12 trajectories showed S-CH₃ bond breaking before 500 fs. Adding a F substituent in SCH₃F, 12 trajectories from the 25 trajectories ran until 500 fs, while 13 trajectories did not complete to the full time. The breaking of the S-CH₃ bond is observed and some trajectories show dissociation of the SCH₃ moiety. For SCH₃Cl (Cl substituent), 13 trajectories from 25 trajectories

ran the full 500 fs matching the SCH₃ system. 12 trajectories that did not run for the full time showed similar trajectories to those found in SCH₃F. From all active trajectories, the benzene ring of SCH₃, SCH₃F, and SCH₃Cl seems to be planar. The rotation of the C1C2SC7 angle ranges from ~ 0-20 degrees at 0-100 fs for SCH₃, SCH₃F and SCH₃Cl (Figure 2). For SCH₃, the C1C2SC7 angle starts to rotate ~40 degrees from 200 fs and becomes twisted to nearly 90 degrees between 250 and 500 fs, as shown in Figure 2a. The C1C2SC7 angle of SCH₃F twists to nearly 90 degrees between 100-500 fs but is partially twisted to 120 degrees between 300-350 fs in Figure 2b, indicating that the twisting torsion plays a role in the structural stability of the excited state. However, the rotation of C1C2SC7 in SCH₃Cl shows lower fluctuation as shown in Figure 2c, with a possibility density in the range not exceeding 40 degrees from 0-500 fs, but in some parts twisting in the range of 40-160 degrees is observed. This is due to the heavy atom Cl substituent. In addition, the substituent also affects the twist angle at the position where the substituent is added, causing different twists because of the size of the substituent. The C1C2C3H angle of SCH₃ in Figure 3a shows a twist density in the range of 160-180 degrees. For the C1C2C3F angle of SCH₃F, the twist angle density is mostly found in the range of 180 degrees (Figure 3b). In addition, the C1C2C3Cl angle of SCH₃Cl shown in Figure 3c reveals twisting in the range of 120-180 degrees because of the properties and size of the substituent. The H atom is very small, and has a lower electronegativity (EN), causing a flexible movement. The F atom has high EN and a larger atomic size than H, resulting in the position of the F atom substituent being only slightly rotated in the range of 180 degrees and the Cl atom is the largest among all the substituents in this work resulting in an unstable substitution causing the Cl atom to be twisted 120 degrees. Although the Cl atom is bigger than a F atom, fluorine is much more electronegative. This means fluorine pulls electrons toward itself more strongly than chlorine does. Because of this strong pull, the F atom is less free to move compared to Cl. In this case, chlorine's electron-withdrawing effect is stronger than any electron-donating effects, which makes the positive charge (or "positive hole") on the benzene ring even stronger instead of canceling it out. As a result, the part of the molecule with the C1C2C3Cl structure has to twist (increase its torsion angle) more to reduce the effect of this positive charge. This behavior is different from what we see in a molecule like SCH₃Cl, where chlorine's substituent effect is more nuanced.

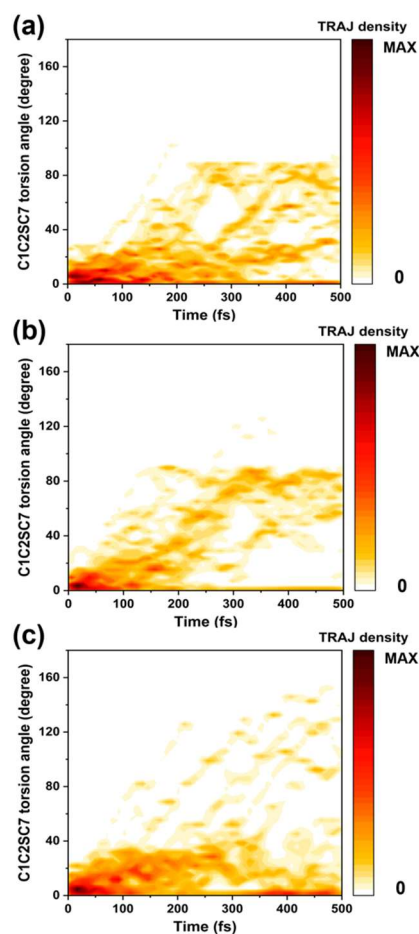


Figure 2. Evolution of C1C2SC7 torsion angles (degree) of (a) SCH₃, (b) SCH₃F, and (c) SCH₃Cl through all trajectories

Emission spectra from excited state dynamics

Emission maxima of the simulated spectra from S₁→S₀ states with on-the-fly dynamic simulations of SCH₃, SCH₃F, and SCH₃Cl (A representative trajectory over 25 trajectories) are depicted in Figure 4. The maximum peak of SCH₃F is found to be slightly blue shift from 371 nm to 365 nm when compared with SCH₃, and red shifted from 371 nm to 424 nm for SCH₃Cl. The F atom tends to withdraw electron density from the neighboring atoms due to its high electronegativity. This electron-withdrawing effect can lead to a decrease in the electron density around the S atom and its attached hydrogen atoms. Consequently, the electron transition energies associated with absorption spectra are typically shifted to higher energies, resulting in a blue shift. In contrast, when a Cl atom is added to the molecule, it also affects the electron density around the S atom, but to a lower extent compared to F. Cl is less

electronegative than F and exhibits a weaker electron-withdrawing effect. Therefore, the addition of a Cl atom may lead to a smaller decrease in electron density compared to F. This results in a red shift in the absorption spectra, where the transition energies are shifted to lower energies.

Relationship between emission and torsion

The torsion angle between the substituent and the main moiety can be one of the effects for the electronic structure, leading to a change in the excitation energy required for electronic transitions. This is particularly relevant in conjugated systems, where the delocalization of electrons along the π -system can be influenced by the spatial orientation of the substituents (Brédas *et al.*, 1999). To determine the correlation between fluorescence

emission energies and torsion angles, 15 geometries of each system were randomly selected to demonstrate the structural change in the excited state.

For the fluorescence, its photophysical behavior is relatively conventional, with fluorescence observed from the $S_1 \rightarrow S_0$ transition in accordance with Kasha's rule. All trajectories were simulated at TD-B3LYP/TZVP level with time steps of 1 fs and maximum time up to 500 fs to cover the change reflecting the geometrical stability. A method of choice using TD-B3LYP gives quite reliable results to explore the dynamics behavior in the excited state. In addition, the relationship between S_1 emission (eV) and C1C2SC7 torsion over time of (a) SCH₃, (b) SCH₃F, and (c) SCH₃Cl is presented in Figure 5.

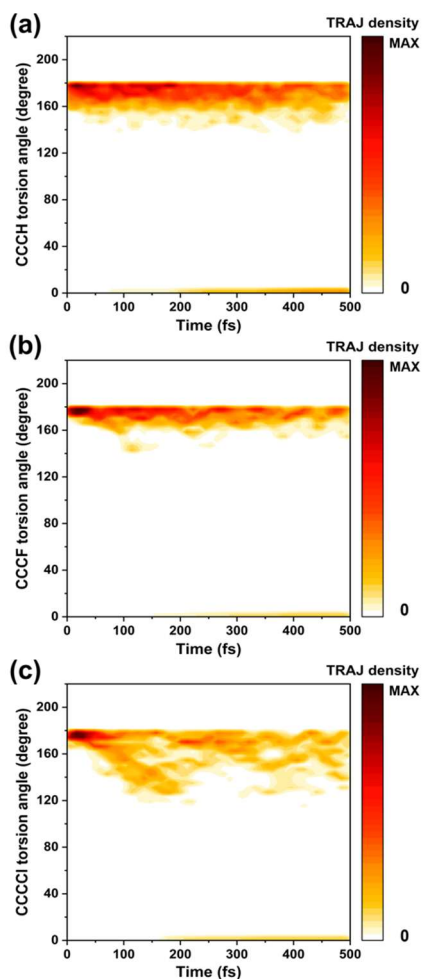


Figure 3. Evolution of C1C2C3X (X is H, F, and Cl) torsion angle across all trajectories over the simulation time of (a) SCH₃, (b) SCH₃F, and (c) SCH₃Cl

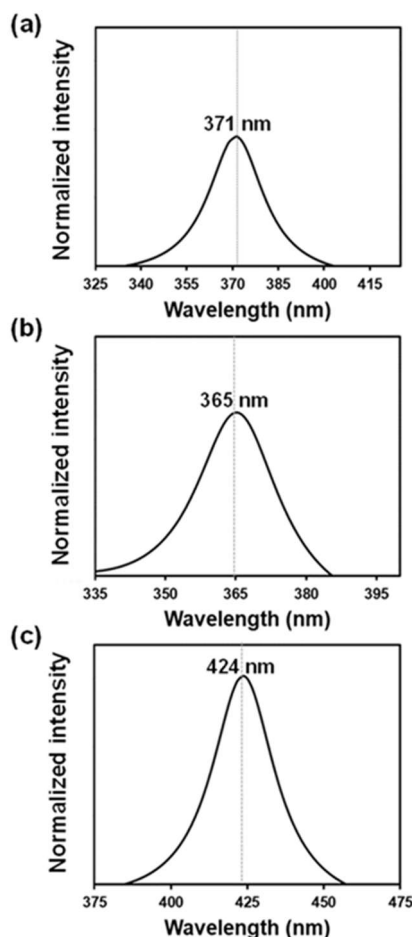


Figure 4. Emissions spectra from selected dynamics geometry of (a) SCH₃, (b) SCH₃F, and (c) SCH₃Cl computed at TD-B3LYP/TZVP level of theory. (A representative trajectory from 25 trajectories)

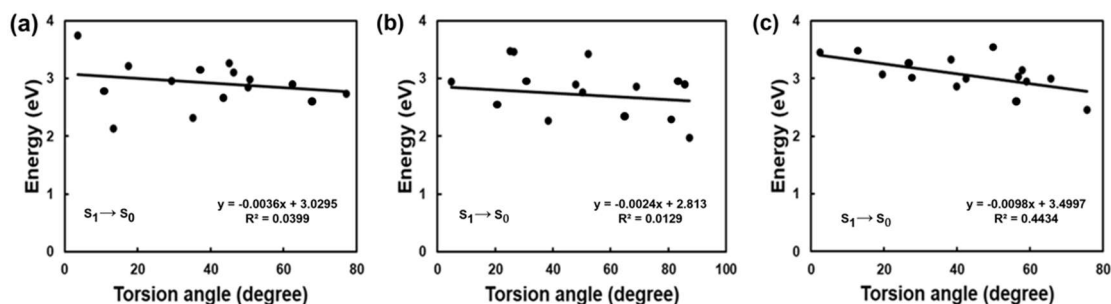


Figure 5. Relationship between S₁ emission (eV) and C1C2SC7 torsion over 15 selected geometries of (a) SCH₃, (b) SCH₃F, and (c) SCH₃Cl

There is a relationship between the S₁ emission energy and the C1C2SC7 dihedral angle (15 sampling geometries from 25 trajectories) of SCH₃, SCH₃F, and SCH₃Cl. From Figure 5, energy gaps between S₁ and S₀ decrease as the dihedral angle is twisted. The energy of SCH₃ decreases from ~4-3 to 2.8 eV (Figure 5a) when the dihedral angle is twisted from 10-20 degrees as shown in Figure 6 where snapshots of the SCH₃ dynamic structure over a simulation time of 500 fs are shown. Between 0 fs and 200 fs, the C1C2SC7 torsion angle of SCH₃ has a slight distortion of about 10 degrees. As time progresses from 300 fs to 500 fs, the C1C2SC7 torsion angle of SCH₃ fluctuates from 10 to 20 degrees, which is slightly more twisted than before. For SCH₃F, the transition energy decreases from about 3 to 2 eV (Figure 5b), when the dihedral angle twists from 0 to 90 degrees (or nearly perpendicular to the benzene ring). Figure 7 shows that at 0 fs the SCH₃F molecule has a C1C2SC7 torsion angle 0 degrees, indicating no initial twist. However, as time progresses to 100-200 fs, the torsion angle begins to twist slightly reaching approximately 10-20 degrees. After 300 fs, the C1C2SC7 torsion angle becomes twisted up to 45 degrees and further increases to 90 degrees, or perpendicular to the benzene ring at 400 fs. For the SCH₃Cl molecule (Figure 8), the SCH₃ angle is only slightly twisted up to 200 fs. At 300 fs the C1C2SC7 torsion angle is nearly 90 degrees and is twisted to almost 80 degrees at 400 to 500 fs. It is shown that when the dihedral angle twists from 0 to nearly 80 degrees, the transition energy drops from 3.5 to 2.5 eV (Figure 5c) confirming that all molecules lose energy upon twisting. This relationship between emission energy and dihedral angle affects fluorescence intensity. The relationship between energy and the torsion of the three molecules can be expressed using the following equations: SCH₃; $y = -0.0036x + 3.0295$, $R^2 = 0.0399$, SCH₃F; $y = -0.0024x + 2.813$, $R^2 = 0.0129$ and SCH₃Cl; $y = -0.0098x + 3.4997$, $R^2 = 0.4434$. From these three

equations, we observe that as the value of the x-axis increases the y-axis values decrease. This indicates that internal conversion becomes more dominant as molecular twisting increases, resulting in lower energy gaps between the S₁ and S₀ states. These twists involve rotations around single bonds within the molecular structure.

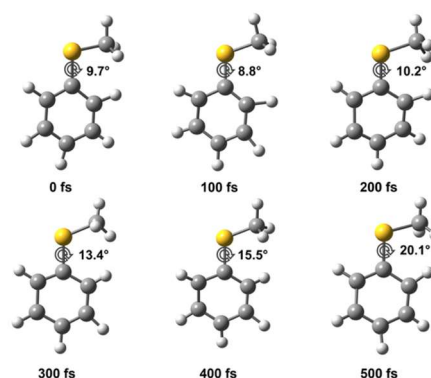


Figure 6. Snapshots of the SCH₃ dynamics showing the structure over a simulation time of 500 fs

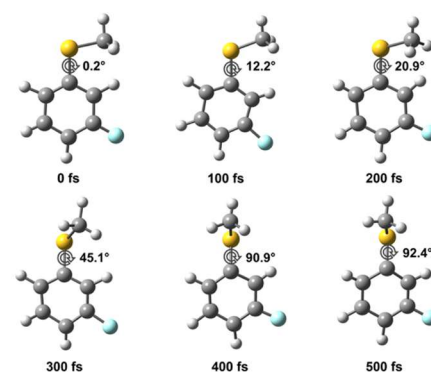


Figure 7. Snapshots of the SCH₃F dynamics showing the structure over a simulation time of 500 fs

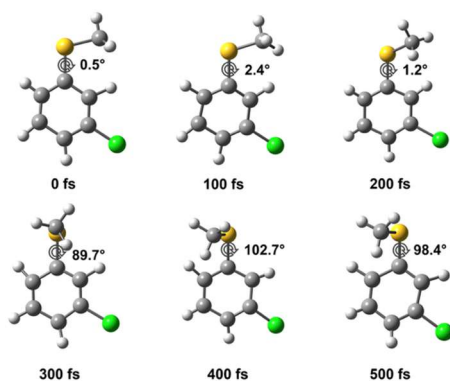


Figure 8. Snapshots of the SCH₃Cl dynamics showing the structure over a simulation time of 500 fs

Conclusions

The static and dynamic properties of SCH₃, SCH₃F, and SCH₃Cl were systematically investigated using B3LYP and TD-B3LYP methods with a TZVP basis set. Substitution with chlorine (SCH₃Cl) resulted in a red shift in absorption (λ_{max} at 271 nm), while fluorine substitution (SCH₃F) caused a slight blue shift (λ_{max} at 263 nm). The maximum absorption wavelengths from static calculations of SCH₃ (λ_{max} 268 nm) were significantly lower than from the experimental value of 334 nm at low temperatures. Simulated emission spectra showed that both Cl and F substitutions at the meta position enable observable S₁→S₀ transitions. SCH₃Cl exhibited red-shifted emission, whereas SCH₃F displayed a blue shift. These shifts are primarily influenced by the molecular planarity and torsional effects in the excited state. Slight shortening of the S–C bonds was observed in all compounds upon excitation, with the C–F bond in SCH₃F being shorter and stronger than the C–Cl bond in SCH₃Cl. All compounds retained their planar structure, suggesting minimal steric hindrance and sustained electronic delocalization. Transitions to the first excited state (S₁) were observed at 4.63 eV, 4.72, and 4.57 eV for SCH₃, SCH₃F, SCH₃Cl, respectively. The study showed a relationship between the torsion angles and excitation energies revealing that an increase in dihedral angles reduces the S₁ and S₀ energy gap, indicating that the substituents influence transition energies through structural distortion. In summary, quantum dynamics simulations used in this work provided insights into molecular behavior not accessible through static calculations alone. Thus, this approach is a valuable tool for understanding the

impact of structural stability on fluorescence intensity.

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