Photoionization Spectroscopic and Theoretical Study on the Molecular Structures of cis- and trans-3-Chlorothioanisole

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ABSTRACT: Resonance-enhanced two-photon ionization (R2PI) and mass-analyzed threshold ionization (MATI) spectra are measured for the cis- and trans-3-chlorothioanisole (3CITA). The first electronic excitation energy (E_1) and the adiabatic ionization energy (IE) of the cis-rotamer are determined to be 33 959±3 and 65 326±5 cm⁻¹, respectively, and those of the trans-rotamer are determined to be 34 102±3 and 65 471±5 cm⁻¹, respectively. Density functional theory (DFT) calculations confirm that both the cis- and trans-rotamers of 3CITA are stable and coexist in their respective S₀, S₁, and D₀ states. Both rotamers adopt planar structures with cis- being slightly more stable than trans- in the respective S₀, S₁, and D₀ states. The conformation, substitution, and isotope effects on the molecular structure, active vibrations, and electronic transition and ionization energies of 3CITA are analyzed.

1. INTRODUCTION

There have been numerous experimental and theoretical studies for investigating the stable structures and properties of anisole and thioanisole (TA) derivatives in their electronic ground (S₀), first excited (S₁), and cationic ground (D₀) states.¹⁻⁹ Due to strong conjugation effect between the benzene ring and the substituent functional groups, most of those molecules are found to be planar. However, several exceptions have been observed. For example, a nonplanar stable structure was observed for trans-2-fluoroanisole (2-F anisole) in its Sₐ state with Fourier transform infrared (FTIR) spectroscopy¹⁰ and a small structure tilt was observed for trans-2-fluorothioanisole (2FTA) in its Sₐ state through resonance-enhanced two-photon ionization (R2PI) spectroscopy.¹¹ In 2FTA, the enhanced steric effect and inductive effect caused by the 2-substituted (ortho-substituted) F atom play important roles.

For TA derivatives, there exist a lot of controversies, from previous calculations and spectroscopic results,⁶,⁹,¹²⁻¹⁴ about their stable structures, particularly in their S₁ states. Some theoretical calculations predict their molecular skeletons to be nonplanar in the S₁ state,¹³,¹⁵ in which the thiomethyl (–SCH₃) group is nearly perpendicular to the benzene ring. The whole molecule has a vertical gauche-like structure. This contradicts the general rule that the benzene ring tends to keep a planar structure as favored by π-orbital delocalization.¹⁶

The nonplanar structures obtained by theoretical calculations do not exactly agree with the spectroscopic experiments.⁶,⁹,¹⁵ Nevertheless, most TA derivatives have now been determined to be planar or quasi-planar,⁶,⁹,¹²⁻¹⁵ and the competition between the steric effect and the inductive effect caused by –SCH₃ was used to explain the difference between calculations and spectroscopic measurements.⁶,⁹,¹⁵ However, the reason for the structure tilt seen in the theoretical calculation is still unclear, and it is worthwhile to investigate the stable structures of halogen-substituted anisole and TA derivatives in various electronic states.

The deformation changes of benzene derivatives upon photoexcitation and photoionization are usually similar to each other for molecules with similar structures.¹,⁶,¹⁰⁻²³ For example, benzene ring is usually enlarged in the S₁ state and a quinoidal structure is often found in the D₀ state. It is reasonable to assume that the conjugation effects of –OCH₃ and –SCH₃ groups with the benzene ring are similar since O and S atoms belong to the same group in the periodic table. Compared with the O atom, the S atom is larger in size, which could make the –SCH₃ group more flexible than the –OCH₃ group.²,¹⁴ Investigation on how the –SCH₃ group substitution affects the molecular properties is limited.

Besides the conjugation effect mentioned above, the steric effect and inductive effect caused by the halogen substitutions should also be considered. For example, the cis-rotamer is observed to be stable for 3-fluoroanisole (3-F anisole)²¹ but not for 2-F anisole.¹⁰,²² That is due to the fact that the steric effect between the F atom and the –OCH₃ group is weaker in

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3-substituted (meta-substituted) anisole than that in the 2-substituted one. The transition energies (E_i) of Cl-substituted anisoles were found to be red-shifted compared to those of anisole, while those of F-substituted anisoles were found to be blue-shifted. This is mainly caused by the different inductive effects of F and Cl atoms.

Based on the above discussion, the 3-chlorothioanisole (3ClTA) molecule can be a suitable system for simultaneously comparing the substitution effects between −SCH3 and −OCH3 groups and between Cl and F atoms. To the best of our knowledge, the vibrational spectra of 3ClTA in both S_0 and D_0 states have not been reported, and its structural properties have not been investigated. In this work, we reported a combined theoretical and spectroscopic study on the cis- and trans-rotamers of 3ClTA. The vibrational spectra of 3ClTA in S_1 and D_0 states were measured by R2PI and mass-analyzed threshold ionization (MATI) spectroscopy. The stable molecular structures and the rotational barriers between the cis- and trans-rotamers of 3ClTA are calculated by comparing the spectroscopic measurements with the theoretical calculations. The structural changes induced by photoexcitation and photoionization are discussed in detail.

2. RESULTS

2.1. Calculated Results. The chemical structures and the atomic labelings of cis- and trans-3ClTA are shown in Figure 1.

The optimized geometric parameters and atomic charges for the two rotamers in S_0, S_1, and D_0 states are listed in Table 1, and their Cartesian coordinates are provided in the Supporting Information (Table S1). The calculated one-dimensional potential energy curves (PECs) of 3ClTA in S_0, S_1, and D_0 states are presented in Figure 2. All PECs were scanned along the C2−C1−S−C8 dihedral angle from −10° to 190° in a 5° increment, and all other structural parameters were optimized without any constraints. The presented energies for the stationary points corresponding to minimum structures include zero-point energy (ZPE) corrections, but ZPE corrections are not included for other points on the PECs.

The calculations indicate that different chlorine isotopes have negligible effects on the investigated properties of 3ClTA, such as molecular geometry, excitation (E_i) and ionization (IE) energies, and vibrational frequencies. Such finding is similar to previous studies on several aromatic molecules containing the chlorine substituent. Hence, we will focus on the results of the 35Cl-substituted 3ClTA in the following sections for clarity.

The PECs presented in Figure 2 indicate that the cis-rotamer of 3ClTA is slightly more stable than its trans-rotamer in S_0 and D_0 states, while the calculated energies including ZPE corrections for the stationary points in the S_1 state show that the trans-rotamer is slightly more stable than the cis-rotamer. Nonetheless, these energy differences are relatively small, and a more confident assignment needs experimental support. In the S_0 state, the calculated energy difference between the cis- and trans-rotamers is 68 cm⁻¹, including ZPE corrections, and the isomerization energy barrier is about 500 cm⁻¹ with respect to the cis-rotamer. A previous study showed that flexible organic molecules with interconversion barriers larger than 400 cm⁻¹ would not relax significantly during the supersonic expansion. Hence, both the cis- and trans-rotamers of 3ClTA could exist in the supersonic molecular beam with an estimated population ratio N_{cis}/N_{trans} of about 1.4 according to the Maxwell–Boltzmann distribution under the assumption of thermal equilibrium.

It is noted that in the calculated PEC for the S_1 state (Figure 2), the benzene ring is distorted and the Cl atom is optimized to be out-of-plane for most of the data points, except at the points where the C2−C1−S−C8 dihedral angles are 0 and 180°. Similar behavior has been found previously for the S_1 state of TA. Therefore, caution should be taken for quantitative evaluation of the calculated PEC and rotational barrier of 3ClTA in the S_1 state. Nonetheless, at the C2−C1−S−C8 dihedral angles of 0 and 180°, the benzene ring was all optimized to be planar with the Cl atom in the same plane for S_0, S_1, and D_0 states.

A discontinuity at 90° was noted in the PEC of the D_0 state. It is mainly caused by the rotation of the −CH3 group, and such discontinuity does not affect the optimized results for both cis- and trans-rotamers at 0 and 180° in the D_0 state. Similar discontinuities were observed previously in the PECs of 2-N-methylaminopyridine. In this regard, the calculated IEs and relative stabilities of the two rotamers in the D_0 state are assumed to be not affected by the discontinuity at 90°.

2.2. 1C-R2PI Spectra. A typical time-of-flight (TOF) mass spectrum of 3ClTA recorded at the UV wavelength of ~285 nm is presented in Figure 3. The mass peaks at 159 and 161 amu are assigned, respectively, to the ion signals of 35Cl-3ClTA and 35Cl-37Cl-3ClTA isotopomers, showing that the mass resolution of the setup is enough for collecting the individual spectra of the two isotopomers of 3ClTA. The 1C-R2PI spectra of the 35Cl and 37Cl isotopomers of 3ClTA in the range of 0–1200 cm⁻¹ are shown in Figure 4. Tentative assignments of the observed vibrational features are listed in Table 2, and the Varsányi’s labeling system is adopted to approximately describe the observed benzene-like vibrational modes of 3ClTA, which should be classified as an meta-di-heavy substituted benzene derivative.

As shown in Figure 4, the first electronic excitation energies of cis- and trans-3Cl-3ClTA are identical to those of 35Cl-3ClTA, confirming that the Cl isotope substitution has negligible effects on the first electronic excitation energies of 3ClTA. Most of the vibrational frequencies are close to each other for the two 3ClTA isotopomers within 3 cm⁻¹. For example, the 6v_0, 2ν_1, and 1v_2 bands locate at 349, 617, and 953 cm⁻¹ for 35Cl-3ClTA, and 351, 615, and 955 cm⁻¹ for 37Cl-3ClTA, respectively. The relative intensities of several vibrational bands are different between the two isotopomers, which is presumably attributed to the edge eliminating effect in choosing the mass range to obtain the reduced spectra during experiments. Those experimentally observed similarities between the two 3ClTA isotopomers verified our predictions.
Table 1. Calculated Geometric Parameters and Atomic Charges of cis- and trans-Rotamers of 3CITA

| Bond Length (Å) | S₀ | S₁ | D₀ |
|-----------------|----|----|----|
| S–CH₃          | 1.815 | 1.804 | 1.809 |
| S–C1           | 1.774 | 1.754 | 1.717 |
| C1–C2          | 1.394 | 1.395 | 1.406 |
| C2–C3          | 1.389 | 1.434 | 1.377 |
| C3–C4          | 1.385 | 1.401 | 1.415 |
| C4–C5          | 1.392 | 1.390 | 1.393 |
| C5–C6          | 1.384 | 1.440 | 1.378 |
| C6–C1          | 1.400 | 1.403 | 1.427 |
| C3–C1          | 1.755 | 1.746 | 1.719 |

| Bond Angle (°) | S₀ | S₁ | D₀ |
|----------------|----|----|----|
| C8–C1–C2      | 103.9 | 106.9 | 106.7 |
| S–C1–C2       | 124.1 | 122.2 | 125.1 |
| S–C1–C6       | 116.5 | 112.9 | 114.2 |
| C2–C1–C6      | 119.4 | 124.9 | 120.7 |
| C1–C2–C3      | 119.2 | 116.0 | 118.6 |
| C2–C3–C4      | 121.1 | 120.7 | 121.0 |
| C3–C4–C5      | 118.2 | 122.0 | 120.2 |
| C4–C5–C6      | 121.0 | 119.0 | 119.9 |
| C5–C6–C1      | 120.2 | 117.5 | 119.6 |
| C2–C3–C1      | 118.6 | 118.8 | 120.3 |

| Atomic Charges (e) | H of –CH₃ group | C8 | S | C1 | C2 (H⁺) | C3 | C4 (H⁺) | C5 (H⁺) | C6 (H⁺) | Cl |
|-------------------|-----------------|----|---|---|--------|----|---------|---------|---------|----|
|                   | 0.208           | -0.705 | 0.270 | -0.137 | -0.279 | 0.017 | -0.251 | -0.165 | -0.230 | -0.018 |
|                   | 0.238           | -0.736 | 0.638 | -0.195 | -0.348 | 0.028 | -0.153 | -0.281 | -0.320 | -0.031 |
|                   | 0.248           | -0.729 | 0.668 | -0.170 | -0.241 | 0.040 | -0.079 | -0.181 | -0.117 | 0.116 |
|                   | 0.218           | (0.208) | (0.208) | 0.261 | (0.240) | (0.223) | (0.212) | (0.243) | (0.204) | (0.239) |
|                   | 0.207           | -0.704 | 0.270 | -0.136 | -0.257 | 0.014 | -0.250 | -0.162 | -0.253 | -0.015 |
|                   | 0.235           | -0.738 | 0.646 | -0.200 | -0.372 | 0.014 | -0.153 | -0.301 | -0.282 | -0.044 |
|                   | 0.261           | -0.729 | 0.681 | -0.169 | -0.199 | 0.014 | -0.074 | -0.072 | -0.162 | 0.104 |

*The H atom in parentheses is directly connected to the C atom before the parentheses.*

derived from theoretical calculations, allowing us to discuss only the spectrum of 35Cl-3CITA in the following sections.

3CITA has 42 normal modes, and the intensity of the vibronic bands is proportional to the Franck–Condon factors (FCFs), and thus not all vibrational modes, for instance, in the cases of very small FCFs, could be observed in the 1C-R2PI process. The assignments of the observed bands to a specific rotamer have been confirmed by measuring the respective IEs using the MATI spectroscopic method.

According to the calculations, the cis-rotamer is slightly more stable than the trans-rotamer in the S₀ state and should have a higher population in the supersonic molecular beam and thus corresponds to a stronger band origin peak in the 1C-R2PI spectrum. Hence, the observed vibrational band at 33959 cm⁻¹ is tentatively assigned to the cis-rotamer’s band origin (S₁ ← S₀ 0₀₀ band). This band origin corresponds to E₁. The band at 34102 cm⁻¹ is tentatively assigned to the trans-rotamer’s 0₀₀ band. The experimentally measured 0₀₀ band of the trans-rotamer is blue-shifted by 143 cm⁻¹ with respect to that of the cis-rotamer. These assignments are also consistent with the calculated results that the cis-rotamer is more stable than the trans-rotamer in the D₀ state. However, these results seem not to be consistent with the calculations in the S₁ state. Such discrepancy could be attributed to the expected difficulty of TDDFT in accurately predicting the electronically excited states.

Besides the 0₀₀ bands, the bands at 46 and 97 cm⁻¹ are assigned as the methyl torsion vibrational mode τ₁ and its overtone τ₃ of the cis-rotamer, in good agreement with the calculated methyl torsion vibration of 48 cm⁻¹ and its overtone of 96 cm⁻¹ (Table 2; also see Figure S1 in the Supporting Information for the vibrational vectors); the band at 209 cm⁻¹ is assigned as the cis-1S₀ mode, and the corresponding calculated value is 213 cm⁻¹; the bands at 349, 617, 815, and 953 cm⁻¹ are assigned to the in-plane ring deformation modes 6a₂, 6b₂, 12₆, and 1₃ of the cis-rotamer, also agreeing with the calculated values of 360, 621, 790, and 960 cm⁻¹; and a combination band of 6a₁ and τ₀ is observed at 409 cm⁻¹.
Figure 2. Calculated one-dimensional potential energy curves (PECs) along the dihedral angle between the $\text{SCH}_3$ group and the benzene ring in $S_0$, $S_1$, and $D_0$ states of 3ClTA. The presented energies for the stationary points corresponding to minimum structures include zero-point energy (ZPE) corrections, but ZPE corrections are not included for intermediate points on the PECs.

(Figure 4; the calculated $6a_0^1 + \tau_0^1$ sum frequency is 408 cm$^{-1}$). As for the trans-rotamer, the observed bands at 24 and 41 cm$^{-1}$ are assigned to the methyl torsion mode $\tau_0^1$ and its overtone $\tau_0^2$, and the band at 963 cm$^{-1}$ is assigned to the in-plane ring deformation mode $\nu_0^1$. Those measured values are well reproduced by the calculations, i.e., 33 and 954 cm$^{-1}$ for $\tau_0^1$ and $\nu_0^1$, respectively. The above mode assignments are summarized in Table 2, and in Figure S1 in the Supporting Information, their vibrational vectors are provided.

2.3. MATI Spectra. The MATI spectra and the assignments of the vibrational bands observed for the cis- and trans-rotamers of $^{35}$Cl- and $^{37}$Cl-3ClTA are presented in this section. For the cis-rotamer, MATI spectra were recorded via the vibrational peaks at 0, 46, 349, and 409 cm$^{-1}$, which show relatively high intensities in the 1C-R2PI spectra; for the trans-rotamer, MATI spectra via the band origin $00^0$ at 0 cm$^{-1}$ and the $\tau_0^1$ mode at 24 cm$^{-1}$ were collected. Except for several vibrational peaks that were not observed due to the low intensity, the MATI spectra of $^{37}$Cl-3ClTA are nearly identical to those of $^{35}$Cl-3ClTA for both rotamers (Figure 5). All vibrational frequencies of the two isotopomers were observed within 7 cm$^{-1}$, close to the experimental uncertainty ($\pm 5$ cm$^{-1}$). Thus, only the MATI spectra of $^{35}$Cl-3ClTA are discussed here.

Table 2. Observed Vibrational Frequencies (in cm$^{-1}$) in the 1C-R2PI Spectra of cis- and trans-3ClTA and Their Tentative Assignments

| cis-3ClTA | trans-3ClTA |
|-----------|-------------|
| expl.      | vib. | theo. | assignment$^b$ | expl.      | vib. | theo. | assignment$^b$ |
| 33 959     | 0    | 48   | band origin    | 34 102     | 0    | 33   | band origin    |
| 34 005     | 46   | 96$^c$ | $\tau_0^1$torsion | 34 126     | 24   | 66$^c$ | $\tau_0^1$torsion |
| 34 056     | 97   | 213  | $\tau_0^1$torsion | 34 143     | 41   | 66$^c$ | $\tau_0^1$torsion |
| 34 168     | 209  | 360  | $6a_0^1$, $\beta(C-C-C)$ | 35 065     | 963  | 954  | $\nu_0^1$, breathing |
| 34 308     | 349  | 408$^c$ | $6a_0^1\nu_0^1$ | 34 308     | 408$^c$ | 617  | $\nu_0^1$, stretching |
| 34 368     | 617  | 621  | $\nu_0^1$, stretching | 34 368     | 617  | 621  | $\nu_0^1$, stretching |
| 34 576     | 815  | 790  | $12\nu_0^1$, $\beta(C-C-C)$ | 34 576     | 815  | 790  | $12\nu_0^1$, $\beta(C-C-C)$ |
| 34 912     | 953  | 960  | $\nu_0^1$, breathing | 34 912     | 953  | 960  | $\nu_0^1$, breathing |

$^a$The theoretical values have been scaled by a scaling factor of 0.967. $^b$The torsion vibration and stretching vibration are denoted by $\tau$ and $\nu$, respectively. The bending mode is designated by $\beta$. $^c$The calculated frequency for these overtone and combination modes are taken from the sum of the calculated individual frequency of each mode.
and 65.471 ± 5 cm⁻¹, giving a measured difference of IE values to be 145 cm⁻¹. These values agree reasonably with the calculated respective values of 63.205, 63.456, and 251 cm⁻¹ including ZPE corrections (Figure 2).

The assignments of all of the vibrational modes observed in the MATI spectra are listed in Table 3. Most of the observed active vibrations are found to be related to the ring deformation and substituent-sensitive modes. For the cis-₃⁵Cl-₃ClTA, the bands at 88 and 177 cm⁻¹ are assigned as the methyl torsion vibrational mode \( \nu^t \) and its overtone \( \nu^{2t} \), respectively. Note that the calculated methyl torsion vibrational frequency is 83 cm⁻¹. The bands at 223, 652, and 980 cm⁻¹ are assigned as the vibrational modes of \( \nu^{1s} \), \( \nu^{0s} \), and \( \nu^{1s} \), respectively, agreeing with the calculated respective values of 270, 629, and 978 cm⁻¹; the bands at 289 and 446 cm⁻¹ are assigned as combination modes. The assignment of the prominent band at 398 cm⁻¹ in the MATI spectra via the \( 0^0 \) mode (Figures 5 and 6) is uncertain. It could be due to either the \( 6a^1 \) or \( 16b^1 \) mode. The \( 6a^1 \) mode is observed to be prominent in the 1C-R2PI spectra (Figure 4) with a vibrational frequency of 349 cm⁻¹. This observation seems to support the assignment of the calculated 381 cm⁻¹ band to the \( 6a^1 \) mode. However, the vibrational frequency of the \( 6a^1 \) mode is measured to be ~366 cm⁻¹ instead of 398 cm⁻¹ in the MATI spectra when the \( \tau^0_0 \) and \( 6a^0_0 \) modes in the \( S_0 \) state were used as the intermediate levels (Figure 7b,d). Similar phenomena have been observed previously for 2FTA.¹¹ For example, the \( 6a^1 \) band in the \( D_0 \) state of 2FTA was observed at 411 cm⁻¹ via the \( 0^0 \) mode in the \( S_1 \) state, while it was measured to be 400 cm⁻¹ when the \( \tau^0_0 \) mode was used as the intermediate level. For the trans-₃⁵Cl-₃ClTA, the frequencies of most benzene-ring-related vibrational modes are observed to be close to those of the cis-₃⁵Cl-₃ClTA. The most prominent peak in the MATI spectrum of trans-₃⁵Cl-₃ClTA via the methyl torsion mode \( \tau^0_0 \) at 24 cm⁻¹ (Figure 7e) is tentatively assigned as \( \nu^t(CSCH_3) + \nu^t(C-Cl) \), in reasonable agreement with the calculated value of 154 cm⁻¹ (Table 3; see also Figure S1 in the Supporting Information for the vibrational vectors). The vibrational frequency for overtone \( \tau^0_0 \) should be also close to ~120 cm⁻¹, while activation of \( \tau^0_0 \) is usually highly unfavorled.

In Figure 7, MATI spectra via several other vibrational bands are presented. It can be seen that when the MATI spectra were recorded via the in-plane ring deformation modes \( 6a_{sb} \), \( \nu^t \), and the combination mode \( 6a^0_{sb} \) as the intermediate levels, the most intensive vibrational peaks observed in the MATI spectra correspond to the same modes of the intermediate levels (Figure 7b,d). This indicates that the molecular geometry and the corresponding vibrational coordinates of the \( 6a^0_{sb} \) \( \nu^t \), and \( 6a^0_{sb} \) modes do not change much upon photoionization from the \( S_0 \) state to the \( D_0 \) state, as verified by the RMSD analysis (Figure S2). Similar phenomena via the benzene-ring-related vibrational levels were previously observed for anisole and its derivatives.¹⁷,21,23,30 However, when the methyl torsion mode \( \tau^0_0 \) was used as the intermediate level, the MATI spectra showed dramatically different characteristics as those via the benzene-ring-related vibrational levels. For the cis-rotamer, the most prominent peak was due to the \( 0^0 \) band, and many other vibrational modes were also significantly excited (Figure 7a). The MATI spectrum of the trans-rotamer via the methyl torsion mode \( \tau^0_0 \) at 24 cm⁻¹ is completely different from that of the cis-rotamer, the \( 0^0 \) band was much weaker, and several low-frequency vibrational modes were strongly excited (Figure 7e).
Table 3. Observed Vibrational Frequencies (in cm\(^{-1}\)) in the MATI Spectra of the cis- and trans-Rotamers of 3CITA and Their Tentative Assignments

|       | cis- |       |       |       | trans- |       |       |       |
|-------|------|-------|-------|-------|--------|-------|-------|-------|
|       | exp. |       |       |       | theor. |       |       |       |
|       |       |       |       |       |        |       |       |       |
| via 0\(_0\) | via 46 cm\(^{-1}\) | via 349 cm\(^{-1}\) | via 409 cm\(^{-1}\) | via 617 cm\(^{-1}\) | theor. | exp. |       |       |
| 0     | 0    | 0     | 0     | 0     | 0      | 0     | 0     | 0     |
| 88    |      |       |       |       | 83     |       |       |       |
| 177   |      |       |       |       | 166    |       |       |       |
| 223   |      |       |       |       | 270    | 15\(^1\) |       |       |
| 289   |      |       |       |       | 353\(^1\) | 15\(^1\) |       |       |
| 398   |      |       |       |       | 381    | 62\(^{a}\) or 16\(^{b}\) |       |       |
| 446   |      |       |       |       | 446\(^{a}\) | 62\(^{a}\) |       |       |
| 652   |      | 653   | 629   |       | 655    | 627   | \(\nu^1\) |       |
| 980   |      | 978   |       |       | 981    | 968   | 1\(^{1}\) |       |

\(^{a}\)The theoretical values have been scaled by a factor of 0.967. \(^{b}\)The assignments are according to the 1C-R2PI spectra in Table 2, and the torsion vibration and stretching vibration are denoted by \(r\) and \(\nu\), respectively. The bending mode is designated by \(\beta\). **The calculated frequency for these overtone and combination modes are taken from the sum of the calculated individual frequency of each mode.**

3. DISCUSSION

3.1. Molecular Structures of cis- and trans-3CITA in S\(_0\), S\(_1\), and D\(_0\) States. 3.1.1. Molecular Structures in S\(_0\) State. Both cis- and trans-3CITA are stable and adopt planar structures possessing a \(C_\alpha\) point group in the S\(_0\) state. The cis-rotamer is slightly more stable than the trans-rotamer, suggesting that the inductive effect of the Cl atom dominates over the steric effect between the two substituent groups in determining the relative stability of the two rotamers. As seen in Table 1, the S–C8 bond in the S\(_0\) state is 1.815 Å in the cis-rotamer and trans-rotamer, and S–C1C2 is 124.1° in the cis-rotamer and 116.0° in the trans-rotamer. The slightly larger S–C1C2 in the cis-rotamer may arise from the larger steric repelling effect between the Cl atom and the S–CH\(_3\) group in the cis-rotamer than that in the trans-rotamer. This is similar to the larger S–NC1C2 in cis-3-Cl-N-methylaniline than that in the trans-rotamer.\(^{16}\)

As for the benzene ring, all of the calculated bond length differences between the two rotamers are less than 0.007 Å and all the bond angle differences are less than 0.4°, indicating that the influences on the structure of the benzene ring caused by the different orientations of the S–CH\(_3\) groups in the two rotamers are small.

From the perspective of intramolecular charge distributions, the two rotamers are close to each other. Table 1 shows that their calculated atomic charges in the S\(_0\) state are almost identical, except for the C2 and C6 atoms. The C2 atom is more negative in the cis-rotamer (−0.279 e for the cis-rotamer and −0.257 e for the trans-rotamer), while the C6 atom is more negative in the trans-rotamer (−0.230 e for the cis-rotamer and −0.253 e for the trans-rotamer). This could be caused by the electron-donating effect of the −CH\(_3\) group, and the C atom closer to the −CH\(_3\) group gets more negative charge.

3.1.2. Structural Changes during the S\(_1\) ← S\(_0\) Transition. The intense 0\(_0\) bands observed in the 1C-R2PI spectra in Figure 4 suggest that there are only minor geometric changes upon excitation from the S\(_0\) state to the S\(_1\) state, as verified by the RMSD analysis (Figure S2). According to the calculated results shown in Table 1, the C1–C2, C2–C3, C3–C4, C5–C6, and C6–C1 bonds in the benzene ring become a little longer upon excitation while the C4–C5 bond stays about the same for the cis-rotamer; for the trans-rotamer, the C1–C2, C2–C3, C3–C4, and C5–C6 bonds become longer during the S\(_1\) ← S\(_0\) transition, while the C3–C4 and C6–C1 bonds are contracted by 0.001 and 0.006 Å, respectively. The above observations are consistent with the previous studies, which showed that the S\(_1\) ← S\(_0\) transitions of benzene derivatives are mainly subject to the \(\pi^* \leftarrow \pi\) electronic excitation and a benzene ring distortion usually occurs, making it deviate from a perfect hexagon.\(^{31,32}\) Such transition scheme is confirmed by analyzing the molecular orbitals involved in the first electronic transition (Figure S3).

Besides the benzene ring distortion, the C3–Cl bond connecting the benzene ring and the Cl atom is shortened by 0.009 Å for the cis-rotamer during the S\(_1\) ← S\(_0\) transition, while it is elongated slightly by 0.007 Å for the trans-rotamer. This may indicate that the steric effect between the Cl atom and the −CH\(_3\) group becomes weaker and/or the interaction between the Cl atom and the benzene ring becomes stronger in the S\(_1\) state for the cis-rotamer. The −SCH\(_3\) group is also distorted during the S\(_1\) ← S\(_0\) transition. The S–Cl bond connecting the −SCH\(_3\) group with the benzene ring is shortened by 0.020 Å for the cis-rotamer and 0.021 Å for the trans-rotamer. The S–C8 bond connecting the S atom with the −CH\(_3\) group is shortened by 0.011 Å for the cis-rotamer and 0.009 Å for the trans-rotamer. This is consistent with the change of the intramolecular charge distribution upon photoexcitation. As shown in Table 1, all H atoms in the −CH\(_3\) group and the S atom become more positive upon the excitation, while all H atoms directly connected to the benzene ring and all of the C atoms of the benzene ring become more negative in the S\(_1\) state, except for C4, which becomes less negative and is furthest from the −SCH\(_3\) group. The shortened bond lengths and the intramolecular charge distribution changes in the S\(_1\) state enhance the \(p\pi\) conjugation interaction between the −SCH\(_3\) group and the benzene ring (Figure S3). Some anisole
derivatives, such as 3-F anisole\textsuperscript{11} and 3-Cl anisole,\textsuperscript{23} undergo similar ring deformation upon excitation from the S\textsubscript{0} state to the S\textsubscript{1} state.

3.1.3. Structural Changes during Photoionization. Both the measured spectra and theoretical calculations suggest that both of the 3CITA rotamers adopt a stable planar structure in the D\textsubscript{0} state. The calculated results show that for both rotamers, the benzene ring of 3CITA has longer C1–C2, C3–C4, C4–C5, and C6–C1 bonds and shorter C2–C3 and C5–C6 bonds in the D\textsubscript{0} state than those in the S\textsubscript{0} state, showing a quinoidal structure. The chlorine atom and all the C atoms of the benzene ring except for C1 that connects with the —SCH\textsubscript{3} group become more positive (or less negative) in the D\textsubscript{0} state (1.718 Å for the cis-rotamer and 1.716 Å for the trans-rotamer) than that in S\textsubscript{0} (1.774 Å for the cis-rotamer and 1.775 Å for the trans-rotamer) and S\textsubscript{1} states (1.754 Å for the cis-rotamer and 1.754 Å for the trans-rotamer). This is consistent with the spectroscopic measurements that the frequencies of the methyl torsion mode \( \nu^1 \) for both rotamers become significantly larger in the D\textsubscript{0} state (88 cm\textsuperscript{-1} for the cis-rotamer and 34 cm\textsuperscript{-1} for the trans-rotamer) than those in the S\textsubscript{1} state (46 cm\textsuperscript{-1} for the cis-rotamer and 24 cm\textsuperscript{-1} for the trans-rotamer). The above observations indicate that the conjugation interaction between the p orbital occupied by the remaining nonbonding electron on the S atom and the \( \pi \) orbital on the benzene ring is enhanced in the photoionization process.

For the —SCH\textsubscript{3} group, the S–C1 bond shows a very strong double bond character in the D\textsubscript{0} state, and it is significantly shorter (1.718 Å for the cis-rotamer and 1.716 Å for the trans-rotamer) than that in S\textsubscript{0} (1.774 Å for the cis-rotamer and 1.775 Å for the trans-rotamer) and S\textsubscript{1} states (1.754 Å for the cis-rotamer and 1.754 Å for the trans-rotamer). The above observations indicate that the conjugation interaction between the p orbital occupied by the remaining nonbonding electron on the S atom and the \( \pi \) orbital on the benzene ring is enhanced in the photoionization process.

For the Cl atom, the C3–Cl bond is also significantly shorter in the D\textsubscript{0} state (1.719 Å for the cis-rotamer and 1.722 Å for the trans-rotamer) than that in S\textsubscript{0} (1.755 Å for the cis-rotamer and 1.754 Å for the trans-rotamer) and S\textsubscript{1} states (1.746 Å for the cis-rotamer and 1.761 Å for the trans-rotamer). The Cl atom can interact with the benzene ring through the p–\( \pi \) conjugative effect, which arises from the donation of a lone pair electron from the Cl atom to the benzene ring, thus the conjugative effect between the Cl atom and the benzene ring may also be enhanced due to the shortened C3–Cl bond in the D\textsubscript{0} state and the rigidity of the benzene ring could be increased. This is in accordance with the spectroscopic observations. For example, the frequencies of the in-plane ring deformation mode \( \nu^1 \) in the D\textsubscript{0} state (980 cm\textsuperscript{-1} for the cis-rotamer and 981 cm\textsuperscript{-1} for the trans-rotamer) are slightly larger than those in the S\textsubscript{1} state (953 cm\textsuperscript{-1} for the cis-rotamer and 963 cm\textsuperscript{-1} for the trans-rotamer), indicating a more rigid benzene ring in the D\textsubscript{0} state.

3.2. Active Vibrational Modes and Their Frequencies. The present 1C-R2PI and MATI spectroscopic measurements show that the in-plane ring deformation modes \( \nu^6_{0,1} \), \( \nu^4_{1,2} \), and \( \nu^5_{1,2} \) of the cis-rotamer have frequencies of 349, 617, and 953 cm\textsuperscript{-1} in the S\textsubscript{1} state, and, respectively, become 366 (or 398), 652, and 980 cm\textsuperscript{-1} in the D\textsubscript{0} state; the in-plane ring deformation mode \( \nu^6_{1,0} \) of the trans-rotamer has a frequency of 963 cm\textsuperscript{-1} in the S\textsubscript{1} state, and becomes 981 cm\textsuperscript{-1} in the D\textsubscript{0} state. Thus, almost all of the benzene ring-related vibrational modes have higher frequencies for both the cis- and trans-rotamers during the photoionization process, indicating that the conjugation effects between the benzene ring and the substituent groups are enhanced in the D\textsubscript{0} state. This increases the rigidity of the benzene ring. Similar vibrational frequency enhancement by photoionization was observed for the substituent-sensitive modes, for example, the methyl torsion mode \( \nu^1_{0,1} \) as presented above.

The current study along with several previous studies on other anisole derivatives\textsuperscript{21,23,27,30} and TA derivatives\textsuperscript{6,11} show that the frequencies of the benzene-ring-related modes are not very sensitive to the orientations of the substituents. In this study, the frequencies of the substituent-sensitive modes, e.g., the methyl torsion mode \( \nu^1_{0,1} \) are measured for both the cis- and trans-3CITA. Its frequency for the cis-rotamer is 46 cm\textsuperscript{-1} in the S\textsubscript{1} state, and 88 cm\textsuperscript{-1} in the D\textsubscript{0} state, while it is only 24 and 34 cm\textsuperscript{-1} in the S\textsubscript{1} and D\textsubscript{0} states of the trans-rotamer. The MATI spectra via the methyl torsion mode \( \nu^1_{0,1} \) for the two rotamers as shown in Figure 7a–e show that the coupling scheme of the methyl torsion mode \( \nu^1_{0,1} \) to other vibrational modes is strongly rotamer-dependent. This may be caused by the different through-space interactions between the two substituents Cl and —SCH\textsubscript{3} in the two rotamers. The two substituents are closer to each other, and thus should have stronger through-space interaction in the cis-rotamer than that in the trans-rotamer. That makes the methyl group in the cis-rotamer harder to move, resulting in a larger vibrational frequency.
It should also be noted that the methyl torsion mode \( \tau_i \) has been observed to be active in TA,\(^6,9,12\) trans-2FTA,\(^11\) and cis- and trans-3CITA, while it was not observed for stable anisole derivatives, such as 2-F anisole,\(^22\) 3-Cl anisole,\(^23\) and 3-F anisole.\(^21\) This indicates that the methyl group on the more flexible \(-\text{SCH}_3\) group is easier to be activated.

### 3.3. Substitution Effect on the Electronic Excitation and Ionization Energies

The measured electronic excitation transition energies \( E_1 \) and ionization energies \( IE \) of several anisole and TA derivatives are listed in Table 4. It can be seen that the \( E_1 \) and IE values depend on both the nature and location of the substituent halogen atom.

For \( E_1 \) values shown in Table 4, the \( E_1 \) values of the Cl-substituted TA derivatives, cis- and trans-3CITA, are red-shifted by 547 and 404 cm\(^{-1}\), respectively, relative to that of TA,\(^6,9,12\) while the \( E_1 \) values of the F-substituted TA derivatives, the trans-2FTA,\(^11\) and cis- and trans-3FTA, are all blue-shifted compared to that of TA.\(^6,9,12\) Similar phenomena have been observed between anisole and its F- and Cl-substituted derivatives.\(^5,20,21\)

A previous study showed that the substitution of a functional group on the benzene ring can lower its zero-point energy (ZPE) level.\(^21\) The red-shifted \( E_1 \) values of 3CITA imply that the interaction of Cl with the benzene ring is stronger in the S\(_1\) state than that in the S\(_0\) state, resulting in a larger ZPE lowering of the S\(_1\) state than that of the S\(_0\) state.

### 4. CONCLUSIONS

The 1C-R2PI and MATI spectra of cis- and trans-3CITA are obtained, implying that both the cis- and trans-rotamers coexist in the experiment and have planar structures in their respective S\(_0\), S\(_1\), and D\(_0\) states. The cis-rotamer is slightly more stable than the trans-rotamer with an isomerization barrier of \( \sim 500 \text{ cm}^{-1} \).

The first photoelectron and ionization energies of cis-3CITA are determined to be 33 959.3 ± 3 and 65 326 ± 5 cm\(^{-1}\), and those of trans-3CITA to be 34 102 ± 3 and 65 471 ± 5 cm\(^{-1}\), respectively. The two Cl isotopes are found to have negligible effects on the molecular properties of 3CITA. The \( E_1 \) and IE values are red-shifted by the Cl substitution for both rotamers, similar to the anisole derivatives.

Most of the active vibrations are found to be the in-plane ring deformation and substituent-sensitive modes. Their vibrational frequencies are generally measured to be higher in the D\(_0\) state than those in the S\(_1\) state, indicating that the conjugation interaction between the benzene ring and the substituted functional groups and the through-space interaction between the two substituents are enhanced during the photoionization process. This is confirmed by the molecular structural changes due to photoionization as revealed by theoretical calculations. The frequencies of the in-plane ring deformation modes are found to be not sensitive to the relative orientation between the two substituents, while the frequencies of the substituent-sensitive modes and their coupling schemes with other vibrational modes are found to be strongly rotamer-dependent.

### 5. EXPERIMENTAL AND COMPUTATIONAL METHODS

#### 5.1. Experimental Methods

The photoionization time-of-flight (TOF) mass spectrometer used in the current study has been described previously,\(^5,20\) and only a brief description is given here. The 3CITA sample with a purity of 99% was purchased from Alfa Aesar and used without further purification. It was seeded in the Ar carrier gas (\( \sim 2 \text{ atm} \)) and then expanded into a vacuum chamber through a pulsed General valve with a nozzle diameter of 0.25 mm. The molecular beam passed through a skimmer with a diameter of 1 mm located at 20 mm downstream from the nozzle and then entered the photoionization region of the mass spectrometer, which is 70 mm from the nozzle. In the photoionization region, the molecular beam was crossed by one or two ultraviolet (UV) laser beams perpendicularly and photoionized for detection.

In the one color resonant two-photon ionization (1C-R2PI) spectroscopic measurement, only one UV laser beam was used. The 3CITA molecule absorbed a single UV photon to be excited to the S\(_1\) state first, and then the 3CITA molecule in the S\(_1\) state absorbed a second UV photon to go above the photoionization threshold. The ions thus produced by the UV laser were immediately accelerated by two direct-current electric fields of 200 and 2100 V/cm, respectively. In the MATI experiment, two counterpropagating UV laser beams of different wavelengths were used. The first UV laser beam was the same as that used in the 1C-R2PI experiment and was used to excite the 3CITA molecule to its S\(_1\) state; the second UV beam excited the molecules from the S\(_1\) state to the high-\(n\)-Rydberg states, which are slightly below the ionization thresholds. The photoionization region was field-free during the photoexcitation process, and after about 200 ns, a pulsed electric field of \(-0.3 \text{ V/cm}\) was switched on to reject the prompt ions, which were usually generated together with the high-\(n\)-Rydberg neutrals. After a delay of 11 \( \mu s \), two pulsed electric fields of \(+200 \) and \(+2000 \text{ V/cm}\) were switched on synchronously to field ionize the high-\(n\)-Rydberg neutrals and accelerate the produced ions to the detector. The ions produced in the above two processes were focused by an Einzel lens and flew through a 1.0 m long field-free tube toward a dual-stacked microchannel plate (MCP) detector.
After passing through a preamplifier (SR445, Stanford Research System), the TOF signal was amplified by 25 times and collected by a multichannel scaler (SR430, Stanford Research System).

The UV lasers used in this experiment were generated by doubling the outputs of two tunable dye lasers (Sirah-CSTR), which were pumped by the second harmonic output of an Nd:YAG laser (Quanta-Ray, Pro-230-10E) at a repetition rate of 10 Hz. Three laser dyes, Pyromethene 597, Pyromethene 580, and DCM, were used in this work. Two pulse delay generators (DG535, Stanford Research System) were used to synchronize the whole system. Typical pressures of ∼3.0 × 10⁻⁷ and ∼3.0 × 10⁻⁸ Pa were maintained in the source and ionization chambers during operation.

5.2. Computational Methods. All calculations in this study were carried out with the Gaussian09 program package. The stable structures and harmonic vibrational frequencies of 3CITA in S₀, S₁, and D₀ states were calculated with density functional theory (DFT), in which time-dependent DFT (TDDFT) was used for the excited state S₂. The B3LYP functional and cc-pVTZ basis set were employed for all the calculations, and no imaginary frequencies were found for the optimized stationary points. The relaxed potential energy curve (PEC) in the S₀ state was scanned to illustrate the isomerization barrier between the cis- and trans-3CITA. The calculated vibrational frequencies of 3CITA in S₀, S₁, and D₀ states were scaled by 0.96741 to approximately account for the vibrational anharmonicity effect. The charge distributions based on natural population analysis (NPA) were conducted by Natural Bond Orbital (NBO) version 3.1 program implemented in the Gaussian09 program package.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06003.

Vibrational vectors of selected modes (Figure S1), overlaid structures and RMSD values for distances (Figure S2), molecular orbitals (Figure S3), Cartesian coordinates (Table S1), and numerical data of Figures 4–7 (Tables S2–S5) (PDF)

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Notes

The authors declare no competing financial interest.

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