Conformer specific nonadiabatic reaction dynamics in the photodissociation of partially deuterated thioanisoles (C₆H₅S-CH₂D and C₆H₅S-CHD₂)

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In this work, we have investigated nonadiabatic dynamics in the vicinity of conical intersections for predissociation reactions of partially deuterated thioanisole molecules: C₆H₅S-CH₂D and C₆H₅S-CHD₂. Each isotopomer has two distinct rotational conformers according to the geometrical position of D or H of the methyl moiety with respect to the molecular plane for C₆H₅S-CH₂D or C₆H₅S-CHD₂, respectively, as spectroscopically characterized in our earlier report [J. Lee, S.-Y. Kim and S. K. Kim, J. Phys. Chem. A, 2014, 118, 1850]. Since identification and separation of two different rotational conformers of each isotopomer have been unambiguously done, we could interrogate nonadiabatic dynamics of thioanisole in terms of both H/D substitutional and conformational structural effects. Nonadiabatic transition probability, estimated by the experimentally measured branching ratio of the nonadiabatically produced ground-state channel giving C₆H₅S \( (\bar{X}) \) versus the adiabatic excited-state channel leading to the C₆H₅S \( (\bar{A}) \) radical, shows resonance-like increases at symmetric \( (\nu_3) \) or asymmetric \( (7a) \) S-CH₂D (or S-CHD₂) stretching mode excitation in \( S_1 \) for all conformational isomers of two isotopomers. However, absolute probabilistic value of the nonadiabatic transition is found to vary quite drastically depending on different conformers and isotopomers. The experimental finding that nonadiabatic transition dynamics are very sensitive to subtle changes in the nuclear configuration within the Franck-Condon region induced by the H/D substitution indicates that the \( S_1/S_2 \) conical intersection seam is quite narrowly defined in the multi-dimensional nuclear configurational space as far as the S-methyl predissociation reaction is concerned. In order to understand the relation between molecular structure and nonadiabaticity of reaction, potential energy surfaces near \( S_1/S_2 \) conical intersections have been theoretically calculated along \( \nu_3 \) and 7a normal mode coordinates for all conformational isomers. Slow-electron velocity map imaging (SEVI) spectroscopy is employed to unravel the extent of intramolecular vibrational redistribution (IVR) for particular mode excitations of \( S_1 \), providing insights into the dynamic interplay between IVR and nonadiabatic transition probability near the conical intersection seam.

Introduction

Photodissociation dynamics of heteroaromatic molecules such as phenol,\(^{1-15}\) thiophenol,\(^{8,16-24}\) pyrrole,\(^{25-35}\) thioanisole,\(^{36-40}\) or aniline\(^{41-45}\) have been quite intensively studied in recent decades. This is because intriguing nonadiabatic dynamics are involved in the relaxation of electronically excited states of those systems, providing insights into the detailed mechanisms of nonradiative transitions and/or predissociation reactions. Understanding these systems is also essential for explaining photochemical processes of biologically important chromophores. As many excellent review articles regarding this subject are already available,\(^{46-51}\) we are going to directly focus on our system. For thioanisole, in the diabatic picture, the first electronically excited state \( (S_1) \) is the bound \( \pi \pi^* \) state whereas the second excited \( \pi \pi^* \) state \( (S_2) \) is repulsive in nature along the S-CH₃ bond elongation.\(^{16-28}\) The most interesting aspect in the thioanisole predissociation dynamics is that there exist two conical intersections along the S-CH₃ bond dissociation coordinate (Fig. 1). The first conical intersection results from crossing of \( S_1 \) and \( S_2 \) near the Franck-Condon region whereas the second conical intersection is generated at the later stage of reaction as the ground state \( (S_0) \) crosses with \( S_2 \). The repulsive \( S_3 \) state diabatically correlates to the ground channel giving the asymptotic products of \( ^*CH_3 + C_6H_5S(\bar{X}) \), while the excited

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A great opportunity to spectroscopically characterize the conical intersection in terms of its nuclear configuration by measuring the nonadiabatic transition probability as a function of the initial excitation energy. Spectroscopic characterization of the conical intersection could be more advanced for thioanisole-d$_1$ ($C_{6}H_{5}S$-CD$_3$) as one could observe multiple $S_1$ vibronic bands showing resonance-like enhancements of the nonadiabatic transition probability. This experiment has confirmed that those nonadiabatic dynamic resonances are strongly mode-dependent, indicating that the nonadiabaticity is determined by the proximity of the nuclear configuration spanned by the specific vibronic transition to that of the $S_1$/$S_2$ conical intersection. Multiple dynamic resonances observed for $C_{6}H_{5}S$-CD$_3$ represent projections of the conical intersection onto several key normal coordinates, also demonstrating that the conical intersection is on the multidimensional seam in nature. It also seems that the $S_1$/$S_2$ conical intersection seam is narrowly defined as subtle changes of nuclear rearrangements in the nuclear configuration space by the isotopic substitution induce huge differences in dynamic resonances. Similar but different nonadiabatic dynamic features have been reported for predissociation of ammonia$^{51-56}$ Specific vibrational mode excitations and/or deuteration of ammonia were found to significantly influence bifurcation dynamics at the conical intersection. Recent multidimensional dynamics calculations seem to be successful in clarifying the nonadiabatic transition mechanism$^{57,58}$ though the experiment could not be fully explained yet.

Herein, we have further explored nuclear configurations near the $S_1$/$S_2$ conical intersection by investigating the photodissociation dynamics of partially deuterated thioanisole species such as thioanisole-d$_1$ ($C_{6}H_{5}S$-CH$_3$D) or thioanisole-d$_2$ ($C_{6}H_{5}S$-CHD$_2$). Spectroscopic characteristics of these isotopomers have already been studied in detail in our earlier report. Interestingly, two different conformational isomers of each isotopomer could be unambiguously identified spectroscopically. For example, the deuterium atom of the methyl moiety in $C_{6}H_{5}S$-CH$_3$D is geometrically positioned either in or out of the molecular plane. Similarly, for $C_{6}H_{5}S$-CHD$_2$, H of the methyl moiety this time could be either in or out of the molecular plane to give two distinct conformers. Partial deuteration of the methyl moiety in thioanisole is not expected to influence potential energy surfaces in terms of both energetics and topographic landscapes. Vibrational frequencies and nuclear displacements associated with normal modes are, however, supposed to be changed by the H/D substitution and/or conformational arrangements. As demonstrated in the thioanisole-d$_1$ experiment$^{58}$ the H/D substitution effect on nonadiabatic dynamics could be quite substantial, giving another opportunity to unravel multidimensional aspects of the conical intersection seam.

**Experimental**

Detailed experimental setup has been described in detail previously.$^{54,53}$ Thioanisole-d$_1$ and -d$_2$ ($\sim 100\%$ purity for d$_1$ and $\sim 99\%$ for d$_2$) were synthesized by MediGen. The sample...
was heated to \( \sim 50^\circ C \), seeded in the argon carrier gas, and expanded into vacuum through a nozzle orifice (General Valve) with a backing pressure of \( \sim 3 \) bar. The supersonic molecular beam was collimated through a 0.5 mm diameter skimmer (Beam Dynamics) before being intersected with UV pulses at right angles. To carry out resonant-enhanced two-photon ionization (R2PI), velocity map ion imaging (VMI)\(^{54,55}\) and slow electron velocity map imaging (SEVI)\(^{56,57}\) experiments, the pump laser pulse in the region of 272.5–290.25 nm was generated by frequency doubling of the dye laser output (Spectra-Physics, ScanmateII) pumped by the second harmonic of a Nd:YAG laser (Spectra-Physics, GCR-150). The probe laser pulse was generated in the energy range of 333.4–333.5 nm to excite Q-branches in the \( 3P_z^2A'(\nu = 0) \rightarrow \bar{X}^2A'' \) transition of the partially deuterated methyl radicals (*CH\(_2\)D or *CHD\(_2\)) for ionization. In order to obtain SEVI spectra, the pump laser wavelength was fixed at a specific \( S_1 \) vibrational level whereas the ionization laser frequency was tuned to obtain photoelectrons near vibrationally adiabatic ionization thresholds. In the VMI or SEVI setup, ions or electrons were velocity-mapped onto the position sensitive detector (Burle, \( \varnothing = 40 \) mm) coupled to a computer interfaced CCD camera (Sony XC-ST50, 768 494 pixels). Raw images were acquired with the IMACQ acquisition software\(^{58}\) and reconstructed using a BASEX algorithm.\(^{59}\)

All calculations were performed with Molpro (2010.1)\(^{60}\) and Gaussian09 packages\(^{61}\) and the Franck–Condon simulations were carried out using the FClabII program.\(^{62,63}\) Equilibrium configurations, harmonic vibrational frequencies, and potential energy surfaces including minimum energy conical intersection (MECI) were obtained using the state-averaged complete active space self-consistent field method\(^{64,65}\) (SA4-CASSCF(12,11)) with a 6-311+G(d,p) basis set. The same level of theory with (11,11) active space and TDDFT/6-311++G(3df,3pd) calculations were carried out for the cationic ground state (\( D_0 \)). The second order multi-reference perturbation corrections\(^{66}\) (CASPT2, level shift = 0.4) were applied in the calculations of the \( S_1 \) minimum energy structure and MECI including crossing points between \( S_1 \) and \( S_2 \) electronic states.

### Results and discussion

Partial deuteration of the methyl moiety of thioanisole is not expected to influence electronic states in terms of their energetics and associated potential energy landscapes. Therefore, ironically, within the Born–Oppenheimer approximation, the conical intersection seam is rather invariant with isotopic substitution in the nuclear configuration space. On the other hand, moments of inertia associated with normal vibrational modes are certainly modified by the partial deuteration of the methyl group, giving a different set of multidimensional normal modes for the spectroscopic characterization of the conical intersection seam. As described above and also in our earlier report,\(^{52}\) the R2PI spectrum of thioanisole-\( d_1 \) represents two distinct conformational isomers depending on the relative orientation of D of the methyl moiety with respect to the molecular plane, giving either conformer A1 where D is on the molecular plane or conformer B1 in which D is positioned out of the molecular plane (Fig. 2). Statistically, B1 is two times more populated in the jet compared to A1. For thioanisole-\( d_2 \),

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**Fig. 2** Hole-burning spectra corresponding to the \( S_1 \rightarrow S_0 \) R2PI spectrum (top) and \( \bar{X}/\bar{A} \) product branching ratios obtained from the translational distributions of the \( ^{*}\text{CH}_2\text{D} \) fragment (bottom) for the jet-cooled thioanisole-\( d_1 \)-A1 (a) and -B1 (b). The \( v_4 \) and 7a mode excitations show striking increases in the \( \bar{X}/\bar{A} \) branching ratio. Orange triangles represent measurements where A1 and B1 are not spectroscopically well separated.
the H atom of the CHD$_2$ moiety could be either on the plane or out of the plane to give conformer A2 or B2, respectively, where the latter is twice more populated than the former (Fig. 3). Spectral assignments had been appropriately carried out using the SEVI technique for each conformational isomer. Here, we have obtained images of the methyl fragment departed from these thioanisole isotopomers excited at specific vibronic upper states.

A typical image of the *CH$_3$D ($\nu = 0$) fragment, for instance from thioanisole-d$_1$, shows two distinct rings of which the outer ring corresponds to the nonadiabatic C$_6$H$_5$S(A) + *CH$_3$D channel whereas the inner ring is associated with the adiabatic channel giving C$_6$H$_5$S(A) and *CH$_3$D products at the asymptotic level. After the processes of 3D reconstruction and Jacobian correction combined with kinematic analysis, the total kinetic energy distribution of fragments could be obtained. As the energetic gap between C$_6$H$_5$S(A) and C$_6$H$_5$S(A) has been precisely known to be 3000 ± 7 cm$^{-1}$, the bimodal kinetic energy distribution could be unambiguously deconvoluted to give the $\tilde{X}/\tilde{A}$ branching ratio which is proportional to the nonadiabatic transition probability. Overall, the $\tilde{X}/\tilde{A}$ branching ratio is as low as 0.04 at the S$_1$ origin and increases slowly with increasing internal energy to give a value of 0.08 at ~950 cm$^{-1}$ above the origin (Fig. 2). It is interesting to recall that dynamic resonance is observed only at the 7a mode excitation for undeuterated thioanisole (thioanisole-h$_3$) whereas both $\nu_6$ and 7a mode excitations lead to striking increases of the $\tilde{X}/\tilde{A}$ branching ratio for thioanisole-d$_3$ (C$_6$H$_5$SCD$_3$). Now, for singly deuterated isotopomers of A1 and B1, we could observe nonadiabatic transitions enhanced at both $\nu_6$ and 7a mode excitations. Incidentally, it is noteworthy that vibrational frequencies of 7a modes for A1 and B1 conformers are quite close to each other giving 712 and 708 cm$^{-1}$, respectively, whereas those of $\nu_6$ are quite distinct for the A1 or B1 conformer giving 659 or 678 cm$^{-1}$, respectively. In order to estimate conformer specific $\tilde{X}/\tilde{A}$ branching ratios at the 7a mode excitation of thioanisole-d$_1$, SEVI spectra are obtained at many different excitation energies where methyl fragment images are taken (Fig. 4(a) and (b)). This allows us to correlate the $\tilde{X}/\tilde{A}$ branching ratio with the nature of the S$_1$ vibronic transition in terms of its conformational structure and vibrational character. The SEVI peak due to 7a$^+$ found in the 725–732 cm$^{-1}$ region, even though it is less distinct, shows a gradual blue shift as the S$_1$ internal energy (of A1) increases from 708 to 714 cm$^{-1}$, reflecting the A1 to B1 conformational change of the 7a mode frequency in the corresponding energy range. This SEVI spectral pattern is quite consistent with the hole-burning spectroscopic result in our earlier report. Judging from SEVI spectra taken as a function of the S$_1$ internal energy from 715 to 737 cm$^{-1}$, it is quite obvious that the 7a mode character gradually disappears as the S$_1$ internal energy increases (Fig. 4). This is well correlated with the decrease of the $\tilde{X}/\tilde{A}$ branching ratio. Now for the A1 isomer, it is estimated that the $\tilde{X}/\tilde{A}$ branching ratio is (0.13 ± 0.01) or (0.19 ± 0.01) at the S-CH$_3$D symmetric stretching ($\nu_6$) mode of 659 cm$^{-1}$ or the 7a mode excitation of 712 cm$^{-1}$, respectively. For the B1 conformational isomer, however, the branching ratio at $\nu_6$ of 678 cm$^{-1}$ decreases to (0.11 ± 0.01) while it remains more or less the same to give (0.17 ± 0.01) at the 7a mode excitation of 708 cm$^{-1}$. Phenomenologically, thioanisole-d$_1$ shows the intermediate case between thioanisole-h$_3$ and thioanisole-d$_3$.
in terms of mode specificity of nonadiabatic transitions at the conical intersection seam. Namely, the experimental finding that 7a is the more effective vibrational mode for driving nonadiabatic transition than $n_s$ for thiaonsole-d$_1$ is more consistent with the result of undeuterated thioanisole in which the nonadiabatic transition probability is enhanced only at the 7a mode excitation. However, the fact that $n_s$ is nonadiabatically active in thioanisole-d$_1$ is rather similar to the case of thioanisole-d$_3$ as both $n_s$ and 7a modes had been found to be active in the latter. It is also noteworthy that the nonadiabatic transition probability of the A1 conformer at $n_s$ (0.13 ± 0.01) is slightly higher than that of B1 at $n_s$ (0.11 ± 0.01), suggesting that the H to D substitution of the methyl moiety on the molecular plane could be more effective in tuning the corresponding normal mode toward the $S_1$/$S_2$ conical intersection seam compared to that placed out of the molecular plane.

For thioanisole-d$_2$, two distinct outer and inner rings associated with the $C_6H_5S \cdot (X) + CHD_2$ channel and the adiabatic channel correlating to $C_6H_5S \cdot (A)$ and $CHD_2$ products, respectively, are observed. Similar to the case of thioanisole-d$_1$, the $X/A$ branching ratio is estimated to be $\sim 0.04$ at the $S_1$ origin and increases monotonically with the increase of the internal energy to give a value of $\sim 0.08$ at $950$ cm$^{-1}$ above the origin. For doubly deuterated isotopomers of A2 and B2, we could also observe sharp increases of the nonadiabatic transition probability at both $n_s$ and 7a mode excitations (Fig. 3). Similar to the case of thioanisole-d$_1$ species, vibrational frequencies of 7a modes for A2 and B2 conformers of thioanisole-d$_2$ are closely
spaced giving their respective values of 707 and 705 cm\(^{-1}\) whereas those of \(v_6\) are quite distinct for the A2 or B2 conformer giving 676 or 658 cm\(^{-1}\), respectively. In this case, the 7a mode of A2 is spectrally overlapped with other vibronic modes of B2. SEVI spectra taken as a function of the S\(_1\)-S\(_0\) excitation energy turn out to be quite helpful to disentangle mode-dependent nonadiabatic reactions in a conformer-specific way (Fig. 4(c) and (d)). Namely, the \(\hat{X}/\hat{A}\) branching ratio for the 7a mode of each conformer could be appropriately estimated from analyses of SEVI spectra based on the propensity rule of \(\Delta\nu = 0\) in the D\(_0\)-S\(_1\) ionization process. As a result, the \(\hat{X}/\hat{A}\) branching ratio of the A2 conformer is estimated to be \((0.11 \pm 0.01)\) at both S-CHD\(_2\) symmetric stretching (\(v_6\)) of 676 cm\(^{-1}\) and 7a mode (707 cm\(^{-1}\)) excitations. For the B2 conformational isomer, the situation becomes quite different, giving the branching ratio of \((0.30 \pm 0.02)\) at \(v_6\) (658 cm\(^{-1}\)) and \((0.14 \pm 0.02)\) at 7a mode (706 cm\(^{-1}\)) excitation. From the phenomenological view employed for the thianisole-d\(_3\) case above, the experimental finding that both \(v_6\) and 7a modes are driving the reaction nonadiabatically for A2 and B2 conformers of thioanisole-d\(_3\) is similar to the case of thioanisole-d\(_3\), which sounds reasonable as dynamics of thioanisole-d\(_3\) are supposed to be closer to those of thioanisole-d\(_3\) compared to the undeuterated one. Conformer specificity of nonadiabatic dynamics of thioanisole-d\(_3\) is remarkable on the other hand. As described above, for the A2 conformer where H of the methyl moiety is on the molecular plane, nonadiabatic transition probabilities at both \(v_6\) and 7a mode excitations are quite low. When one of the D atoms of CHD\(_2\) is positioned on the molecular plane in the B2 conformational isomer, however, the nonadiabatic transition probability peaked at \(v_6\) is quite high whereas that observed at the 7a mode is still low (vide supra). The fact that the H to D substitution of methyl on the molecular plane, compared to that placed out of the plane, is more effective in tuning the \(v_6\) normal mode toward the S\(_1\)/S\(_0\) conical intersection seam coordinate seems to be also true for thioanisole-d\(_3\).

Even though it is a formidable task to fully characterize the conical intersection seam, experimental observation of dynamic resonances in nonadiabatic transitions of thioanisole isotopomers in this and previous works\(^{36,38}\) provides us very important clues for spectroscopic description of the conical intersection seam in the multi-dimensional normal mode space. Furthermore, the extent of the nonadiabatic transition which varies with different conformational isotopomers may reflect many different facets of conical intersection dynamics. These include energetic gaps between S\(_1\) and S\(_0\) at nuclear configurations spanned by dynamic resonant vibronic modes, revealing the proximity of the corresponding reactive flux to the conical intersection seam in terms of energetics and molecular structure. Another key factor determining the \(\hat{X}/\hat{A}\) branching ratio would be the extent of IVR by which the vibrational energy is randomized among isoenergetic quantum states after the zeroth-order bright state preparation. If the IVR rate exceeds the chemical reaction rate, no mode dependent nonadiabatic dynamics would be expected whatsoever.

It should be emphasized here that the \(\hat{X}/\hat{A}\) branching ratio is determined by nonadiabatic bifurcation of the reactive flux at the S\(_0\)/S\(_2\) conical intersection which is located quite far from the Franck–Condon region (Fig. 1). Our argument here is, therefore, based on the assumption that the optically accessible S\(_1\)/S\(_2\) conical intersection is the fingerprint for the S\(_0\)/S\(_2\) conical intersection. As these two S\(_1\)/S\(_0\) and S\(_0\)/S\(_2\) conical intersections are both generated in the planar geometry and connected by the repulsive S\(_2\) potential energy surface,\(^{40}\) it could be rationalized that the quantum nature of the reactive flux at the S\(_1\)/S\(_2\) conical intersection especially with respect to vibrational modes perpendicular to the reaction coordinate may be little altered at the S\(_0\)/S\(_2\) conical intersection.\(^{37}\) On the other hand, quantitative correlation between Franck–Condon overlap with the conical intersection seam and nonadiabaticity of chemical reaction is still not straightforward, as both conical intersection seam and reaction coordinates are multi-dimensional in nature and the nonadiabatic reaction path would be the consequence of complicated coupling of those two coordinates. Nonetheless, theoretical calculations of the conical intersection seam with respect to nuclear displacements associated with normal modes and their comparison with experiment would provide nice platforms for the spectroscopic characterization of the conical intersection seam. Instead of using internal coordinates for the comparison between normal modes and conical intersection seam which had been employed for the explanation of dynamic resonances observed in thioanisole-d\(_3\),\(^{38}\) S\(_1\) and S\(_2\) energies are calculated here with respect to nuclear displacements associated with normal modes showing dynamic resonances (Fig. 5). Here, the molecule adopts a planar geometry and both \(v_6\) and 7a modes belong to \(a^\prime\). Interestingly, for thioanisole-h\(_3\), S\(_1\) and S\(_2\) give a crossing point when these states calculated along the 7a normal mode coordinate are drawn at both CASSCF and CASPT2 levels. The crossing point found at the CASPT2 level is energetically lowered and geometrically positioned at the smaller displacement vectors compared to that of CASSCF. More interesting point is that S\(_1\) and S\(_2\) do not cross along the \(v_6\) normal mode coordinate for thioanisole-h\(_3\) at both calculation levels. This is quite consistent with our earlier experimental observation that the 7a mode is the only vibronic mode giving the nonadiabatic dynamic resonance for thioanisole-h\(_3\).\(^{36}\) Subtle changes of normal mode coordinates induced by the CH\(_3\)/CD\(_3\) substitution give very different behaviors of electronic states in the curve crossing region. For thioanisole-d\(_3\), for instance, S\(_1\) and S\(_2\) show crossing points with respect to both 7a and \(v_6\) normal mode coordinates at the CASPT2 level. This is quite consistent with our earlier experimental result in which both 7a and \(v_6\) had been identified as vibronic modes which enhance nonadiabatic transitions at the asymptotic level.\(^{38}\) This calculation confirms again that direct access to the S\(_1)/S\(_0\) conical intersection seam mediated by the one-photon vibronic transition is responsible for the resonance-like behavior of the nonadiabatic transition probability. Now, for partially deuterated species, S\(_1\) and S\(_2\) cross along the 7a normal mode coordinate for A1 and A2 conformers while they avoid crossings for B1 and B2 conformers at the CASSCF level as these conformers now belong to C\(_1\) instead of C\(_6\). Even in these cases of avoided crossings along one degree of freedom (7a), it is most likely that same-symmetry
conical intersections are developed in the multi-dimensional seam for B1 and B2 conformers. In this sense, significant state mixings of \( \text{S}_1 \) and \( \text{S}_2 \) along the 7a normal mode coordinate are also expected for B1 and B2, as depicted in Fig. 5. This now seems to be consistent with the experiment as nonadiabatic resonances are found at 7a mode excitations for all A1, B1, A2, and B2 isomers. Along the \( \nu_s \) normal mode displacement, except for the case of A1, \( \text{S}_1 \) and \( \text{S}_2 \) states seem to cross at the CASPT2 level for the B1, A2, and B2 isotopomers within our calculation range although these crossings are only roughly predicted from smooth interpolation among several different points. Crossing regions found for A2 and B2 are located at smaller displacement vectors of the \( \nu_s \) normal mode coordinates compared to that found for A1, implying that the \( \nu_s \) normal mode character of thioanisole-d₂ (A2 and B2) is more similar to that of thioanisole-d₃ than that of thioanisole-d₁ (A1 or B1). It is interesting to note

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**Fig. 5** Calculated potential energy profiles of the first (\( \text{S}_1 \), red) and second (\( \text{S}_2 \), blue) electronically excited states along the symmetric stretching (\( \nu_s \), left) and the asymmetric stretching (7a, right) normal mode coordinates, obtained by SA4/CASSCF (dashed line) and CASPT2 (solid line) level of theory for \( \text{h3}(a), -\text{d3}(b), \text{A1}(c), \text{B1}(d), \text{A2}(e) \) and \( \text{B2}(f) \). The green star indicates the CASSCF \( \text{S}_1/\text{S}_2 \) crossing point and the purple rhombus in B1 and B2 isomers represents \( \text{S}_1/\text{S}_2 \) state mixing regions resulting from the lowered C1 symmetry. Potential energy curves have been calculated also in the negative region, and yet contracted bond length of S–CH₃ seems to ruin our (12,11) active space in CASSCF calculations giving unreasonable energetics. All normal mode vectors corresponding to the scale of 1.0 on the abscissa are listed in Table S8 (ESI†) while energetics regarding ZPE on the \( \text{S}_1 \) minimum and crossing points (or MECI) are depicted in Fig. S6, ESI.†
that $S_1$ and $S_2$ states become energetically close very quickly along the $\nu_s$ normal coordinate for B1 whereas there is no sign of curve crossing even at large displacement vectors of $\nu_s$ for thioanisole-d$_3$ (Fig. 5). This nicely explains why we could observe nonadiabatic resonances at $\nu_s$ vibronic transitions of all partially deuterated conformers while no dynamic resonance was observed at $\nu_s$ for thioanisole-d$_3$. Quantitatively, however, the energetics of curve crossing points calculated for all isotopomers with respect to their $S_1$ minimum energies are considerably higher than the vibrational energies of $\nu_s$ or 7a modes. This suggests that our calculations of excited-state potential energy surfaces along calculated harmonic normal modes are overestimated. It should be noted here that even though the conical intersection seam is narrowly defined along the multi-dimensional space its dynamic property regarding nonadiabaticity may be extended in the nuclear configurational space within the effective dynamic volume depending on the coupling strengths of two adiabats and their variation upon nuclear displacements in the vicinity of the conical intersection. In this sense, our experimental results could be very important clues for stringent tests of high-level multi-dimensional potential energy surface calculations in the conical intersection region, which are yet to come.

Now, regarding the extent of the nonadiabatic transition probability which is manifested by the $\tilde{X}/\tilde{A}$ branching ratio, it seems to be hardly explainable by our calculated potential energy curves alone. For example, it is nontrivial to explain why the $\tilde{X}/\tilde{A}$ branching ratio of 0.30 estimated at the $\nu_s$ vibronic mode of B2 is much larger than the value of 0.14 found at 7a of the same conformational isomer. The $\tilde{X}/\tilde{A}$ branching ratio may reflect the extent of the spatial overlap between phase space of the reactive flux and that of the conical intersection seam. Therefore, as long as the reactive flux maintains its initial character of the phase space given by a specific vibronic transition of $\nu_s$ or 7a giving nonadiabatic resonances, the extent of the nonadiabatic transition probability may reflect the relative amplitude of the vector component of the conical intersection seam along the corresponding normal mode coordinate being excited. In other words, the nonadiabatic transition becomes more probable as the spatial overlap between the reactive flux and the conical intersection seam increases in the nuclear configurational space.67 On the other hand, when the energy randomization process such as IVR takes place, initial memory of the stationary state will be washed out and no mode dependent nonadiabatic dynamic behavior would be expected. Therefore, the averaging effect of IVR should be also carefully considered. Measuring the extent or rate of IVR in polyatomic molecules is not always straightforward.68–75 Generally, the IVR rate increases with increasing internal energy as the density of states exponentially increases with the increase of the internal energy. For thioanisole, $S_1/S_2$ curve crossings are apparently located in the 600–800 cm$^{-1}$ region of the $S_1$ internal energy where density of states is calculated to be about 7 cm$^{-1}$ which is quite low. In this respect, IVR in the $S_1$ state of thioanisole in the conical intersection region, because of its low density of states, is expected to be not significant and initial vibrational eigenstates may maintain their original characters in $S_1$ until their couplings to continuum.

However, it is well known that the IVR process is rather complicated and not governed by the density of states alone,68–70,74 suggesting that one should take a close look at IVR dynamics in terms of its extent or rate in order to judge whether or not an initially prepared $S_1$ bright state remains stationary. Even though high resolution and/or time-resolved spectroscopic studies would be ideal for unraveling the detailed mechanism of IVR, SEVI spectroscopy employed here provides very clear information about the onset of IVR in $S_1$.71–75 The SEVI spectrum obtained by (1 + 1’’) two color ionization mediated by a specific $S_1$ vibronic state is supposed to reflect any structural change upon $D_0$–$S_1$ ionization according to the Franck–Condon overlap. When the structural difference between $S_1$ and $D_0$ is little which is the case of thioanisole, the propensity rule of $\Delta\nu = 0$ holds to give 1:1 correspondence between $S_1$ and $D_0$ vibrational levels. A specific $S_1$ vibrational level could be then characterized from appropriate assignment of the most prominent peak in the corresponding SEVI spectrum using normal mode calculations for $D_0$, which would be otherwise nontrivial.52,76 This assignment strategy for $S_1$ vibronic levels using ionization spectroscopy has been very successful52,76 but also it provides very useful information about IVR. Namely, when the initial $S_1$ bright state is coupled to isoenergetic dark states, the SEVI spectrum becomes structureless as the ionization efficiency is spread out into different manifolds in $D_0$.68–70,72 In the case of complete IVR where the signature of the bright state is gone, the only constraint would be conservation of the internal energy in the ionization process.

SEVI spectra taken via the $\nu_s$ or 7a mode in $S_1$ for A1 and B1 isotopomers, in addition to the peak expected by the propensity rule of $\Delta\nu = 0$ due to the cationic $\nu_s$ or 7a mode, show broad featureless signals in the internal energy region higher than the threshold energy of the $\nu_s$ or 7a$^+$ mode, respectively (Fig. 6). This indicates that significant IVR in $S_1$ takes place already at such a low internal energy of $\sim 700$ cm$^{-1}$ although the stationary character given by the initial vibronic transition still remains quite strong. This may represent a typical situation of the so-called intermediate IVR.71–75 The extent of IVR simply judged from the relative amplitude of the broad background signal compared to the main prominent cationic peak in SEVI seems to be significant for the $\nu_s$ mode in B1. Qualitatively speaking, this trend seems to be consistent with the experiment. That is, the $\tilde{X}/\tilde{A}$ branching ratio of 0.11 measured for the $\nu_s$ mode in B1 is quite small compared to that of (0.20 ± 0.01) estimated for the 7a mode in A1 or B1. This is even smaller than (0.13 ± 0.01) measured for the $\nu_s$ mode in A1. Much clearer evidence for the IVR effect on nonadiabaticity could be found for thioanisole-d$_3$ isomers. The SEVI spectrum taken via the $\nu_s$ mode in B2 shows a single prominent $\nu_s$ peak with little background signal indicating that IVR is not in serious action yet, which means that the initially prepared $\nu_s$ mode in $S_1$ mostly remains stationary (Fig. 7). Now, this does not seem to be coincidental with the experimental fact that the $\tilde{X}/\tilde{A}$ branching ratio of 0.30 estimated for the $\nu_s$ mode of B2 is quite large. Meanwhile, SEVI spectra taken via the 7a mode for A2 and B2 isomers show strong background spectral features indicating
that IVR processes at these levels in S1 are already quite significant. At these levels, \( \langle \chi | A \rangle \) branching ratios estimated for A2 or B2 are 0.11 or 0.14, respectively, which are quite small probably due to the decrease of the stationary character of the initial vibronic state. The SEVI spectrum \( \text{via} \nu_s \) mode of A2 also shows a strong signature of IVR, and this is also consistent with the small \( \langle \chi | A \rangle \) branching ratio of 0.11. However, it should be emphasized here that this argument regarding the effect of IVR on nonadiabaticity of chemical reaction is only primitive and relative. It is interesting to note that no significant IVR in S1 had been observed for thioanisole-h3 or thioanisole-d3 isotopomers in the 600–800 cm\(^{-1}\) region as presented in our earlier reports.\(^{36,38,51}\) Abnormal increases of the density of states for partially deuterated thioanisoles are not expected as the number of internal degrees of freedom is not influenced by the H/D substitution. The change of symmetry properties of rovibrational levels due to different orientations and numbers of deuterium atoms in the methyl moiety could possibly contribute to the change of coupling strengths of bright states to dark states. This and related discussions regarding IVR, however, are nontrivial at the present time without highly resolved spectroscopic or time-resolved data and are subject to further studies.

**Conclusions**

The present study of nonadiabatic predissociation dynamics of partially deuterated thioanisole molecules (C\(_6\)H\(_5\)S-CH\(_2\)D and C\(_6\)H\(_5\)S-CHD\(_2\)) has revealed spectroscopic features of the S1/S2 conical intersection seam overlapped with the Franck–Condon region in the S1–S0 optical excitation. As each isotopomer has two distinct rotational conformers depending on the geometrical position of D or H of the leaving methyl moiety, H/D substitutional and conformational structural effects on nonadiabaticity near the conical intersection could be systematically investigated. Nonadiabatic transition probability shows resonance-like increases at symmetric (\( \nu_s \)) or asymmetric (7a) S-CH\(_2\)D (or S-CHD\(_2\)) stretching mode excitation in S1 for all isotopomers though absolute values are quite different for different conformational isotopomers. Excited-state potential energy surfaces calculated along \( \nu_s \) and 7a normal mode coordinates, even though they are one-dimensional calculations, turn out to be very helpful to gain insights into the structural aspect of the conical intersection seam and its Franck–Condon accessibility via different vibronic transitions. Our results on nonadiabatic dynamics of partially deuterated thioanisoles have revealed new dynamic facets of the conical intersection seam using different sets of normal mode coordinates influenced by the H/D isotopic substitution in a conformer-specific way. This, with the aid of high-level potential energy surface calculations, will contribute to the better understanding of nonadiabatic reaction dynamics occurring in the vicinity of the multidimensional conical intersection seam. Slow-electron velocity map imaging (SEVI) spectroscopy is used to estimate the extent of intramolecular vibrational redistribution for particular mode excitations of S1. Indeed, we have found that IVR averages out

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**Fig. 6** (1 + 1') SEVI spectra taken via \( \nu_s \) or 7a levels of the S1 state of TA-d1: (a) \( \nu_s \) (659 cm\(^{-1}\)) and (b) 7a (712 cm\(^{-1}\)) for A1; (c) \( \nu_s \) (678 cm\(^{-1}\)) and (d) 7a (708 cm\(^{-1}\)) for B1. Nuclear displacement vectors associated with the corresponding normal modes of D0 are shown in the inset. Stick spectra shown below each SEVI represent Franck–Condon overlaps between one quantum vibronic level for \( \nu_s/7a \) on S1 and D0 minimum. Note that the internal energy of each conformer is depicted.

**Fig. 7** (1 + 1') SEVI spectrum taken via \( \nu_s \) or 7a levels of the S1 state of TA-d2: (a) \( \nu_s \) (676 cm\(^{-1}\)) and (b) 7a (707 cm\(^{-1}\)) for A2; (c) \( \nu_s \) (658 cm\(^{-1}\)) and (d) 7a (706 cm\(^{-1}\)) for B2. In (b), the 7a* mode corresponds to the 725 cm\(^{-1}\) band whereas the most intense peak at 758 cm\(^{-1}\) is assigned as the cationic \( \text{A}_{\text{ex}}\text{S}_{\text{a}}\text{a}_{\text{ex}} \) level, indicating that the vibrational character of the 707 cm\(^{-1}\) band is a mixture of the 7a and bending modes of A2. Nuclear displacement vectors associated with the corresponding normal modes of D0 are shown in the inset. Stick spectra shown below each SEVI represent Franck–Condon overlaps between one quantum vibronic level for \( \nu_s/7a \) on S1 and D0 minimum. As in Fig. 6, the internal energy of each conformer is depicted.
the mode effect on nonadiabaticity in the vicinity of the conical intersection, confirming that whole nonadiabatic dynamics, in principle, could be controlled by the appropriate selection of the stationary quantum state.

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Notes and references
