**ABSTRACT:** For benzene, toluene, aniline, fluorobenzene, and phenol, even sophisticated treatments of electron correlation, such as MRCI and XMS-CASPT2 calculations, show oscillator strengths typically lower than experiment. Inclusion of a simple pseudo-diabatization approach to perturb the \( S_1 \) state with approximate vibronic coupling to the \( S_2 \) state for each molecule results in more accurate oscillator strengths. Their absolute values agree better with experiment for all molecules except aniline. When the coupling between the \( S_1 \) and \( S_2 \) states is strong at the \( S_0 \) geometry, the simple diabatization scheme performs less well with respect to the oscillator strengths relative to the adiabatic values. However, we expect the scheme to be useful in many cases where the coupling is weak to moderate (where the maximum component of the coupling has a magnitude less than 1.5 au). Such calculations give an insight into the effects of vibronic coupling of excited states on UV/vis spectra.

**INTRODUCTION**

Small monosubstituted benzenes serve as model systems for biological chromophores, helping to understand the structure of proteins and hydrogels. Both their electronically excited states and their vibrational spectra have been widely investigated. For example, the aromatic groups of tyrosine and phenylalanine contribute to the electronic circular dichroism of proteins in the near ultraviolet, while IR spectroscopy is widely used to probe the conformational landscape of proteins. Toluene plays a role in atmospheric chemistry, oxidizing in the troposphere and playing a role in the secondary organic aerosol formation. Toluene is also important for the synthesis of industrial polymers, and excited states have a key role in the radiolysis of aromatic compounds. A comprehensive description of the spectroscopy of individual chromophores is a pre-requisite for understanding the often complex spectra of dimers and higher aggregates present in many types of macromolecular systems. We have a long-standing interest in the accurate and efficient description of the spectroscopy of toluene as a model of phenylalanine for electronic circular dichroism calculations. Such calculations determine parameters for our DichroCalc software. In particular, we are interested in a simple, efficient, and quantitative approach to the calculation of vibronic coupling of different electronically excited states in such molecules to improve the fine structure of the electronic transitions and corresponding transition dipole moments.

To glean useful information from calculations of the electronic excited states of benzene and monosubstituted benzene derivatives, one must understand the nature of the transitions being studied: in our case, the \( S_1 \leftarrow S_0 \) transition. In benzene, the \( S_1 \leftarrow S_0 \) (\( A^1B_2u \leftarrow X^1A_1g \)) transition is formally forbidden, but it becomes allowed because of vibronic coupling to the optically allowed \( C^1E_{1u} \) state. Monosubstituted halobenzenes have \( C_{3v} \) symmetry, and so the \( S_1 \leftarrow S_0 \) transition becomes formally allowed, exhibiting a larger oscillator strength than benzene, although still weak. This is often stated as the electronic structure of monosubstituted benzenes having a "memory" of the \( D_{3h} \) symmetry and vibronic nature of the transition. Experimental studies have consistently shown some intensity, with activity in the \( b_1 \) vibrational modes in the \( S_1 \leftarrow S_0 \) spectra. The \( S_2 \) state is known to have a conical intersection, leading to fast internal conversion to the \( S_1 \) state, with the \( S_2 \) state having a lifetime of less than 100 fs. Once on the \( S_1 \) surface, the excitation wavepacket is able to decay along two channels: the first to the nearby \( S_1/S_0 \) conical intersection and the second to the \( S_1 \) minimum. The \( S_1 \) state is longer lived, with a lifetime of \( \sim 4 \) ps.

There have been several different computational approaches to the accurate description of \( S_1 \) vibrational frequencies of aromatic molecules and vibronic coupling of \( S_1 \) states to higher electronic states for benzene, toluene, and other monosubstituted benzene derivatives. The vibronic bands in benzene have been investigated using multireference approaches, and coupling between different states has been considered in the interpretation of the photochemistry observed experimentally (see also ref 23 for a useful review by Suzuki). Tew et al. investigated the anharmonic nature of the \( S_1 \) vibrational...
f_{ij}(\mathbf{R}) = \langle \Psi_j(\mathbf{R}) | \frac{\partial}{\partial q} | \Psi_i(\mathbf{R}) \rangle \tag{1}

where \( f_{ij} \) are the non-adiabatic coupling matrix elements (NACMEs) and \( \mathbf{R} \) are the nuclear coordinates. The effects of vibronic coupling were included using the simple diabatization scheme of Simah et al.\(^{(34)}\) (based on the work by Domcke and Woywod\(^{(35)}\)), in which the overlap of the orbitals from a reference geometry and target geometry is optimized and the resulting pseudo-adiabatic orbitals are used to transform the wavefunction at the target geometry. In our case, we chose the reference geometry to be the MECI of the S\(_2\)/S\(_1\) conical intersection seam, as this is the point at which the two states involved in the intensity borrowing process interact most strongly. The target geometry is the S\(_0\) optimized geometry as this represents the geometry at which the Franck–Condon (FC) excitation occurs. The diabatic states (denoted by the superscript \( d \)) are considered to be a minor perturbation to the adiabatic states and are found by a unitary transformation of the S\(_1\) and S\(_2\) diabatic states (denoted by a superscript \( a \))

\[
\Psi_n^{d} = \sum_n \Psi_n^{a} U_{nm} \tag{2}
\]

The unitary transformation matrix is chosen such that the NACME vector, \( X_2 \)

\[
X_2 = \langle \Psi_m^{d} | \frac{\partial}{\partial q} | \Psi_n^{d} \rangle \tag{3}
\]

is minimized for all of the internal coordinates, \( q \). For a two-state diabatization, the unitary transformation matrix, \( U \), is given as

\[
U = \begin{bmatrix}
\cos \theta & \sin \theta \\
-\sin \theta & \cos \theta
\end{bmatrix} \tag{4}
\]

where a single non-adiabatic mixing angle, \( \theta \), can be used to describe the mixing of the adiabatic states. In the approximate scheme used in this work, the CI coefficients from an MRCI or XMS-CASPT2 calculation were transformed by maximizing the overlap of the CASSCF orbitals at the S\(_0\) geometry with those obtained at a reference geometry, generating a pseudo-adiabatic set of orbitals:

\[
|\langle \phi_i(q') | \phi_j(q) \rangle |^2 + |\langle \phi_i(q) | \phi_j(q') \rangle |^2 \tag{5}
\]

where the overlap is computed over all active orbitals \( i \) and \( j \) at the current geometry \( q \) with those at the reference geometry \( q' \), which in this case was the S\(_2\)/S\(_1\) MECI. In all cases, we assume that this MECI lies close to the S\(_1\) minimum and the proximity of the electronic states allows them to interact (see Figure 2 for a qualitative overview). The diabatic wavefunction, \( \Psi_m^{d} \), is constructed from the pseudo-adiabatic orbitals as

\[
\Psi_m^{d} = \sum_{j} d_{jm} \Phi_j^{d} \tag{6}
\]

At the target geometry, the matrix \( d \) is related to the adiabatic wavefunctions by the transformation \( d = cU \), where \( c \) is the coefficient matrix of the adiabatic wavefunctions and \( U \) is determined using the condition that \( d \) remains as close as possible to the matrix \( d^{ref} \) at the reference geometry:

\[
U = \mathbf{V}(\mathbf{V})^{-1/2} \tag{7}
\]

where
The oscillator strength can then be calculated:
\[ f = \frac{2}{3} (E_{S_1}^d - E_{S_0}^d) |\langle \Psi^d_{S_1} | \mu | \Psi^d_{S_0} \rangle|^2 \] (11)

While in eq 11, we use an adiabatic description of the \( S_0 \) state and pseudo-diabatic representation for \( S_1 \), the pseudo-diabatic representation is essentially only a perturbation to the adiabatic \( S_1 \) state. As such, where there is very strong coupling between \( S_1 \) and \( S_2 \) states, we expect this simple approximation to break down as the pseudo-diabatization scheme is based on the assumption that the orbitals and CI coefficients change very little as a function of geometry; this is not always true in the vicinity of a conical intersection. In the original scheme of Simah et al., the reference geometry is ideally chosen where the adiabatic and diabatic states are identical (e.g., due to symmetry). In the current work, the use of the \( S_1/S_2 \) MECl is a compromise between accuracy and computational cost. Additionally, the reference orbitals at the MECI geometry may have poor overlap with those at the target geometry \( S_0 \). If the MECI is far from the FC region of the \( S_1 \) state, then the current scheme is likely to show limited vibronic coupling, even if there is true coupling between the two states.

Adiabatic XMS-CASPT2 calculations were performed within the single-state single-reference contraction scheme (SS-SR) and a real shift of 0.2 au, using the cc-pVTZ basis set, the cc-pVTZ-JKFIT auxiliary basis set, using the BAGEL software. Adiabatic time-dependent density functional theory (TDDFT) calculations within the Tamm–Dancoff approximation were performed with the B3LYP, CAM-B3LYP, M06-2X, and \( \omega \)B97X-D functionals. Single-reference EOM-CCSD, ADC(2), and ADC(3) calculations were also performed. TDDFT and single-reference wavefunction theory calculations were performed using the Q-Chem software. The diabatic transformation calculations (using both internally contracted MRCI and XMS-CASPT2) were performed with the Molpro software suite. The \( S_0 \) and \( S_1/S_2 \) calculated geometries were superposed based on minimizing the RSMD of all atoms. In all cases, the cc-pVTZ basis set was employed as it represents a good compromise between accuracy and computational cost.

In addition, for toluene, a vibrationally resolved spectrum was determined by calculating the FC factors between the \( S_0 \) and \( S_1 \) harmonic vibrational modes and frequencies. The spectrum was calculated using the ezSpectrum software at a temperature of 10 K.

### RESULTS AND DISCUSSION

We first consider the \( S_0 \) and \( S_1 \) states of toluene. In Table 1 are the calculated XMS-CASPT2 harmonic vibrational frequencies.

<table>
<thead>
<tr>
<th>assignment ( a )</th>
<th>XMS-CASPT2</th>
<th>Expt. ( b )</th>
<th>XMS-CASPT2</th>
<th>Expt. ( b )</th>
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<td>( m_1 )</td>
<td>3072</td>
<td>3087</td>
<td>3086</td>
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<td>( m_2 )</td>
<td>3052</td>
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<td>3076</td>
<td>3077</td>
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<td>( m_3 )</td>
<td>3038</td>
<td>3055</td>
<td>3066</td>
<td>3063</td>
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<td>1605</td>
<td>1411</td>
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<tr>
<td>( m_5 )</td>
<td>1439</td>
<td>1494</td>
<td>1401</td>
<td></td>
</tr>
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<td>( m_6 )</td>
<td>1179</td>
<td>1210</td>
<td>1162</td>
<td>1193</td>
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<td>( m_7 )</td>
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<td>( m_8 )</td>
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<td>1030</td>
<td>921</td>
<td>935; 934</td>
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<td>( m_9 )</td>
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<td>1003</td>
<td>904</td>
<td>966</td>
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<td>( m_{10} )</td>
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<td>785</td>
<td>719</td>
<td>736; 753</td>
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<td>457</td>
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<td>( m_{20} )</td>
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<td>( m_{27} )</td>
<td>1136</td>
<td>1155</td>
<td>1110</td>
<td></td>
</tr>
<tr>
<td>( m_{28} )</td>
<td>1049</td>
<td>1080</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>( m_{29} )</td>
<td>587</td>
<td>623</td>
<td>514</td>
<td>532</td>
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<tr>
<td>( m_{30} )</td>
<td>317</td>
<td>342</td>
<td>309</td>
<td>332; 331</td>
</tr>
</tbody>
</table>

*a Assignments taken from ref 14. b Experimental data taken from refs 16, 56, 58. c Harmonic frequencies are scaled by 0.954. See the Supporting Information for full details of the scaling parameter.

The scaled harmonic vibrational frequencies show fair agreement with experiment, with a maximum error of 316 cm\(^{-1}\) for one of the low frequency carbon–carbon bend modes (\( m_{33} \)) and average errors of 55 and 29 cm\(^{-1}\) for the \( S_0 \) and \( S_1 \) frequencies, respectively, after scaling. The average error for the \( S_0 \) vibrations is 45 cm\(^{-1}\), neglecting the \( m_{33} \) frequency. Tew et al. employed the CC2/cc-pVTZ approach to calculate...
The differences exhibited between the XMS-CASPT2 and experimental $S_1$ frequencies are likely due to a combination of anharmonicity, for which CC2/cc-pVTZ performs well, and potential issues in the XMS-CASPT2 accuracy. In particular, the $m_{14} m_{15} m_{16} m_{18} m_{23}$, and $m_{25}$ modes all show larger differences to the CC2 values (and experiment); these were modes identified as genuinely anharmonic. Battaglia and Lindh determined XMS-CASPT2 excitations to be poor relative to MS-CASPT2 in regions where potential surfaces are energetically well separated (i.e., at or near minima); they developed an alternative approach to XMS-CASPT2 termed extended dynamically weighted CASPT2 (XDW-CASPT2). The results presented here suggest that stationary points and their frequencies may be similarly affected. These frequencies have been used to generate a vibrationally resolved spectrum (Figure 3). The dominant transition is the $0^−0$ vibrational line, with a handful of other vibrational lines about two orders of magnitude smaller.

We now turn to the calculation of the oscillator strengths for the $S_1 ← S_0$ transition for toluene, benzene, and three monosubstituted benzene derivatives. The $S_2/S_1$ MECI structures for each of the molecules considered are shown in Figure 4. With the exception of aniline, all exhibit a prefulvene-like structure typical of the MECI geometries of aromatic molecules. Aniline exhibits geometrical distortion of the $-NH_2$ group relative to the ring, with the atoms in the ring remaining planar. This is similar to that seen for the $1\pi^*\pi$ MECI in the recent work of Ray and Ramesh. The MECI geometry for toluene has a peaked topology, while the rest have a sloped topology.

The computed transition energies are given in Table 2 (0−0 transitions) and Table 3 (Franck–Condon transitions), along with the calculated oscillator strengths. The MECIs lie 1.14, 0.89, 0.52, 0.59, and 1.10 eV above the $S_1$ minima and 0.97, 0.73, 0.28, 0.42, and 1.03 eV above the Franck–Condon transition energy ($S_1 ← S_0$) for benzene, toluene, aniline, fluorobenzene, and phenol, respectively. The magnitudes of the calculated and experimental oscillator strengths are compared in Figure 5. The single-reference methods generally overestimate the oscillator strength, although for benzene (data shown in Table 3) and toluene, they are between 0 and 50% of the experimental value. The multireference methods both underestimate the oscillator strengths in comparison to experiment and the single-reference methods (DFT, EOM-CCSD, and ADC approaches), with the exception of phenol, where the XMS-CASPT2 oscillator strength is the largest of all the methods considered. The pseudo-diabatic oscillator strengths are given in Table 3 and Figure 5 for MRCI and XMS-CASPT2. The calculated oscillator strengths are enhanced relative to the adiabatic values for all molecules except aniline, where the pseudo-diabatic values are ~50% of the adiabatic values and ~10% of the experimental value for both MRCI and XMS-CASPT2. In this case, we can see that the $S_2$ state is energetically close to the $S_1$ state across the potential energy surface connecting the $S_0$ minimum and $S_2/S_1$ conical intersection (see Figure S1), deviating by no more than ~1.1 eV. In contrast, the other molecules have energy gaps
greater than 1.5 eV at the S₀ minima. In Figure 6, we present visual representations of the XMS-CASPT2 calculated non-adiabatic coupling vector between the S₂ and S₁ states at the S₀ geometry. It is clear for aniline that the coupling is much stronger than that seen for the other molecules. This is also reflected in the Franck−Condon excitation energy being less than 0.3 eV lower than the S₂/S₁ MECI relative to the S₀ energy. Interestingly, the coupling is strongest for the atoms in the ring and relatively low for the −NH₂ group, in contrast to the 1ππ*/1πσ* conical intersection.61 Worth and co-workers demonstrated two 3p Rydberg states between the S₁ and S₂ states. These also couple to the S₁ state,25 but they are not considered in the current study. We propose that, in this case, the approximate diabatization scheme would need to be replaced with a more robust approach (possibly including Franck−Condon factors and explicit integration of the NACMEs) to give a more accurate oscillator strength as vibronic coupling between the S₁ and S₂ states is stronger than the other molecules considered. Given in Figure S2 are the maximum and average coupling values compared to the difference in oscillator strength between the calculated and experimental oscillator strengths. For the molecules consid-
Figure 6. Visual representation of the non-adiabatic coupling vectors between the S₂ and S₁ states at the S₀ optimized geometries for benzene (top left), toluene (bottom left), aniline (center), fluorobenzene (top right), and phenol (bottom right).

Figure 7. (a) Two-dimensional potential energy surface scanned along the torsion angle C(aromatic)−C(aromatic)−C(aromatic)−C(methyl) and the bond angle C(aromatic)−C(aromatic)−C(methyl); kcal mol⁻¹, contour value of 0.025 kcal mol⁻¹. (b) Calculated oscillator strength as a function of the bond angle C(aromatic)−C(aromatic)−C(methyl) (see key for details of the methods).
the accuracy of the current method deteriorates when an individual atom’s NACME vector has a magnitude greater than 1.5 au (or the average magnitude of the NACME vector across all atoms is greater than \( \sim 0.7 \) au). The coupling between electronically excited states for phenol in this study is between two \( \pi \sigma^* \) states, while the true \( S_2 \) state is of a \( \pi \pi^* \) character.\(^{63}\) This is a consequence of the approach taken in this study, namely, choosing the simple \( \pi \)-electron active space and not expanding to include \( \sigma^* \) orbitals.

For each of the molecules considered, the point-group symmetry of the geometry of the \( S_0 \) state is \( D_{6h} \) (benzene), \( C_1 \) (toluene), \( C_2 \) (aniline), \( C_{3v} \) (fluorobenzene), and \( C_i \) (phenol). Breaking of the planar aromatic ring would therefore be assumed to be responsible for an enhancement in the oscillator strength of the \( S_1 \leftarrow S_0 \) transition. The effect of symmetry breaking upon the calculated oscillator strength is given in Figure 7 for toluene. As the torsion angle (between three aromatic carbon atoms and the methyl carbon) is decreased by \( \sim 10^\circ \), the energy of the \( S_0 \) state increases by only 1 kcal mol\(^{-1} \) (Figure 7a). As such, there is effectively little to no barrier to symmetry breaking at finite temperature. While there is a small change in the oscillator strength as the symmetry of the molecule is broken, this is a small effect (Figure 7b).

We now consider the extent to which the \( S_1 \) and \( S_2 \) states are mixed in the pseudo-diabatization procedure. In Table 4 are the calculated diabatic rotation angles for MRCI and XMS-CASPT2 for each of the molecules considered. While these rotation angles have an effect on the diabatic energies (eq 7), the effect on the oscillator strengths is determined by the mixing of the CI coefficients. As noted above, the coupling between the \( S_2 \) and \( S_1 \) states is strong for aniline with analytic NACMEs at the \( S_0 \) geometry, in contradiction to the rotation angle calculated using the approximate diabatization procedure. This provides further evidence that, in the event of strong coupling, the pseudo-diabatization procedure becomes less reliable.

### CONCLUSIONS

We have applied a simple pseudo-diabatization scheme to benzene, toluene, and three other monosubstituted benzenes to account for the vibronic coupling between the \( S_2 \) and \( S_1 \) states and the effect this has upon the transition properties of the \( S_1 \leftarrow S_0 \) excitation using multireference approaches. In the adiabatic basis, MRCI and XMS-CASPT2 exhibit oscillator strengths lower than the experimental values. Inclusion of approximate vibronic coupling effects through the pseudo-diabatization states results in improved quantitative values of the oscillator strength for all molecules except aniline. In this case, the vibronic coupling was determined to be strong relative to that seen in the other molecules; the success of the simple approach adopted here is predicated on weak coupling of the \( S_1 \) and \( S_3 \) states; in the case of aniline, this coupling is strong, leading to a poor description of the oscillator strength.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at [https://pubs.acs.org/doi/10.1021/acs.jpca.1c01685](https://pubs.acs.org/doi/10.1021/acs.jpca.1c01685).

Potential energy scans for aniline, NACME magnitudes, and harmonic vibrational frequency scaling data (PDF)

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Complete contact information is available at: [https://pubs.acs.org/10.1021/acs.jpca.1c01685](https://pubs.acs.org/10.1021/acs.jpca.1c01685)

#### Notes

The authors declare no competing financial interest.

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3599–3600.


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