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The molecular structures of guaiacol (2-methoxyphenol) and mequinol (4-methoxyphenol) have been studied using high resolution electronic spectroscopy in a molecular beam and contrasted with ab initio computations. Mequinol exhibits two low frequency bands that have been assigned to electronic origins of two possible conformers of the molecule, trans and cis. Guaiacol also shows low frequency bands, but in this case, the bands have been assigned to the electronic origin and vibrational modes of a single conformer of the isolated molecule. A detailed study of these bands indicates that guaiacol has a vibrationally averaged planar structure in the ground state, but it is distorted along both in-plane and out-of-plane coordinates in the first electronically excited state. An intramolecular hydrogen bond involving the adjacent –OH and –OCH$_3$ groups plays a major role in these dynamics. © 2015 AIP Publishing LLC.

INTRODUCTION

It is well known that vibrations play a key role in the intramolecular dynamics of electronically excited states. An early example can be found in the experiments of Sur and Johnson, who discovered that the rate of $S_0 \rightarrow S_1$ internal conversion (IC) in the hydrogen-bonded phenol-H$_2$O complex is much lower than in free phenol (PHE). Later, Lipert and Colson showed that replacement of the OH hydrogen atom by deuterium had a similar effect, lowering the rate of IC by more than two orders of magnitude. Both effects were attributed to the reduced ability of the ground state OH vibration to act as an accepting mode in the radiationless transition to the ground state, as lower frequency vibrations have smaller Franck-Condon factors at the excitation energy of the $S_1$ state. Many other examples have been provided by pioneering experiments on intersystem crossing and a wide variety of other dynamical processes at or near conical intersections in large molecules.

In this report, we explore the role of chemical substitution on dynamical processes. Chemical substitution induces several effects; it may change the number and/or type of vibrational modes that might participate in the process, it may introduce new types or kinds of pathways that might be accessed on electronic excitation, and/or it may change the nature of the state(s) that might be excited as the molecule disposes of its excitation energy.

Molecules of interest to us include catechol (CAT) and hydroquinone (HQY) in which a second OH group is attached to either the 2- or 4-position of the PHE aromatic ring, and anisole (ANI), guaiacol (GAU), and mequinol (MEQ) in which one OH group is replaced by a methoxy group, –OCH$_3$. Structures of these are shown in Scheme 1. HYQ and ANI have previously been studied by high resolution techniques. Both of them possess a lowest $S_1$ state that is ππ* in character, with perpendicularly oriented (with respect to the a-inertial axis of the molecular frame) electronic transition moments (ETMs). HYQ has two conformers, cis and trans; neither exhibits intramolecular hydrogen bonds, but both exhibit different intensity patterns in their fully resolved electronic spectra that are a direct consequence of the different point groups to which each conformer belongs. ANI reveals just one conformer in the collision-free experiments.

Bürgi and Leutwyler reported the identification of only one conformer of CAT in the gas phase experiments, the one subtending a hydrogen bond between the two OH groups. The same authors also suggested the existence of a double minimum potential (DMP) in the $S_1$ state along the OH torsional coordinate of the hydrogen-bound hydroxy group, with a barrier height of 145 cm$^{-1}$. Kleinermanns and co-workers studied the vibrational modes of CAT using both experimental and theoretical techniques and concluded that the “free” (non-bound) OH is rotated out of the plane of the molecule by ~24°. King et al. have pointed out that CAT undergoes a change in point group symmetry upon electronic excitation which, together with the presence of the intramolecular hydrogen bond, might enhance the photodissociation dynamics of the electronically excited molecule. Finally, Stavros...
and co-workers\textsuperscript{9} proposed a vibrationally enhanced tunneling mechanism via a $S_0$/$S_2$ conical intersection resulting in a dissociative O–H bond along $S_2$ in the isolated molecule.

Mequinoil shows two conformers (\textit{cis-} and \textit{trans-}) in a supersonic jet expansion, as reported by Patwari \textit{et al.}\textsuperscript{10} and later confirmed by Tzeng and co-workers\textsuperscript{11,12}. The electronic origin transitions and some low frequency vibronic bands of both conformers have been identified in the gas phase experiments.

The final member of this family of molecules, GUA, has received much attention in the recent literature.\textsuperscript{13–17} Weed and co-workers\textsuperscript{13,14} have assigned low-frequency features that appear in its electronic spectrum to different conformers of the molecule and estimated the potential barriers relative to the internal rotation of the methoxy group. Later, Dean \textit{et al.}\textsuperscript{15} revisited GUA and concluded that only the hydrogen-bound conformer was present, as observed in CAT as well.\textsuperscript{5} Additionally, it was found that the low-frequency vibrations of GUA undergo extensive Duschinsky mixing between $S_0$ and $S_1$. Theoretically, Castaño and co-workers\textsuperscript{16} determined that just one conformer is present in the GUA experiments by performing DFT calculations, whereas Agache and Popa\textsuperscript{17} found that the lowest energy conformer of GUA is the one with an \textit{intramolecular} hydrogen bond, whose binding energy is about 18 kJ/mol, determined by MP4 calculations.

In this work, we examine the fully resolved electronic spectra of both MEQ and GUA in the gas phase, and use these data to determine the electronic nature of their $S_1$ states. We also explore the nature of some low frequency vibrations that appear in these spectra, some of which provide clues to their underlying dynamic behavior. We close with some remarks about the effect of chemical substituents on the processes that take place when molecules of this type absorb UV light.

**EXPERIMENTAL**

MEQ and GUA (99\% pure) were purchased from Aldrich and used without further purification. In the vibrationally resolved experiment, the GUA sample was seeded into about 138 kPa of argon gas and expanded into a vacuum chamber (1.33 $\times$ 10$^{-3}$ Pa) through a 1 mm diameter orifice pulsed valve (General Valve Series 9) operating at 10 Hz. Two centimeters downstream of the valve, the sample was excited with the second harmonic of a Quanta Ray Nd$^{3+}$:YAG (Model DCR-1A) pumped dye laser (Model PDL-1). The dye (Rhodamine 575) laser output was frequency doubled with an external $\beta$-barium borate crystal providing a spectral resolution of $\sim$0.6 cm$^{-1}$ in the ultraviolet. From the point of intersection between the free jet and the laser, the molecules were excited and the fluorescence was collected with a photomultiplier tube (PMT). Finally, the collected data were processed by a boxcar integrator (Stanford Research Systems) and recorded with Quick Data Acquisition software version 1.0.5.

Rotationally resolved experiments were performed using a molecular beam laser spectrometer, described in detail elsewhere.\textsuperscript{18} Briefly, the molecular beam was formed by expansion of the vaporized sample, seeded in an argon carrier gas ($\sim$40 kPa), through a heated ($\sim$450 K) 240 $\mu$m quartz nozzle into a differentially pumped vacuum system. The expansion was skimmed once and crossed 15 cm downstream by a collimated CW laser beam. This beam was generated by pumping a dye laser mixture (Kiton Red for MEQ and Rhodamine 110 for GUA) with a single mode Ar$^+$ laser and intracavity frequency doubled with either 600 nm or 560 nm BBO crystals, yielding approximately 350 $\mu$W of UV radiation with a resolution of $\sim$1 MHz. The fluorescence excitation spectra (FES) were detected using spatially selective optics by a PMT and a photon counting system. This signal, together with the iodine absorption spectrum and the relative frequency markers, was simultaneously collected and processed by the JBA95 data acquisition system.\textsuperscript{18} Absolute frequency calibration of the spectra was performed by comparison with the I$_2$ absorption spectrum.\textsuperscript{19} Relative frequency markers were obtained from a stabilized etalon having a free spectral range of 299.7520 $\pm$ 0.0005 MHz in the fundamental of the dye.

**COMPUTATIONAL DETAILS**

The ground-state structures of MEQ and GUA were fully optimized using the B3LYP density functional approach employing a 6-31G(d,p) basis set. Optimizations of the first excited state were carried out using the time-dependent density functional theory (TD-DFT) method, employing the same level as for the ground state. It is well known that B3LYP is not the best functional to describe the energy of a system; thus, we tested several combinations of functionals and basis set in order to have good rotational constants because they are the parameters that we would like to reproduce in this manuscript. To our surprise, B3LYP and the 6-31G(d,p) basis set is the best combination that was found to better represent the rotational constants for the title systems for both the ground and the first electronically excited states. Harmonic-frequency computations were performed on both states to characterize the nature of all stationary points and to compute the zero-point energy corrections. The Gaussian 09 program package was employed for all these computations.\textsuperscript{20}
RESULTS

Figure 1 shows the vibrationally resolved resonance-enhanced multiphoton ionization (REMPI) spectrum of MEQ in the gas phase, recorded by Li et al.\textsuperscript{11} This spectrum exhibits two main bands located at 33 569.7 and 33 666.4 cm\(^{-1}\), respectively. In addition, several vibronic bands have been assigned to specific vibrational modes originating from two different conformers of the molecule in the jet expansion. The origin bands (0\( \rightarrow \)0\(_t\)) of MEQ are blue-shifted by \(\sim 69.7\) and \(\sim 132\) cm\(^{-1}\) with respect to the electronic origin bands of the corresponding HYQ conformers.\textsuperscript{3} The relative splitting between the two origin-band transitions of MEQ is about 97 cm\(^{-1}\).

Figure 2 shows the vibrationally resolved FES of jet-cooled GUA in the gas phase. In agreement with previous results,\textsuperscript{13–15} we observe that the electronic origin (0\( \rightarrow \)0\(_t\)) of this molecule is red-shifted by \(\sim 432.5\) cm\(^{-1}\) from that of PHE\textsuperscript{21} and by \(\sim 468\) cm\(^{-1}\) from that of ANI\textsuperscript{5,5} and blue-shifted by \(\sim 267\) cm\(^{-1}\) from that of CAT.\textsuperscript{6} It is evident that the addition of a second functional group to the aromatic ring causes a red frequency shift (GUA vs. PHE or ANI), but in the case of replacing an –OH group by a –OCH\(_3\) group, there is a moderate blue shift due to a considerable decrease of the intramolecular hydrogen bond among these chemical species (GUA vs. CAT). Frequency labels are used to identify the stronger bands in the studied low-frequency region. Band B, located at 139.5 cm\(^{-1}\) to the blue of the origin band (A), does not show up in the FES spectra of either PHE or ANI.\textsuperscript{22} However, the band located at 223.7 cm\(^{-1}\) (C) resembles the 18\(b_1\) band observed in ANI at \(\sim 260\) cm\(^{-1}\) above the electronic origin.\textsuperscript{22,23}

Figure 3(a) shows the high resolution fluorescence excitation spectrum of the 0\( \rightarrow \)0\(_t\) band of trans-MEQ in the gas phase at 33 569.7 cm\(^{-1}\). This spectrum spans approximately 2.9 cm\(^{-1}\) and exhibits mostly b-type character. Thus, the ETM vector lies nearly parallel to the b-inertial axis of the molecule. To fit this spectrum, we first generated \(\sim 3000\) b-type transitions based on \textit{ab initio}\textsuperscript{20} estimates of rotational constants and rigid rotor Hamiltonians in both electronic states. Then, we made quantum number assignments of single transitions in the simulated spectrum to the corresponding transitions in the experimental spectrum, using the JB95 program.\textsuperscript{24} Finally, we used a least-squares fitting procedure to optimize the inertial parameters, based on comparisons of the observed and calculated line positions. The final fit used about 200 assigned lines out of \(\sim 3000\) transitions and resulted in a standard deviation of 3.80 MHz.

Figure 3(b) shows the corresponding high resolution spectrum of the 0\( \rightarrow \)0\(_t\) band of cis-MEQ in the gas phase at 33 666.4 cm\(^{-1}\). This spectrum spans approximately 2.3 cm\(^{-1}\) and also exhibits mostly b-type character. The final fit of this band used about 110 assigned lines out of \(\sim 2800\) transitions and resulted in a standard deviation of 4.40 MHz. The quality of the fits of the two spectra of MEQ is shown in the bottom panel of the figure, where portions of each spectrum are shown together with their corresponding simulations.

Figure 4 shows the rotationally resolved S\(_1\) \(\leftarrow\) S\(_0\) fluorescence excitation spectrum of the 0\( \rightarrow \)0\(_t\) band of the lowest energy conformer of GUA in a molecular beam at 35 916.2 cm\(^{-1}\). The spectrum spans approximately 2.4 cm\(^{-1}\) and exhibits mostly a-type character. The final fit utilized about 115 lines of the \(\sim 1000\) simulated rotational transitions and resulted in a standard deviation [observed minus calculated (OMC)] of

![FIG. 1. One-color REMPI spectrum of 4-methoxyphenol (MEQ) in the gas phase. The transition origins of the trans (t) and cis (c) rotamers appear at about 33 570 and 33 666 cm\(^{-1}\), respectively.][1]

![FIG. 2. Vibrationally resolved fluorescence excitation spectrum of 2-methoxyphenol (GUA) in the gas phase. The feature labeled with the asterisk is the hydrogen-bonded water complex formed in the jet with the conformer shown in the inset picture.][2]
2.38 MHz. The quality of the fit is shown in the bottom panel of the figure. Here, a portion of the experimental spectrum and its corresponding (Voigt line shape function) simulated spectrum are shown at full experimental resolution. The full width at half maximum (FWHM) linewidth of this spectrum is 36 MHz, with 18 MHz Gaussian and 30 MHz Lorentzian components, respectively. From the measured Lorentzian linewidth, the lifetime of GUA in the $S_1$ state is determined to be 5.3 ns. The rotational temperature of the fit is 4.0 K.

Figures 5 and 6 show the high resolution spectra of two low-frequency vibronic bands (B and C) of GUA at $+139.5$ and $+223.7$ cm$^{-1}$ above the origin band, respectively. These two bands also reveal mostly $a$-type polarized spectra and the same values of rotational constants in the ground electronic state ($S_0$). Analyses of these spectra proceeded in a manner similar to the previously described procedure. In the case of the $+139.5$ band (see Figure 5), $1400 a$- and $b$-type rovibronic transitions were simulated. Of these, 107 lines were assigned and fit using rigid rotor Hamiltonians for both electronic states. In the bottom panel of Figure 5, the experimental trace and the corresponding simulations, with and without a line shape function, are also shown. The OMC of the fit is 4.51 MHz; the Voigt line shape profile has 18 MHz Gaussian and 25 MHz Lorentzian components. The rotational temperature of the fit is 5.0 K. For the $+223.7$ cm$^{-1}$ band (see Figure 6), the experimental trace obtained requires the use of two simulated spectra to properly fit it. About 100 out of $\sim1000$ lines in each simulated spectrum were assigned, resulting in standard deviations of 3.95 MHz for both sub-bands. The rotational temperatures of the fits are 10 and 13 K, respectively. Voigt profile components similar to those used in the $+139.5$ band were used in these fits. The bottom panel of Figure 6 shows the quality of the fit. Clearly evident is the presence of two sub-bands in the spectra, separated by a splitting of $\sim161$ MHz. The inertial parameters of the studied bands of GUA are summarized in Table II.

**DISCUSSION**

**Nature of the $S_1$ states of MEQ and GUA**

Figure 7 depicts the measured ETM orientations of MEQ, GUA, and the reference molecules discussed in this work.

<p>| TABLE I. Theoretical and experimental inertial parameters of the trans- and cis-conformers of MEQ in the gas phase. |</p>
<table>
<thead>
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<th>Parameter</th>
<th>$O_0^0(r)$</th>
<th>trans-B3LYP/6-31G(d,p)</th>
<th>$O_0^0$</th>
<th>cis-B3LYP/6-31G(d,p)</th>
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<td></td>
<td></td>
<td></td>
</tr>
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<td>4 888.8</td>
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<td></td>
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<tr>
<td>$A'$ (MHz)</td>
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<td>4 672.2</td>
<td>4 630.0 (1)</td>
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*Standard deviations shown in parentheses are relative to the last significant figure.*
FIG. 4. Rotationally resolved fluorescence excitation spectrum of the $S_1 \leftarrow S_0$ electronic origin band of the lowest energy conformer of GUA in the gas phase, at 35 916.2 cm$^{-1}$. A portion of the $P$-branch of the fully resolved experimental spectrum and its corresponding simulated spectrum are shown in the bottom panel.

(PHE, CAT, HYQ, and ANI). All ETMs lie (approximately) in the $ab$ plane; thus, the $S_1$ states of all six molecules are $\pi\pi^*$ in nature. As Platt showed many years ago,26 and revisited often (see, for example, the work of Kroemer et al.,27), two kinds of $\pi\pi^*$ states of singly substituted benzenes with $C_2v$ or higher symmetry exist, $^1L_a$ and $^1L_b$. $^1L_a$ states show $a$-oriented ETMs and $^1L_b$ states $b$-oriented ETM’s. Thus, PHE, ANI, HYQ, and MEQ all possess $S_1$ states that are $^1L_b$ in character, as is the case for most molecules of this type. Their $S_1 \leftrightarrow S_0$ ETMs are all perpendicular to the attached OH and/or OCH$_3$ groups, in the plane and parallel to the $b$-inertial axis.

More interesting are CAT and GUA, since they have adjacent substituents. If both molecules have $S_1 \leftrightarrow S_0$ ETMs in character, and the two substituents are “equivalent,” one would expect ETMs that lie in the $ab$ plane and make an angle of approximately 30° with the $a$-inertial axis (this is because the attachment of the second substituent rotates the inertial axes by approximately 60°). The $S_1$-$S_0$ origin band of GUA was found to be an in-plane hybrid band, with 79% $a$-type and 21% $b$-type character. The two low-frequency vibronic bands of GUA exhibit similarly polarized, principally $a$-type spectra. Interpreting these results in the usual way yields the magnitude of the orientation of the ETM with respect to the $a$-inertial axis of $\theta = \pm 28^\circ$, as shown in Fig. 7, where the negative sign has been chosen in terms of chemical intuition (the vector lies nearly perpendicular to the methoxy group). Similar results

FIG. 5. Rotationally resolved $S_1 \leftarrow S_0$ fluorescence excitation spectrum of the +139.5 band (Band B) of the lowest energy conformer of GUA in the gas phase, at 36 055.7 cm$^{-1}$. A portion of the $R$-branch of the fully resolved experimental spectrum and its corresponding simulated spectrum are shown in the bottom panel.

FIG. 6. Rotationally resolved $S_1 \leftarrow S_0$ fluorescence excitation spectrum of the +223.7 band (Band C) of the lowest energy conformer of GUA in the gas phase at 36 139.9 cm$^{-1}$. A portion of the $Q$-branch of the fully resolved experimental spectrum and its corresponding simulated spectra are shown in the bottom panel.
would be expected for CAT, though no reports about its experimental ETM orientation were found. However, we determined by theory (TD-DFT/B3LYP/6-31G(d,p)) its relative orientation within its inertial framework. Thus, we conclude that the lowest excited singlet states in all six molecules are $\pi\pi^*$ states of $^1L_b$ character.

While the theoretical values of the excitation energies of the different methoxyphenol isomers (35 744 cm$^{-1}$ for MEQ and 37 950 cm$^{-1}$ for GUA) are different from experiment (33 570 and 35 916 cm$^{-1}$, respectively), their relative values are correctly predicted by the calculations. Figure 8 shows the molecular orbitals involved in the excitation of GUA to its $S_1$ state. For GUA, cis-MEQ, and trans-MEQ, the $S_1$-$S_0$ transition involves primarily a HOMO-LUMO+1 excitation with a minor contribution from HOMO-1 to LUMO, which is a classical $\pi\pi^*$ excitation of a $^1L_b$ state. The calculated transition moment orientations agree with experiment.

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<th>Parameter</th>
<th>Band A</th>
<th>Band B</th>
<th>Band C (red)$^b$</th>
<th>Band C (blue)$^b$</th>
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<td>$B''$ (MHz)</td>
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<td>$C''$ (MHz)</td>
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$^a$Standard deviations shown in parentheses are relative to the last significant figure.

$^b$See Figure 6 for further details.

**FIG. 7.** Experimentally measured electronic transition moment (ETM) vector orientations of PHE, HYQ, CAT, ANI, cis-MEQ, and the lowest energy conformer of GUA. The ETM vectors are determined with respect to the inertial frame but the orientations shown here have been displaced from the center of mass for ease of viewing. $^*$The ETM of CAT has not been measured experimentally, but it has been estimated by theoretical calculations.
FIG. 8. Frontier molecular orbitals (and their eigenvalues in eV) involved in the electronic excitation of GUA.

Structures of the $S_0$ and $S_1$ states of MEQ and GUA

The computed (equilibrium) $S_0$ and $S_1$ rotational constants of the lowest energy conformers of the two molecules are in excellent agreement with the vibrationally averaged experimental values (cf. Tables I and II). For the ground states, the maximum deviation between theory and experiment is less than 10 MHz. For the excited states, the deviations are only slightly higher (<32 MHz). Thus, we can safely use theory to give us at least a qualitative picture of the structures of the two molecules in both states.

Figure 9 shows the computed lowest energy conformers of MEQ in its $S_0$ and $S_1$ states. The energy difference of the two MEQ conformers (cis and trans) is negligible (~7 cm$^{-1}$), with the cis conformer being the more stable structure. All structures are (heavy-atom) planar in their ground states. However, there is a slight deviation of planarity upon excitation revealed by the methoxy group dihedral angle ($\phi$) measured with respect to the aromatic plane of the molecule and confirmed by the inertial defect small increment obtained from the experimental fits (see Table I). We did the frequency analysis for planar and nonplanar systems. For planar systems, there is one negative frequency, and the rotational constants are much different to those computed for the nonplanar structure, which is a local minimum. So, this is a proof that at least at this level, the system is not planar.

Additionally, Figure 10 shows the calculated lowest-energy conformer of GUA, which appears to exhibit an intramolecular hydrogen bond (as previously described by several groups for CAT$^6,7$ and GUA$^{15-17}$). The distance between the OH hydrogen and the oxygen atom of the methoxy group is 2.077 Å. Likely, this hydrogen bond explains why GUA is ~805 cm$^{-1}$ more stable than MEQ in the ground state. The meta form (3-methoxyphenol) was theoretically predicted to be less stable than GUA, but only by ~175 cm$^{-1}$. The calculated OH rotational barriers of GUA, MEQ, and 3-methoxyphenol in their ground states are 2310, 875, and 1260 cm$^{-1}$, respectively.

From theoretical calculations, the differences in the ground state rotational constants of the different geometrical isomers (cis and trans) of the two molecules are relatively small, less than 50 MHz. Nonetheless, the experimental, vibrationally averaged values of these constants obtained by fitting the high resolution spectra are accurate enough to distinguish among them. Thus, we are able to assign specific spectral transitions to specific isomers. The inertial parameters reported for the two studied bands of MEQ confirm the earlier assignments$^{11}$ of the red-shifted band to the trans-conformer and the blue-shifted band to the cis-conformer. The ~100 cm$^{-1}$ separation of these two bands is typical of the separations observed in previous studies of the electronic spectra of geometric conformers of large molecules.$^{28}$ The different features

FIG. 9. Structures of the lowest energy conformers of MEQ in their $S_0$ and $S_1$ states. The relative energy differences (in wavenumbers) are shown for comparison. The dihedral angle ($\phi$) of the methoxy group increases from 0$^\circ$ in $S_0$ to ~1.5$^\circ$ in $S_1$, in both conformers.

FIG. 10. Structures of the lowest energy conformer of GUA in its $S_0$ and $S_1$ states. The relative energy differences (in wavenumbers) are shown for comparison. The dihedral angle ($\phi$) of the methoxy group is theoretically predicted to increase from 0 to ~13.5$^\circ$ upon electronic excitation.
in the spectrum of GUA (see Figure 2) are assigned to the lowest energy cis-conformer, in agreement with the previous IR/UV study reported by Castaño and co-workers. Further high resolution experiments will be necessary to confirm the suggestion of Konijn et al. that other conformers contribute to the electronic spectrum of GUA.

The excited state values of $A$, $B$, and $C$ of GUA and the corresponding $A$ and $C$ values of both isomers of MEQ are smaller than their ground state counterparts, owing to the small ring expansions that are typical of $\pi\pi^*$ states. More importantly, the lowest energy conformers of GUA, cis-MEQ, and trans-MEQ are not planar in their $S_1$ states. Experimentally, this is revealed by an increase in the magnitude of the inertial defect. The data in Table II show that $\Delta I = -3.46 \pm 0.03 \text{ u Å}^2$ for GUA in its $S_0$ state and $\Delta I = -4.13 \pm 0.03 \text{ u Å}^2$ in its $S_1$ state. (The expected value for a methyl group is $\Delta I = -3.4 \text{ u Å}^2$.) According to theory (see Fig. 10), the methoxy group of GUA is rotated out of the aromatic plane by $\sim 13.5^\circ$. For cis-MEQ and trans-MEQ, this rotation is less; the methoxy group is rotated out-of-plane by no more than $2^\circ$. Consequently, transfer of electrons from the $-\text{OCH}_3$ group to the aromatic plane is inhibited on excitation of both molecules to their $S_1$ states.

**Dynamical properties of the $S_1$ state in GUA**

Two vibronic bands of GUA have been studied at high resolution in this work, Band “B” at 139.5 cm$^{-1}$ above the $S_1$ origin and Band “C” at 223.7 cm$^{-1}$ above the $S_1$ origin. Previous studies of these two bands by Zwier and co-workers have shown that Band B should be assigned to 44$_2^0$, the first overtone of the out-of-plane-flapping mode of the attached $-\text{OCH}_3$ group, and that Band C should be assigned to 30$_0^1$, an in-plane scissoring mode of the linked OH $\cdots$ OCH$_3$ groups. A theoretical/experimental contrast of the low-frequency modes of GUA with their suggested assignment is shown in Table III. While the frequency of 30$_0^1$ changes little on $S_1$ excitation, the frequency of 44$_2^0$ drops significantly in $S_1$ relative to $S_0$, owing to the non-planar nature of the $S_1$ state.

The high resolution studies described here provide further insight into the nature of these two bands. First, we note that the upper state inertial defects ($\Delta I$) derived from the measured rotational constants are different from those of the ground state, see Table II. Thus, Bands B and C both originate in the zero-point level of the ground electronic state, which has $\Delta I = -3.46 \text{ u Å}^2$, and terminate in two different vibrational levels of the $S_1$ state which have very different inertial defects, $\Delta I = -5.44 \text{ u Å}^2$ (44$_2^0$) and $-3.95 \text{ u Å}^2$ (30$_0^1$), respectively. Significantly, these two $\Delta I$ values also are different from the zero point vibrational level (ZPL) of the $S_1$ state, $\Delta I = -4.13 \text{ u Å}^2$. Since the upper state $\Delta I$ value in Band B is larger in magnitude than that of the $S_1$ ZPL, we can conclude that this state has out-of-plane vibrational character. Similarly, we conclude that Band C terminates in an in-plane vibrational level, since its inertial defect is smaller in magnitude than that of the $S_1$ ZPL. Both of these conclusions are consistent with the assignments of Dean et al.

More interesting is the observation that Band C is split into two components, separated by 161.32 MHz. One possible explanation for this splitting is that the vibrational coordinate which is accessed in this transition ($v_{30^1}$) is governed by a double minimum potential. But $v_{30^1}$ is an asymmetric in-plane mode, so this seems unlikely. Alternatively, $v_{30^1}$ could be coupled to another vibrational coordinate that is governed by a double minimum potential (DPM). But $v_{30^1}$ is an asymmetric in-plane mode, so this seems unlikely. Alternatively, $v_{30^1}$ could be coupled to another vibrational coordinate that is governed by a DMP. Indeed, in their study of GUA, Dean et al. found that the dispersed fluorescence spectrum of 30$_0^1$ exhibited a false origin and a pair of sidebands assigned to the out-of-plane combinations 44$_2^0$(4) and 43$_3^0$(4), signaling the presence of a Fermi resonance between these combination bands and the 30$_0^1$ levels. (Extensive Duschinsky mixing of the four lowest frequency modes was also suggested.) These authors further showed that the Franck-Condon progression along mode $v_{44}$ (the out-of-plane flapping mode) in the fluorescence excitation spectrum could be fit by a double minimum potential with a 195 cm$^{-1}$ barrier and a 0°/0° splitting of 13 cm$^{-1}$. So, we speculate that a coupling between the electronic transitions involving $v_{30^1}$ and $v_{44}$ and/or $v_{45}$ is responsible for the observed splitting in the high resolution spectrum, as illustrated in Fig. 11. If this is correct, then the observed splitting of 161.32 MHz is a direct measure of the magnitude of this interaction. A similar mode coupling was observed in previous high resolution experiments on 9,10-dihydrophenanthrene.

As was first pointed out by Weisshaar and co-workers, and further elaborated by Trachsel et al., $\pi\pi^*$ transitions of molecules containing methyl (or methoxy) groups often show strong fundamentals of out-of-plane modes, since ($a'' +$ internal rotation) excitations can be totally symmetric. Essential

**TABLE III.** Some theoretical and experimental vibrational mode frequencies (in wavenumbers) of the $S_1$ state of GUA.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Experimental frequency$^{ab}$</th>
<th>Theoretical frequency$^a$</th>
<th>Mode description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_{45}(a'')$</td>
<td>45.9</td>
<td>48.7</td>
<td>Out-of-plane methoxy flapping</td>
</tr>
<tr>
<td>$v_{44}(a'')$</td>
<td>69.7</td>
<td>102.6</td>
<td>Out-of-plane methoxy Rocking</td>
</tr>
<tr>
<td>$v_{43}(a'')$</td>
<td>180.5</td>
<td>138.4</td>
<td>Out-of-plane butterfly</td>
</tr>
<tr>
<td>$v_{42}(a'')$</td>
<td>...</td>
<td>146.0</td>
<td>Out-of-plane methoxy twisting</td>
</tr>
<tr>
<td>$v_{41}(a')$</td>
<td>223.7</td>
<td>216.1</td>
<td>In-plane methoxy-bending</td>
</tr>
<tr>
<td>$v_{40}(a')$</td>
<td>...</td>
<td>314.0</td>
<td>In-plane methoxy-hydroxy scissoring</td>
</tr>
</tbody>
</table>

$^a$Mode assignments are taken from Ref. 15.
$^b$Experimental values are the results of this work.
$^c$Theoretical frequencies [B3LYP/6-31G(d,p)] have been reduced by using the correction factor 0.9408.

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CONCLUSIONS

Rotationally resolved electronic spectroscopy in a molecular beam has been used to assign the electronic origins and a few low frequency bands that appear in the $S_1 \leftarrow S_0$ spectra of mequinol and guaiacol and to study their ensuing dynamics. Both molecules contain $\text{-OH}$ and $\text{-OCH}_3$ groups attached to an aromatic ring. Mequinol exhibits conformational isomerism since the two substituents are widely separated, but guaiacol exhibits an intramolecular hydrogen bond since the two substituents are adjacent to each other. On this respect, in GUA, it is evident that the chemical substitution (i.e., the two substituents are adjacent to each other). Further studies of these eects, but GUA does, owing to the proximity of its hydrogen-bonded $\text{-OH}$ and $\text{-OCH}_3$ groups. Further studies of other bands in the high resolution spectra will be needed to map out the couplings that govern the dynamics of GUA and related molecules. But even at this very early stage, it is already clear that these dynamics will be significantly influenced by both the position and type of chemical substitution.

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