

# Structure Determination of Resorcinol Rotamers by High-Resolution UV Spectroscopy

Grzegorz Myszkiwicz,<sup>[a]</sup> W. Leo Meerts,<sup>\*[a]</sup> Christian Ratzler,<sup>[b]</sup> and Michael Schmitt<sup>\*[b]</sup>

The rotationally resolved  $S_1 \leftarrow S_0$  electronic origins of several deuterated resorcinol rotamers cooled in a molecular beam have been recorded. An automated assignment of the observed spectra has been performed using a genetic algorithm approach with an asymmetric rotor Hamiltonian. The structures of resorcinol A and resorcinol B were derived from the rotational constants of twenty deuterated species for both electronic states. The lifetimes of different resorcinol isotopomers in the  $S_1$  state are also reported.

As is the case for phenol, these lifetimes mainly depend on the position of deuteration. A nearly perfect additivity of the zero-point energies after successive deuterations in resorcinol rotamers has been discovered and subsequently used in the full assignment of the previously reported low-resolution spectra of deuterated resorcinol A. An analogous spectrum is also predicted for the resorcinol B rotamer.

## 1. Introduction

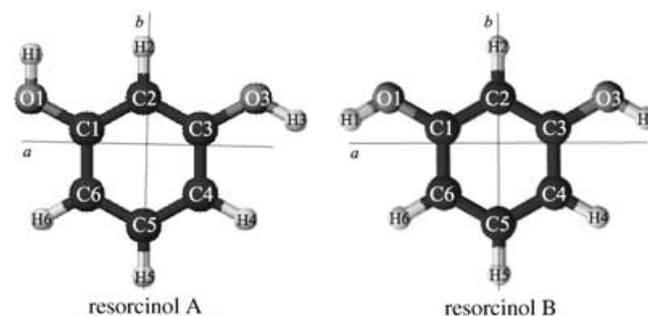
The three dihydroxybenzenes catechol (1,2-dihydroxybenzene), resorcinol (1,3-dihydroxybenzene), and hydroquinone (1,4-dihydroxybenzene) are the building blocks of many biologically important groups of molecules, such as flavanones, flavones, flavonols, and anthocyanins. As such, their structure is essential in understanding the chemistry and dynamics of these biomolecules. Another interesting topic is that hydroquinone possesses two isomers, which are distinguished by the relative orientation of their two  $-OH$  groups (*cis-trans* isomerism). For resorcinol and catechol, even three such rotamers are expected, although for catechol one of these three will have a strong steric hindrance. It is therefore not surprising that dihydroxybenzenes have been the topic of many scientific publications.

Low-resolution spectra (for example laser induced fluorescence—LIF, resonance enhanced multiphoton ionization—REMPI or dispersed fluorescence—DF) help to understand the vibrational activity in different electronic states of the molecules. REMPI spectra of dihydroxybenzenes up to about  $300\text{ cm}^{-1}$  were recorded by Dunn et al.<sup>[1]</sup> and different rotamers were tentatively assigned. However, as shown by Gerhards et al.,<sup>[2]</sup> earlier assignments of resorcinol rotamers were incorrect. Using spectral-hole burning, Gerhards et al. observed two series of transitions arising from two different rotamers of resorcinol, and attributed the band at  $35944\text{ cm}^{-1}$  to the  $S_1 \leftarrow S_0$  origin of structure A, and the band at  $36196\text{ cm}^{-1}$  to the  $S_1 \leftarrow S_0$  origin of structure B (see Figure 1). Later, low-resolution studies on resorcinol, its cations and deuterated isotopomers combined experimental and theoretical approaches,<sup>[3,4,5]</sup> and yielded a better understanding of the structure and vibrations in the  $S_0$ ,  $S_1$ , and  $D_0$  electronic states.

Microwave (MW) spectroscopy of *cis*-hydroquinone<sup>[6]</sup> allowed the structure of the  $-COH$  groups in its electronic ground state to be determined. MW spectra of resorcinol<sup>[7]</sup> yielded the rotational constants of the ground state of all three possible ro-

tamers. Unfortunately, no isotopic substitutions were done, and consequently no structural parameters were derived. On the other hand, rotational constants predicted from theoretical structures of resorcinol<sup>[2,3]</sup> do not compare very well with the microwave data.<sup>[7]</sup> This indicates that higher level calculations are needed.

Since MW spectroscopy gives only rotational constants of the electronic ground-state, high-resolution laser induced fluo-



**Figure 1.** Rotamers of resorcinol studied herein. Numbering of the atoms is used in the text to refer to the different deuterated species. The inertial axes *a* and *b* are also shown, the *c* axis is perpendicular to the *ab* plane.

[a] G. Myszkiwicz, Dr. W. L. Meerts  
Molecular and Biophysics Group, Institute for Molecules and Materials  
Radboud University Nijmegen  
P.O. Box 9010, 6500 GL Nijmegen (The Netherlands)  
Fax: (+33) 24-356-3311  
E-mail: Leo.Meerts@science.ru.nl

[b] Dr. C. Ratzler, Dr. M. Schmitt  
Heinrich-Heine-Universität, Institut für Physikalische Chemie  
40225 Düsseldorf (Germany)  
Fax: (+49) 211-81-15195  
E-mail: mschmitt@uni-duesseldorf.de

rescence spectroscopy has to be applied for information about the electronically excited states. The structure of the  $S_1$  state of phenol was derived from high-resolution LIF data of several isotopomers.<sup>[8]</sup> The *trans* and *cis* rotamers of hydroquinone were identified in the high-resolution  $S_1 \leftarrow S_0$  fluorescence excitation experiments by Humphrey and Pratt.<sup>[9]</sup> They determined the structural change of hydroquinone upon electronic excitation, and deduced a quinoidal structure in the electronic  $S_1$  state.

Herein, we determine the pseudo- $r_s$ -structures<sup>[10]</sup> of the A and B rotamers of resorcinol in their  $S_0$  and  $S_1$  electronic states (see Figure 1). A total of 24  $S_0 \leftarrow S_1$  electronic origins of deuterated species of resorcinol A and B were measured using rotationally resolved LIF. We fit the obtained spectra with a genetic algorithms (GA) automated assignment<sup>[11,12]</sup> to an asymmetric rotor Hamiltonian. The GA prove to be very useful in analysis of the multitude of spectra acquired in this experiment. All spectra can be described within experimental accuracy as  $a$ -type spectra. As in the case of phenol,<sup>[8]</sup> the  $S_1$  lifetimes of the deuterated molecules depend mainly on the position of deuteration. We also show extreme additivity of the zero-point energies after successive deuterations in resorcinol rotamers. Finally, we use this fact to correct the assignment of the low-resolution spectra of deuterated resorcinol A<sup>[3]</sup> and to predict such a spectrum for resorcinol B.

## Experimental Section

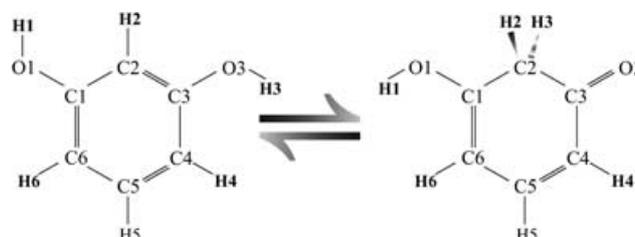
**Apparatus:** The experimental setup for the rotationally resolved LIF is described elsewhere.<sup>[13]</sup> In short, the vacuum system consists of three differentially pumped vacuum chambers that are linearly connected by two skimmers (1 mm and 2 mm). The skimmers collimate the molecular beam and hence reduce the Doppler contribution to the measured linewidth to 25 MHz of full width at half maximum (FWHM).

The laser part consists of single-frequency ring dye laser (Coherent 899-21), pumped with 7 W of the 514 nm line of an argon ion laser. Rhodamine 110 was used in the dye laser as a lasing medium. The fundamental light from the dye laser was coupled into an external delta cavity (Spectra Physics) for second harmonic generation (SHG). The UV radiation at  $\approx 278$  nm was generated in this cavity by an angle-tuned, Brewster-cut beta-barium-borate (BBO) crystal. The cavity length was locked to the dye laser frequency by a frequency modulation technique.<sup>[14,15]</sup> Typically  $\approx 20$  mW of UV radiation was available for the experiment.

The UV laser crosses the molecular beam 360 mm downstream from the nozzle under right angles. The molecular fluorescence was collected perpendicular to the plane defined by the laser and molecular beams by an imaging optics. The total fluorescence was detected by a photomultiplier tube, whose output was digitized by a photon-counter and sent to a PC for data acquisition and processing. The relative frequency was determined using a quasi-confocal Fabry–Perot interferometer with a free spectral range of 149.9434(56) MHz. For the absolute frequency calibration, an iodine spectrum was recorded and compared with tabulated data.<sup>[16]</sup>

Commercially available undeuterated resorcinol was used without further purification. To substitute different hydrogen atoms from resorcinol with deuterium atoms, it was mixed with a surplus of  $D_2O$  in the source container. Firstly, the hydroxy groups are deuter-

ated. Subsequently, all hydrogen atoms except H5 can be exchanged by deuterium atoms, owing to a keto–enol tautomerism (see Figure 2). To increase the vapor pressure of resorcinol, the source was heated to 180 °C. Subsequently, the molecular beam is formed by expanding a mixture from the source, seeded in 600 mbar of argon, through a 100  $\mu\text{m}$  hole into the vacuum system.



**Figure 2.** Keto–enol tautomerism in the resorcinol A rotamer. Owing to this mechanism, the hydrogen atoms shown in bold are easily deuterated.

**Spectra of Deuterated Species:** First, we tried to obtain the rotationally resolved LIF spectra of the  $S_1 \leftarrow S_0$  origins of the undeuterated resorcinol A and B. Although we searched for the spectra within  $\pm 10$   $\text{cm}^{-1}$  from the origins given by ref. [2], we failed to detect any signal. This must be due to a very short lifetime of the  $S_1$  electronic state of resorcinol, which is apparently much shorter than those of phenol<sup>[8]</sup> and hydroquinone.<sup>[9]</sup>

We therefore based our experiments on the deuterated species using the assignment of the mass-resolved R2PI spectra of deuterated resorcinol A reported in ref. [3]. Since we expected short lifetimes (that is, possibly weak or undetectable spectra) for all hydroxy undeuterated resorcinol isotopomers, we focused on the bands originating from isotopomers with at least one deuterated hydroxy group. The results will be presented in the following section.

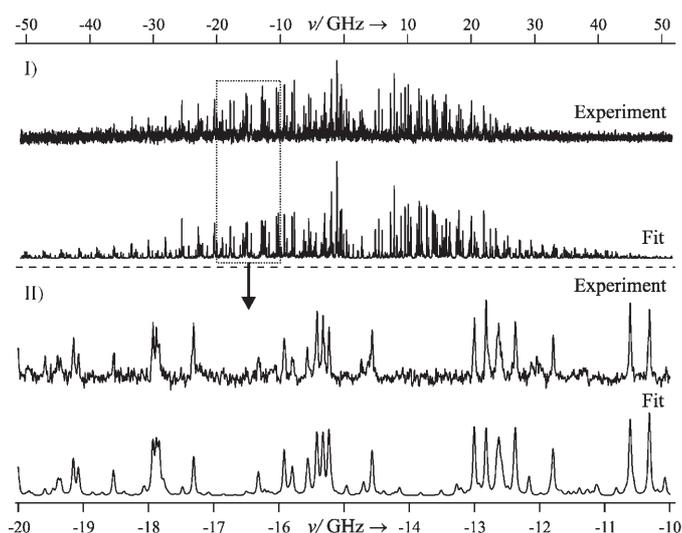
The numbering of the atoms used further in the text is presented in Figure 1. For designation of the different deuterated species, we put the number of hydrogen atoms replaced by deuterium atoms in brackets, and, if necessary, separated by commas. For example, (1,3) means the resorcinol isotopomer with deuterium atoms in positions H1 and H3.

## 2. Results and Discussion

### 2.1. Analysis of the Spectra

All spectra were analyzed with a rigid, asymmetric rotor Hamiltonian<sup>[17]</sup> with a two-temperature model.<sup>[18]</sup> To fit the spectra, we used an automatic assignment GA program, which was developed in our group.<sup>[11,12]</sup> This GA-based approach confirmed its usefulness in the assignment of the many (24), frequently overlapping, spectra present in our study.

In general, the spectra of resorcinol A were found to be weaker than those of B. At first sight this is surprising, because the low-resolution LIF spectra from ref. [5] show a slightly weaker signal for rotamer B than for A. Ab initio calculations<sup>[2,19]</sup> also confirmed a lower stability of rotamer B. However, it has been found from our analysis that, in general, the isotopomers of resorcinol A have shorter lifetimes and thus might indeed have weaker rotationally resolved spectra, due to lifetime broadening. This will be discussed in Section 2.6.



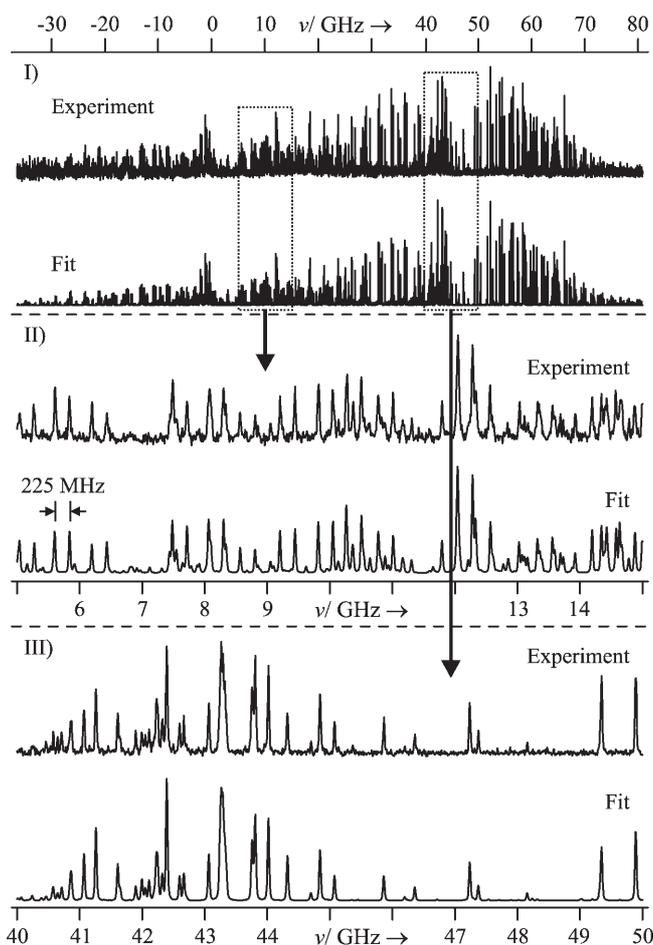
**Figure 3.** Experimental and fitted spectra of (1,3,4,6) and (1,4,6) deuterated resorcinol A. I) Full spectra. II) 10 GHz zoom-in. The zero in the frequency scale corresponds to the origin of the (1,3,4,6) transition,  $\nu_0$  of the (1,4,6) species was shifted from the other band by +3661(7) MHz.

Within experimental accuracy, all the bands analyzed in this work were found to be pure  $\alpha$ -type transitions. The  $-\text{OH}$  torsional splittings remained unresolved for all hydroxy undeuterated resorcinol isotopomers. A sample of the spectra and the GA fit of the  $+65.60\text{ cm}^{-1}$  band of resorcinol A is presented in Figure 3. The spectrum of three overlapping bands at around  $+75\text{ cm}^{-1}$  originating from the three different isotopomers of rotamer B is compared with the GA fit in Figure 4. GA fits of the other spectra of resorcinol A and B were of similar quality. In the two-temperature model<sup>[18]</sup> implemented in the GA fits, typical values for the rotational temperatures were  $T_1 \approx 1.8\text{ K}$ ,  $T_2 \approx 3\text{--}8\text{ K}$  and the weighting factor  $w$  was about 0.04–0.1.

## 2.2. Nuclear Spin Statistics

Rotamer A of resorcinol belongs to the molecular symmetry (MS) group isomorphic with point group  $C_s$ . Consequently, we do not expect any influence of the nuclear spin statistics on the rotational spectra of any of its isotopomers. This is in agreement with the experimental finding.

On the other hand, rotamer B can be characterized by the MS group  $C_{2v}$ . Therefore, the ratio of the line intensities for  $K_a + K_c = \text{odd}$  to the  $K_a + K_c = \text{even}$  should be 6:10. This is characteristic for the molecules with  $C_{2v}$  symmetry with two pairs of equivalent hydrogen atoms, where the  $C_2$  axis coincides with the  $b$  inertial axis. However, for most isotopomers of this resorcinol rotamer, the  $C_{2v}$  symmetry is lost, and hence the spin statistics no longer influence the rotational spectra. The only isotopomers that will still possess  $C_{2v}$  symmetry are the ones that are symmetrically substituted with respect to the inertial  $b$  axis, namely (1,3), (4,6), (1,2,3), (2,4,6), (1,3,4,6), and (1,2,3,4,6). (Position 5 could not be deuterated in our experiment). The first four species contain a pair of equivalent hydrogen atoms, as well as a pair of equivalent deuterium atoms. In



**Figure 4.** Experimental and fitted spectra of (1,2,4), (1,2,6) and (1,2,3,4) deuterated resorcinol B. I) Full spectra. The zero in the frequency scale corresponds to the origin of the (1,2,4) isotopomer. II) 10 GHz zoom-in of the part belonging to the (1,2,4) and (1,2,6) isotopomers. A small splitting of 225 MHz between these two bands is also shown. III) 10 GHz zoom-in of the origin vicinity of the (1,2,3,4) species.

this case, the ratio of the line intensities for  $K_a + K_c = \text{odd}$  to  $K_a + K_c = \text{even}$  was 7:5. For the (1,3,4,6) and (1,2,3,4,6) isotopomers, two pairs of equivalent deuterium atoms gave an intensity ratio of  $K_a + K_c = \text{odd}$  to  $K_a + K_c = \text{even}$  of 4:5.

## 2.3. Molecular Constants

The rotational constants of resorcinol A and B, together with the other parameters obtained from the GA fits of the 20 experimental spectra are given in Tables 1 and 2, respectively. Parameters presented in these tables were typically averaged over five different GA fits of the same spectrum started from different initial parameter values. Owing to the weak spectra of bands (2,3,4), (2,4), (2,3,6), and (2,6) of resorcinol A, ten runs of GA fits were averaged in these cases. Simulated spectra with averaged parameters as well as the ones from the single fits always gave a perfect or very good match with the observed spectra, both in intensity and positions of the transitions.

Averaging also gives an estimate of the errors of the fitted parameters using standard deviations of the averages. Subse-

**Table 1.** Molecular constants of ten differently deuterated resorcinol A isotopomers.  $\Delta\nu_0 = \nu_0 - 35\,944\text{ cm}^{-1}$ . For overlapping spectra that we could paste together, we also determined the relative shift between the spectra. Here,  $\Delta\nu_0^{\text{prev}}$  represents the shift from the previous column (isotopomer) origin. For the numbering of the substitution positions, see Figure 1.

Substitution	(1,3,6)	(1,6)	(1,3,4)	(1,4)	(1,3,4,6)
A'' [MHz]	3591.1(49)	3605(12)	3594.2(66)	3608.8(90)	3520.9(61)
B'' [MHz]	1711.08(40)	1770.8(11)	1709.56(51)	1765.96(61)	1683.00(50)
C'' [MHz]	1159.01(27)	1185.47(70)	1158.75(42)	1185.06(49)	1139.14(33)
$\nu_0$ [cm <sup>-1</sup> ]	35978.745(10)	35978.836(10)	35980.395(10)	35980.513(10)	36009.596(10)
$\Delta\nu_0$ [cm <sup>-1</sup> ]	34.745(10)	34.836(10)	36.395(10)	36.513(10)	65.596(10)
$\Delta\nu_0^{\text{prev}}$ [MHz]		2741.5(64)	46717.6(42)	3550.2(51)	
A' [MHz]	3463.9(49)	3478(12)	3467.8(66)	3481.4(90)	3400.3(61)
B' [MHz]	1702.62(40)	1761.2(11)	1701.00(51)	1756.50(61)	1674.28(50)
C' [MHz]	1142.25(27)	1167.83(70)	1142.03(42)	1167.52(49)	1122.94(33)
$\tau$ [ns]	6.8(15)	3.6(4)	5.5(9)	4.0(6)	7.1(16)
Substitution	(1,4,6)	(2,3,6)	(2,6)	(2,3,4)	(2,4)
A'' [MHz]	3524.5(80)	3573.8(84)	3574(11)	3569(10)	3566(16)
B'' [MHz]	1739.41(76)	1739.61(73)	1800.4(10)	1741.93(85)	1800.2(14)
C'' [MHz]	1164.98(45)	1170.19(50)	1197.63(68)	1170.29(57)	1197.51(94)
$\nu_0$ [cm <sup>-1</sup> ]	36009.718(10)	36024.826(10)	36024.910(10)	36026.557(10)	36026.670(10)
$\Delta\nu_0$ [cm <sup>-1</sup> ]	65.718(10)	80.826(10)	80.910(10)	82.557(10)	82.670(10)
$\Delta\nu_0^{\text{prev}}$ [MHz]	3660.7(53)		2531.0(81)	49374.7(74)	3379.9(93)
A' [MHz]	3402.8(80)	3441.4(84)	3441(11)	3438(10)	3433(16)
B' [MHz]	1730.03(76)	1730.75(73)	1791.0(10)	1733.06(85)	1790.7(14)
C' [MHz]	1147.90(45)	1152.41(50)	1178.75(68)	1152.52(57)	1178.76(94)
$\tau$ [ns]	2.3(3)	3.0(3)	2.7(2)	3.8(4)	2.5(3)

**Table 2.** Molecular constants of ten differently deuterated resorcinol B isotopomers.  $\Delta\nu_0 = \nu_0 - 36\,196\text{ cm}^{-1}$ . For spectra where the pasting of overlapping scans was possible,  $\Delta\nu_0^{\text{prev}}$  represents the shift from the previous column (isotopomer) origin. For the numbering of the substitution positions, see Figure 1.

Substitution	(1,4)	(1,6)	(1,3,4)	(1,2)	(1,2,3)
A'' [MHz]	3670(12)	3678(11)	3672.3(57)	3632.4(75)	3630.9(58)
B'' [MHz]	1742.50(83)	1744.94(84)	1687.59(42)	1773.01(63)	1714.87(47)
C'' [MHz]	1183.30(61)	1183.77(55)	1156.53(30)	1192.14(43)	1164.84(30)
$\nu_0$ [cm <sup>-1</sup> ]	36227.801(10)	36227.809(10)	36229.237(10)	36237.829(10)	36239.322(10)
$\Delta\nu_0$ [cm <sup>-1</sup> ]	31.801(10)	31.809(10)	33.237(10)	41.829(10)	43.322(10)
$\Delta\nu_0^{\text{prev}}$ [MHz]		242.8(65)	42832.9(47)		44752.8(44)
A' [MHz]	3543(12)	3551(11)	3546.7(57)	3501.7(75)	3500.9(58)
B' [MHz]	1726.93(83)	1728.89(84)	1672.62(42)	1756.86(63)	1699.73(47)
C' [MHz]	1163.30(61)	1163.76(55)	1137.42(30)	1171.23(43)	1144.87(30)
$\tau$ [ns]	4.7(9)	4.6(10)	13.2(22)	5.1(8)	11.2(16)
Substitution	(1,4,6)	(1,3,4,6)	(1,2,4)	(1,2,6)	(1,2,3,4)
A'' [MHz]	3605.9(59)	3597.1(46)	3571.8(57)	3570.4(54)	3559.2(44)
B'' [MHz]	1716.49(47)	1661.59(34)	1743.01(47)	1745.37(46)	1687.43(32)
C'' [MHz]	1163.20(32)	1137.32(25)	1171.14 (32)	1171.34(32)	1145.25(24)
$\nu_0$ [cm <sup>-1</sup> ]	36260.428(10)	36261.845(10)	36270.382(10)	36270.389(10)	36271.864(10)
$\Delta\nu_0$ [cm <sup>-1</sup> ]	64.428(10)	65.845(10)	74.382(10)	74.389(10)	75.864(10)
$\Delta\nu_0^{\text{prev}}$ [MHz]		42476.4(38)		224.6(42)	44209.3(36)
A' [MHz]	3485.3(59)	3477.3(46)	3446.6(57)	3445.8(54)	3435.1(44)
B' [MHz]	1700.54(47)	1646.60(34)	1727.00(47)	1728.90(46)	1672.30(32)
C' [MHz]	1143.72(32)	1118.73(25)	1150.75 (32)	1151.09(32)	1125.82(24)
$\tau$ [ns]	5.6(10)	9.4(17)	6.5(13)	6.6(14)	15.1(29)

quently, we derived a final uncertainty (containing correlations between the parameters) utilizing a least-squares program,<sup>[20]</sup> with the line positions calculated from the averaged GA results. In these calculations, we manually included only lines with a large enough intensity, that is, the lines which would be used in the "classical" assignment. The upper limit for the error of the absolute origin  $\nu_0$  and  $\Delta\nu_0$  was estimated from the absolute frequency calibration to the iodine lines.<sup>[16]</sup> It amounts  $0.010\text{ cm}^{-1}$ .

All analyzed bands were attributed to isotopomers on the basis of the structure fit to the inertial parameters and their shifts from undeuterated species. Details are discussed in the following sections. We also note here that the spectra of the (1) and (1,3) isotopomers of resorcinol A, and the (4) and (4,6) isotopomers of resorcinol B were too weak for reliable GA fits. However, after successful structure fits, these spectra could be reproduced with rotational constants derived from the calculated structural parameters.

## 2.4. Structure Fit

### 2.4.1. Models

From the experiment, we obtained the rotational constants  $B_g^0$ , which are related to the vibrationally averaged moments of inertia of the molecule  $I_g^0$  via Equation (1):

$$I_g^0 = h/4\pi B_g^0 \quad (1)$$

where  $g$  designates the principal axes of inertia of the molecule  $a, b, c$ . However, if possible, one prefers to determine the equilibrium structure of the molecule, which is directly related to the minimum of the potential energy of the electronic state. These latter structures are marked with the superscript  $e$ .

There are a few methods to correct the experimental moments of inertia for vibrational effects. As a crude approximation, one can neglect these effects and force the relation  $I_g^0 = I_g^e(r_0)$ . The result is called the  $r_0$ -structure. However, these structures give typically overestimated bond lengths,<sup>[21]</sup> and depend strongly on the choice of isotopomers.<sup>[22]</sup> In the  $r_s$  structures<sup>[22,23]</sup> Equation (2) is used to take into account average vibrational effects along every principal axes:

$$I_g^0 = I_g^e(r_s) + \frac{1}{2} \varepsilon_{0g} \quad (2)$$

The  $\varepsilon_{0g}$  contain the average vibrational contributions with respect to the inertial axes  $g$ . Unfortunately, the substitution method generally does not allow the use of multisubstituted isotopomers in the fit of the structure (with the exception of some highly symmetric multisubstitutions), but it gives better estimates of the hypothetical equilibrium structure and is largely independent of the studied isotopic substitutions.

The third way to include the vibrational corrections is the *pseudo Kraitchman* approach.<sup>[10]</sup> Here, Equation (2) is utilized in a global, nonlinear fit of all the isotopomers (also multisubstituted) in order to obtain the pseudo  $r_s$ -structure. We used this model in our structure fits, because it allows the inclusion of vibrational effects on the structure with only three additional parameters (the three  $\varepsilon_{0g}$ ), while simultaneously multisubstitutions can be considered. The fitting program utilized has been described in detail in ref. [8]. More models for the determination of structures from rotational constants have been discussed,<sup>[24–27]</sup> but they are not used here, since they require additional parameters to be fit.

### 2.4.2. Structural Constraints

Since we studied only a limited number of isotopically substituted resorcinols, we had to impose constraints on the geometry of the molecules in the structure fit. Both rotamers of resorcinol in the ground and excited states were treated as planar molecules. This is certainly a good assumption for the ground states, for which MW on resorcinol<sup>[7]</sup> predict very small inertial defects  $\Delta I(A) = -0.083$  and  $\Delta I(B) = -0.081$ . We do not report the inertial defects for the electronically excited states of the resorcinol rotamers, because of the large uncertainty in the ro-

tational constant  $A$ . However, in phenol<sup>[8]</sup> as well as in hydroquinone,<sup>[9]</sup> the  $S_1$  state was found to be planar and there should be no reason for resorcinol to behave differently.

In the case of resorcinol B, the following restrictions are justified by the symmetry: distance C1–C2 is set equal to C2–C3; C1–C6 equals C3–C4, and similarly C4–C5 equals C5–C6. Both –COH groups are equivalent, and the inner angles of the benzene ring are set equal in the following pairs: C6–C1–C2 with C2–C3–C4 and C1–C6–C5 with C3–C4–C5. Additionally, we fix the outer C–C–H angles such that the C–H bonds bisect the inner C–C–C angles. Finally, all C–H bonds were treated as identical, and the sum of all the inner angles in the benzene ring was fixed to 720°.

In principle, resorcinol A does not have the  $C_{2v}$  symmetry of resorcinol B. However, in our structure fits we found that the aforementioned constraints are also valid for resorcinol A. For example, if the distance C1–C2 is uncoupled from C2–C3, identical values within their uncertainties were found. The same holds for the other C–C pairs mentioned in the previous paragraph, as well as for the inner C–C–C angles. For resorcinol A we also fixed the two, in principle different, –COH groups to the same geometry. This is justified by the fact that the hydroxy groups are in *meta* positions and therefore their electronic and steric interactions are small. The other constraints imposed on the resorcinol B geometry were also applied in the final fit of resorcinol A structure.

### 2.4.3. Fit

We started the structure fits with resorcinol A, since we expected some help with the assignment of different isotopomers from the low-resolution R2PI spectra.<sup>[3]</sup> As starting parameters, we used the bond lengths and –COH group geometry from phenol,<sup>[8]</sup> and additionally fixed the inner benzene ring angles and outer C–C–H angles to 120°. In this way, the initial guess of the rotational constants of all possible deuterated isotopomers of resorcinol A was made. These preliminary rotational constants agreed reasonably well with the MW constants<sup>[7]</sup> obtained for the undeuterated resorcinol. Furthermore, from the guess, we could unambiguously assign most of the isotopomers and include them in the fit. The remaining bands were assigned from the improved structural parameters. Only in the case of pairs (2,3,4) with (2,3,6), and (2,4) with (2,6) were the differences in the rotational constants too small for definitive assignment. These bands were tentatively distinguished using their shifts from undeuterated species. For details see Section 2.5.

Fitting of some of the parameters from our model made the fit numerically unstable. This was most likely caused by the large uncertainties in the rotational constants, in particular  $A$ , but might also be caused by the low number of measured isotopically substituted species. Therefore, in the next step, we tried to fix different combinations of geometrical parameters to the values found in phenol.<sup>[8]</sup> However, for consistency reasons, after the successful resorcinol B structure fit, we repeated the structure fit of rotamer A with parameters fixed to values

**Table 3.** Pseudo- $r_s$  structural parameters of resorcinol A and B in the  $S_0$  and  $S_1$  electronic states. All bond lengths are given in Å, and angles in degrees.

Parameter	A		B	
	$S_0$	$S_1$	$S_0$	$S_1$
C2–C3	1.388(28)	1.450(18)	1.3944(27)	1.438(18)
C3–C4	1.388(32)	1.418(21)	1.3963(44)	1.425(28)
C4–C5	1.408(29)	1.469(16)	1.4071(77)	1.449(23)
C–H	1.091(27)	1.074 <sup>[a]</sup>	1.0856(57)	1.074(18)
C–O	1.371(64)	1.307(37)	1.3569(56)	1.3286(92)
O–H	0.959(48)	0.975(34)	0.9547(85)	0.947(57)
C1–C2–C3	119.68 <sup>[a]</sup>	116.1 <sup>[a]</sup>	119.68(52)	116.1(14)
C2–C3–C4	120.68 <sup>[a]</sup>	122.61 <sup>[a]</sup>	120.68(29)	122.61(69)
C3–C4–C5	119.41 <sup>[a]</sup>	120.46 <sup>[a]</sup>	119.41(36)	120.46(73)
C4–C5–C6	120.14 <sup>[a]</sup>	117.8 <sup>[a]</sup>	120.14(54)	117.8(13)
C3–C2–H2	120.16 <sup>[a]</sup>	121.97 <sup>[a]</sup>	120.16(26)	121.97(71)
C5–C4–H4	120.29 <sup>[a]</sup>	119.77 <sup>[a]</sup>	120.29(18)	119.77(37)
C6–C5–H5	119.93 <sup>[a]</sup>	121.11 <sup>[a]</sup>	119.93(27)	121.11(64)
C4–C3–O3	119.6(20)	118.7(18)	122.18(54)	121.0(16)
C–O–H	108.55 <sup>[a]</sup>	110.0 <sup>[a]</sup>	108.55(21)	110.0(30)
$\epsilon_A$	0.0548(21)	0.180(83)	0.05370(94)	0.220(61)
$\epsilon_B$	0.0552(19)	0.180(83)	0.05396(94)	0.217(61)
$\epsilon_C$	–0.0557(10)	–0.180(83)	–0.05393(94)	–0.217(61)

[a] Fixed in the final fit to the value found for resorcinol B.

found for resorcinol B. The final structural parameters for resorcinol A are presented in Table 3.

In contrast to rotamer A, the fit of resorcinol B geometry was straightforward. With the parameters from the species A fit, a very good estimate of the rotational constants of all the rotamer B isotopomers was obtained. All the resorcinol B bands shown in Table 2 were unambiguously identified. The results of structure fits for both electronic states are presented in Table 3.

The structure fits for both resorcinol rotamers in the  $S_0$  and  $S_1$  electronic states reproduce the rotational constants of all isotopomers very well. The uncertainties of parameters from Table 3 include parameter correlations. It is important to notice that the fitting program is a local optimizer. To exclude convergence to local solutions, the fits were repeated with different starting parameters.

#### 2.4.4. Ground and Excited Electronic-State Structures

From Table 3, it is evident that, within the given uncertainties, both resorcinol rotamers are structurally very similar. This also holds for the excited electronic states. The aromatic ring of resorcinol expands upon electronic excitation rather equally in all directions (benzenoidal), though there seems to be a trend for elongating the whole molecule more along the  $b$  inertial axis than  $a$  axis.

The most significant differences between resorcinol and phenol<sup>[8]</sup> are observed for the C–C bond lengths of the benzene frame. For resorcinol, the longest bond seems to be the C–C5 bond, which is far from the hydroxy groups; and the shortest, the bond between the two hydroxy groups C2–C3. In contrast, in phenol, the largest one is the  $C_{\text{OH}}-C_{\text{ortho}}$  distance (1.4187(139) Å), closest to the –OH group and the smallest distance (1.3912(34) Å) is the “middle” one ( $C_{\text{ortho}}-C_{\text{meta}}$ ). This can

be explained by some collective electronic influence of the hydroxy groups on the benzene skeleton in the *ortho* and *para* positions.

Resorcinol is a slightly stronger acid than phenol<sup>[28]</sup> ( $pK_a^{\text{(resorcinol)}} = 9.45$  versus  $pK_a^{\text{(phenol)}} = 9.96$ ) in the  $S_0$  electronic state. This seems to be confirmed by the –COH group structures for both molecules. Although the C–O bonds are equal, the O–H bond of the resorcinol tends to be longer than the corresponding one in phenol.<sup>[8]</sup> Upon electronic excitation, we clearly see the shortening of the C–O bonds and a possible elongation of the O–H bonds. This suggests a similar increase in acidity upon electronic excitation in resorcinol, compared to phenol.

Finally, we can compare the  $\epsilon_g$  parameters, which represent the averaged effect of vibrations along the  $g$  inertial axis. From Table 3, it is clear that on average both rotamers experience similar vibrational motions in the ground electronic state. This is not surprising in light of the dispersed fluorescence experiments of Imhof et al.<sup>[5]</sup> on resorcinol A and B, which reported very similar vibrational frequencies for both rotamers. Upon electronic excitation, a significant increase in the vibrational activity ( $\epsilon_g$ ) is noticed. This is caused by a shallowing of the potential energy surface for most of the normal modes in the  $S_1$  state, and consequently a decrease in the corresponding vibrational frequencies. Again, this is in agreement with the reported vibrational frequencies for both resorcinols in the  $S_1$  state.<sup>[5]</sup>

## 2.5. The Zero-Point Energies

### 2.5.1. Additivity and Assignment of Electronic Shifts

In the Born–Oppenheimer approximation, all isotopomers of the same resorcinol rotamer share the same potential energy surface. Within this approximation, the differences between shifts of the band origins from the undeuterated origin  $\Delta\nu_0$  can be identified with the differences in the zero-point energies (ZPE) between ground and excited states  $\Delta ZPE = ZPE' - ZPE''$  for different isotopomers. Moreover, one can easily calculate the  $\Delta ZPE$ s corresponding to subsequent substitutions of all the atoms in the molecule. In our case, only hydrogen atoms were substituted. The results for resorcinol B and A are presented in Tables 4 and 5.

We start with a discussion of resorcinol B, in which the assignment of isotopomers was more straightforward. It is clear from Table 4 that for resorcinol B the  $\Delta ZPE$ s after successive deuterations are extremely additive (to within below  $0.1 \text{ cm}^{-1}$ ). This additivity of  $\Delta ZPE$  is not completely surprising, since it

**Table 4.** Differences in the  $\Delta ZPE$  for the observed isotopomers of resorcinol B ( $\Delta ZPE \equiv \Delta \nu_0$ ). Each column named with “+ (...)” contains  $\Delta ZPE$  after additional substitution of the isotopomer given in the first column. All numbers are in  $\text{cm}^{-1}$ .

	$\Delta \nu_0$	+ (2)	+ (3)	+ (4)	+ (6)	+ (1,3)	+ (2,3)	+ (3,4)	+ (3,6)
(4) <sup>[a]</sup>	30.39				32.64	2.84			
(1,4)	31.80	42.58	1.44		32.63		44.06		
(1,6)	31.81	42.58		32.62				34.04	34.04
(1,3,4)	33.24	42.63			32.61				
(1,2)	41.83		1.49	32.55	32.56			34.03	
(1,2,3)	43.32			32.54					
(4,6) <sup>[a]</sup>	63.03					2.81			
(1,4,6)	64.43		1.42						
(1,3,4,6)	65.84								
(1,2,4)	74.38		1.48						
(1,2,6)	74.39								
(1,2,3,4)	75.86								

[a] Origins found for isotopomers with spectra too weak for reliable GA fits. Later fitted with rotational constants predicted from the structure fits.

**Table 5.** Differences in the  $\Delta ZPE$  for the observed isotopomers of resorcinol A ( $\Delta ZPE \equiv \Delta \nu_0$ ). Each column named with “+ (...)” contains  $\Delta ZPE$  after additional substitution of the isotopomer from the most left column in the position from “+ (...)”. All numbers are in  $\text{cm}^{-1}$ .

	$\Delta \nu_0$	+ (3)	+ (4)	+ (6)	+ (3,4)	+ (3,6)	+ (4,6)
(1,3) <sup>[a]</sup>	5.54		30.86	29.21			60.06
(1) <sup>[a]</sup>	5.63	-0.09	30.89	29.21	30.77	29.12	60.09
(1,3,6)	34.74		30.85				
(1,6)	34.84	-0.09	30.88		30.76		
(1,3,4)	36.39			29.20			
(1,4)	36.51	-0.12		29.21		29.08	
(1,3,4,6)	65.60						
(1,4,6)	65.72	-0.12					
(2) <sup>[b]</sup>	51.76						
(2,3,6)	80.83						
(2,6)	80.91	-0.08					
(2,3,4)	82.56						
(2,4)	82.67	-0.11					

[a] Origins found for isotopomers with spectra too weak for reliable GA fits. Later fitted with rotational constants predicted from the structure fits. [b] Origin predicted from the average of four ZPE differences.

has already been observed, for example, for phenol.<sup>[8]</sup> It clearly points to a very local character of CH and OH stretching and COH bending vibrations in resorcinol B.

For resorcinol A, we consider first the upper eight rows of Table 5. These data represent the  $\Delta ZPE$ s of isotopomers unambiguously assigned by the structure fits. With high confidence, it can be assumed that the substitutions in positions (1), (2), and (3) will also be additive. This assumption is based on the observations that both in resorcinol B and in phenol the  $\Delta ZPE$ s add up very well. Furthermore, the substitutions at positions (4) and (6) (next to any of the two hydroxy groups) in resorcinol A seem to be perfectly additive as well.

From these facts, it can be concluded that of the four possible assignments of the isotopomers (2,3,6), (2,3,4), (2,6), and (2,4), only the one presented in Table 5 gives additive shifts for substitutions in positions (2) and (3). For the other three possibilities, the  $\Delta ZPE$  after deuteration of either H2 or H3 differ

within each column by  $\approx 3.47 \text{ cm}^{-1}$ . We did not observe such large deviations, even in phenol. Moreover, in phenol<sup>[8]</sup> the  $\Delta ZPE$  clearly gets smaller in deuterated isotopomers from -CH groups with increasing distance from the hydroxy group. This agrees perfectly with a smaller origin shift for the + (6) column (*trans* position with respect to -OH group) compared to the + (4) column (*cis* position with respect to -OH group).

### 2.5.2 Prediction of the $S_1 \leftarrow S_0$ Spectrum for Deuterated Resorcinol Rotamers

On the basis of the additivity of the origin shifts with subsequent deuterations, and the average shifts from Tables 5 and 4, we can predict the full  $S_1 \leftarrow S_0$  spectrum of deuterated resorcinol A and B. The results are presented in Table 6, where they are also compared with the results of the low-resolution ex-

**Table 6.** Comparison of predicted electronic shifts from the undeuterated origin for all resorcinol A isotopomers, deuterated in positions 1–6 (excluding 5), with experimentally observed values  $\Delta \nu_0^{\text{measured}}$ . All numbers are given in  $\text{cm}^{-1}$ .

	Substitution	$\Delta \nu_0^{\text{pred.}}$	$\Delta \nu_0^{\text{measured}}$
d1	(3)	-0.10	
	(1)	5.64	5.63
	(6)	29.21	
	(4)	30.87	
d2	(2)	51.76	
	(1,3)	5.53	5.54
	(3,6)	29.10	
	(3,4)	30.77	
	(1,6)	34.84	34.84
	(1,4)	36.50	36.51
	(2,3)	51.65	
	(1,2)	57.39	
	(4,6)	60.07	
	(2,6)	80.96	80.91
d3	(2,4)	82.62	82.67
	(1,3,6)	34.74	34.74
	(1,3,4)	36.40	36.39
	(1,2,3)	57.29	
	(3,4,6)	59.97	
	(1,4,6)	65.71	
	(2,3,6)	80.86	80.83
	(2,3,4)	82.52	82.56
	(1,2,6)	86.60	
	(1,2,4)	88.26	
d4	(2,4,6)	111.83	
	(1,3,4,6)	65.61	65.60
	(1,2,3,6)	86.49	
	(1,2,3,4)	88.16	
d5	(2,3,4,6)	111.73	
	(1,2,4,6)	117.47	
	(1,2,3,4,6)	117.36	

periment from ref. [3]. Clearly for rotamer A, the derived origin shifts,  $\Delta\nu_0^{\text{pred.}}$ , are in perfect agreement with the observed ones,  $\Delta\nu_0^{\text{measured}}$ . Furthermore, after taking into account the FWHM of  $\approx 3 \text{ cm}^{-1}$  of the low-resolution study, estimated on the basis of Figure 5 from ref. [3], we conclude a very good agreement between frequencies. However, in view of our study, some of the bands from ref. [3] had to be reassigned.

For resorcinol B, the electronic origin of the undeuterated species that was not observed in the present investigation can be determined using the nearly perfect additivity of the ZPE shifts. The values given in Table 4 were used to determine  $\nu_0^{\text{undeuterated}}$ . The resulting average value of  $36193.78(4) \text{ cm}^{-1}$  gives a perfect agreement (to within below  $0.1 \text{ cm}^{-1}$ ) of the predicted and measured origin shifts of all isotopomers. This origin of the undeuterated resorcinol B is certainly within the experimental error of the low-resolution experiments, which previously reported the origin at  $36196 \text{ cm}^{-1}$ .<sup>[3]</sup>

## 2.6. S<sub>1</sub> Electronic-State Lifetimes

For both resorcinol rotamers, the trend of increasing the excited state lifetimes with subsequent deuterations of the hydroxy groups is similar (compare Tables 1 and 2). For the rotamer A, the lifetime of isotopomers with 1 and 3 positions substituted ranged from 5.5 to 7.1 ns, for either 1 or 3 substituted from 3.0 to 4.0 and for deuterated isotopomers with neither 1 nor 3 substitution from 2.5 to 2.7 ns. One exception to this rule is the (1,4,6) isotopomer, with the short lifetime of 2.3 ns, which is shorter than that of the hydroxy-undeuterated species.

For rotamer B, no hydroxy-undeuterated species could be observed. An increase in the S<sub>1</sub> lifetime for the resorcinol B isotopomers was found with respect to the respective isotopomers of resorcinol A. Substitution of both hydroxy hydrogen atoms led to lifetimes between 9.4 ns and 15.1 ns, while single hydroxy deuteration resulted in lifetimes between 4.6 and 6.6 ns.

## 3. Summary

All 24 studied spectra were interpreted utilizing the GA automated assignment<sup>[11,12]</sup> with an asymmetric rotor Hamiltonian. The GA again proved its usefulness in the analysis of the many spectra acquired in this experiment. All spectra could be described within experimental accuracy as *a*-type spectra and the –OH torsional splittings remained unresolved for all resorcinol isotopomers.

We determined the pseudo *r<sub>s</sub>*-structures of the resorcinol A and B rotamers in the S<sub>0</sub> and S<sub>1</sub> electronic states. Within the obtained uncertainties and assumed model, both rotamers could be described with very similar geometrical parameters for both electronic states. The aromatic ring of resorcinol expands symmetrically, although there exists a trend for a slightly larger elongation of the whole molecule along the *b* inertial axis.

The extreme additivity of the zero-point energies after successive deuterations of the resorcinol rotamers was proven,

and subsequently used in the full assignment of the previously reported low-resolution spectrum of deuterated resorcinol A.<sup>[3]</sup> An analogous spectrum is also predicted for the resorcinol B rotamer. For that rotamer, the additivity led to a correction of the undeuterated S<sub>1</sub>←S<sub>0</sub> origin to  $36193.78(4) \text{ cm}^{-1}$ . The additivity of the ZPE shifts is a clear indication of the local oscillator behavior of the CH and OH vibrations in these molecules.

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