Vibrational OH-Stretching Overtone Spectroscopy of Jet-Cooled Resorcinol and Hydroquinone Rotamers

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We have measured the OH-stretching fundamental and overtone spectra of resorcinol and hydroquinone in a supersonic jet using nonresonant ionization detected infrared/near-infrared spectroscopy. Anharmonic oscillator local mode calculations of the OH-stretching frequencies and intensities and Boltzmann populations of the stable rotamers have been calculated at the B3LYP/6-311++G(3df,2pd) level to help interpret the observed spectra. Resorcinol has three stable rotamers and in the recorded second and third OH-stretching overtone spectra there is evidence of two distinguishable rotamers. Hydroquinone has two stable rotamers; however, the OH-stretching oscillators of each rotamer are so similar in nature that even up to the fourth OH-stretching overtone the transitions coincide. These results place a limit on the ability of the jet-cooled overtone spectroscopy technique to distinguish between rotamers.

Introduction

Dihydroxybenzenes exhibit both structural and rotational isomerism, caused by the relative positions and conformations of the hydroxyl substituents. There are three structural isomers of dihydroxybenzene: catechol (*o*-dihydroxybenzene), resorcinol (*m*-dihydroxybenzene), and hydroquinone (*p*-dihydroxybenzene). Dihydroxybenzenes are good models for key biological molecules, such as dopamine, adrenaline, flavones, and flavonoles. In large biological systems, macromolecules are able to recognize and distinguish between individual rotamers. This is one reason that the conformations and populations of these rotamers have attracted significant attention.[1−14]

In terms of rotational isomerism, catechol is perhaps the simplest of the three dihydroxybenzenes. Catechol has two stable rotamers, however the two neighboring hydroxyl groups can form a weak intramolecular hydrogen bond and as a result, the cis rotamer is strongly favored.[1−3,15] The stable rotamers of resorcinol and hydroquinone are shown in Figure 1 with labels.

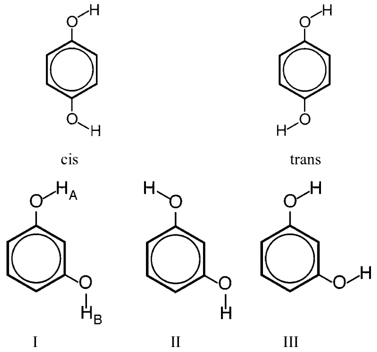

Figure 1. The three rotamers of resorcinol are shown in the lower panels and the two rotamers of hydroquinone in the upper panels.

The relative populations of the three rotamers in resorcinol have been studied by several groups but the reported results are not consistent.[1,9−14] Rotamers I, II, and III were all identified by millimeter wave spectroscopy at 115 °C.[10] On the other hand, only two rotamers were found in other spectroscopic studies.[9,11−13,14] Two electronic origins of the S_1 excited-state were assigned to rotamers I and II in the electronic spectrum of jet-cooled resorcinol investigated by resonance-enhanced multiphoton ionization (REMPI) and hole-burning spectroscopy.[11] Furthermore, the ionic ground state of rotamers I and II were found in mass analyzed threshold ionization (MATI) and infrared photoinduced Rydberg ionization (IR-PIRI) spectroscopy.[9,12] Recently all deuterated resorcinol isomers were investigated by high-resolution laser induced fluorescence (LIF) spectroscopy.[14] The rotational analysis of LIF supported the hypothesized existence of two rotational isomers, rotamer I and II, but no positive evidence was found for the existence of rotamer III. From the millimeter wave experiment the rotamer III was found to have significantly higher energy which could explain its lack of observation with the other techniques.[10]

In both *cis*- and *trans*-hydroquinone, there is little interaction between the two hydroxyl groups, and the spectroscopy of the two rotamers is expected to be similar. The S_1-S_0 electronic transition of the cis and trans rotamers are separately observed at 33 535 and 33 500 cm^{-1}, respectively.[4] The species were assigned from the analysis of the rotational structure in the high-resolution LIF spectrum. Similar populations of the two rotamers

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have been experimentally determined with the trans rotamer slightly lower in energy (10 cm^{-1}) in the electronic ground state. The structure of the cis rotamer was confirmed and refined by microwave spectroscopy; however, the trans rotamer could not be measured due to the lack of a permanent dipole.[7]

Recently, we proposed a new method of distinguishing rotamers based on a combination of nonresonant ionization detected infrared and near-infrared spectroscopy (NID-IR/NIR) and ab initio local mode calculations.[16] The study of vibrational overtone transitions is a suitable method to study subtle differences in molecular conformation, such as OH bond length, because a slight difference in the fundamental frequency of vibration of any given bond is exaggerated in higher overtones. We interpret the OH-stretching overtone spectra in terms of a local mode model.[17,18] We calculate the fundamental and overtone stretching frequencies and intensities with an anharmonic oscillator (AO) local mode model with dipole moment functions obtained from density functional theory calculations.[19,20] However, vibrational overtone spectra are often measured at room temperature using sensitive techniques such as photoacoustic and cavity ring-down spectroscopy but the broad bands observed at ambient temperatures make it difficult to distinguish rotamers.[21,22] This problem can be overcome by recording the spectra in the low-temperature environment of supersonic jet expansions; however a highly sensitive spectroscopic technique must be employed due to the low concentration of sample in jet-cooled conditions. One such technique is NID-IR/NIR spectroscopy.[23] The high sensitivity of NID spectroscopy has been demonstrated by the previous measurement of overtone OH-stretching transitions in phenol, catechol and aminophenol.[3,16,24,25] The advantage of vibrational overtone spectroscopy in jet-cooled conditions was demonstrated by the resolution of geometrically similar rotamers in the spectra of *m*-aminophenol.[16]

In the present study, we apply the combination of NID spectroscopy and AO local mode calculations with Boltzmann population analyses to the rotamers of resorcinol and hydroquinone. The chemical environment of the hydroxyl groups of resorcinol and hydroquinone is predicted to be very similar, and this overtone spectroscopic study will provide an indication of the differences in local environment present in these molecules. In addition it will provide limitations on the sensitivity of this NID overtone spectroscopy in distinguishing rotamers.

Experimental

The nonresonant ionization detected (NID) infrared/near-infrared (IR-NIR) spectroscopic technique has been described in detail previously.[23,25] Briefly, NID is an IR-NIR/UV double resonance technique that selectively ionizes a vibrationally excited molecule by nonresonant two-photon excitation. The selective ionization can be achieved by choosing the frequency of the ionization laser to be slightly lower than half the ionization potential. The UV radiation for the ionization laser is generated by a frequency doubled dye laser (LAMBDA PHYSIK: SCANMATE, Lumonics HD-500), which is pumped by the second harmonic of a Nd^{3+}:YAG laser (Spectra Physics: INDI, Spectra Physics: GCR170). The wavelength of UV radiation used was 305 nm for the measurement of resorcinol and 320 nm for hydroquinone. Tunable IR radiation from 2600 to 5600 cm^{-1} was obtained by the differential mixing technique between the fundamental or second harmonics of the YAG laser and the dye laser output. Tunable NIR radiation was obtained from an OPO laser (Spectra Physics: MOPO-HF/PRO250) in the 5600−11400 cm^{-1} range, and with a dye laser (Lumonics HD-500) in the 13 200−14 200 cm^{-1} and 16 500−16 800 cm^{-1} range, using the LDS751 dye and R610/R640 dye mixture, respectively. The line width of the IR/NIR lasers was less than 0.1 cm^{-1} in all regions. The laser power used to measure the OH-stretching regions corresponding to $\Delta v_{\mathrm{OH}} = 1$, 2, 3, and 4 were 0.5, 1.5, 10, and 40 mJ, respectively.

The UV and IR-NIR beams were introduced coaxially (from opposite directions) and simultaneously into the vacuum chamber and focused where they crossed a supersonic jet. The cations generated by IR-NIR/UV excitation were pushed into a detector chamber where they were detected by a channel multiplier (Murata Ceratron) through a quadrupole mass-filter (EXTREL). The ion signal was amplified by a preamplifier (EG&G PARC 115) and was integrated by a digital boxcar (EG&G PARC 4420/4422). The integrated signal was recorded as a function of the IR-NIR laser wavelength. The observed band shape was deconvoluted into Lorentzian functions with use of the Igor Pro (v. 4.02) curve-fitting program.

Resorcinol vapor at 351 K and hydroquinone vapor at 393 K were seeded in 3 atm of He gas and were expanded into the vacuum chamber through a solenoid valve with a 0.8 mm diameter orifice. We estimate the rotational temperature to be about 1 K in the supersonic jet.[24] The samples were purchased from Wako (99% purity) and were used after purification by vacuum sublimation.

Theory and Calculations

The three rotamers of resorcinol and two rotamers of hydroquinone were optimized at the B3LYP level of theory with the 6-311++G(3df,2pd) basis set within Gaussian03.[26] The Opt = Tight keyword was used to ensure tight convergence criteria on the structures. Harmonic frequency calculations yielded no imaginary eigenvalues for each of the rotamers, indicating each rotamer is at a minimum on the potential energy surface.

We use the local mode model to describe the nonequivalent OH-stretching vibrations of the different rotamers.[17] Previous studies on 1,3-butadiene have shown that coupling between CH-stretching local mode oscillators is generally only significant if the oscillators share a common heavy atom;[27] therefore, the OH-stretching overtone vibrations in resorcinol and hydroquinone can to a good approximation be described as isolated local modes. We use Morse oscillators to describe each of the nonequivalent OH-stretching modes, each defined by a local mode frequency $\tilde{\omega}$ and anharmonicity $\tilde{\omega}x$. We calculate fundamental and overtone OH-stretching frequencies and intensities from the Morse oscillator wavefunctions and a B3LYP calculated dipole moment function.[19,20] We express the intensity by the dimensionless oscillator strength f, which is given by[28]

$$f = 4.702 \times 10^{-7}\,[\mathrm{cm\ D^{-2}}]\tilde{\nu}_{v0}|\vec{\mu}_{v0}|^2 \qquad (1)$$

where $\tilde{\nu}_{v0}$ is the transition frequency in cm^{-1} and $\vec{\mu}_{v0} = \langle v|\vec{\mu}|0\rangle$ is the transition dipole moment in Debye (D).

The dipole moment function for each of the nonequivalent OH oscillators is approximated as a series expansion in the internal OH-stretching coordinate. The expansion coefficients are determined from the B3LYP calculated dipole moment at the equilibrium geometry and at geometries in which the bond length is incremented from its equilibrium position. The dipole moment is calculated at nine points obtained by stretching the bond by ±0.2 Å in steps of 0.05 Å. We have limited the series expansion of the dipole moment to fifth order.[19,27,29]

We have used B3LYP energies calculated at these 9 points (potential energy curves) to determine the local mode frequency

TABLE 1: Relative Energies (cm^{-1}) and Percentage Population of the Three Unique Resorcinol Rotamers at 351 K[a]

rotamer	ΔE^b	$\Delta E_0{}^c$	ΔG^d	F (%)
I	0	0	0	74
II	15	1	334	19
III	241	229	557	7

[a] Energies calculated with the B3LYP/6-311++G(3df,2pd) method. [b] Relative electronic energy. [c] ZPVE corrected energy. [d] Free energy including degeneracy contribution.

and anharmonicity for each of the nonequivalent OH oscillators. We have attempted to compensate for deficiencies in the chosen ab initio method and thereby improve the spectroscopic accuracy by scaling the calculated local mode parameters.[29] Phenol was chosen as the basis for the scaling factors since its OH-stretching fundamental and overtone spectra have been observed and because of its chemical similarity to resorcinol and hydroquinone. Scaling factors were determined by comparison of the local mode parameters obtained from a Birge−Sponer type fit to the observed $\Delta v_{\mathrm{OH}} = 1-4$ transitions of phenol[24,25] to those calculated. The B3LYP/6-311++G(3df,2pd) calculated local mode parameters for phenol are $\tilde{\omega} = 3840.8\ \mathrm{cm}^{-1}$ and $\tilde{\omega}x = 98.08\ \mathrm{cm}^{-1}$. The local mode parameters obtained from the observed spectra of phenol are $\tilde{\omega} = 3824.6 \pm 0.3\ \mathrm{cm}^{-1}$ and $\tilde{\omega}x = 84.35 \pm 0.1\ \mathrm{cm}^{-1}$, which gives scaling factors of 0.99577 and 0.8600 for $\tilde{\omega}$ and $\tilde{\omega}$, respectively, for the B3LYP/6-311++G(3df,2pd) method.

A theoretical population analysis was performed at the B3LYP/6-311++G(3df,2pd) level to provide an estimate of the rotamer ratios present at our experimental conditions. We calculate ΔE, ΔE_0, and ΔG, where E is the electronic energy with the given theoretical method and E_0 includes the zero point vibrational energy correction. The Gibbs free energy is calculated from equilibrium statistical mechanics and includes the contribution from the structural degeneracy Ω. The structural degeneracy contributes $-RT \ln \Omega$ to the free energy. More details can be found in the paper by Howard et al. and references therein.[30] The two possible dihedral angles about the two C−O bonds of resorcinol and hydroquinone yield a total of four torsional combinations for each molecule. For resorcinol, symmetry reduces the number of unique conformers to three. Conformer I has $\Omega = 2$ while II and III each have $\Omega = 1$. The two unique conformers of hydroquinone both have $\Omega = 2$. The relative populations of the different rotamers in both resorcinol and hydroquinone have been calculated from the Gibbs free energy differences.

Results and Discussion

Resorcinol. The relative energies of the three different rotamers and percentage populations are presented in Table 1. The electronic and zero-point corrected energies of rotamers I and II are nearly identical, with rotamer III about 240 cm^{-1} higher in energy. These results are in reasonable agreement with the relative energies extracted from the millimeter wave spectra of about 0 cm^{-1}, 20 cm^{-1} (±70 cm^{-1}) and 410 cm^{-1} (±70 cm^{-1}).[10] However due to the difference in degeneracy the free energy difference between rotamer I and II is significantly higher at approximately 330 cm^{-1} in favor of I and leads to a population that strongly favors rotamer I at the 351 K temperature of our sample reservoir.

The NID spectra of jet-cooled resorcinol are shown in Figure 2. The spectra are drawn on a relative wavenumber axis. The region of the OH-stretching fundamental vibration is centered at 3656 cm^{-1}. The variation in IR laser power for this region, due to the absorption by atmospheric water, is also shown. The dip in the $\Delta v_{\mathrm{OH}} = 1$ peak coincides with a sharp drop in the IR laser power. Thus the two peak appearance of the fundamental band is artificial and due to the variation of the IR laser power.

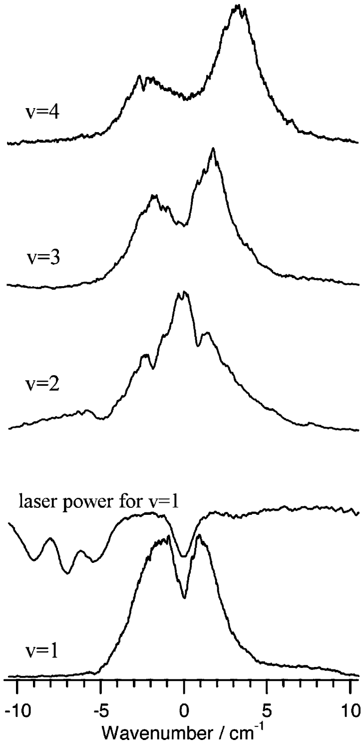

Figure 2. NID spectrum of jet-cooled resorcinol in the $\Delta v_{\mathrm{OH}} = 1$ region centered at 3656 cm^{-1}. IR laser power spectrum in the $\Delta v_{\mathrm{OH}} = 1$ region. NID spectrum of jet-cooled resorcinol in the $\Delta v_{\mathrm{OH}} = 2-4$ regions centered at 7142, 10460, and 13616 cm^{-1}, respectively.

For the OH-stretching overtones the variation in laser power is negligible. Much like the fundamental, the $\Delta v_{\mathrm{OH}} = 2$ region is essentially a single band. However, in the $\Delta v_{\mathrm{OH}} = 3$ region more structure is revealed and at least two peaks are observed. The $\Delta v_{\mathrm{OH}} = 4$ region looks similar to $\Delta v_{\mathrm{OH}} = 3$ with more separation between the peaks, a typical property of overtone spectra.[16,18,30]

We have labeled the different OH bonds by their rotamer label and for rotamer I the two nonequivalent OH bonds are labeled IA and IB. Calculated OH bond lengths are useful as a first approximation as to how the overtone spectra will appear. The B3LYP calculated OH bond lengths of the three rotamers are similar with a maximum difference of less than 3×10^{-4} Å between that of IA and III. Based on such small bond length differences alone, the OH-stretching transitions of the rotamers are predicted to lie close together. The calculated OH bond lengths are given in Supporting Information.

We have simulated the OH-stretching transition of resorcinol in the $\Delta v_{\mathrm{OH}} = 1$ and 4 regions based on our AO local mode calculations and our Boltzmann populations of the rotamers, and show these simulated stick spectra in Figures 3 and 4, respectively. The observed transition frequencies and local mode parameters are given in Table 3 and the calculated local mode parameters, transition frequencies and intensities in the Supporting Information. In the fundamental region, the transitions of all conformers lie within approximately 3 cm^{-1} of each other. This close overlap is in agreement with the observation of a rather broad single peak. The width of each peak is expected to be about 2 cm^{-1} at an experimental rotational temperature of about 1 K.[24] In the $\Delta v_{\mathrm{OH}} = 4$ region, the transitions are more

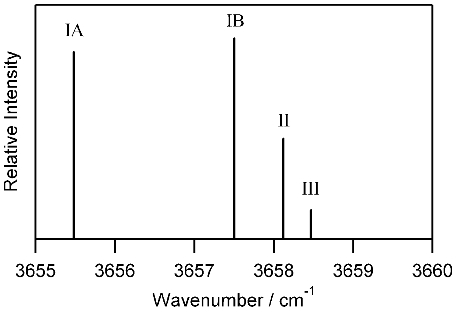

Figure 3. Calculated spectrum of resorcinol in the $\Delta\upsilon_{OH} = 1$ region at 351 K.

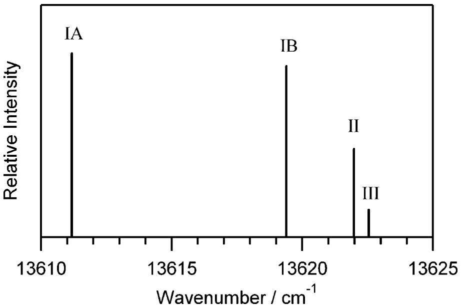

Figure 4. Calculated spectrum of resorcinol in the $\Delta\upsilon_{OH} = 4$ region at 351 K.

TABLE 2: Relative Energies (cm^{-1}) and Percentage Population of the Two Unique Hydroquinone Rotamers at 393 K[a]

rotamer	ΔE[b]	ΔE_0[c]	ΔG[d]	F (%)
trans	0	0	0	53
cis	37	31	28	47

[a] Energies calculated with the B3LYP/6-311++G(3df,2pd) method. [b] Relative electronic energy. [c] ZPVE corrected energy. [d] Free energy.

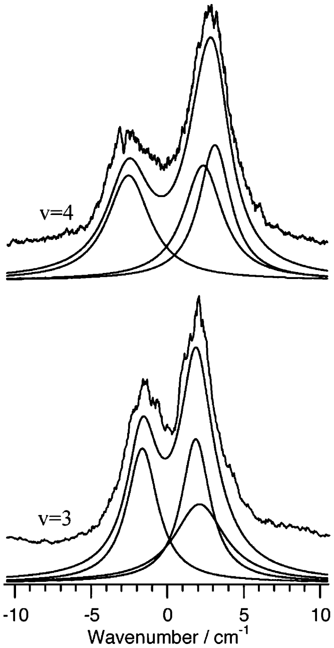

Figure 5. NID spectra of jet-cooled resorcinol in the $\Delta\upsilon_{OH} = 3$ and 4 regions. The deconvoluted Lorentzian functions and the fitted spectrum are shown below the observed spectrum.

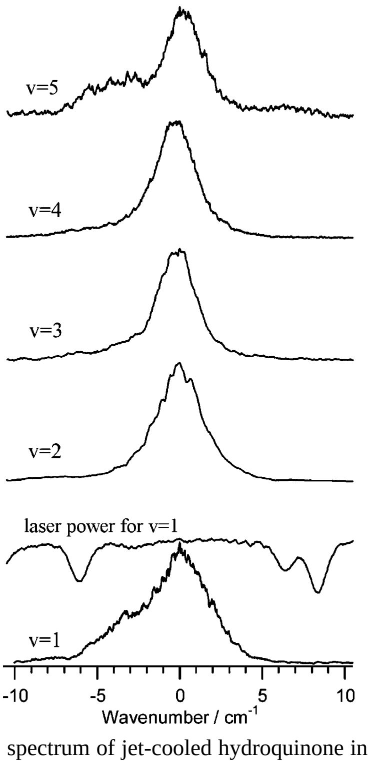

Figure 6. NID spectrum of jet-cooled hydroquinone in the $\Delta\upsilon_{OH} = 1$ region. IR laser power spectrum in the $\Delta\upsilon_{OH} = 1$ region. NID spectrum of jet-cooled hydroquinone in the $\Delta\upsilon_{OH} = 2-5$ regions.

spread out with the transition due to IA about 8 cm^{-1} lower in energy than IB. The transitions due to II and III are calculated to be nearly degenerate and are at slightly higher energy than IB, and unlikely to be resolved from the IB transition. The calculation is in good agreement with experiment, where essentially two well-defined peaks are observed. The single peak lying to lower energy is assigned as IA while the higher energy peak with greater intensity has contributions from IB, II and III.

We have deconvoluted the observed $\Delta\upsilon_{OH} = 3$ and 4 spectra of resorcinol and the results are shown in Figure 5. Three Lorentzian functions were used in the procedure, which correspond to transitions for IA, IB and a combination of II plus III. We constrained the fitting by requiring the two Lorentzian functions corresponding to IA and IB to have the same area as the calculated oscillator strengths of IA and IB are almost equal. The deconvolution was optimized by the least-squares method. The observed spectral profile is reproduced very well by three Lorentzians and clearly shows that additional intensity is present in the region of the IB transition. From our calculations including both relative abundances and intensities the ratio of intensity of lower energy to higher energy region is 1:1.8 and 1:1.6 for the $\Delta\upsilon_{OH} = 3$ and 4 overtones, respectively, in good agreement with the ~1:2 ratio obtained from our deconvolutions.

Hydroquinone. The relative free energies of the two hydroquinone rotamers are similar, with the trans favored by approximately 30 cm^{-1} at the B3LYP/6-311++G(3df,2pd) level, in reasonable agreement with the experimental result.[4] These results suggest an almost equal population at 393 K with the trans rotamer making up 53% of the population as seen in Table 2. In both rotamers the two OH bonds are equivalent and the OH bonds in the *cis* rotamer are very similar to those in the trans rotamer. The B3LYP calculated OH bond length difference between the cis and trans rotamers of hydroquinone is less than 4×10^{-5} Å. Bond length distanes quoted to such high accuracy are unlikely to be meaningful, but it does indicate the nearly identical character of the OH bonds between the two rotamers.

Figure 6 shows the NID spectrum of jet-cooled hydroquinone in the $\Delta\upsilon_{OH} = 1-5$ regions. Only a single strong peak is found for $\Delta\upsilon_{OH} = 1-4$. The power spectrum of the IR laser is also shown for the $\Delta\upsilon_{OH} =1$ region, which does not interfere with

TABLE 3: Observed Transition Frequencies and Local Mode Parameters (cm^{-1})

	resorcinol			hydroquinone	catechol[a]		
Δv_{OH}	IA	IB	II(III)	cis/trans	$\mathrm{OH_b}$	$\mathrm{OH_f}$	phenol[b]
1	3656	3656	3656	3662	3611	3668	3656
2	7142	7142	7142	7153	7063	7188	7143
3	10458	10461	10462	10476	10318	10512	10461
4	13613	13618	13619	13638	13406	13679	13612
5				16627			
$\tilde{\omega}^{c}$	3821.5 ± 2.7	3819.9 ± 1.3	3819.6 ± 1.4	3829.2 ± 0.3	3788 ± 7	3839 ± 8	3824.6 ± 0.3
$\tilde{\omega}x^{c}$	83.71 ± 0.65	83.10 ± 0.32	83.00 ± 0.33	84.02 ± 0.30	87.1 ± 1.8	83.5 ± 2.2	84.35 ± 0.09

[a] From Kjaergaard et al.[3] [b] From Ishiuchi et al.[24,25] [c] Uncertainties are one standard deviation.

the observed transition. The shoulder seen to the red in the $\Delta v_{\mathrm{OH}} = 1$ region is likely caused by a resonance, similar to what we have previously been observed in the spectra of phenol.[24] In contrast to resorcinol, no obvious splitting was found in the $\Delta v_{\mathrm{OH}} = 3$ and 4 regions. For $\Delta v_{\mathrm{OH}} = 5$, a weak satellite band at 16 624 cm^{-1} appears at the lower frequency side of the major peak at 16 627 cm^{-1}. However, the splitting due to rotamers will increase systematically in going to higher overtone, as was observed for resorcinol, thus it is not reasonable to assign the satellite band in the hydroquinone spectrum as due to the other rotamer. The satellite band is thought to be a combination vibration similar to what we have observed in the spectra of phenol.[24] The observed band positions and local mode frequencies are given in Table 3.

The results of the AO local mode calculation for hydroquinone are given in the supplementary deposit. The calculated OH-stretching frequencies of the two rotamers are within 1 cm^{-1} and with virtually identical intensities in each overtone up to $\Delta v_{\mathrm{OH}} = 5$. This result is in full agreement with the observation of a single peak for the fundamental and overtone transitions. Thus we conclude that the two rotamers have almost identical overtone frequencies and are not possible to resolve them in the NID overtone spectrum. The band observed in the $v = 4$ spectrum appear to have a somewhat flat top, which could arise from the sum of two closely lying Lorentzian peaks.

Dihydroxybenzenes. A summary of the observed OH-stretching transitions and extracted local mode parameters for phenol and the dihydroxybenzenes are shown in Table 3. The local mode anharmonicity $\tilde{\omega}x$ is virtually the same for all OH oscillators within the experimental uncertainties. The exception is the hydrogen bond ($\mathrm{OH_b}$) of catechol which is about 3 cm^{-1} larger. Such a difference is expected due to its weak interaction with the neighboring free hydroxyl ($\mathrm{OH_f}$) group.[3] The transition frequencies in resorcinol are similar to those observed in phenol. The local mode frequency $\tilde{\omega}$ decreases systematically by about 10 cm^{-1} from the $\mathrm{OH_f}$ in catechol (ortho) to hydroquinone (para) and to resorcinol (meta), with a similar pattern for the transition frequencies. This is indicative of a stronger OH bond in the ortho and para positions.

In previous work the OH-stretching transitions in *cis*- and *trans*-*m*-aminophenol were separated at the $\Delta v_{\mathrm{OH}} = 3$ and 4 overtone despite their calculated bond lengths differing by only 2×10^{-5} Å (with the B3LYP/6-311++G(2d,2p) method).[16] In resorcinol and hydroquinone the bond length differences are of a similar magnitude, however distinguishing between the different OH-stretching transitions is much less transparent. Thus it seems that one cannot makes these arguments based on a simple bond length argument alone. Another important factor to distinguish isomers is the difference in anharmonicity. In *m*-aminophenol, the difference in OH-stretching anharmonicity is ~0.2 cm^{-1} between cis and trans isomers, while the OH-bonds in the three resorcinol isomers have nearly identical anharmonicities. Although the overtone spectroscopy is sensitive to femtometer differences in bond length, such an identical anharmonicity causes limitation to distinguish isomers. A practical problem in overtone spectra is the broadening of the bands. An overtone transition usually shows the Lorentzian shape due to the intramolecular vibrational redistribution. Even in an ultracold condition of a supersonic jet, the bandwidth becomes a few wavenumbers or more. Such a broadening also gives the limitation to distinguish the isomers by overtone transitions. Nevertheless, we would like to emphasize the advantage of the overtone spectroscopy in identification of isomers. As we have shown here and in previous studies, the overtone transitions are well predicted by the theoretical calculations of the different isomers. Thus once transitions originated from isomers are distinguished, we can easily assign the overtone transitions in terms of species and population. This analysis is easier than the high-resolution spectroscopies for isomer assignments, and will be feasible for larger and more flexible molecules such as biological building blocks.

Conclusions

The OH-stretching overtone transitions of resorcinol and hydroquinone in a supersonic jet were observed by NID spectroscopy. Anharmonic oscillator local mode calculations and Boltzmann population analyses were performed to help interpret the observed spectra. The second and third OH-stretching overtones of resorcinol show clear splitting due to the two nonequivalent OH bonds in the dominant rotamer I. The existence of the other two rotamers (II and III) of resorcinol is not clear from the overtone spectra. However, comparison of the calculated and observed relative intensities, indicate that the less abundant rotamers are also present. The OH stretching transitions of the two rotamers of hydroquinone cannot be resolved thus indicating that the OH bonds are essentially identical.

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Supporting Information Available: Table of B3LYP/6-311++G(3df,2pd) calculated OH bond lengths. Two tables of observed and calculated local mode parameters and two tables of calculated OH stretching frequencies and intensities. This material is available free of charge via the Internet at http://pubs.acs.org.

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