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Observation of Hydrogen-Bonded Rotational Isomers of the Resorcinol·Water Complex

Wolf D. Geppert, Caroline E. H. Dessent, Susanne Ullrich, and Klaus Müller-Dethlefs*

Department of Chemistry, University of York, Heslington, York, YO10 5DD, U.K.

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Three rotational isomers of resorcinol(1,3-dihydroxybenzene)·H_2O have been identified using resonance-enhanced multiphoton ionization (REMPI), zero electron kinetic energy (ZEKE) spectroscopy, and ab initio calculations. Hole-burning spectroscopy was employed to confirm the presence of three isomers in the REMPI spectrum. The frequencies of the intermolecular vibrations and the S_10^0 and ionization energy red shifts reveal that the water molecule hydrogen bonds more weakly to resorcinol than phenol. We discuss the spectral characteristics of the rotational isomers by considering the extent to which the second OH group of resorcinol perturbs the resorcinol·H_2O hydrogen bond.

I. Introduction

The preference of a solvent molecule for certain binding sites on a solute molecule is a problem of general chemical interest. In the low-temperature environment of a free jet expansion, isomeric molecular complexes can be generated with a single solvent molecule ‘frozen’ at different binding sites on the solute when the barrier for interconversion between isomers is sufficiently high. Complexes can then be interrogated with a variety of high-resolution spectroscopic methods such as laser-induced fluorescence and REMPI for probing neutral states[1,2] and ZEKE photoelectron spectroscopy for studying cationic states.[3−8] Hole-burning spectroscopy[9,10] is a powerful tool for identifying spectral contributions from different isomers. These techniques are sufficiently sensitive to allow the identification of the low-frequency, intermolecular vibrations which characterize the intermolecular potential energy surface.

Dihydroxybenzenes can exist in different isomeric forms that are related through rotations of the OH groups.[10−15] The rotational barrier heights are thought to be substantial (∼1200 cm^{-1}),[13,15] allowing the various rotational isomers to be isolated in a supersonic expansion. Two rotational isomers of resorcinol, pictured in Figure 1, were recently identified in a REMPI study by Gerhards et al.[10] We have built on this work by conducting a combined REMPI and ZEKE study of resorcinol·H_2O clusters to explore different solvent binding sites which are available in these isomers. In the related phenol·H_2O complex, which has been extensively studied as a prototype for hydrogen-bonding interactions,[16,17] the water molecule bonds to the phenol OH group through its oxygen atom. We anticipate that this primary interaction should dominate binding in resorcinol·H_2O leading to the three possible isomeric complexes pictured in Figure 2. The resorcinol·H_2O intermolecular bond should then be perturbed to varying degrees by the second OH group.

Experimental observations of intermolecular binding energies, vibrational frequencies, and Franck−Condon (FC) patterns of vibrational excitation provide excellent benchmarks for ab initio calculations. The characterization of structurally similar isomeric complexes is a stringent test of the performance of such calculations, allowing several local minima on the potential energy surface to be analyzed. Calculations using the 6-31G* basis set were employed by Hobza and co-workers[17] to assign spectra of the phenol·H_2O complex, although the calculated intermolecular frequencies were considerably higher than those observed experimentally.[16] In this work, we employ the cc-pVDZ basis set to obtain structures and intermolecular vibrational frequencies for the neutral and cationic resorcinol·H_2O complexes, since it has proven reliable for calculating structures of clusters involving water molecules.[18−21]

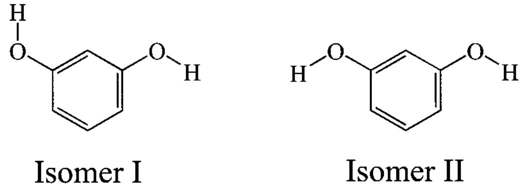

Figure 1. Rotational isomers of resorcinol observed by Gerhards et al.[10]

II. Experimental Section

The experimental apparatus has been described in detail previously[22] and will only be reviewed briefly here. Resorcinol·H_2O clusters were produced in a supersonic jet expansion of resorcinol vapor seeded in a water/neon mixture at 0.5−1.5 bar. The sample reservoir was located immediately behind the valve (General Valve Series 9, 500 μm nozzle) and heated to 370−420 K. We estimate that the composition of the expansion mixture was approximately 1% resorcinol, 4% water, and 95% neon.

The skimmed supersonic beam was intersected 20 cm downstream by two coaxial, counterpropagating, synchronously pumped dye lasers (the pump laser employed was a Lambda Physik EMG 1003i excimer). The frequency-doubled output of a Radiant Narrowscan laser was used to perform the initial excitation to an S_1 intermediate state, while the undoubled output of a Lambda Physik FL 3002 laser promoted ionization. Laser wavelengths were calibrated by simultaneously recording iodine spectra[23] with all quoted laser photon energies having been converted from air to vacuum. The pulse sequences, timings, and field strengths used to ionize the Rydberg states are identical to those in ref 22.

The hole-burning experiments were performed using a Nd:YAG (Continuum Precision PL 8020) pumped dye laser (Radiant Narrowscan) which was set to the respective $S_1 \leftarrow S_0$ transition. The excimer pumped Radiant Narrowscan dye laser

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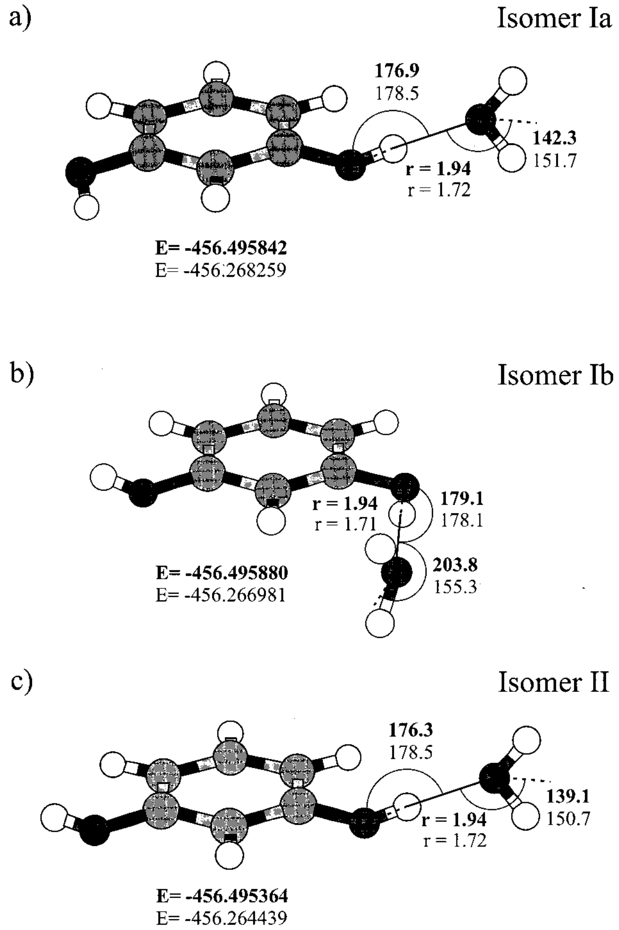

Figure 2. Geometrical structure and energies of the resorcinol•H_2O isomers. Numbers in bold refer to the neutral complexes calculated at the RHF/cc-pVDZ level, while numbers in plain text refer to the cationic complexes calculated at the UHF/cc-pVDZ level. Energies are given in hartrees, bond lengths in Å, and angles in degrees. The dihedral angle between the H_2O and phenyl plane is 90.0° in all of the complexes.

described above was then used as the probe laser. The two laser beams were coaxially overlapped, with the probe laser being fired 400−600 ns after the hole-burning laser. The ions were retrieved by a 305 V/cm pulsed electrical field commencing 1 μs before the burn laser.

III. Results and Discussion

A. Ab Initio Calculations of Resorcinol•H_2O. Geometric structures of the neutral (S_0) and cationic (D_0) ground-state resorcinol•H_2O were obtained from ab initio calculations at the R(U)HF/cc-pVDZ level of theory using GAUSSIAN 94.[24] Harmonic frequencies were calculated to confirm that optimized structures corresponded to local minima and to aid assignment of the ZEKE spectra. Local minima structures were identified by applying an intermolecular geometry analogous to that of phenol•H_2O as a starting point for the calculations. Only structures based on resorcinol isomers I and II were pursued. The energies and intermolecular geometrical parameters for the neutral and cationic ground states of the isomers are included in Figure 2, while the intermolecular vibrational frequencies of the cations are listed in Table 1.

TABLE 1: Ab Initio Harmonic Frequencies (in cm^{-1}) of the Intermolecular Vibrations of the Rotational Isomers of [Resorcinol•H_2O]$^+$ at the UHF/cc-pVDZ Level of Theory^a

mode	isomer Ia	isomer Ib	isomer II
β''	59.8	69.4 (63^b)	59.0
β'	91.4	79.8 (71)	90.8
τ	179.3	167.1	179.2
σ	209.7 (215)	216.1 (223)	208.7 (214)
γ'	366.8 (369^c)	341.8 (311)	370.8 (370^c)
γ''	382.9	381.9	383.2

^{a} Experimental frequencies are displayed in parentheses. ^{b} Calculated from $2\beta''$. ^{c} The assignment presented for this mode is the favored assignment. See text for details.

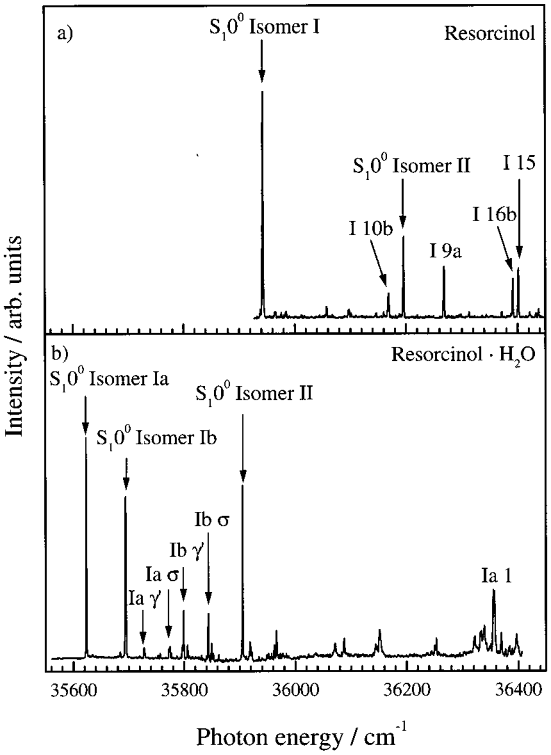

Figure 3. Two-color (1 + 1′) REMPI spectra of (a) resorcinol and (b) resorcinol•H_2O recorded with the ionizing laser set to 30 300 cm^{-1}.

The C_s symmetry ab initio structures obtained for each of the isomers resemble the structure of phenol•H_2O,[17,20] with the water molecule hydrogen bonding to one OH group of resorcinol through its oxygen atom. The solvent therefore adopts a localized binding site on the surface of resorcinol, rather than interacting with the overall dipole moment of the solute. In neutral isomers Ia and II, the angles of the C_{2v} axis of the water molecule to the OH group (142.3 and 139.1°) are very similar to the angle of 141.2° found in phenol•H_2O.[17,20] However, in neutral isomer Ib, this angle is considerably distorted (203.8°). The calculations predict that a substantial geometry change occurs along this coordinate between the S_0 and D_0 states for isomer Ib, with the effect that this angle is similar in the three cationic complexes.

On the basis of the ab initio calculations, we anticipate that the REMPI and ZEKE spectra of isomers Ia and II should be similar (and resemble the spectra of phenol•H_2O), while isomer Ib should display distinctive spectral characteristics. The similarity of structures Ia and II is reflected in the intermolecular frequencies displayed in Table 1, which suggest that the isomers will be difficult to assign on the basis of their ZEKE spectra alone.

B. REMPI Spectra of Resorcinol•H_2O. The two-color (1 + 1′) REMPI spectrum of the resorcinol monomer is displayed in Figure 3a. This spectrum agrees well with the previously recorded one-color (1 + 1) spectrum,[10] where the prominent features at 35 944 and 36 196 cm^{-1} were assigned to the S_10^0

TABLE 2: Frequencies of Vibrational Features Observed in the REMPI Spectrum of Resorcinol·H$_2$O[a]

$S_0 \rightarrow S_1$ energy/cm^{-1}	assignment	$S_0 \rightarrow S_1$ energy/cm^{-1}	assignment
35624s	Ia 0^0	36071w	Ia 16b
35695s	Ib 0^0	36088w	Ia 15
35728w	Ia γ'	36151w	Ia 6a
35774w	Ia σ	36253w	Ia 16a
35799m	Ib γ'	36322w	Ib 16a
35843m	Ib σ	36339w	II 16b
35905s	II 0^0	36356m	Ia 1
35919w	Ib 10b	36397w	Ia 11
35966w	Ia 9a		

[a] w denotes weak, m medium, and s strong.

transitions of isomers I and II, respectively. The (1 + 1′) two-color REMPI spectrum of resorcinol·H$_2$O is displayed in Figure 3b. The ionization laser was set to 30 300 cm^{-1} for both REMPI spectra to avoid fragmentation and dissociation of higher clusters into the resorcinol·H$_2$O mass channel.

The REMPI spectrum of resorcinol·H$_2$O is dominated by three strong features at 35624 ± 1, 35695 ± 1, and 35905 ± 1 cm^{-1}, which we assign as the $S_1 0^0$ transitions of isomers Ia, Ib, and II, respectively. These features can be related to the rotational isomers of resorcinol by considering the spectral shifts of the cluster $S_1 0^0$ transitions compared to the origin transitions in the monomer REMPI spectrum. In phenol·H$_2$O,[16] the $S_1 0^0$ transition is red shifted by 352.5 cm^{-1} relative to the corresponding transition in phenol, and we anticipate that similar red shifts should be observed for the resorcinol·H$_2$O complexes. The features at 35624 ± 1 and 35695 ± 1 cm^{-1} can therefore be associated with water complexing to isomer I, with spectral red shifts of 320 and 249 cm^{-1}, respectively. Since the ab initio results suggest that the structure of neutral isomer Ib (Figure 2b) deviates most from the structure of phenol·H$_2$O,[17,20] it seems probable that the feature at 35695 ± 1 cm^{-1} (red shift = 249 cm^{-1}) can be attributed to the $S_1 0^0$ transition of isomer Ib. This assignment is confirmed by an analysis of the ZEKE spectra presented in section III.C. The feature at 35 905 cm^{-1} is red shifted by 291 cm^{-1} compared to the $S_1 0^0$ transition of resorcinol isomer II and can therefore be straightforwardly assigned as resorcinol·H$_2$O isomer II (Figure 2c).

The REMPI spectrum of resorcinol·H$_2$O also displays numerous smaller intensity features, which can be tentatively assigned by comparison with the REMPI spectrum of phenol·H$_2$O[16] and calculations of resorcinol.[10] A list of spectral features and assignments are included in Table 2. The features 104 and 148 cm^{-1} above the $S_1 0^0$ origin of isomer Ib are particularly distinctive and are assigned as the in-plane wag (γ') and the intermolecular stretch (σ). The strength of these features implies that a substantial geometry change occurs upon excitation to the S_1 state for isomer Ib.

C. ZEKE Spectra of Resorcinol·H$_2$O. ZEKE spectra recorded via the $S_1 0^0$ transitions of the resorcinol·H$_2$O isomers are displayed in Figure 4. The lowest energy feature in each spectrum is assigned to the vibrational ground state of the cation ($S_1 \rightarrow D_0$), giving ionization energies[25] (computed as the sum of the $S_1 0^0$ transition and the vibrationless $S_1 \rightarrow D_0$ transition) of 62635 ± 4 (Ia), 62771 ± 4 (Ib), and 63085 ± 4 (II) cm^{-1}. The observation of three distinct ionization energies is a strong indication that three different isomeric species are present in the S_1 state spectrum. The ionization energies correspond to red shifts of 4060 ± 8 (Ia), 3924 ± 8 (Ib), and 4063 ± 8 cm^{-1} (II) compared to the respective monomer transitions,[27] all of which are considerably smaller than the ionization energy red shift of 4601 ± 8 cm^{-1} observed in the phenol·H$_2$O cluster.[16] As with the $S_1 0^0$ transitions, the ionization energy red shift for isomer Ib deviates most from the phenol·H$_2$O value.

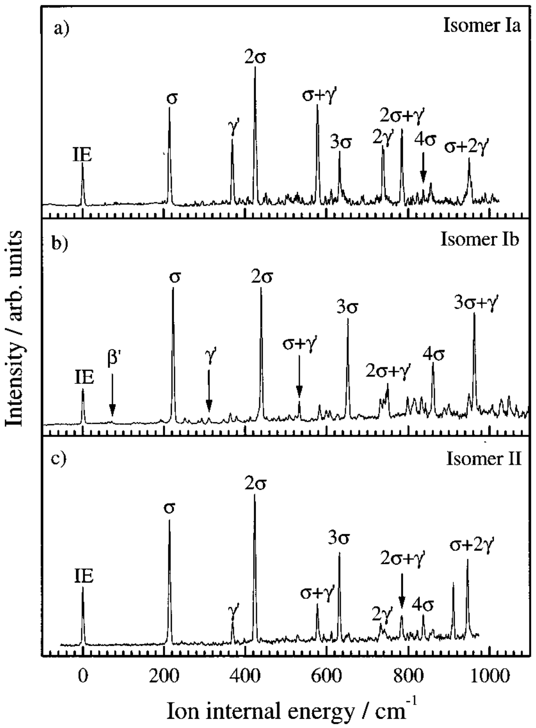

Figure 4. ZEKE spectra of resorcinol·H$_2$O recorded via the $S_1 0^0$ state of (a) isomer Ia, (b) isomer Ib, and (c) isomer II. Each spectrum is displayed relative to the respective ionization energy. Assignments of the in-plane bend (β'), in-plane wag (γ'), and intermolecular stretch (σ) modes are included on the spectra.

TABLE 3: Frequencies (in cm^{-1}) of Vibrational Features Observed in the ZEKE Spectra of the Resorcinol·H$_2$O Isomers Recorded via the Respective $S_1 0^0$ States[a]

isomer Ia	isomer Ib	isomer II	assignment[b]
	71w		β'
215s	223s	214s	σ
369s	311w	370m	γ'
425s	439s	424s	2σ
579s	534m	578m	$\sigma + \gamma'$
632s	652s	631s	3σ
738s	608w	733m	$2\gamma'$
784s	748m	784m	$2\sigma + \gamma'$
837w	861s	836m	4σ
856m			?
		915m	?
950s		945s	$\sigma + 2\gamma'$
	962s		$3\sigma + \gamma'$

[a] The frequencies are given relative to the ionization energies, and w denotes weak, m medium, and s strong. ? indicates a feature which could not be assigned. [b] The assignment presented in this table is the favored assignment. See text for details.

The ZEKE spectra of all three isomers display extensive vibrational features (listed in Table 3) that can mainly be attributed to two modes, one displaying a progression spaced by ~220 cm^{-1} and the other by ~340 cm^{-1}. If we compare these frequencies with the ab initio values presented in Table 1, the 220 cm^{-1} progression can clearly be assigned to the intermolecular stretch (σ), while the modes spaced by ~340 cm^{-1} can either be assigned to the in-plane wag (γ') or the first overtone of the torsion mode (2τ). We would not expect this mode to correspond to the out-of-plane wag (γ'') since it is generally not observed for C_s symmetry structures.[16,22,28] In isomer Ib, this mode (311 cm^{-1}) can be assigned with some certainty to γ', since we were able to record a ZEKE spectrum via the γ' mode in the REMPI spectrum which confirmed the assignment. We also favor the γ' assignment for the ZEKE spectra of isomers Ia and II through a comparison of ab initio and experimental results for phenol·H_2O. The frequency of τ in ab initio calculations is generally much larger than the experimental frequency.[20] This general trend would be at odds with the assignment of the ~340 cm^{-1} progression to 2τ, leading us to the assignment presented in Table 1. (We also note that the 4τ vibration was never observed in phenol·H_2O, which again favors the γ' assignment.) While this point is currently ambiguous, it could be clarified by obtaining additional ZEKE spectra through other S_1 state vibrations or isotopic substitution of resorcinol·H_2O. In some respects, the uncertainty in the identity of this mode reflects ambiguities that still exist in the assignment of vibrations in the phenol·H_2O spectra,[16] illustrating the need for further investigations of this prototype system.

Next, we consider the assignment of the ZEKE spectra to the rotational isomers by comparing the experimental frequencies of the intermolecular vibrations to the ab initio results. Since isomer II has already been assigned on the basis of the $S_1 0^0$ transition red shift, we are primarily concerned with confirming the assignment of isomers Ia and Ib. The stretching mode occurs at a higher frequency in the ZEKE spectrum of isomer Ib, in line with the results of the ab initio calculations. We are unable to make a direct comparison of the γ' mode in the spectra of isomers Ia and Ib due to the uncertainty in the γ' assignment for isomer Ia. Nonetheless, the experimental frequency of the γ' mode of isomer Ib is closest to the relatively low ab initio value found for this isomer, again favoring the suggested assignment.

The experimental frequencies of the σ and γ' vibrations are relatively similar for isomers Ia and II, as expected from the ab initio results. The calculations do appear to recover the experimental result that σ appears at a slightly higher frequency in isomer Ia compared to isomer II, while γ' occurs at a slightly lower frequency. An assignment of the vibrational features observed in the Figure 4 ZEKE spectra is included in Table 3.

A vibrational progression in the σ mode dominates all of the ZEKE spectra presented in Figure 4, illustrating that a substantial decrease of the equilibrium intermolecular bond length occurs upon ionization. As in other phenol·ligand complexes,[16,22,28] combination bands of σ with γ' are also prominent. The FC envelopes of the σ progressions in the ZEKE spectra of the three isomers are similar, indicating that the intermolecular bond length changes by a comparable amount for each complex. It is notable that this observation is in line with the ab initio results. The σ progression is also prominent in the phenol·H_2O ZEKE spectrum via $S_1 0^0$ [16] and again displays a similar FC envelope. In phenol·H_2O, the anharmonicity constant of this mode is 0.75 cm^{-1} whereas the values are somewhat higher in the resorcinol·H_2O isomers (1.5, 1.9, and 1.5 cm^{-1} for isomers Ia, Ib, and II, respectively).

ZEKE spectra recorded via the $S_1\gamma'$ and σ states of isomer Ib are presented in Figure 5. The lowest energy features in both spectra appear at 62771 ± 4 cm^{-1}, in excellent agreement with the adiabatic ionization energy obtained for excitation via $S_1 0^0$. This confirms that the Ib 0^0, γ', and σ features in the REMPI spectrum can in fact be attributed to the same isomer. Vibrational features observed in the spectra shown in Figure 5 are listed in Table 4. The γ' mode is enhanced in the spectrum recorded via $S_1\gamma'$ (Figure 5a), in line with the "$\Delta\nu = 0$" propensity rule.[3] Combinations of this mode with σ are also enhanced compared to the spectrum recorded via the $S_1 0^0$ state. These results confirm the assignment of the γ' feature in the $S_1 0^0$ ZEKE spectrum. We note that the intermolecular bending modes (β' and β'') are also clearly present in this spectrum. Figure 5b presents the ZEKE spectrum of isomer Ib recorded via the $S_1\sigma$ state. The FC pattern of the σ mode in this spectrum is characteristic of phenol·ligand ZEKE spectra recorded via the $S_1\sigma$ state,[16,20,28] and confirms the σ assignment.

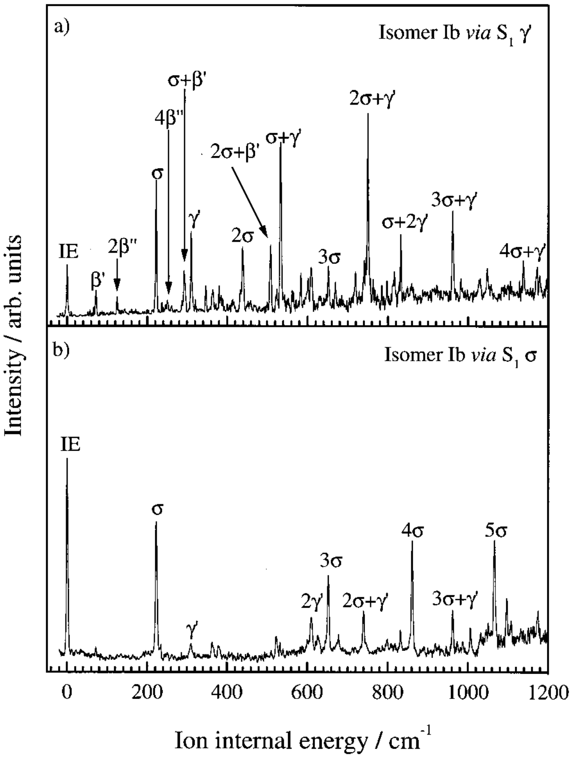

Figure 5. ZEKE spectra of isomer Ib of resorcinol·H_2O recorded via (a) the $S_1\gamma'$ and (b) the $S_1\sigma$ intermediate levels, displayed relative to the ionization energy. Assignments of the in-plane bend (β'), out-of-plane bend (β''), in-plane wag (γ'), and intermolecular stretch (σ) modes are included on the spectra.

TABLE 4: Frequencies (in cm^{-1}) of Vibrational Features Observed in the ZEKE Spectra of Isomer Ib of Resorcinol·H_2O Recorded via the $S_1\gamma'$ and $S_1\sigma$ Intermediate States[a]

via $S_1\gamma'$	via $S_1\sigma$	assignment	via $S_1\gamma'$	via $S_1\sigma$	assignment
72w	72vw	β'	584w		$2\sigma + 2\beta'$
125w		$2\beta''$	609m	610m	$2\gamma'$
223s	223s	σ	652m	652s	3σ
250w		$4\beta''$	750s	740m	$2\sigma + \gamma'$
294m		$\sigma + \beta'$	831m	832w	$\sigma + 2\gamma'$
310s	310w	γ'		861s	4σ
363vw		$\sigma + 2\beta'$	961s	962m	$3\sigma + \gamma'$
439m		2σ		1066s	5σ
509m		$2\sigma + \beta'$	1139m		$4\sigma + \gamma'$
534s		$\sigma + \gamma'$			

[a] The frequencies are given relative to the ionization energy and vw denotes very weak, w denotes weak, m medium, and s strong.

D. Hole-Burning Spectra. Hole-burning (HB) spectra were recorded to confirm the assignment of the resorcinol·H_2O REMPI spectrum. A one-color (1 + 1) REMPI spectrum of resorcinol·H_2O is displayed in Figure 6a for comparison. Figure 6b presents the spectrum obtained with the burn laser set to the isomer Ia $S_1 0^0$ transition. Inspection of this spectrum reveals that the bands assigned to Isomers Ib and II are unaffected by the burn laser, whereas the $S_1 0^0$ band of isomer Ia is clearly diminished. The HB spectrum recorded with the burn laser set to the $S_1 0^0$ transition of isomer Ib (Figure 6c) shows that while the $S_1 0^0$ transition and σ and γ' modes are reduced in intensity, the $S_1 0^0$ transitions of the other isomers are unaffected. Finally,

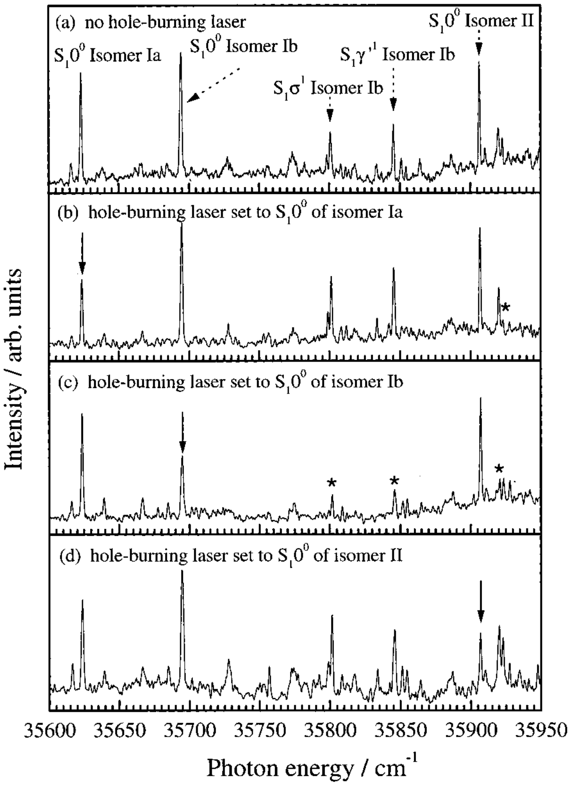

Figure 6. Hole-burning spectra of one-color (1 + 1) REMPI spectra of resorcinol·H_2O with (a) no hole-burning laser, and with the hole-burning laser set to the $S_1 0^0$ transition of (b) isomer Ia, (c) isomer Ib, and (d) isomer II. The arrows represent the positions of the hole-burning lasers and bands affected are marked with asterisks.

Figure 6d shows the spectrum obtained with the HB laser set to the $S_1 0^0$ transition of isomer II, confirming that no other major features are associated with this isomer. The HB spectra therefore confirm the presence of three isomers, and the assignment of the intermolecular vibrations of isomer Ib. They also exclude the existence of other isomers over this region of the spectrum, since all of the significant spectral features can be associated with isomers Ia, Ib, and II.

IV. Further Discussion

A. Comparison of Resorcinol·H_2O and Phenol·H_2O. Despite the overall similarities of the resorcinol·H_2O and phenol·H_2O spectra,[16] subtle differences in the spectra of the two complexes illustrate the influence of the second OH group. In the phenol·H_2O REMPI spectrum,[16] the γ' and σ modes display frequencies of 121 and 157 cm^{-1}, respectively. These values are somewhat larger than those observed for isomers Ia (104 and 150 cm^{-1}) and Ib (104 and 148 cm^{-1}), indicating that water interacts more strongly with phenol than resorcinol in the S_1 state. The σ mode occurs at 240 cm^{-1} in the phenol·H_2O ZEKE spectrum,[16] compared to 215, 223, and 214 cm^{-1} in the spectra of isomers Ia, Ib, and II, which again indicates that the intermolecular bond is stronger in $[\text{phenol}\cdot H_2O]^+$ than in each of the $[\text{resorcinol}\cdot H_2O]^+$ isomers. These conclusions are substantiated by the comparatively weaker $S_1 0^0$ and ionization energy red shifts displayed by all three resorcinol·H_2O isomers.

The ab initio calculations[29] offer a possible explanation for the weaker resorcinol·H_2O bond. A higher positive charge localizes on the hydroxyl group hydrogen atom in phenol·H_2O compared to resorcinol·H_2O, implying that phenol is more polarizable than resorcinol. We note that the lower interaction energy of water with resorcinol compared to phenol is unexpected in the context of the comparatively higher gas-phase acidity of resorcinol. (Previous studies have established a correlation between the acidity of phenols and their propensity to hydrogen bond.[30,31])

B. Comparison of the Resorcinol•H_2O Isomers. The spectra of isomer Ib deviate most from the spectra of the other resorcinol·H_2O isomers, and from the spectra of phenol·H_2O.[1b] The ab initio results indicate that this effect originates from the considerable distortion of the water molecule−resorcinol OH group geometry from the optimal geometry for hydrogen bonding in the neutral cluster, presumably due to the hydrogen atoms of the water molecule being stabilized by an interaction with the oxygen atom of the second OH group. This interaction may explain the blue shift of the $S_1 0^0$ transition compared to the other resorcinol·H_2O isomers, since a similar interaction in the phenol dimer cluster results in a blue shift of the $S_1 0^0$ transition compared to the phenol monomer.[32] A comparison of the σ mode frequencies for the three isomers (215 (Ia), 223 (Ib), and 214 cm^{-1} (II)) illustrates that isomer Ib is the most strongly bound cation. It would be useful to obtain MATI dissociation spectra[28] of the three resorcinol·H_2O isomers to allow a quantitative comparison of the interaction energies.

The ab initio calculated geometries of the intermolecular bonds in isomers Ia and II are quite close to that of phenol·H_2O,[17,20] although in isomer Ia the water molecule tilts slightly away from the free OH group of resorcinol (compared to the angle it adopts in phenol·H_2O) presumably due to a slightly repulsive interaction between the water hydrogens and the hydrogen of the free OH group. This situation is reversed in isomer II, where the water molecule tilts slightly toward the second OH group (compared to the phenol·H_2O angle) due to an interaction with the oxygen of this OH group. This difference may explain the blue shift in the $S_1 0^0$ transition of isomer II compared to isomer Ia.

We are aware of no other REMPI/ZEKE studies where direct comparisons can be made with the results of this work. Only a single isomer was identified in a REMPI study of catechol·H_2O.[12] Two rotational isomers have been identified in the 1,4-dimethoxybenzene·Ar cluster,[33] but in this system, the dominant intermolecular interaction consists of dispersion forces between the rare gas atom and the aromatic ring. The argon atom is thought to bind above the aromatic ring, and the intermolecular bond is relatively insensitive to the orientation of the methoxy groups.

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