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Observation of Rotational Isomers II: A ZEKE and Hole-Burning Spectroscopy Study of Hydrogen-Bonded 3-Methoxyphenol·Water Clusters

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Three rotational isomers of 3-methoxyphenol·water have been identified using resonance-enhanced multiphoton ionization (REMPI) and hole-burning and zero electron kinetic energy (ZEKE) photoelectron spectroscopies with the aid of ab initio and density functional theory calculations. The S_1 band origins of the isomers were measured as 35 822, 35 834, and 36 019 ± 1 cm^{-1} and the adiabatic ionization energies as 61 049, 61 801, and 62 120 ± 5 cm^{-1} for isomers IV, I, and III, respectively. The frequencies of the intermolecular vibrations and the $S_1 0^0$ and ionization energy red shifts reveal that the water molecule hydrogen bonds more weakly to 3-methoxyphenol than to phenol. We discuss the spectral characteristics of the rotational isomers by considering the perturbation of the 3-methoxyphenol·H_2O intermolecular hydrogen bond by the −OCH_3 group.

I. Introduction

3-Methoxyphenol (3MP) can exist in different isomeric forms that are related through the rotations of −OH and −OCH_3 substituent groups.[1−3] A substantial rotational barrier exists (∼1050 cm^{-1}),[1] allowing various rotational isomers to be isolated in a supersonic jet expansion. Isomeric molecular complexes can then be generated with a single solvent molecule frozen at different binding sites on the solute if the barrier for interconversion between isomers is sufficiently high.[4−10] This paper reports a spectroscopic study of the rotational isomers of 3MP·H_2O illustrated in Figure 1. We find that the water ligand in 3MP·H_2O hydrogen bonds to the phenolic −OH group, letting us probe the varying extent to which the intermolecular bond is perturbed by the −OCH_3 group in different isomers. These studies also allow us to investigate subtle differences in the binding site adopted by a solvent molecule on a series of similar solutes.

In a previous study,[7] we identified three rotational isomers of resorcinol·H_2O using a combination of REMPI and ZEKE spectroscopy.[11−13] These techniques have been demonstrated to be powerful tools for probing the structure of neutral and cationic molecular complexes.[14] Hole-burning spectroscopy[15] was employed to confirm that three isomers were present in the REMPI spectrum. A careful analysis of the spectra aided by ab initio calculations led to the identification of the rotational isomers and therefore allowed an analysis of the extent to which the resorcinol·H_2O intermolecular hydrogen bond was perturbed by the second −OH group in each of the rotational isomers. One of the notable results of the resorcinol·H_2O study was that the water molecule hydrogen bonds more weakly to resorcinol than to phenol. By considering differences in the spectral characteristics of the resorcinol·H_2O isomers compared to those of phenol·H_2O, we concluded that the dominant effect of the second −OH group is electronic. The effect was tentatively attributed to the resorcinol −OH groups being less polarizable than the single −OH group of phenol. A subsequent study of the rotational isomers of resorcinol·CO also indicated that CO hydrogen bonds more weakly to resorcinol than phenol.[8]

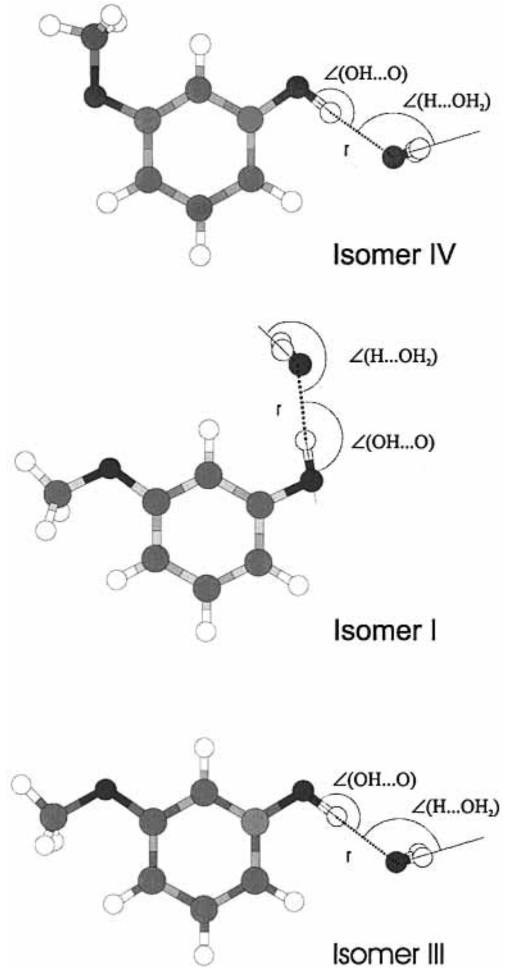

Figure 1. Geometrical structures of the 3MP·H_2O isomers. Table 1 lists the intermolecular parameters obtained from the HF/cc-pVDZ and B3LYP/cc-pVDZ calculations. The dihedral angle between the H_2O and phenyl plane is 90.0° in all the complexes.

The methoxy group in 3MP may exert both electronic and steric perturbations on the intermolecular hydrogen bond compared to the −OH group in resorcinol·H_2O, which should

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TABLE 1: Intermolecular Geometric Parameters (Figure 1) Obtained from HF/cc-pVDZ and DFT/cc-pVDZ Calculations of the S_0 and D_0 States of the Rotational Isomers of 3MP·H_2O[a]

		isomer I	isomer III	isomer IV
HF	r/Å	1.954	1.948	1.945
		(1.727)	(1.743)	(1.735)
	∠(OH···O)/deg	177.8	178.4	176.8
		(178.4)	(178.4)	(178.6)
	∠(H···OH_2)/deg	207.7	141.8	146.2
		(152.7)	(148.7)	(150.4)
DFT	r/Å	1.807	1.813	1.810
		(1.599)	(1.615)	(1.608)
	∠(OH···O)/deg	178.5	177.8	177.6
		(176.6)	(177.6)	(177.6)
	∠(H···OH_2)/deg	131.3	128.6	129.0
		(142.1)	(140.6)	(141.9)

[a] Values for the D_0 state are shown in parentheses.

be evident in the REMPI and ZEKE spectra of the 3MP·H_2O complexes. HF/cc-pVDZ and B3LYP/cc-pVDZ calculations are presented to aid the interpretation of the spectra. Methoxyphenols form integral parts of lignin and other biologically important substances,[16] so an understanding of the geometric structures of simple 3MP complexes could lead to a better understanding of these larger systems. We are unaware of any previous studies of van der Waals or hydrogen-bonded complexes of 3MP.

II. Experimental Section

3MP·H_2O clusters were produced in a supersonic jet expansion of 3MP 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 140−160 °C. The apparatus and techniques used in this study were described in detail in the previous paper.[3]

III. Results and Discussion

A. Ab initio and Density Functional Theory Calculations of 3MP·H_2O. Geometric structures of the neutral (S_0) and cationic (D_0) ground-states of 3MP·H_2O were obtained from HF/cc-pVDZ and B3LYP/cc-pVDZ calculations using GAUSSIAN 98.[17] Calculations at the MP2 level of theory were considered to be beyond the scope of this work due to the expense of calculating harmonic frequencies. The cc-pVDZ basis set was chosen because it has been shown to give reliable results for water clusters.[7,18]

Harmonic frequencies were computed to confirm that optimized structures corresponded to local minima and to determine zero point energy (ZPE) corrections. The reported vibrational frequencies are not scaled, and no scaling factor was applied when calculating the ZPE corrections due to the uncertainty in appropriate scaling factors for cations. Spin-unrestricted orbitals were employed in the D_0 state calculations. As in the 3MP calculations,[3] the expectation value of the S^2 operator was substantial in the HF calculations (0.929−0.933), leading us to view these results with some caution. The density functional theory (DFT) calculations are not susceptible to this limitation.[19]

Only complexes based on the previously observed 3MP monomers (I, IV, and III) with 3MP as the proton donor were studied, since the observation of the respective isomer in the jet expansion is a necessary prerequisite to observing the corresponding isomeric complex. An intermolecular geometry analogous to that of phenol·H_2O was used as a starting point in all calculations.[20,21] Intermolecular geometrical parameters for the neutral and cationic states of the rotational isomers are included in Table 1. A second, higher-energy S_0 state isomer I was also identified in the HF calculations.[22] No analogous isomer was found in resorcinol·H_2O, and we anticipate that the barrier height for interconversion of the two structures should be modest so that the system is quenched into the lowest-energy minimum in the jet expansion. A calculation of the potential energy surface of isomer I was beyond the scope of this work.

The C_s symmetry structures obtained for each of the 3MP·H_2O isomers resemble the structure of phenol·H_2O, with the water molecule hydrogen bonding to the −OH group through its oxygen atom. As in resorcinol·H_2O, the solvent adopts a localized binding site on the surface of 3MP, rather than interacting with the overall dipole moment of the solute. In neutral isomers III and IV, the H···OH_2 angles of the water molecule to the OH group (141.8° and 146.2°) are similar to the angle of 141.2° found in phenol·H_2O.[21] However, in neutral isomer I, this angle is considerably distorted (207.7°). The calculations predict that a substantial geometry change occurs along this coordinate between the S_0 and D_0 states for isomer I, with the effect that the angle is similar in the three cationic complexes (~150°). For each isomer, the intermolecular bond length, r, contracts considerably from S_0 to D_0 due to the introduction of the charge−dipole interaction in the cation.

Table 2 displays the absolute energies of the S_0 states of the rotational isomers along with the ZPE-corrected values. Basis set superposition error (BSSE) corrected binding energies of the complexes are also presented. Isomer IV is the lowest-energy isomer in both sets of calculations, although the absolute energies of isomers I and IV are close. Isomer I represents the most strongly bound neutral complex in the DFT calculations, while isomer IV is the most strongly bound complex in the HF calculations. However, it is notable that the calculated binding energies of the three neutral complexes are extremely close.

The absolute energies and ZPE-corrected values for the D_0 states of the rotational isomers are displayed in Table 3, along with BSSE-corrected binding energies. Isomer IV is the lowest-energy isomer in both the HF and DFT calculations and represents the most strongly bound cationic complex. The calculated adiabatic ionization energies (IE) represent the difference between the total energy of the optimized neutral and the corresponding optimized cation. Relative IEs are

TABLE 2: Absolute Energies of the S_0 States of the Rotational Isomers of 3MP·H_2O Obtained from HF/cc-pVDZ and B3LYP/cc-pVDZ Calculations[a]

	HF (Hartrees)	DFT (Hartrees)	relative energy (cm^{-1})		binding energy (cm^{-1})	
			HF	DFT	HF	DFT
isomer I	−495.517 629	−498.456 685	31	30	1937	2270
	(−495.345 196)	(−498.295 884)	(29)	(48)		
isomer III	−495.516 984	−498.456 312	142	112	1951	2261
	(−495.344 700)	(−498.295 600)	(138)	(110)		
isomer IV	−495.517 631	−498.456 822	0	0	1954	2267
	(−495.345 328)	(−498.296 103)	(0)	(0)		

[a] Zero-point energy-corrected values are given in parentheses. Relative energies and BSSE-corrected binding energies are also presented.

TABLE 3: Absolute Energies of the D_0 States of the Rotational Isomers of 3MP·H_2O Obtained from HF/cc-pVDZ and B3LYP/cc-pVDZ Calculations[a]

			IE (cm^{-1})		relative IE (cm^{-1})		BE (cm^{-1})[b]
	HF (Hartrees)	DFT (Hatrees)	HF	DFT	HF	DFT	DFT
isomer I	−495.292621	−498.194490	49350	57542	834	800	6691
	(−495.120 893)	(−498.033 650)	(49 268)	(57 550)	(793)	(704)	
isomer III	−495.290 012	−498.192 598 7	49 812	57 875	1296	1029	6833
	(−495.118 365)	(−498.031 880)	(49 672)	(57 876)	(1197)	(1030)	
isomer IV	−495.296 564	−498.198 270	48 516	56 742	0	0	6911
	(−495.124 445)	(−498.037 076)	(48 475)	(56 846)	(0)	(0)	

[a] Zero-point energy-corrected values are given in parentheses. Ionization energies (IEs) and BSSE-corrected binding energies (BEs) are also presented. [b] B3LYP/cc-pVDZ.

TABLE 4: Harmonic Frequencies (in cm^{-1}) of the Intermolecular Vibrations of the Rotational Isomers of $[3MP\cdot H_2O]^+$ from HF/cc-pVDZ and B3LYP/cc-pVDZ Calculations[a]

	isomer I		isomer III		isomer IV	
	HF	DFT	HF	DFT	HF	DFT
β''	67	70	49	51	54	57
β'	73 (64)	80	89 (75)	93	87 (79)	95
τ	167	179	195	192	195	196
σ	203 (203)	218	196 (194)	213	185 (181)	190
A'	263 (253)	270	257 (242)	254	257 (251)	274
γ'	334	347	366	361	362 (353)	359
γ''	372	377	370	373	375	375

[a] Experimental frequencies are shown in parentheses.

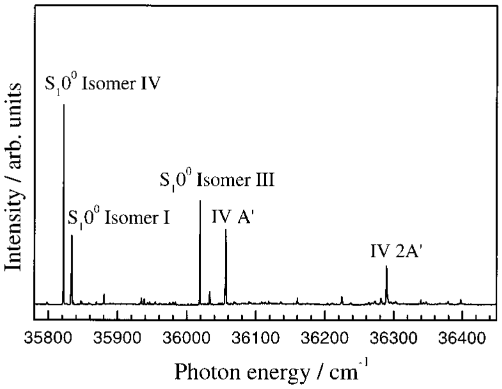

Figure 2. Two-color (1 + 1′) REMPI spectrum of the 3MP·H_2O cluster recorded with the ionization laser set to 27 000 cm^{-1}.

TABLE 5: Frequencies of Vibronic Features Observed in the REMPI Spectrum of the 3MP·H_2O Cluster[a]

$S_1 \leftarrow S_0$ energy/cm^{-1}	assignment	$S_1 \leftarrow S_0$ energy/cm^{-1}	assignment
35822s	IV 0^0	36057m	IV A'
35834s	I 0^0	36160w	?
35880w	?	36224w	?
36019m	III 0^0	36289m	IV $2A'$
36033w	?		

[a] Intensities are denoted by w (weak), m (medium), and s (strong), and ? denotes a peak which could not be assigned.

included in Table 3 to facilitate comparison with the experimental results. Both sets of calculations predict that the IEs should increase substantially in the order of isomer IV < isomer I < isomer III, and the rotational isomers should therefore be readily distinguishable.

Table 4 lists the intermolecular vibrational modes of the D_0 states of the rotational isomers. 3MP·H_2O should display six intermolecular frequencies, namely, out-of-plane bend (β''), in-plane bend (β'), torsion (τ), stretch (σ), in-plane wag (γ'), and out-of-plane wag (γ''). Inspection of the calculated harmonic vibrations reveals that an additional mode, A', which appears at ∼260 cm^{-1}, corresponds to a large degree of intermolecular vibration. This mode is nominally an intramolecular in-plane bend of the $-OCH_3$ group (appearing at ∼250 cm^{-1} in the monomers) but contains a substantial contribution from the γ' and σ intermolecular vibrations.

The calculated frequencies indicate that it should be possible to identify the isomers by comparing intermolecular vibrations which appear in the ZEKE spectra of the complexes. σ should appear at a lower frequency for isomer IV than for isomers I and III, while β' should occur at a lower frequency for isomer I than for isomers III and IV.

B. REMPI Spectra of 3MP·H_2O. Figure 2 displays the two-color (1 + 1′) REMPI spectrum of 3MP·H_2O obtained with the ionization laser set to 27 000 cm^{-1}. The REMPI spectrum is dominated by three strong features at 35 822, 35 834, and 36 019 ± 1 cm^{-1}, which are assigned as the S_10^0 transitions of isomers IV, I, and III. These features can be related to the rotational isomers of 3MP by considering the spectral shifts of the cluster S_10^0 transitions compared to the origin transitions in the monomer REMPI spectrum.[3] In phenol·H_2O,[20] the S_10^0 transition is red-shifted by 352.5 cm^{-1} relative to the corresponding monomer transition, and we anticipate that similar red shifts should be observed for the 3MP·H_2O complexes. The feature at 36019 cm^{-1} is red-shifted by 183 cm^{-1} relative to the S_10^0 transition of 3MP isomer III and can be straightforwardly assigned to isomer III of 3MP·H_2O. The features at 35 822 and 35 834 cm^{-1} are then assigned as the S_10^0 transitions of isomers IV and I of 3MP·H_2O, respectively. This assignment is primarily based on the IE red shifts presented in section III.D. The S_10^0 red shifts of isomers IV and I are therefore 212 and 140 cm^{-1}, respectively. For each of the rotational isomers, the red shifts are considerably smaller than the values for both the phenol·H_2O and resorcinol·H_2O isomers (320, 249, and 291 cm^{-1} for isomers Ia, Ib, and II).[7]

Table 5 lists the frequencies of vibronic features observed in the 3MP·H_2O REMPI spectrum. Apart from the S_10^0 transitions, the only notable features occur at 36 057 and 36 289 cm^{-1} and are assigned to a progression built off the isomer IV S_10^0 transition with a frequency of 235 cm^{-1}. This feature appears to represent the same vibronic mode observed 224 cm^{-1} above the origin in the REMPI spectrum of the monomer and is assigned to the A' intramolecular mode on the basis of a ZEKE spectrum recorded via this S_1 intermediate level (section III.D). The observation of an A' progression built of the isomer IV band origin is evidence that the isomers are correctly assigned. Finally, we note that the weak intensity of any intermolecular vibrations in the REMPI spectrum indicates that the intermolecular bonds in the three complexes undergo little structural change upon $S_1 \leftarrow S_0$ excitation.

C. Hole-Burning Spectra of 3MP·H_2O. Hole-burning spectra were recorded to confirm the existence of three isomers

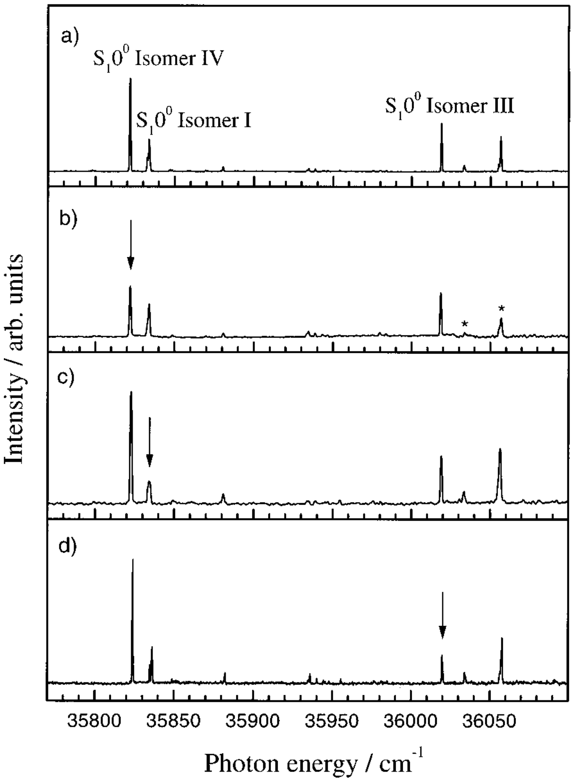

Figure 3. Hole-burning spectra of two-color (1 + 1′) REMPI spectra of $3MP{\cdot}H_2O$ (a) without the hole-burning laser and with the hole-burning laser set to the S_10^0 transition of (b) isomer IV, (c) isomer I, and (d) isomer III. The arrows represent the positions of the hole-burning laser, and the bands affected are marked with asterisks. The ionization laser was set to 27 000 cm^{-1}.

in the REMPI spectrum of $3MP{\cdot}H_2O$. As in 3MP,[3] hole-burning was applied with two-color (1 + 1′) REMPI excitation, since one-color (1 + 1) excitation resulted in extensive fragmentation. A two-color (1 + 1′) REMPI spectrum of $3MP{\cdot}H_2O$ is displayed in Figure 3a for comparison with the hole-burning spectra (Figure 3b−d).

Figure 3b shows the spectrum obtained with the burn laser set to the isomer IV S_10^0 transition. Inspection of this spectrum reveals that the features assigned to the isomer I and III S_10^0 transitions are unaffected by the burn laser, whereas the S_10^0 band of isomer IV is clearly diminished. The features at 36 033 and 36 057 cm^{-1} are also reduced in intensity by the burn laser and are therefore associated with isomer IV. Figure 3c shows the hole-burning spectrum recorded with the burn laser set to the S_10^0 transition of isomer I, and illustrates that the S_10^0 transitions of isomers IV and III are unaffected. Finally, Figure 3d displays the spectrum obtained with the hole-burning laser set to the S_10^0 transition of isomer III and shows that this feature represents a distinct band origin. The hole-burning spectra therefore confirm the presence of three isomers and the assignment of the isomer IV *A*′ progression. In addition, they exclude the existence of other isomers over this region of the spectrum, since all of the significant spectral features can be associated with isomers IV, I, and III.

D. ZEKE Spectra of $3MP{\cdot}H_2O$. ZEKE spectra recorded via the S_10^0 transitions of the $3MP{\cdot}H_2O$ isomers are presented in Figure 4. The spectra display rich excitations of a number of low-frequency modes, indicating that a substantial change in the intermolecular geometry occurs between the S_1 and D_0 states. In each spectrum, the lowest-energy feature is assigned to the vibrational ground state of the cation ($D_0 \leftarrow S_1$), giving IEs of 61 049 (IV), 61 801 (I), and 62 120 (III) ± 5 cm^{-1}. The observation of three distinct IEs is a strong indication that three different isomeric species are present in the S_1-state spectrum. The IEs correspond to red shifts of 3692 (IV), 3427 (I), and 3528 ± 10 cm^{-1} (III), all of which are considerably smaller than the phenol·H_2O red shift of 4601 cm^{-1} [20] and somewhat smaller than the red shifts of the resorcinol·H_2O isomers [4060 (Ia), 3924 (Ib), and 4063 (II)].[7] We note that if the assignments of the S_10^0 transitions of isomers IV and I are reversed, significantly different red shifts are obtained [2940 (IV) and 4179 (I)]. It is highly unlikely that rotational isomers would display such different red shifts, since the ligand binding should only be moderately different in the three complexes. Furthermore, the DFT calculations predict that the IEs of the $3MP{\cdot}H_2O$ isomers should increase in the order of IV < I < III, with the values for isomers I and III being 704 and 1030 cm^{-1} higher. This prediction is in excellent agreement with the experimental values of 752 and 1071 ± 10 cm^{-1}.

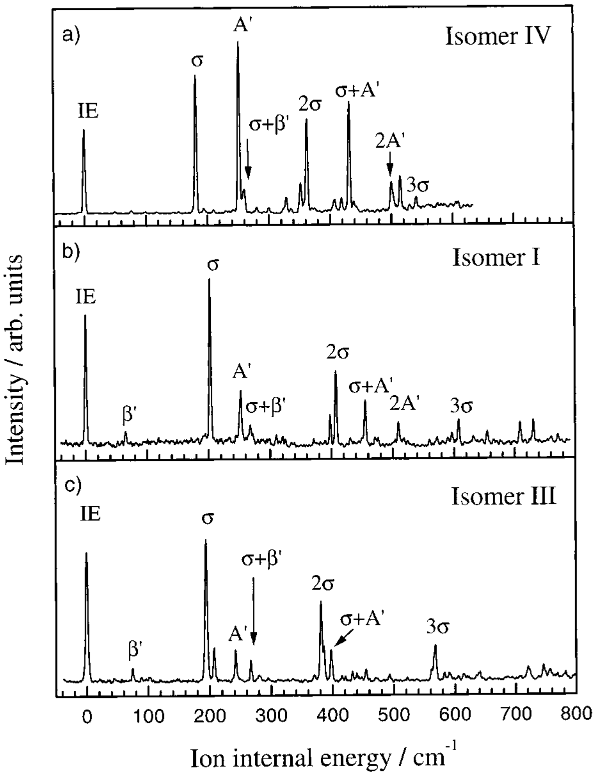

Figure 4. ZEKE spectra of $3MP{\cdot}H_2O$ recorded via the S_10^0 state of (a) isomer IV, (b) isomer I, and (c) isomer III. Each spectrum is displayed relative to the respective ionization energy. Assignments of the in-plane bend (β'), intramolecular $-OCH_3$ in-plane bend (A'), and intermolecular stretch (σ) are included on the spectra.

The ZEKE spectra of all three isomers display a prominent vibrational progression spaced by ~190 cm^{-1}, which can be assigned by comparison with the calculations (Table 4) and the ZEKE spectra of resorcinol·H_2O as σ. More than three quanta of excitation are evident in this mode due to the ionization-induced contraction of the intermolecular bond.[20,23−25] In contrast to σ progressions of the phenol·H_2O and resorcinol·H_2O, the σ progressions in the $[3MP{\cdot}H_2O]^+$ spectra appear to be harmonic within the experimental resolution. The feature at approximately 70 cm^{-1} is assigned to β' and also appears in combination with σ.

Progressions and combinations of a third mode, which displays a frequency of ~250 cm^{-1}, are also evident in the three ZEKE spectra. In resorcinol·H_2O, γ' occurs around 370 cm^{-1} for isomers I and II, and the calculations predict that it should appear at ~350 cm^{-1} in the $[3MP{\cdot}H_2O]^+$ isomers. Therefore,

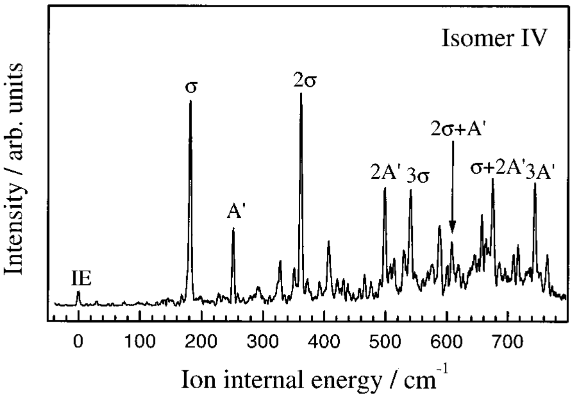

Figure 5. ZEKE spectrum of $3MP{\cdot}H_2O$ recorded via the S_1 *A′* state of isomer IV. The spectrum is displayed relative to the ionization energy. Assignments of the in-plane bend (β'), intramolecular $-OCH_3$ in-plane bend (*A′*), and intermolecular stretch (σ) are included on the spectrum.

TABLE 6: Frequencies (in cm^{-1}) of Vibronic Features Observed in the ZEKE Spectra of the $3MP{\cdot}H_2O$ Isomers Recorded via the S_10^0 States and the S_1 *A′* State of Isomer I[a]

isomer IV via S_10^0	isomer I via S_10^0	isomer III via S_10^0	isomer IV via $S_1\,9a_1$	assignment
79	64w	75w	–	β'
181s	203s	194s	182s	s
		207m		?
251s	253m	242m	252m	A'
260w	268w	267m	–	$\sigma + \beta'$
			293w	$9a_1$
328w			327m	*b*
353m			350w	γ'
	397			?
362s	407m	381m	361s	2σ
			371w	$9a_1 + \beta'$
			393w	?
407w			407m	327 $cm^{-1} + \beta'$
419w				?
431s	445m	398		$\sigma + A'$
		456		$2\sigma + \beta'$
501s	510m	–	499m	$2A'$
515m				?
			530	$\sigma + \gamma'$
540w	608w	569m	541m	3σ
			589m	$9a_2$
–	655w	–	610m	$2\sigma + A'$
			657m	*b*
–	709w	–	675m	$\sigma + 2A'$
	730w			?
			709w	?
			718w	4σ
		720w		?
–	–	–	745m	$3A'$

[a] The frequencies are given relative to the IE. Intensities are denoted by w (weak), m (medium), and s (strong). ? indicates a feature which could not be assigned. [b] In an alternative assignment, these features could represent $9a_1$ and $9a_2$.

the mode at 250 cm^{-1} is assigned to the *A′* intramolecular vibration. The prominent appearance of this mode in the ZEKE spectra appears to arise from it being coupled to σ (and γ'), and it is particularly strong in the ZEKE spectrum of isomer IV. γ' does not appear prominently in any of the ZEKE spectra.

A ZEKE spectrum recorded via the S_1 *A′* state of isomer IV is shown in Figure 5, and the vibronic features observed in this spectrum are included in Table 6. The lowest-energy feature appears at 61 042 ± 5 cm^{-1}, in excellent agreement with the IE obtained from the spectrum recorded via the S_10^0 transition and confirming that the IV S_10^0 and *A′* features in REMPI spectrum can be attributed to the same isomer. In accord with the $\Delta\nu = 0$ propensity rule,[12] excitation of *A′* in this ZEKE spectrum is enhanced compared to the spectrum recorded via S_10^0. It is possible that the feature at 293 cm^{-1} (with an overtone at 589 cm^{-1}) corresponds to the $9a_1$ internal rotational transition discussed in the previous paper.[3]

An assignment of the features observed in the ZEKE spectra of the $3MP{\cdot}H_2O$ isomers in Figures 4 and 5 is included in Table 6. The frequencies of the intermolecular vibrations are in excellent agreement with the calculated values and confirm the identity of the isomers. For example, β' appears at the lowest frequency for isomer I, and σ appears at the lowest frequency for isomer IV.

IV. Further Discussion

A. Comparison of the $3MP{\cdot}H_2O$ isomers. As in resorcinol·H_2O, differences in the ZEKE spectra of the three rotational isomers of $3MP{\cdot}H_2O$ allow us to assign the isomers and provide insight into the properties of the different binding sites displayed by the isomeric complexes. The calculations predict that the intermolecular bond in isomer I of $3MP{\cdot}H_2O$ is significantly distorted compared to phenol·H_2O and the other $3MP{\cdot}H_2O$ isomers, due to the hydrogen atoms of the water molecule interacting with the distant oxygen atom of the $-OCH_3$ group. This effect is evident in the comparatively smaller S_10^0 and IE red shifts, and may explain the blue shift of the S_10^0 transition of isomer I compared to the other isomers of $3MP{\cdot}H_2O$, since a similar interaction in the phenol dimer cluster results in a blue shift of the S_10^0 transition.[29]

For all three rotational isomers of $3MP{\cdot}H_2O$, little intermolecular vibrational excitation is observed in the S_1 state spectrum, indicating that the intermolecular geometry changes between the S_0 and S_1 states are small. However, isomer IV displays prominent excitation of the *A′* vibration, in contrast to the other isomers. It is possible that the oxygen lone pairs of the $-OH$ group are interacting with the methoxy hydrogen atoms in this conformation and promoting a $S_1 \leftarrow S_0$ geometry change. The water molecule seems to promote this effect because the Franck−Condon factors for *A′* excitation are greater in the cluster spectrum compared to in the monomer specturm.[3] If we compare the Franck−Condon patterns of vibrational features in the ZEKE spectra of the $3MP{\cdot}H_2O$ isomers, the most notable difference occurs in excitation of the *A′* mode. This appears extremely strongly in the isomer IV spectrum and can again be attributed to an interaction of the $-OH$ oxygen lone pairs with the methoxy hydrogen atoms.

The magnitude of the IE red shifts should indicate the relative strength of binding of the water molecule in the three cationic clusters. Isomer IV displays the largest IE red shift, indicating that the water is bound most strongly in this isomer, in line with the calculated BSSE-corrected binding energies (Table 3). It would be useful to obtain the MATI dissociation spectra of the $[3MP{\cdot}H_2O]^+$ isomers to provide experimental binding energies for the S_0, S_1, and D_0 states.[24,30]

Finally, we note that the relative intensities of the S_10^0 transitions of the three isomeric complexes in the REMPI spectrum of $3MP{\cdot}H_2O$ are strikingly different from the corresponding features in the monomer REMPI spectrum.[3] The intensities of the S_10^0 transitions are fairly similar in the monomer spectra, whereas the isomer IV band origin is approximately twice as intense as the isomer I and III origins for the complexes. For a series of rotational isomers, we expect the $S_1 \leftarrow S_0$ transition moments to be similar, and the relative intensities of the S_10^0 features should therefore reflect either the relative stability or relative rates of formation of the ground-state complexes. The ab initio and DFT calculations predict comparable binding energies for the 3MP·H_2O complexes, which could indicate that isomer IV is formed more rapidly than the other rotational isomers under the experimental conditions employed. We note that it is also possible that the relative stabilities of larger water clusters might influence the observed concentrations of the 1:1 complexes, and ab initio calculations of the structures and binding energies of the 1:2 complexes could shed light on the observed intensities.

B. Comparison of 3MP·H_2O with Phenol·H_2O and Resorcinol·H_2O. The 3MP·H_2O rotational isomers studied in this work, like the related isomers of resorcinol·H_2O, share many characteristics with phenol·H_2O. In all of these complexes, the water ligand adopts a localized binding site at the phenolic −OH group and hydrogen bonds through its oxygen atom. While the REMPI spectra display relatively little intermolecular excitation, the ZEKE spectra display rich vibrational excitation of intermolecular modes, in line with a substantial change in the intermolecular geometry upon ionization. Despite the overall similarities, subtle differences in the spectra of the three systems illustrate the influence of additional substituents on the intermolecular hydrogen bond.

In resorcinol·H_2O,[7] the most notable effect of substitution was an electronic effect which resulted in the water molecule being less strongly bound to resorcinol than to phenol. This was evident in the lower spectral red shifts and lower frequency intermolecular modes. Steric and direct electrostatic interactions between the hydrogen-bonded water and the remote second −OH group appeared to play a smaller role. These results are reflected in the REMPI and ZEKE spectra of the 3MP·H_2O isomers. The spectral red shifts and intermolecular vibrational frequencies again indicate that the water ligand is less strongly bound to 3MP than to both phenol and resorcinol. For example, the IE red shift of phenol·H_2O is 4601 cm^{-1}, and the red shifts of the resorcinol·H_2O isomers lie between 3924 and 4063 cm^{-1}, whereas the red shifts of the 3MP·H_2O isomers are 3427−3692 cm^{-1}. In addition, the σ vibration in the $[\text{phenol}\cdot H_2O]^+$ and $[\text{resorcinol}\cdot H_2O]^+$ isomers appear at frequencies of 240 cm^{-1} and 214−223 cm^{-1}, respectively, whereas the $[\text{3MP}\cdot H_2O]^+$ isomers display much smaller σ frequencies of 181−203 cm^{-1}.

The comparatively weaker intermolecular bond in resorcinol compared to that of phenol was attributed to the phenolic −OH group being less polarizable in resorcinol. A similar, but more substantial, effect appears to be operating in 3MP.[31] The $-OCH_3$ group of 3MP is regarded as more inductively "electron donating" than the −OH group of resorcinol and therefore reduces the polarity of the phenol group involved in the hydrogen bond. In future work, it would be useful to test this hypothesis by investigating the REMPI and ZEKE spectra of a phenolic molecule with an electron withdrawing group, e.g., 3-nitrophenol or 3-cyanophenol.

It is of particular interest to compare the spectral characteristics of isomer I of 3MP·H_2O with isomer Ib of resorcinol·H_2O,[7] since the water molecule is able to interact directly with the substituent group in these isomers. (In isomer Ib of resorcinol·H_2O, the solvent adopts a geometry with respect to the solute similar to the geometry in isomer I of 3MP·H_2O, where its hydrogen atoms can interact with the oxygen of the second functional group.) The spectra of isomer I should therefore provide information on the extent to which the larger methoxy group influences the intermolecular hydrogen bond. Both isomers display the smallest $S_1 0^0$ and IE red shifts, and their ZEKE spectra show the highest-frequency σ vibration, leading to a picture where isomer I of 3MP·H_2O and isomer Ib of resorcinol·H_2O share a number of spectral characteristics.

One important difference between the REMPI and ZEKE spectra of isomer Ib of resorcinol·H_2O and isomer I of 3MP·H_2O is the Franck−Condon factors for excitation of intermolecular modes. The S_1 state spectrum of isomer Ib of resorcinol·H_2O displays strong σ and γ' features, and the excitation of γ' is markedly different in the ZEKE spectra of resorcinol·H_2O isomers I and II compared to the ZEKE spectra of isomer Ib. These results are in line with a substantial geometry change occurring in isomer Ib upon $S_1 \leftarrow S_0$ excitation. However, no intermolecular modes are evident in the 3MP·H_2O isomer I S_1 state spectrum, and γ' excitation is not prominent in the ZEKE spectrum. It is possible that the larger methoxy group in 3MP reduces the propensity for the excitation of the intermolecular wag. Alternatively, these observations may suggest that we are observing the higher-energy undistorted isomer I geometry.[22] We currently favor the assignment of isomer I as the distorted structure due to the similarities of the $S_1 0^0$ and IE red shifts to isomer Ib of resorcinol·H_2O. In addition, it is unclear whether the prediction of two isomer I structures is reliable due to the low level of theory employed. Higher level (CASSCF) calculations are underway for both sets of complexes and may help to clarify the spectral results.[33]

Prior to our study of resorcinol·H_2O,[7] no other ZEKE studies of hydrogen-bonding rotational isomers were available. However, Fujii and co-workers have recently presented ZEKE spectra of the cis and trans isomers of *m*-cresol·H_2O.[9] The emphasis of this study was on how the intermolecular bond affected the $-CH_3$ internal rotational barrier. Once again, it is notable that the substituent group acts to weaken the intermolecular bond, since the σ feature appears at 227 cm^{-1} in cis-*m*-cresol·H_2O and 219 cm^{-1} in trans-*m*-cresol·H_2O. From an analysis of the ZEKE spectra of the two clusters, Fujii and co-workers concluded that the methyl rotation does not interact directly with the σ vibration. However, complexation clearly affects the internal rotational barrier, since the S_1-state barrier was enhanced by cluster formation while the D_0 barrier was lowered. Both isomers displayed the same trend, indicating that the effect of cluster formation was mostly electronic, in broad agreement with our results.

In summary, three rotational isomers of 3MP·H_2O have been observed in the REMPI and ZEKE spectra of the complex. Ab initio and density functional theory calculations have facilitated assignment of the isomers, allowing an analysis of the extent to which the intermolecular $-OH\cdots OH_2$ hydrogen bond is perturbed by the methoxy group. The perturbation is greatest for the isomer I complex, where the water molecule is closest to the $-OCH_3$ functional group. For all three complexes, the methoxy group is seen to exert an electronic effect on the $-OH\cdots OH_2$ bond, which weakens the intermolecular interaction compared to phenol·H_2O. In future work, it would be of interest to study water complexes of other substituted phenols to further investigate how the strength of intermolecular hydrogen bonds vary as a function of the substituent group.

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