

S₁-State Decay Dynamics of Benzenediols (Catechol, Resorcinol, and Hydroquinone) and Their 1:1 Water Clusters

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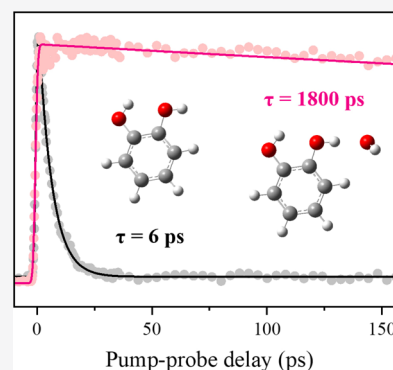


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ABSTRACT: The S₁-state decaying rates of the three different benzenediols, catechol, resorcinol, and hydroquinone, and their 1:1 water clusters have been state-specifically measured using the picosecond time-resolved parent ion transients obtained by the pump (excitation) and probe (ionization) scheme. The S₁ lifetime of catechol is found to be short, giving $\tau \sim 5.9$ ps at the zero-point level. This is ascribed to the H-atom detachment from the free OH moiety of the molecule. Consistent with a previous report (*J. Phys. Chem. Lett.* **2013**, 4, 3819–3823), the S₁ lifetime gets lengthened with low-frequency vibrational mode excitations, giving $\tau \sim 9.0$ ps for the 116 cm⁻¹ band. The S₁ lifetimes at the additional vibronic modes of catechol are newly measured, showing the nonnegligible mode-dependent fluctuations of the tunneling rate. When catechol is complexed with water, the S₁ lifetime is enormously increased to $\tau \sim 1.80$ ns at the zero-point level while it shows an unusual dip at the intermolecular stretching mode excitation ($\tau \sim 1.03$ ns at 146 cm⁻¹). Otherwise, it is shortened monotonically with increasing the internal energy, giving $\tau \sim 0.67$ ns for the 856 cm⁻¹ band. Two different asymmetric or symmetric conformers of resorcinol give the respective S₁ lifetimes of 4.5 or 6.3 ns at their zero-point levels according to the estimation from our transients taken within the temporal window of 0–2.7 ns. When resorcinol is 1:1 complexed with H₂O, the S₁ decaying rate is slightly accelerated for both conformers. The S₁ lifetimes of *trans* and *cis* forms of hydroquinone are measured to be more or less same, giving $\tau \sim 2.8$ ns at the zero-point level. When H₂O is complexed with hydroquinone, the S₁ decaying process is facilitated for both conformers, slightly more efficiently for the *cis* conformer.



INTRODUCTION

Understanding the excited-state dynamics of polyatomic molecules is one of the most challenging subjects in chemical physics. This is because the close-lying excited states are strongly coupled to give surface crossings among various electronic states. The resultant conical intersections are extended along the multidimensional seam coordinates, and it is nontrivial to distinguish and follow the adiabatic/nonadiabatic reaction pathways. Accordingly, many experimental and theoretical studies revealing multiple facets of the excited-state dynamics are definitely needed for grasping the whole dynamic picture of the polyatomic systems. In this aspect, a series of the recent studies on the $\pi\sigma^*$ -mediated nonadiabatic predissociation and/or tunneling dynamics is quite noteworthy. For instance, predissociation dynamics in the vicinity of the S₁($\pi\pi^*$)/S₂($\pi\sigma^*$) conical intersection have been both extensively and intensively investigated for phenols, thiophenols, thioanisoles, and many other heteroaromatic molecules.^{1–8} Overall reaction dynamics are found to be largely influenced by the subtle structural change of the reactive flux, which could be manipulated by the specific vibronic coupling,^{9–12} chemical substitution,^{13–18} or solvent clustering.^{1,14,19–22}

Herein, we have investigated the S₁ excited-state dynamics of three different dihydroxybenzenes (benzenediols): catechol

(1,2-dihydroxy benzene), resorcinol (1,3-dihydroxy benzene), and hydroquinone (1,4-dihydroxy benzene). The 1:1 water clusters with these molecules are also studied. Actually, spectroscopy and dynamics of the excited states of all three dihydroxybenzenes had been much studied to date.^{16,23–44} For instance, the state-specific S₁ lifetime of catechol was reported to be 7 or 11 ps at the S₁ origin and first quantum of the OH torsional mode, respectively.²⁹ This is more or less consistent with the results that was independently obtained from the femtosecond (fs)^{16,30} or picosecond (ps)^{32,33} time-resolved studies. It has been well established that the major S₁ decaying process of catechol is the H-atom detachment reaction from the free OH moiety.^{16,27} The decrease of the H-atom tunneling rate upon the out-of-plane torsional mode excitation had been attributed to the nonplanarity of the S₁ catechol.²⁹ The S₁ lifetimes of the other benzenediols had been reported numerous times but mostly at their zero-point energy (ZPE)

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levels. The S_1 lifetime of hydroquinone (though it was not conformer-selective) had been consistently reported to be 2.7–3.0 ns in several other studies, whereas the S_1 lifetime of resorcinol seems to be scattered in the literature, giving the lifetime in the 2.7–4.5 ns range.^{30,32,33,37} Though the lifetimes of benzenediols had been measured in the high- S_1 internal energy region using the fs pump–probe scheme, as the energetic window of the fs pulse is wide, the lifetime measurement was not conformer-specific.³⁰ It is interesting to note that the S_1 lifetime of the partially deuterated resorcinol, estimated from the high-resolution spectroscopic study, was reported to be in the 2.3–6.6 ns range,³⁶ indicating that the OH/OD substitution of resorcinol does not significantly impede the S_1 relaxation.³⁷ When benzenediols are complexed with a single water molecule, Morishima and co-workers^{32,33} had shown that the S_1 relaxation dynamics are significantly influenced by the modified potential energy surfaces especially in the vicinity of the $\pi\pi^*/\pi\sigma^*$ curve crossing regions.^{1,14} Consequently, it may open new S_1 relaxation pathways such as the excited-state hydrogen transfer (ESHT) or the bimolecular complex pair formation in the cluster in addition to the H-atom detachment and radiative/nonradiative transitions (internal conversion or intersystem crossing) which are more common for the monomer species.

In this work, we report the state-specific S_1 lifetimes of catechol at various vibronic levels employing the pump–probe scheme where the yield of parent or fragment ions is monitored as a function of the delay time between the pump (excitation) and probe (ionization) laser pulses. Using the narrow-band picosecond laser pulses ($\Delta E \sim 20 \text{ cm}^{-1}$ and $\Delta t \sim 1.7 \text{ ps}$), we could unambiguously identify individual conformers of resorcinol and hydroquinone in the jet. This makes possible to investigate the effect of the conformational structure on the S_1 decaying dynamics of these systems. The dynamic differences among three different benzenediols are discussed with the aid of ab initio calculations. Additionally, the S_1 -state lifetimes of 1:1 clusters of water with catechol, resorcinol, and hydroquinone are also estimated in a conformer-specific way. As the spectroscopic structures of those clusters are well documented in the literature, the relationship between the structure and dynamics in the cluster could be inferred from the present experimental results.

EXPERIMENTAL METHOD

Experimental details had been described elsewhere.^{12,45} Briefly, catechol, resorcinol, and hydroquinone were heated in a stainless-steel reservoir and vaporized to be mixed with a neon carrier gas of 2.4 bar. The gas mixture was then expanded into a high vacuum chamber (10^{-8} Torr) through an Even-Lavie pulsed valve ($\phi \sim 100 \mu\text{m}$) operating at a repetition rate of 200 Hz. The molecular beam was collimated by a 2 mm skimmer and crossed by picosecond pump–probe laser pulses ($\Delta E \sim 20 \text{ cm}^{-1}$ and $\Delta t \sim 1.7 \text{ ps}$). The parent or H fragment ions were accelerated into a time-of-flight tube and detected using a microchannel plate detector coupled with a phosphor screen. The ion signal was digitized using an oscilloscope and further processed using the home-built LabVIEW software. The decay time constants were extracted from the fits to the parent ion transients using the exponential decay function with the convolution of the Gaussian instrumental response function.^{12,18,45} The picosecond pump (270–280 nm) and probe (290 nm) pulses were generated by two separate units of the optical parametric amplifier, which were pumped by the

same fundamental output (791 nm, 1 kHz) of the picosecond Ti:Sapphire regenerative amplifier coupled with an 80 MHz femtosecond oscillator output (Vitara-T-HP, Coherent). The time delay between the pump and probe was controlled by a 220 mm long translational stage (DDS220, Thorlabs) where a hollow retroreflector is placed. During the measurement, the polarization axis of the pump pulse was maintained at the magic angle (54.7°) with respect to that of the probe pulse to avoid the contribution of the rotational dephasing. The equilibrium geometries of dihydroxybenzenes and their water clusters in the ground state were optimized using density functional theory (DFT) based on the M06-2X functional and the cc-pVDZ basis set in the Gaussian 09 program package.⁴⁶ The structures of the conformational isomers of clusters were obtained by repeating the optimization processes with several initial guesses of different geometric configurations. The vertical excitation energies were calculated using the time-dependent DFT at the same level of theory as above. The S_1 potential energy curves of monomers and clusters along the O–H extension coordinate have been obtained by the vertical energy calculations from the ground-state (S_0) geometries obtained by the rigid-scan where only the O–H bond distance is varied while all other geometrical parameters are frozen at the S_0 equilibrium geometries.

RESULTS AND DISCUSSION

The picosecond ($1 + 1'$) resonance two-photon ionization (R2PI) spectrum of the jet-cooled catechol shows distinct S_1 vibronic structures, Figure 1a. In the supersonic jet, the catechol is known to adopt the only one conformational isomer which is planar and one of the OH moieties is hydrogen-bonded to the adjacent OH moiety.^{24–27} Each vibronic band is appropriately assigned, whereas its S_1 lifetime has been measured precisely by the picosecond time-resolved parent ion transient. The lifetime (τ) at the zero-point level (0^0) is found to be $5.9 \pm 0.1 \text{ ps}$. Then it increases to $\tau = 9.0 \pm 0.2 \text{ ps}$ at the 116 cm^{-1} band corresponding to the first symmetry-allowed OH out-of-plane torsional mode (τ^1). It slightly decreases to $\tau = 7.9 \pm 0.5 \text{ ps}$ at the 257 cm^{-1} band (τ^2). The experimental fact that the S_1 lifetime of catechol gets increased with the increase of the vibrational energy is consistent with a previous report by Weiler et al.,²⁹ although absolute lifetime values here are somewhat different from previously reported ones.³² The seemingly unusual behavior of the lifetime with changing the energy should be attributed to the dynamic change of the tunneling barrier, namely, the $S_1(\pi\pi^*)/S_2(\pi\sigma^*)$ curve crossing is avoided more efficiently when the molecule becomes nonplanar, lowering the effective tunneling barrier for the H-atom detachment of catechol adopting the nonplanar geometry at ZPE. This is in accordance with the recent experimental studies on the tunneling dynamics of 2-methoxythiophenol, 2-fluorothiophenol, and 2-chlorothiophenol, although the tunneling rate is accelerated this time by the out-of-plane torsional mode excitations as these molecules adopt the planar geometries with respect to the SH tunneling coordinate at the S_1 ZPE.^{47–50} Dynamic shaping of the tunneling barrier by the upper-lying surface crossings along the multidimensional coordinates has also been nicely demonstrated in phenols⁵¹ and cresol.¹⁸ For catechol, the S_1 lifetimes of a number of vibronic bands in the higher energy region have been precisely measured, Figure 1c. Interestingly, the retardation effect of the torsional mode on the tunneling rate has also been observed for the combination

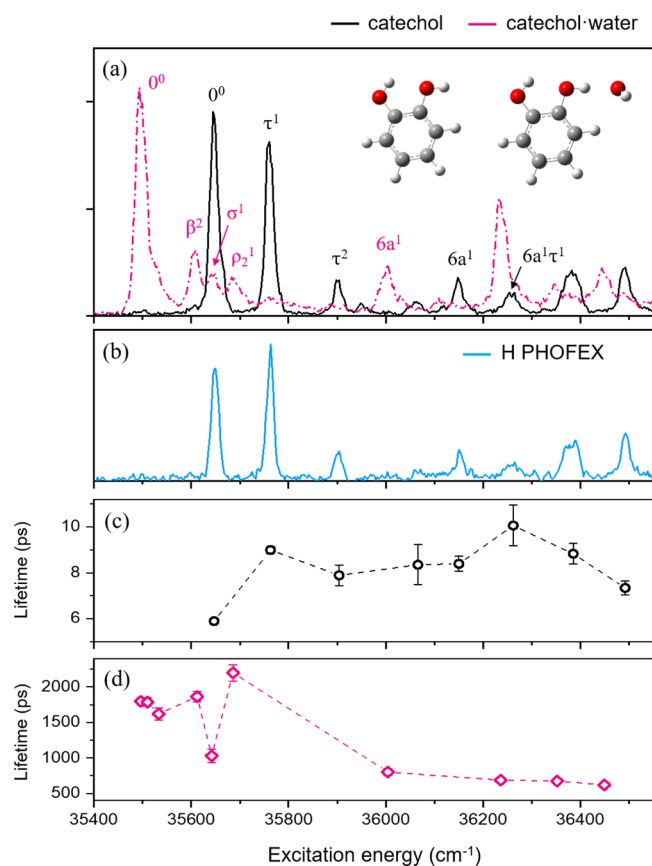


Figure 1. (a) Picosecond ($1 + 1'$) REMPI spectra of catechol (black) and catechol-water 1:1 cluster (magenta) taken at the zero pump-probe time delay. Mode assignments and notations of the vibrational modes of catechol and catechol-water are from the report by Gerhards et al.²⁵ (b) H-atom photofragment excitation (PHOFEX) spectrum in the experimental condition where the monomer and cluster are coexpanded in the molecular beam at a pump-probe delay of 2.7 ns. The state-specific S_1 lifetimes of (c) catechol and (d) catechol-water measured by fitting the transients by the single exponential fits. Error bars represent standard errors derived from the nonlinear least squares fitting algorithm. All other transients are given in the Supporting Information.

modes, giving $\tau = 8.4 \pm 0.3$ or 10.1 ± 0.9 ps for the $6a^1$ (503 cm^{-1}) or $6a^1\tau^1$ (615 cm^{-1}) mode, respectively. Overall, the tunneling rate of the S_1 catechol spans from $(6 \text{ ps})^{-1}$ to $(11 \text{ ps})^{-1}$ in the $0\text{--}900 \text{ cm}^{-1}$ region, indicating that the internal modes other than the OH out-of-plane torsion influence little the tunneling rate.

The catechol-water 1:1 cluster had previously been spectroscopically well characterized, giving the minimum energy structure where the free OH moiety is hydrogen-bonded with the water molecule in both ground (S_0) and excited (S_1) electronic states.^{25,52} The picosecond R2PI spectrum of the catechol-water cluster identifies the S_1 origin band red-shifted from that of the monomer by $\sim 150 \text{ cm}^{-1}$.²⁵ At its ZPE level, the S_1 lifetime of the cluster is estimated to be $\sim 1.8 \text{ ns}$, which is quite close to the lifetime of $\sim 2.0 \text{ ns}$ reported by the Ebata group.³² The 300-fold retardation of the S_1 decay rate by the water clustering could be due to the huge increase of the reaction barrier against the H-atom detachment or the ESHT process.¹ The PHOFEX spectrum taken by monitoring the H-atom fragment as a function of the excitation energy at a reaction time of 2.7 ns reflects the absorption structure of

catechol only even in the experimental condition where the significant amount of the catechol-water cluster is copopulated in the molecular jet, Figure 1b. Namely, no H-atom fragment is produced from the catechol-water cluster, indicating that the H-atom tunneling is completely blocked in the cluster. The nonradiative transitions such as the internal conversion or intersystem crossing might be then largely responsible for $\tau \sim 1.8 \text{ ns}$ at the ZPE of the cluster. Interestingly, however, the S_1 decay rate of the catechol-water cluster is found to be mode-dependent. The S_1 lifetime gets significantly shortened to $\tau \sim 1.03 \text{ ns}$ at the intermolecular stretching mode (σ) excitation at 146 cm^{-1} above the S_1 origin. Upon the excitation of other intermolecular vibrational modes of ρ_2 (H_2O rocking) or β (H_2O wagging) below the internal energy of $\sim 200 \text{ cm}^{-1}$, the S_1 lifetime changes little from that of the ZPE. The S_1 lifetime is increased momentarily to $\tau \sim 2.2 \text{ ns}$ for the 190 cm^{-1} band before it gets rapidly decreased with increasing the excitation energy to give $\tau \sim 670 \text{ ps}$ for the 856 cm^{-1} band. The significant decrease of the S_1 lifetime of the catechol-water cluster at the intermolecular stretching mode excitation suggests that the ESHT through the hydrogen bonding between the catechol and water might take place on the S_1 surface. Actually, the excitation of the intermolecular stretching mode often modifies the tunneling barrier of ESHT in the way of expediting the H-atom transfer process.^{14,19,21,22} Accordingly, the experimental fact that the S_1 lifetime of the catechol-water cluster decreases rather sharply with the increase of the S_1 internal energy, as well as its strong mode dependence, indicates that the ESHT could be significantly responsible for the S_1 -state relaxation, similarly found in the case of the *o*-aminophenol-water complex.⁵³

There are two different conformational isomers of resorcinol: the C_s asymmetric isomer (*cis*) or the C_{2v} symmetric isomer (*trans*). In the previous fs study, *cis* and *trans* isomers could not be separated because of the intrinsic broad bandwidth of the fs laser.^{30,37} Here, using the narrow-band picosecond (ps) laser pulse ($\Delta E \sim 20 \text{ cm}^{-1}$), the *cis* or *trans* isomer of resorcinol could be distinctly identified to give the respective S_1 lifetime of ~ 4.5 or $\sim 6.3 \text{ ns}$ at its ZPE, respectively (Figure 2). The lifetime of the *trans* isomer is about 1.4 times longer than that of the *cis* isomer, though it should be noted that the lifetime estimation here is subject to the further refinement as our experimental temporal window is limited to 2.7 ns. The conformer-selective lifetimes estimated are found to be a bit longer than the previously reported lifetime of 2.7 ns from the fs study.^{30,37} Our measurements are more consistent with the previous other ps study where a lifetime of 4.2 or 4.5 ns was reported for the *cis* or *trans* isomer, respectively.³³ Although these are overall a bit shorter than the present experiment, it seems to be consistent that the S_1 lifetime of the *cis* conformer is shorter than that of the *trans* conformer. The notable difference in the S_1 lifetime between *cis* and *trans* conformers is interesting, and theoretical calculations would be desirable. The relatively long S_1 lifetime of both *cis* and *trans* conformers of resorcinol suggests that the nonadiabatic transition could be more responsible for the S_1 relaxation process compared to the H-atom (tunneling) detachment process in terms of the relative quantum yields.³⁷

It is interesting to note that the resorcinol-water (1:1) clusters give slightly shorter S_1 lifetimes compared to those of monomers. Two different structural isomers of the resorcinol-(*cis*)-water cluster give more or less same S_1 lifetimes of $\tau \sim 3.0 \text{ ns}$, whereas the S_1 lifetime of the resorcinol(*trans*)-water is

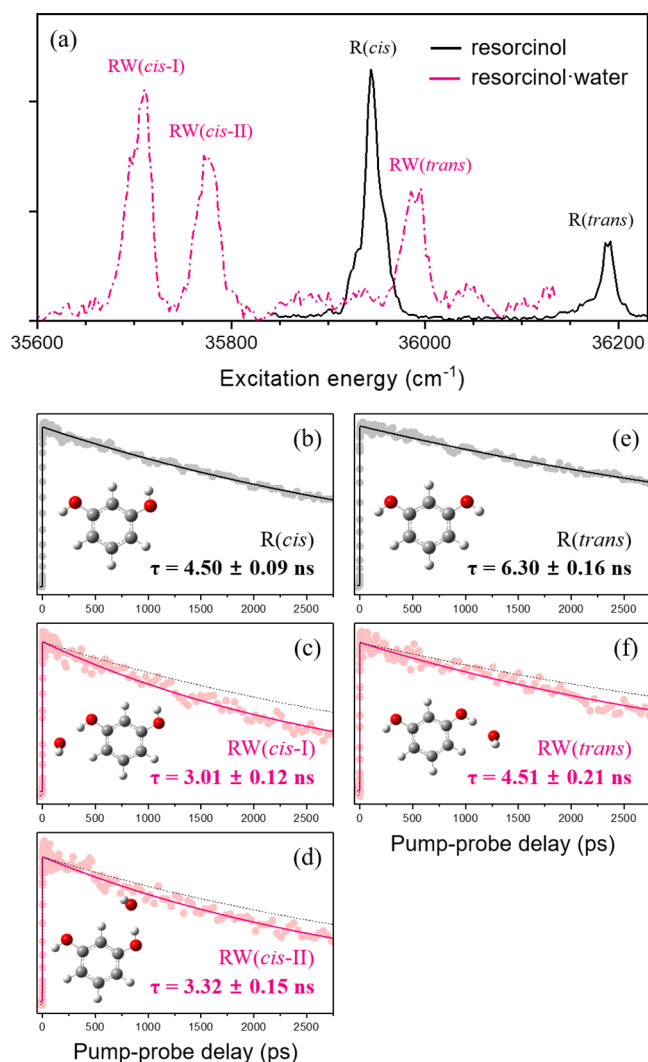


Figure 2. (a) Picosecond ($1 + 1'$) REMPI spectra of resorcinol (black) and resorcinol-water 1:1 cluster (magenta) taken at the zero pump-probe time delay. (b–f) Parent ion transients of the conformational isomers of monomers and clusters at their ZPE levels. ‘R’ or ‘RW’ stands for the resorcinol or resorcinol-water cluster, respectively.

estimated to be ~ 4.5 ns. The most surprising observation is that, for both *cis* and *trans* resorcinol conformers, the S_1 lifetime gets shortened by the 1:1 clustering with water. This is opposite to the case of catechol dynamics where the S_1 dephasing is significantly slowed down by the water clustering. As the H-atom detachment is the main S_1 dephasing process in catechol, its clustering with water practically blocks the H-atom detachment by placing the large barrier to tunneling. The water clustering to catechol thus completely changes the S_1 dephasing process into the otherwise competitive ESHT and/or nonradiative transitions (*vide supra*). In a similar context, one may think that if the S_1 resorcinol decays via the H-atom tunneling, then the S_1 decaying process would have been retarded by the cluster formation with water, which turns out to be not the case. Given the previous reports that the partial or full deuteration of the OH moieties of resorcinol does not bring the significant change of the S_1 lifetime,^{36,37} it seems that the S_1 states of resorcinol and its cluster might decay still preferentially through the nonradiative transitions. Yet, as one of two OH moieties of the resorcinol-water cluster is not

hydrogen-bonded by water, the lowering of the tunneling barrier for the H-atom detachment from the free OH moiety could not be excluded as another possible scenario (*vide infra*).

For hydroquinone, the S_1 lifetime turns out to be not conformer-specific, giving $\tau \sim 2.8$ ns for both *trans* and *cis* conformers, Figure 3. This is quite consistent with the previous

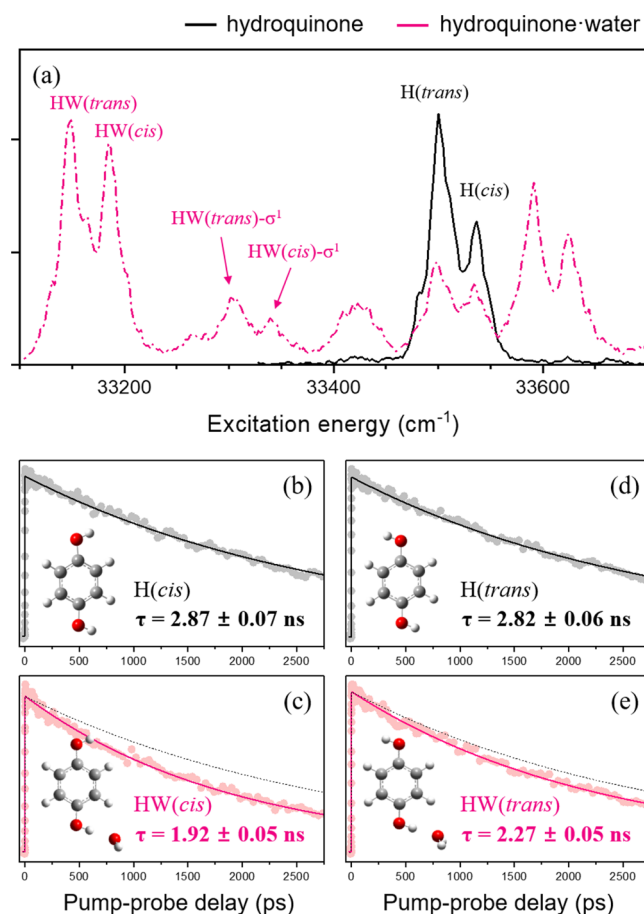


Figure 3. (a) Picosecond ($1 + 1'$) REMPI spectra of hydroquinone (black) and hydroquinone-water 1:1 cluster (magenta) taken at the zero pump-probe time delay. (b–e) Parent ion transients of the conformational isomers of monomers and clusters at their ZPE levels. ‘H’ or ‘HW’ stands for the hydroquinone or hydroquinone-water cluster, respectively.

fs ($\tau \sim 3.0$ ns)³⁰ and ps results ($\tau \sim 2.6$ ns).³³ Spectroscopic identification of *trans* and *cis* conformers of hydroquinone and their water clusters had been well established by the recent Stark deflection experiment.⁴⁴ Differences in dipole moments of different conformers have been reflected in the spatial deflection in the presence of the strong electric field, making possible unambiguous identification of the structural isomers of hydroquinone and the hydroquinone-water cluster. Quite interestingly, the S_1 decay rate is also accelerated by the water clustering for both *trans* and *cis* conformers of hydroquinone, giving $\tau \sim 2.27$ or 1.92 ns, respectively.³³ The expediting effect on the S_1 decay by the cluster formation is slightly more efficient for the *cis* compared to *trans*. In phenol, the H-atom tunneling process in S_1 ($\tau \sim 2.3$ ns) is faster compared to the competitive nonradiative transition processes.^{54–56} In the same context, the S_1 lifetime of the *trans* or *cis* conformers of hydroquinone might largely reflect the H-atom detachment rate. Then, the slight acceleration of the S_1 dephasing rate in

the hydroquinone-water cluster compared to the monomer could be due to the electron-withdrawing effect of hydrogen-bonded water on the OH moiety in the *para* position with respect to the free OH moiety undergoing the H-atom detachment via tunneling.

According to the spectroscopic studies by the Wategaonkar group,^{42,43} the vibronic band located at $\sim 156\text{ cm}^{-1}$ above the S_1 origin of the hydroquinone(*cis*)-water or hydroquinone(*trans*)-water cluster corresponds to the intermolecular hydrogen bond stretching (σ) mode, giving the corresponding S_1 lifetime of ~ 2.10 or ~ 2.31 ns, respectively (Supporting Information). In contrast to the case of the catechol-water cluster where the σ mode excitation accelerates the S_1 relaxation rate twice, the influence of σ mode excitation seems to be little in both conformers of the hydroquinone-water cluster, implying that the ESHT may not be activated. Namely, unlike the catechol-water cluster, one of the OH moieties in the hydroquinone-water is free, and thus the H-atom detachment from the free OH moiety seems to be more responsible for the S_1 relaxation pathway rather than the ESHT in the hydrogen-bonded OH moiety on the *para* position.

Although it is a formidable task to predict the absolute values of the S_1 decaying rates of benzenediols, *ab initio* calculations turn out to be quite valuable in the qualitative interpretation of the experiment. The reaction barrier under the S_1/S_2 conical intersection along the O–H extension coordinate as well as the $S_1(\pi\pi^*) - S_2(\pi\sigma^*)$ energetic gap in the vertical transitions from S_0 is calculated for all systems studied here (Table 1). Upon clustering, the H-atom detachment from the hydrogen-bonded OH moiety becomes less likely because of the much increased tunneling barrier height (Table 1). Interestingly though, in the clusters of resorcinol and hydroquinone, it has been found that the hydrogen bonding of water makes lower the tunneling barrier of the H-atom detachment from the free OH moiety. This explains at least partially why the S_1 decay of resorcinol or hydroquinone is expedited by the water clustering although the quantitative analysis is subject to the further investigation. Regarding the ESHT which could be conceivable in the hydrogen-bonded OH moiety of benzenediols, the reaction barrier of the catechol-water cluster is calculated to be much lower compared to that of the resorcinol-water or hydroquinone-water cluster. This is also consistent with the experiment, as the S_1 lifetime of the catechol-water cluster only is strongly mode- and energy-dependent, suggesting that the ESHT might play an important role in the S_1 -state relaxation (*vide supra*). Conversely, it suggests that the ESHT process may be insignificant in the resorcinol-water or hydroquinone-water cluster, which is also consistent with the present experimental finding.

CONCLUSIONS

In summary, we have investigated the dynamics of the S_1 -state decay of three benzenediols and their 1:1 water clusters in a conformer-specific manner using the ps pump–probe scheme. The mode dependence of the S_1 -state lifetime of catechol has been refined and confirmed that the nonplanar S_1 geometry is responsible for the unusual decrease of the tunneling rate with the OH out-of-plane torsional mode excitation. The enormous increase of the S_1 lifetime of the catechol-water cluster, compared to the monomer, is the consequence from the blocking of the free OH moiety by the hydrogen bonding with water. While the H-atom detachment is blocked, it seems that

Table 1. Calculated Vertical Excitation Energies for the S_1 and S_2 States and Tunneling Barrier Heights (in eV) for Catechol, Resorcinol, and Hydroquinone Monomers and Their 1:1 Water Clusters^a

species	calculated energy (eV)			S_1 lifetime (ns)	
	S_1	S_2	tunneling barrier height	ZPE	mode
catechol					
catechol, free OH	5.289	6.294	0.393	0.006	
catechol-water, H-bonded OH	5.237	6.258	0.560	1.80	1.03
<i>cis</i> -resorcinol (I)					
<i>cis</i> -resorcinol, R(<i>cis</i>)	5.325	6.790	0.612	4.50	
<i>cis</i> -resorcinol-water, RW(<i>cis</i> -I), free	5.279	6.898	0.673	3.01	
<i>cis</i> -resorcinol-water, RW(<i>cis</i> -I), H-bonded	5.280	6.415	0.745		
<i>cis</i> -resorcinol (II)					
<i>cis</i> -resorcinol, R(<i>cis</i>)	5.325	6.790	0.665	4.50	
<i>cis</i> -resorcinol-water, RW(<i>cis</i> -II), free	5.280	6.688	0.590	3.32	
<i>cis</i> -resorcinol water, RW(<i>cis</i> -II), H-bonded	5.280	6.666	0.859		
<i>trans</i> -resorcinol					
<i>trans</i> -resorcinol, R(<i>trans</i>)	5.337	6.741	0.637	6.30	
<i>trans</i> -resorcinol-water, RW(<i>trans</i>), free	5.296	6.812	0.627	4.51	
<i>trans</i> -resorcinol-water, RW(<i>trans</i>), H-bonded	5.296	6.452	0.780		
<i>cis</i> -hydroquinone					
<i>cis</i> -hydroquinone, H(<i>cis</i>)	4.950	6.442	0.661	2.87	
<i>cis</i> -hydroquinone water, HW(<i>cis</i>), free	4.871	6.383	0.625	1.92	2.10
<i>cis</i> -hydroquinone water, HW(<i>cis</i>), H-bonded	4.871	6.081	0.823		
<i>trans</i> -hydroquinone					
<i>trans</i> -hydroquinone, H(<i>trans</i>)	4.940	6.362	0.675	2.82	
<i>trans</i> -hydroquinone water, HW(<i>trans</i>), free	4.862	6.383	0.653	2.27	2.31
<i>trans</i> -hydroquinone water, HW(<i>trans</i>), H-bonded	4.862	6.139	0.855		

^aThe excited-state energy has been calculated at the M06-2X/cc-pVDZ level of theory by scanning the O–H bond length while the other atoms are frozen at the S_0 geometry. The tunneling barrier heights are estimated by the energy difference between the S_2/S_1 crossing and S_1 minimum energy points.

the excited-state hydrogen transfer takes place through the hydrogen bonding between catechol and water instead, giving the strong mode and energy dependences in its S_1 lifetime. The *cis* and *trans* conformers of resorcinol are slightly different in their lifetimes. The S_1 decay of *cis* is slightly faster than that of *trans*. Upon clustering with water, the S_1 decay is expedited in both conformers. Although the S_1 resorcinol seems to decay preferentially via the nonradiative transitions, the H-atom detachment from the free OH moiety should be also significantly responsible for the S_1 -state relaxation. The shortening of the S_1 lifetime in the resorcinol-water cluster thus could be partly due to the lowered tunneling barrier (for the H-atom detachment from the free OH moiety) induced by the hydrogen bonding to the other OH moiety. The S_1 decay dynamics of hydroquinone is not conformer-specific. The

lifetime of S_1 in the hydroquinone-water cluster is slightly increased, implying that the H-atom tunneling barrier is lowered by the hydrogen bonding to the other OH moiety, as in the case of resorcinol. Ab initio calculations support our experiment and present interpretation quite well.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.1c05448>.

State-specific picosecond transients of the catechol and catechol-water cluster, S_1 lifetimes of hydroquinone-water clusters at the σ -mode excitation, DFT calculation of potential energy curves, correlation diagrams between the S_1 lifetimes, and the calculated tunneling barrier (PDF)

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Notes

The authors declare no competing financial interest.

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