

Zero kinetic energy spectroscopy of hydroquinone-water (1:1) complex: A probe for conformer assignment

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Zero kinetic energy (ZEKE) photoelectron spectroscopy of the hydroquinone-water (HQW) complex was carried out to characterize its S_1 - S_0 resonantly enhanced multiphoton ionization (REMPI) spectrum in terms of the *cis* and *trans* conformers. The ZEKE spectra of the hydroquinone isomers show differences in the Franck-Condon (FC) activity of a few ring modes, viz., modes 15, 9*b*, and 6*b*, due to the different symmetries of the two isomers. These modes were used as a “diagnostic tool” to carry out the categorical assignment of the REMPI spectrum of the HQW complex. It was found that the FC activity of these diagnostic modes in the cationic ground state (D_0) of the water complex is similar as that of the monomer. The two lowest energy transitions in the REMPI spectrum of the water complex, 33 175 and 33 209 cm^{-1} , were reassigned as the band origins of the *cis* and *trans* hydroquinone-water complexes, which is opposite of the previous assignment. The intermolecular stretching mode (σ) of the complex shows a long progression, up to $v'=4$, in the cationic ground state and is strongly coupled to other observed ring modes. The Franck-Condon factors for different members in the progression were calculated using the potential energy surfaces computed *ab initio*. These agree well with the observed intensity patterns in the progression. The ionization potential of the *trans* and *cis* complexes was determined to be $60\,071 \pm 4$ and $60\,024 \pm 4$ cm^{-1} , respectively. © 2007 American Institute of Physics. [DOI: 10.1063/1.2780158]

I. INTRODUCTION

In recent years the study of van der Waals and hydrogen-bonded interactions has been a subject of much interest. Weakly bound molecular complexes are intermediates in the transition from the single isolated molecules to the condensed phase. In this context, hydroquinone (HYQ) is an interesting molecule as it forms a giant hydrogen-bonding network due to the presence of two phenolic hydroxyl groups at the *para* position. This leads to the formation of clathrate compounds¹ in the solid state, which have wide industrial applications² in the field of gas separation, lubricants, fuel additive, and many others. Besides the industrial applications, HYQ is important in the field of crystal engineering where microscopic data are needed to fill the gap between the isolated state and the condensed phase. HYQ and its weakly bound complexes with many different solvents have been studied quite extensively in the gas phase up to date and still it is of interest to address many fundamental problems.

HYQ is a planar molecule and exists as two conformers, viz., *cis* and *trans*, depending on the relative orientation of the two hydroxyl groups. These two conformers marginally differ in their energies in the ground state; the *trans* form is lower in energy than the *cis* isomer.³ The S_1 - S_0 fluorescence excitation as well as the resonantly enhanced multiphoton ionization (REMPI) spectrum of HYQ expanded in the su-

personic jet shows the presence of both the conformers⁴ even in the cold beam. The entire spectrum consists of transitions appearing in pairs due to the presence of the two conformers. The similarity in the Franck-Condon activity of various normal modes of these two conformers makes it difficult to assign the spectral features to individual conformers. However, the two-photon spectroscopy³ and high resolution spectroscopy⁵ of the monomer have been successfully used to identify the transitions due to each of the isomers as they belong to two distinctly different point groups (the *trans* form belongs to C_{2h} and the *cis* form belongs to the C_{2v} point group). The lower energy transition of the band origin pair was assigned to the *trans* isomer and the other one to the *cis* isomer.

The H-bonded complex of hydroquinone and water (HQW) has been studied in the gas phase by REMPI technique.⁶ The REMPI spectrum of HQW is quite similar to that of the monomer. The transitions appear in pairs as in the case of the monomer and the two lowest energy transitions are 34 cm^{-1} apart from each other compared to 32 cm^{-1} in the monomer. Hole burning spectrum confirmed the presence of only two species in the jet. A large redshift (~ 330 cm^{-1}) in the lowest energy transition of HQW compared to that in the monomer indicates that two species present in the jet are the ones in which the monomer acts as the hydrogen bond donor, as in the case of other phenolic compounds. This was supported by theoretically calculated binding energy data of the four possible HQW complexes, which showed that the hydrogen bond donor complexes are three times more stable than that of the acceptor complexes. The REMPI spectrum

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was assigned in terms of the two hydrogen bond donor species, namely, *trans*-HQW and *cis*-HQW.

The difficult part was the conformer specific assignment of the spectrum. In the earlier work, the assignments of the spectral features of HQW complexes were carried out using an analogy with the monomer. The most intense lowest energy transition at $33\,175\text{ cm}^{-1}$ was assigned as the *trans*-HQW (HQW-I) complex and the next one at $33\,209\text{ cm}^{-1}$ to the *cis*-HQW (HQW-II) complex. Theoretically obtained binding energy data for the ground state were not of much help because the difference in their energies was very small and the relative energies were dependent on the level of computation (at times, it even altered the relative order). Therefore there is some uncertainty/inconsistency between the theoretical results and experimental inference which needs to be addressed. Also the categorical assignment of the spectrum to individual conformers by some independent method is still pending.

Recent publications of the mass analyzed threshold ionization (MATI) spectroscopy^{7,8} and zero kinetic energy (ZEKE) photoelectron spectroscopy⁹ of HYQ monomer reported that the Franck-Condon (FC) activity in a few ring modes in the cationic ground state of the two conformers was quite different. The *trans* and *cis* isomers of HYQ belong to two different point groups, viz., C_{2h} and C_{2v} , respectively. The C_2 axis is, however, differently oriented in these two isomers; in *trans*-HYQ it passes through the center of the aromatic ring and is perpendicular to the molecular plane, whereas in the case of *cis* isomer, it lies in the plane of the molecule and bisects the two central C–C bonds. This has an interesting consequence with regard to the symmetry species of certain normal modes. Mode 15, which is the in-plane C–X bending mode, is totally symmetric (a_1) for *cis*-HYQ and nontotally symmetric (b_u) for *trans*-HYQ. Mode 9*b* which is another in-plane C–X bending mode is totally symmetric (a_g) for the *trans*-HYQ and nontotally symmetric for *cis*-HYQ. Mode 6*b* which is one of the in-plane ring deformation modes is totally symmetric for *trans*-HYQ and nontotally symmetric for *cis* isomer. This affects the Franck-Condon activity of the aforementioned normal modes in the observed ZEKE and MATI spectra, as reported in Ref. 9. In the *trans*-HYQ spectrum the 15¹ transition is very weak, whereas in the *cis* isomer it appears very prominently. The transitions due to modes 9*b* and 6*b* are active, as expected, in *trans*-HYQ and totally absent in the *cis* isomer. Using the observed differences in the FC activity of the aforementioned normal modes as a “diagnostic tool,” it will be possible to decipher the S_1 - S_0 REMPI spectrum of the two conformers of the HQW complex.

In this paper, we report the vibronic spectroscopy of the cationic ground state of two conformers of HQW using ZEKE photoelectron spectroscopic technique. A specific conformer was excited to a specific intermediate vibrational level in the S_1 state and the ionization laser was scanned to obtain the ZEKE spectrum corresponding to that particular conformer. Throughout this paper the conformer with the band origin (BO) at $33\,175\text{ cm}^{-1}$ is termed as HQW-I and the other one at $33\,209\text{ cm}^{-1}$ is termed as HQW-II and we have refrained from referring to them as *trans*-HQW or *cis*-HQW

until the conclusions were drawn. Four intermediate levels were excited in the case of HQW-I and three in the case of HQW-II in order to help assign the normal modes, determine the vibrational couplings among various normal modes, check the FC activity of different normal modes, and determine the relative potential energy surface shifts between the S_1 and D_0 states. Experimental results were corroborated using *ab initio* calculations at the level of the 6-31G** basis set using the HF/DFT/MP2 level to obtain the vibrational modes, first ionization potential, and binding energy of both the isomers. In addition the configuration interaction singles (CIS) and complete active space self-consistent-field (CASSCF) calculations were performed to determine the S_1 - S_0 excitation energy and the ionization potentials (IPs). All the findings were used to assign the ZEKE spectrum in terms of the two conformers of the HQW complex and deduce the correct assignment of the S_1 - S_0 REMPI spectrum.

II. EXPERIMENTAL DETAILS

The experimental setup, the details of which have been described elsewhere,¹⁰ consisted of two 10 in. diameter differentially pumped stainless steel chambers. A $100\text{ }\mu\text{m}$ pulsed nozzle (General Valve, series 9) housed in the first chamber was used to generate a cold beam of molecules which was collimated before the second chamber by a skimmer located $\sim 25\text{ mm}$ downstream from the nozzle orifice. The time of flight mass spectrometer (TOFMS) with a 20 cm flight tube with a mu metal shield was housed in the second chamber. A 10 mm diameter channeltron (Philips X919AL) was used to detect the electrons. The output of the channeltron was sent to a digitizing storage oscilloscope (Lecroy 9450) that was interfaced to a PC.

For the ZEKE experiments (two color, two photon using pulsed field ionization), a 10 Hz nanosecond Nd^{+3} yttrium aluminum garnet (YAG) (Quantel Brilliant) pumped dye laser (Molelectron DL18P) was used to provide the fixed S_1 - S_0 excitation source and another Nd^{+3} :YAG (Quantel YG781C) laser pumped dye laser (Quantel TDL70) was used to provide the tunable D_0 - S_1 ionization source. The two copropagating beams were spatially and temporally overlapped and were focused onto the molecular beam using a 50 cm focal length lens. The linewidth of the Quantel dye laser was 0.08 cm^{-1} and that of the Molelectron dye laser was 0.3 cm^{-1} . Typical pulse energies were ~ 5 – $10\text{ }\mu\text{J}$ for the excitation laser and $\sim 100\text{ }\mu\text{J}$ for the ionization laser. Excitation pulse energy was maintained low enough to avoid the space charge effects due to the excessive ionization. The ZEKE spectra were recorded using three intermediate levels, viz., the BO, intermolecular hydrogen-bonding stretching mode ($\nu=1$), and the 6*a* ($\nu=1$) level of the S_1 for both the isomers, viz., HQW-I and HQW-II, and additionally through the β_1 mode ($\nu=2$) of the HQW-I conformer. The ionization laser was scanned between $26\,515$ and $27\,710\text{ cm}^{-1}$ by mixing IR (1064 nm)+dye fundamental output of three sets of dyes, namely, R6G+R610, R575+R6G, and R575 (Exciton, Inc.). The dye laser was calibrated by means of the optogalvanic method using a Fe–Ne hollow cathode lamp.

The experiments were carried out using a typical

Wiley-McLaren¹¹ TOFMS with the following pulse sequence to improve the signal to noise (S/N) ratio. Initially both the extraction (bottom) and the acceleration (middle) grids (separated by 35 mm) were held at the same voltage of ~ -80 V with a spoil field of about 600 mV/cm between the two grids so that the ionization occurs *near* field-free region. The bottom grid was pulsed ~ 400 ns (SRS; DG-535) after the laser pulse such that the effective extraction field was 7 V/cm for the duration of 1 μ s. This allows one to extract the ZEKE electrons at very low electric fields and then accelerate them toward the detector using higher acceleration field (~ 55 V/cm), thereby increasing the collection efficiency at the detector.

Hydroquinone is a solid at room temperature. It was heated to about 135 °C to generate a sufficient amount of vapor pressure to record spectra with good S/N ratio. It was purchased from S.D. Fine-Chemicals Ltd. and used without further purification. Helium obtained from local commercial sources was used without further purification as the buffer gas. The buffer gas was flowed over a reagent bottle containing water. The optimum amount of water vapor required for generating the 1:1 complex was maintained by means of a needle valve. The typical backing pressure was 2.5–3 atm. The typical working pressure in the source chamber was $\sim 6 \times 10^{-5}$ Torr and in the TOFMS chamber it was $\sim 2 \times 10^{-6}$ Torr.

III. COMPUTATIONAL DETAILS

To gain more insight into the experimental results, the energy optimized structures and fundamental vibrational modes in different electronic states were calculated using *ab initio* methods. All the calculations were performed using the GAUSSIAN 98 program package.¹² The Hartree-Fock (HF), Møller-Plesset perturbation of second order (MP2), and density functional theory (DFT) methods using the 6-31G** basis set were used to obtain the optimized structures, total energies, and normal mode frequencies for both conformers in the S_0 and the D_0 states. The CIS method was applied to obtain the excited state geometries and frequencies. The ionization potentials were obtained as the difference between the optimized energies of the ground state (S_0) and cationic ground state (D_0). The zero point energy correction (ΔZPE) was included to obtain a more accurate result. The IP and the S_1 - S_0 excitation energy were also calculated using the CASSCF method. The CASSCF calculations were carried out with ten electrons in eight orbitals (10,8) active space for the ground state (S_0) and the first electronic excited state (S_1) and with nine electrons in eight orbitals (9,8) active space for the cationic ground state (D_0). These eight orbitals include all five occupied and the three lowest unoccupied π -type orbitals. The binding energy of the complexes in the cationic ground state was also calculated at all the levels of theory including the basis set superposition error (BSSE) in the counterpoise method.¹³

Potential energy surfaces (PESs) along the intermolecular stretching (σ) normal coordinate of the HQW-I and HQW-II complexes were calculated in order to determine the FC factors corresponding to the long progressions in the σ

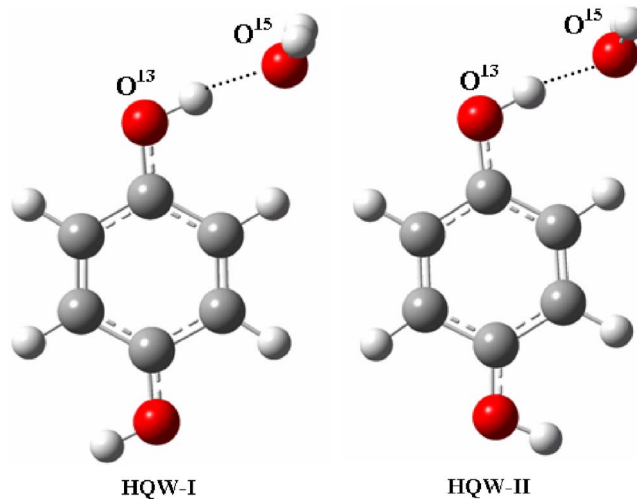


FIG. 1. (Color online) Structure of the H-bonded HQW-I in the cationic ground state optimized at the MP2 level using the 6-31G** basis set.

mode. The complex geometry was frozen at its optimized geometry in each state and the single point energies were calculated at various O¹³-O¹⁵ (Fig. 1) distances incremented by 0.1 Å in each step, which represents the intermolecular stretching normal coordinate. The PESs for the S_0 and D_0 states were calculated at the HF level using the 6-31G* basis set and the same for the S_1 state is calculated at the CIS level using the 6-31G* basis set. The FC factors were calculated using the LEVEL 7.5¹⁴ program. The program solves the radial one dimensional Schrödinger equation for bound levels of any smooth single potential, and calculates the expectation values for the vibrational levels and Franck-Condon factors for various transitions between two electronic states. The PESs obtained by *ab initio* methods were used as the input surfaces. The FC factors were calculated for both the S_1 BO mediated and S_1 stretch mediated ZEKE spectra for the HQW-I complex and these were compared with the experimentally observed intensities.

IV. RESULTS

The S_1 - S_0 REMPI spectrum of the HQW complex reported in the literature⁶ shows that the vibronic features appeared in pairs due to the complex formation with both *cis* and *trans* isomers of the monomer present in the jet. The lowest energy pair of transitions at 33 175 and 33 209 cm^{-1} was assigned to the BOs of these two conformers of HQW, *trans*-HQW and *cis*-HQW (referred to as HQW-I and HQW-II in the present work), respectively. The excitation laser source was tuned to these two energies separately to record the photoionization efficiency curves of the two species using dc extraction field. The photoionization efficiency curves of the HQW-I and HQW-II (128 amu) yielded the rough estimates of the ionization thresholds of the complexes at around 26 820 cm^{-1} for both the conformers. The region around the ionization threshold was scanned using the pulsed field ionization to determine the adiabatic ionization potential and record the ZEKE spectra of the complexes.

TABLE I. Ionization energy obtained via various intermediate levels of the S_1 state.

Intermediate level	HQW-I (cm^{-1})			HQW-II (cm^{-1})	
	0^0	σ_0^1	$\{\beta_1\}_0^2$	0^0	σ_0^1
S_1-S_0 transition	33 175	33 331	33 292	33 209	33 366
D_0-S_1 origin	26 846	26 688	26 727	26 859	26 699
IP	60 021	60 019	60 019	60 068	60 065

A. Ionization energy

The ionization energies were obtained by pumping several intermediate levels in the S_1 state for the individual conformers of the HQW complex and are listed in Table I. For each of the conformer, the ionization potential values obtained as the sum of the S_1-S_0 excitation energy and the band origin of the D_0-S_1 ZEKE spectrum for each intermediate transition are self-consistent within the spectral resolution. The mean IP for HQW-I and HQW-II is $60\,020 \pm 4$ and $60\,067 \pm 4$ cm^{-1} , respectively. The quoted error in the IP values is due to the resolution of the recorded spectrum and the error in laser calibration. The measured IP values need to be corrected for the stray field present in the ionization volume. The field-free ionization potential can be obtained by extrapolation to zero field by determining the field shift (δ) according to the formula δ (cm^{-1}) = $cE^{1/2}$, where c is a constant and E is the field strength in V/cm .^{15,16} For molecular clusters such as phenol-water, the value of c is normally taken as 4.5 (Ref. 17) for all practical purposes. The field shift was calculated to be 4 cm^{-1} for the stray field of 600 mV/cm used in the present experiments. Hence, the field-free IP was derived as $60\,024 \pm 4$ and $60\,071 \pm 4$ cm^{-1} for HQW-I and HQW-II, respectively.

B. ZEKE spectra of HQW-I

Figure 2 shows the pulsed field ionization (PFI)-ZEKE spectra of HQW-I obtained via four different intermediate vibronic levels in the S_1 state; band origin ($33\,175$ cm^{-1}), σ^1 ($33\,331$ cm^{-1}), $\{\beta_1\}_0^2$ ($33\,292$ cm^{-1}), and $6a^1$ ($33\,615$ cm^{-1}). The observed spectral features are the transitions to various vibrational levels in the D_0 state of the cationic complex. Varsanyi's nomenclature¹⁸ was used for the normal mode assignments. The assignment of the spectral features was carried out based on the ZEKE spectroscopy of the monomer⁹ and experimental values available for the corresponding mode in the S_0 and S_1 states, and using the normal mode frequencies calculated at the DFT level using the B3LYP functional and 6-31G** basis set. In the case of S_1 state band origin mediated ZEKE spectrum, the lowest energy transition was observed at $26\,846$ cm^{-1} , as shown in Fig. 2(a). The strongest transition appears at 224 cm^{-1} with a progression up to $v'=3$ in this mode. This transition was assigned to intermolecular stretching vibration (σ). A moderately strong transition at 385 cm^{-1} was assigned to in-plane C–O bending mode, i.e., mode 15. The transitions at 605 and 820 cm^{-1} were assigned to the combination band of mode 15 with the first and second quanta in the stretching mode. The 462 cm^{-1} transition was assigned to $6a_0^1$ transition. The intramolecular modes such as the $6a$ and 15 are almost within a few wave-

numbers of their respective values in the monomer. All the observed transitions are presented in Table II.

Figure 2(b) displays the ZEKE spectrum obtained by exciting the σ^1 ($33\,331$ cm^{-1}) mode in the S_1 state. The lowest energy transition appears at $26\,688$ cm^{-1} with respect to which the spectrum was plotted. As in the case of BO mediated ZEKE spectrum, the progression in the stretch mode was observed up to four quanta; however, the FC activity of the different members of the progression was quite different and would be discussed in detail later. Apart from mode 15 and $6a$ intramolecular transitions at 385 and 462 cm^{-1} , respectively, mode $6b$ was observed at 630 cm^{-1} and mode 1 transition was observed at 867 cm^{-1} . The other observed transitions at 181 and 320 cm^{-1} were assigned to intermolecular vibration modes. The transition observed at 724 cm^{-1} can either be assigned as mode 12 or the combination of 181 and 320 cm^{-1} with one quantum of the intermolecular stretch. The FC activity of the 1_0^1 transition, which was observed at 867 cm^{-1} , is much higher than the other ring modes. Combination band of $6a$ with first and second quanta

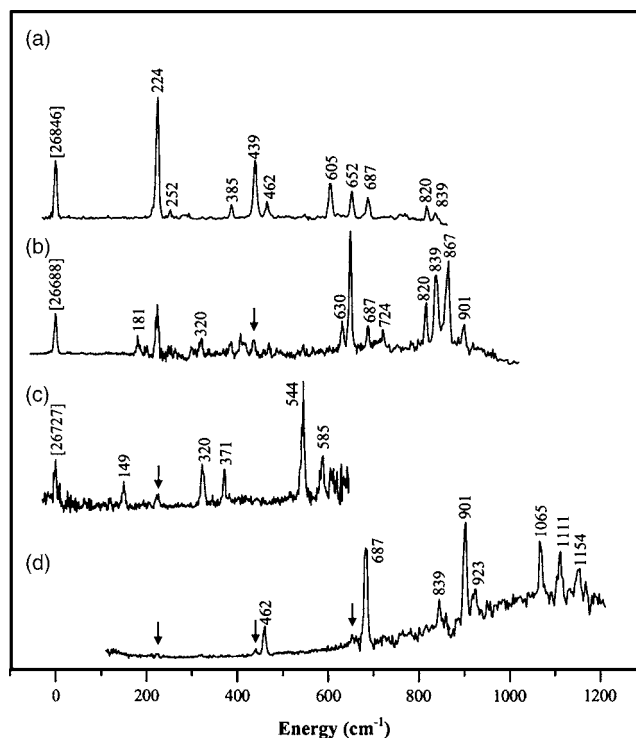


FIG. 2. ZEKE spectrum of HQW-I recorded via (a) $S_1 0^0$ ($33\,175$ cm^{-1}), (b) $S_1 \sigma^1$ ($33\,331$ cm^{-1}), (c) $S_1 \{\beta_1\}_0^2$ ($33\,292$ cm^{-1}), and (d) $S_1 6a^1$ ($33\,615$ cm^{-1}) intermediate states. Traces are plotted with respect to the origin of the D_0-S_1 spectrum in each case. The position of the origin is given in parentheses. The arrows indicate the position of the σ^1 transitions, where $n=0, 1, 2, \dots$.

TABLE II. Observed transitions with their assignments in the ZEKE spectra of HQW conformers.

HQW-I					HQW-II				Mode assignment
Intermediate level in S_1 state					Intermediate level in S_1 state				
0^0	σ^1	$\{\beta_1\}_2^2$	$6a^1$	Theory	0^0	σ^1	$6a^1$	Theory	
		149							$\{\beta_1\}_2^2$
	181					183			X
224	224	224	224	248	223	223	223	248	σ^1
252									Y
	320	320				269			Q
		371							Z
385	385			381					$\{\beta_1\}_2^2 + \sigma^1$
						404		412	15^1
439	439		439		441	441	441		$9b^1$
462	462		462	469	462	462	462		σ^2
		544							$6a^1$
		585							$\sigma^1 + Z$
605					604	604			$\{\beta_1\}_2^2 + \sigma^2$
	630			630		627		629	$15^1 + \sigma^1$
652	652		652		648	648	648		$6b^1$
687	687		687		688		688		σ^3
	724								$\sigma^1 + 6a^1$
						734			X + $\sigma^1 + Z$
820	820					813			$6a^1 + Q$
839	839		839			843			$15^1 + \sigma^2$
	867			853		866			σ^4
	901		901			901	901		1^1
			923				923		$\sigma^2 + 6a^1$
			1065						$6a^2$
			1111				1111		$\sigma^1 + 15^1 + 6a^1$
			1154				1151		$\sigma^3 + 6a^1$
									$\sigma^1 + 6a^2$

of stretch mode was observed at 687 and 901 cm^{-1} , respectively. A combination of mode 15 with two quanta of stretch was observed at 820 cm^{-1} .

Figure 2(c) shows the ZEKE spectrum of HQW-I obtained by the $\{\beta_1\}_0^2$ (33 292 cm^{-1}) excitation in the S_1 state. The lowest transition at 26 727 cm^{-1} matches well with the ionization energy of the complex cation obtained by the other two S_1 state excitations. A new intermolecular mode was observed at 149 cm^{-1} in addition to the 320 cm^{-1} mode observed earlier in the σ^1 excitation [Fig. 2(b)] spectrum. However, the intensity in both these transitions was very prominent in the present spectrum. The absence of the 149 cm^{-1} transition in the other spectra indicates that for this mode, the FC activity is concentrated only in the $\Delta v=0$ transitions and further that the 149 cm^{-1} mode is strongly coupled with the 320 cm^{-1} mode. This transition was assigned as the $\{\beta_1\}_2^2$ transition giving the value of the $\{\beta_1\}$ ($v=2$) level of 149 cm^{-1} for the cation. The appearance of the spectrum indicates that these two modes act as a pseudo-band-origin and within the range that was probed the spectrum appears similar to that of the BO mediated spectrum, i.e., the stretching mode σ was observed in combination with the 149 and 320 cm^{-1} transitions at 371 and 544, respectively.

Figure 2(d) shows the ZEKE spectrum recorded via the

$6a^1$ (33 615 cm^{-1}) excitation in the S_1 state. The expected transition corresponding to the D_0 - S_1 band origin at 26 405 cm^{-1} could not be observed due to the poor FC factor for this transition. The first strong transition was observed at 462 cm^{-1} from the expected band origin with an overtone at 923 cm^{-1} . This 462 cm^{-1} feature was assigned as the $\Delta v=0$ transition in the $6a$ mode and gives the frequency of the $6a$ mode as 462 cm^{-1} compared to 458 cm^{-1} of the monomer.⁹ Like the previous spectrum, the 462 cm^{-1} transition acts as the pseudo-band-origin for the rest of the spectrum, which is very much similar to that in the BO mediated spectrum. A strong progression in the intermolecular stretching mode in combination with the $6a$ mode up to three quanta was observed at 687, 901, and 1111 cm^{-1} . The transition at 1154 cm^{-1} was assigned as the combination band of $6a_0^2$ with one quanta of stretch. The transition at 1065 cm^{-1} was assigned as the combination band of $6a$, σ , and mode 15.

C. ZEKE spectra of HQW-II

Figure 3 shows the ZEKE spectra recorded by ionization of HQW-II via three different intermediate levels in the S_1 state, viz., BO (33 209 cm^{-1}), σ^1 (33 366 cm^{-1}), and $6a^1$ (33 647 cm^{-1}). The $\{\beta_1\}_0^2$ mediated ZEKE spectrum could

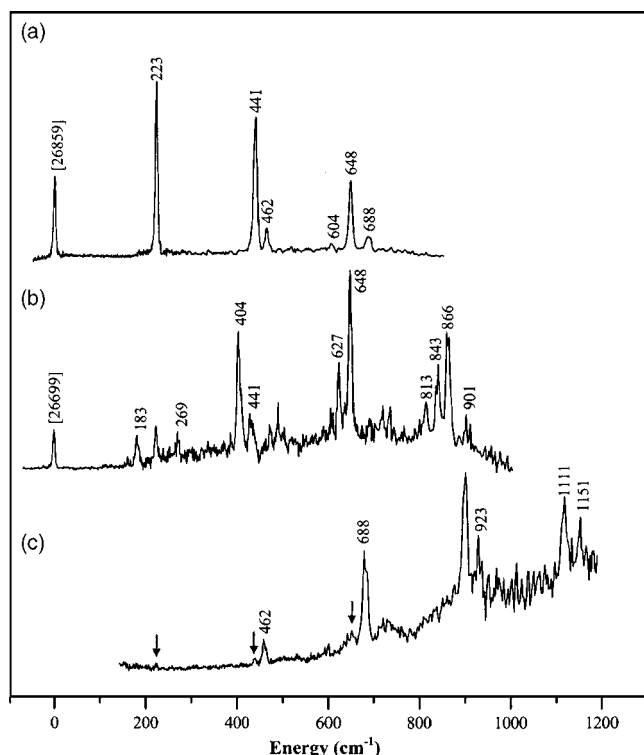


FIG. 3. ZEKE spectrum of HQW-II recorded via (a) $S_1, 0^0$ (33 209 cm^{-1}), (b) S_1, σ^1 (33 366 cm^{-1}), and (c) $S_1, 6a^1$ (33 647 cm^{-1}) intermediate states. Traces are plotted with respect to the origin of the D_0 - S_1 spectrum in each case. The position of the origin is given in parentheses. The arrows indicate the position of the σ^n transitions, where $n=0, 1, 2, \dots$.

not be recorded for this conformer as it is overlapped by the σ^1 transition of the HQW-I in the S_1 - S_0 REMPI spectrum. The BO mediated ZEKE spectrum [Fig. 3(a)] shows that the lowest energy transition occurs at 26 859 cm^{-1} . In stark contrast to the HQW-I case, the spectrum has only two active modes, viz., the intermolecular stretching mode (σ) at 223 cm^{-1} and the $6a$ mode at 462 cm^{-1} . A progression in the 223 cm^{-1} mode was observed up to $\Delta v=3$. The $6a$ mode is also coupled to the stretch mode and their combination band appears at 688 cm^{-1} .

Figure 3(b) displays the spectrum obtained via the σ^1 (33 366 cm^{-1}) excitation in the S_1 state. The lowest energy transition was observed at 26 699 cm^{-1} and the spectrum was plotted with respect to it. The spectrum looked more or less similar to that in the case of the HQW-I spectrum [Fig. 2(b)] with regard to the length of the progression in the stretching mode (σ) as well as the FC activity among its members. However, there were a few differences. A strong transition

was observed at 404 cm^{-1} which was assigned to mode 9b, and mode 15 was absent. Mode 6b at 627 cm^{-1} was also quite prominent. A new intermolecular mode was observed at 269 cm^{-1} along with its combination with mode 6a. FC activity in the 6a mode is very small whereas mode 1 at 866 cm^{-1} is highly FC active. Though mode 15 was not observed, the combination of mode 15 with one and two quanta of stretch was present weakly. The transition at 901 cm^{-1} was assigned as the combination band of 6a with two quanta of stretch.

Figure 3(c) shows the ZEKE spectrum of HQW-II recorded by the $6a^1$ excitation in the S_1 state. As in the case of the corresponding HQW-I spectrum, the expected transition corresponding to the D_0 - S_1 origin at 26 419 cm^{-1} could not be observed. The first strong transition was observed at 462 cm^{-1} from the band origin with an overtone at 923 cm^{-1} . This 462 cm^{-1} transition was assigned as the $\Delta v=0$ transition in the $6a$ mode of the cation and gives the frequency of the $6a$ mode as 462 cm^{-1} compared to 458 cm^{-1} of the monomer.⁹ Intermolecular stretching frequency mode is strongly coupled with the $6a$ mode as a progression in the stretch mode (σ) was observed up to $\Delta v=3$ at 688, 901, and 1111 cm^{-1} . The transition at 1151 cm^{-1} was assigned as the combination of stretch mode with two quanta of mode 6a.

D. Computational results

The two most stable structures (HQW-I and HQW-II) present in the jet⁶ were optimized in their cationic (D_0) ground state. The optimized structures obtained at the MP2 level with the 6-31G** basis set are shown in Fig. 1. Intermolecular hydrogen bond lengths calculated at different levels of theories are given in Table III along with those in the S_0 and S_1 states for the sake of comparison. The hydrogen bond lengths for the two conformers are within 0.01 Å of each other in all the states and at all the levels of theory. At the HF level, the bond length shortens by about 0.06 Å in the S_1 state and by 0.271 Å in the D_0 state relative to that in the S_0 state. Although the hydrogen bond shortening in the D_0 state is calculated at all the levels of theory, it is least at the MP2 level, i.e., 0.199 Å, and greatest at the CASSCF level, i.e., 0.284 Å. The DFT number is close to the HF level, i.e., 0.261 Å. The shortening of the H bond manifests itself in the large blueshift and a long progression observed in the intermolecular stretching mode in the ZEKE spectra.

The binding energies of the optimized structures in the cationic ground state including the BSSE and zero point energy correction (ΔZPE) are listed in Table IV. The ΔZPE

TABLE III. Hydrogen bond lengths of HQW conformers calculated at different levels of theories with the 6-31G** basis set.

Isomer	S_1		D_0^a			
	CIS (Å)	CAS (Å)	HF (Å)	MP2 (Å)	DFT (Å)	CAS (Å)
HQW-I	1.909	1.959	1.696 (1.967)	1.665 (1.864)	1.576 (1.839)	1.691 (1.975)
HQW-II	1.919	1.962	1.698 (1.968)	1.677 (1.866)	1.579 (1.840)	1.664 (1.978)

^a S_0 values are given in parentheses.

TABLE IV. Binding energy of HQW complexes in D_0 state obtained at different levels of theory with the 6-31G** basis set.

	HQW-I (cm^{-1})			HQW-II (cm^{-1})		
	HF	MP2	DFT	HF	MP2	DFT
BE including BSSE correction	6673	7478	7754	6720	7637	7758
–BSSE	168	468	486	193	460	492
Δ ZPE	731	473	721	736	–30	725
BE including BSSE correction and Δ ZPE	5942	7005	7034	5983	7667	7034

value at the MP2 level of the HQW-II complex is erroneous because for some strange reasons it calculates the antisymmetric in-plane OH stretching frequency mode in the D_0 state to be 4136 cm^{-1} which is abnormally high. Taking the same Δ ZPE value as that of the HQW-I conformer, the corrected binding energy comes out to be 7164 cm^{-1} . The HF and MP2 levels of calculation show that the HQW-II (*cis*-HQW) complex is more stable in the D_0 state compared to the HQW-I (*trans*-HQW), whereas at the DFT level, both the conformers are equally stable. The binding energies of the complexes are substantially higher in the cationic state compared to both ground state and first electronic excited state due to the increased partial positive charge on the proton in the cationic state, as listed in Table V. This is consistent with the reduction in the IP by $\sim 4000 \text{ cm}^{-1}$ relative to that of the monomer.

The binding energies of the HQW complexes at the MP2 and DFT levels of theory are in the range of $7000\text{--}7200 \text{ cm}^{-1}$, whereas they are about 6000 cm^{-1} at the HF level. These values can be compared with the empirically determined value of $6520 \pm 50 \text{ cm}^{-1}$ for the phenol-water complex.¹⁹ This is a valid comparison because several parameters such as the redshift in the $S_1\text{--}S_0$ band origin and the redshift in the vibrational frequency of the phenolic OH stretching mode in the two systems are comparable. The agreement between the binding energies computed in this work and the empirical value for the phenol-water system is excellent (i.e., within 10%); the MP2 and DFT values are on the higher side, whereas they are underestimated at the HF level. The magnitude of increase in the binding energy in the cationic state relative the neutral ground state is comparable with that reported for the phenol-water.^{16,19}

The ionization energies were also computed at various levels of theory as the difference between the optimized energies of the ground state (S_0) and cationic state (D_0). The zero point energy correction (Δ ZPE) was also included to

obtain more accurate result. Table VI gives the complete listing of the IP values obtained at the HF, MP2, DFT, and CASSCF levels. As expected the HF values show the largest deviation from the experimental determined IP as they do not account for the correlation energy. The CASSCF value is also 13% off the empirical value, suggesting that the number of orbitals included in the active space is not sufficient. The MP2 value was in excellent agreement followed by the DFT value.

E. Franck-Condon factors

The FC factors for various members of the progression were calculated using the PESs calculated *ab initio* for all the three states and the LEVEL 7.5 program. Figure 4 depicts all three potential energy surfaces that were generated as described earlier. The fully optimized PESs could not be calculated because of the limitations on the computational resources. However, the quality of the potentials is verified as follows. The vibrational levels calculated by the LEVEL 7.5 program using these potentials were 142, 145, and 214 cm^{-1} for the S_0 , S_1 , and D_0 states, respectively. These values are in excellent agreement with the experimentally observed values, viz., 156, 156, and 224 cm^{-1} , respectively. The potentials of the S_0 and S_1 states are very similar in terms of their shape except that the equilibrium $\text{O}^{13}\text{--O}^{15}$ distance is slightly shorter in the S_1 state. This is consistent with the observed REMPI spectrum of HQW,⁶ where the stretch mode (σ) does not show any progression. The D_0 state PES shows a considerable shift along the normal coordinate compared to the S_0 and S_1 state. The equilibrium $\text{O}^{13}\text{--O}^{15}$ distance is 2.659 \AA in the D_0 state which is shorter by $\sim 0.2 \text{ \AA}$ compared to that in the S_1 state. Also, due to the large increase in the binding energy, the potential well is much deeper (more harmonic) in the D_0 state compared to both the

TABLE V. Mulliken atomic charges (in a.u.) on hydrogen and oxygen atoms of isolated monomer calculated at the MP2 and CIS levels of theory using the 6-31G** basis set.

Atom	<i>trans</i> -HYQ			<i>cis</i> -HYQ		
	S_0	S_1	D_0	S_0	S_1	D_0
O	–0.665	–0.638	–0.535	–0.666	–0.639	–0.536
H	0.344	0.349	0.399	0.345	0.350	0.400

TABLE VI. Ionization energy calculated at different levels of theories with the 6-31G** basis set.

	HQW-I (cm ⁻¹)				HQW-II (cm ⁻¹)			
	ΔE	ΔZPE	IP	% error	ΔE	ΔZPE	IP	% error
HF	48 313	299	48 613	19	48 436	286	48 722	19
MP2	56 507	1597	58 104	3	56 524	1714	58 238	3
DFT	54 334	351	54 685	9	54 406	356	54 762	9
CAS	51 327	560	51 887	13	51 437	655	52 092	13

neutral states. This is reflected in the long progression in the stretching mode in the ZEKE spectrum.

Figure 5 shows the FC factors obtained using the aforementioned potentials along with the experimentally observed intensity distribution among the members of the σ_i^f ($i=0,1$; $f=0-4$) progressions. Figure 5(a) pertains to the BO mediated spectrum and Fig. 5(b) is for the σ^1 mediated ZEKE spectrum. It can be seen from Fig. 5(a) that the FC factors calculated using vibrational wavefunctions for the transitions from D_0 - S_1 were in excellent agreement with the observed intensity distribution, whereas the overlap between the S_0 and D_0 wavefunctions is very poor. Similarly for the σ^1 mediated ZEKE spectrum [Fig. 5(b)] the agreement between the observed intensities and the FC factors for the D_0 - S_1 transition was very good compared to the D_0 - S_0 transition.

V. DISCUSSION

The S_1 state BO mediated ZEKE spectra as depicted in Figs. 2(a) and 3(a) clearly show that HQW-I and HQW-II have completely different characteristic Franck-Condon activities in certain modes. The only transitions observed for HQW-II are the progression in the intermolecular stretching mode (σ), mode 6a, and the combination thereof. However, for the HQW-I conformer, in addition, another fundamental transition is observed in mode 15 at 385 cm⁻¹ and its combinations with the σ mode. These observations can be compared with the trend in the monomer ZEKE spectra which is presented in Ref. 9. Mode 15 is active in the *cis*-HYQ monomer whereas it is extremely weak in the *trans* monomer.

Similarly in the case of the stretch mediated ZEKE spectra [Figs. 2(b) and 3(b)] the 15¹ transition is present in HQW-I at 385 cm⁻¹ but totally absent in HQW-II. The spectrum of HQW-II shows a strong transition at 404 cm⁻¹, which has been assigned to 9b based on the calculated value of 412 cm⁻¹ for this mode. The transition at 627 cm⁻¹, which is strong in HQW-II but very weak in HQW-I, was assigned to mode 6b. Therefore it can be summarized that the 9b¹ and 6b¹ transitions were active in the case of HQW-II alone and inactive in HQW-I, similar to the observations in the *trans* and *cis* monomers, respectively. In the case of the 6a excited ZEKE spectra [Figs. 2(d) and 3(c)] also the only difference in the two spectra was that in the case of HQW-I, a combination of mode 15 with mode 6a and σ was prominent, whereas the same was absent in the case of HQW-II.

All of these observations suggest that mode 15 is the allowed mode in the case of HQW-I conformer whereas 9b and 6b modes are the allowed modes in the case of HQW-II conformer. As mentioned earlier these differences arise from the fact that the two isomers belong to two different point groups and the C_2 axis in both cases is oriented differently. This makes mode 15 totally symmetric only for the *cis* isomer and modes 9b and 6b totally symmetric only in the case of the *trans* isomer. Therefore it is inferred that the HQW-I complex is the complex in which water is bound to the *cis* monomer and HQW-II is the water complex with the *trans* monomer. With this new assignment, certain things need to be pointed out with regard to the relative stabilities of the two conformers in the S_1 state. The band origins for the *cis*

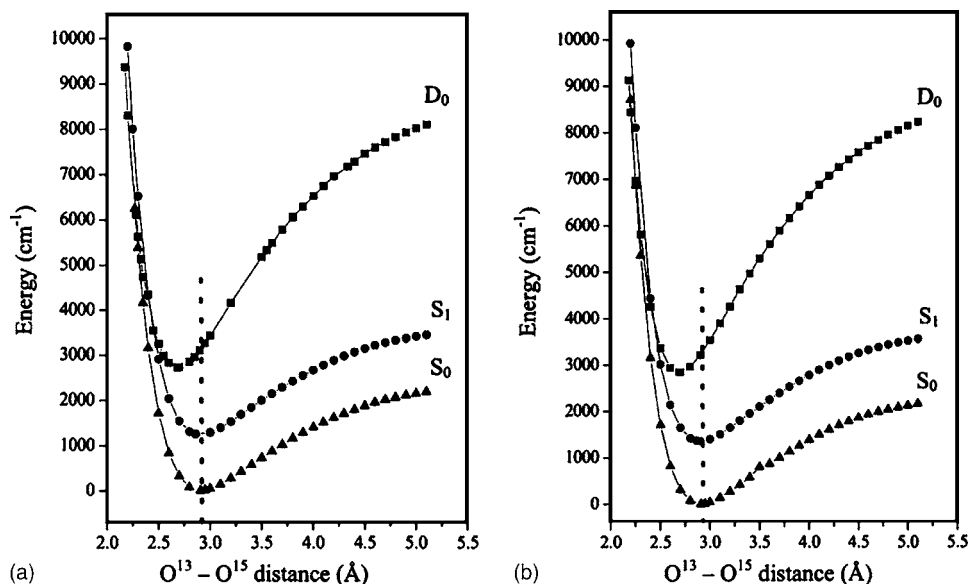


FIG. 4. Potential energy surfaces for (a) HQW-I and (b) HQW-II calculated at the HF level for the S_0 and the D_0 states and the CIS level of theory for the S_1 state using the 6-31G* basis set. The dotted line shows the position of R_{\min} in the S_0 state as a reference. The y axis shows the energy scale corresponding to the S_0 state. The S_1 and D_0 PES were arbitrarily offset in energy for proper representation.

and *trans* monomers occur at 33 540 and 33 508 cm^{-1} and those for their water complexes at 33 175 and 33 209 cm^{-1} , respectively. This makes the redshift in the band origins for the *cis* isomer as 365 cm^{-1} and that for the *trans* isomer as 299 cm^{-1} , suggesting that the water complex in the *cis* conformer is stabilized more than that in the *trans* conformer. This is somewhat intuitive since the *cis* monomer has a net dipole moment, whereas it is almost nonexistent for the *trans* monomer. Therefore, stronger dipole-dipole interaction between the monomer and the water molecule may lead to greater stability for the *cis* conformer.

A. Intermolecular vibrational modes

The main feature in the ZEKE spectra of HQW-I and HQW-II complexes is the progression in the intermolecular stretching vibration (σ) in combination with different intramolecular and intermolecular vibrations. The stretch frequency is measured as 224 and 223 cm^{-1} for HQW-I and HQW-II complexes, respectively. In the case of the ZEKE spectrum via the vibrationless S_1 state, the first member of the progression, i.e., $\Delta v=1$ transition, was the most intense feature for both the conformers and then intensity decreased monotonically. A progression up to three quanta was observed with the frequency separation between the successive members measured as 224 cm^{-1} (223 cm^{-1} for HQW-II), 215 cm^{-1} (218 cm^{-1} for HQW-II) and 213 cm^{-1} (207 cm^{-1}

for HQW-II). Relative FC factors for the different members of the progression are quite similar in the two complexes. A progression up to three quanta in the stretch mode with very small intensity was also seen in the $6a$ mediated ZEKE spectra of HQW-I and HQW-II complexes.

The ZEKE spectrum recorded via the stretch excitation in the S_1 state is very rich with regard to the transitions involving different intermolecular modes. Besides the progression in the stretch mode, several other intermolecular modes, viz., 149, 181, and 320 cm^{-1} , were active in the cationic ground state. (In the case of HQW-II, an additional mode at 269 cm^{-1} was also observed.) The 149 cm^{-1} transition was assigned as $\{\beta_1\}_2^2$, *vide supra*. This gives the value of β_1 normal mode as 75 cm^{-1} ; the computed value for this in-plane bending mode is 87 cm^{-1} . It is not possible to categorically assign any of the other transitions to any modes because the computationally obtained modes do not agree with any of these numbers, perhaps due to the large anharmonicity associated with these low frequency modes, whereas the calculated numbers are for harmonic normal.

B. Franck-Condon factors

The FC factors for the transition between two vibrational levels in a given progression depend on the vibrational wavefunction overlap integral between the initial and final states. In the present case wherein the final state is accessed through a resonant intermediate state, the description of the initial state is ambiguous. The observed intensity pattern is expected to depend on whether or not the system completely adapts to the intermediate S_1 potential energy hypersurface (within the Born-Oppenheimer approximation) before it absorbs the second photon. In the former case the intensities would be governed by the FC factors for a transition between the S_1 and the D_0 state and in the latter case the operative FC factors would depend on the overlap between the vibrationless S_0 state and the D_0 state. In the present work, the progression in the σ mode exhibits different intensity patterns among its members depending on the intermediate vibronic state (BO or σ^1), as it has been observed in similar systems reported in the literature. The very fact that the intensity distributions in the ZEKE spectra obtained via two different intermediate states were different itself suggests that the intermediate state does have an influence on the FC factors. However, for the scheme employed here, i.e., two-color, two-photon ionization, it is possible that the second photon is absorbed *before* the molecular system completely assumes the influence of the S_1 potential energy hypersurface. The time domain studies are better suited to address this question of partial versus complete relaxation which will also be reflected in the intensity distribution in the ZEKE spectrum in the frequency domain studies. In this work what is attempted is to compute the FC factors for the S_1 surface as well as the S_0 surface and compare them with the observed intensity distribution. The quantitative analysis carried out in this work shows that the agreement was excellent between the FC factors calculated for the transition between the S_1 state and the final D_0 state. For the BO mediated spectrum, the agreement was extremely good whereas for the σ^1 mediated

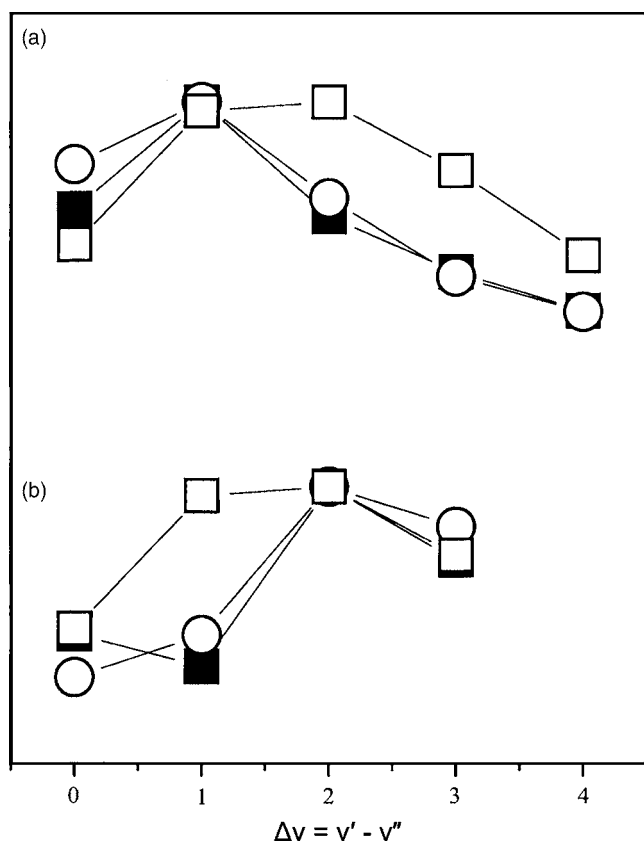


FIG. 5. Plots showing the observed intensity distribution (■) among various members of the σ progression in (a) S_1^0 excited ZEKE spectrum and (b) $S_1^{\sigma^1}$ excited ZEKE spectrum. The normalized FC factors are also shown in the respective plots: (□) FC factors for the D_0 - S_0 (vibrationless) transition and (○) corresponding to the D_0 - S_1 transition.

spectrum, agreement was acceptable. In both cases the FC factors for the transitions between the vibrationless S_0 state (which is the initial state) and the final D_0 state was very poor and there was hardly any scope to invoke the incomplete relaxation to the S_1 potential in both cases. Therefore it can be concluded that in the two-color, two-photon schemes, the intermediate state completely relaxes to its equilibrium S_1 potential while using nanosecond laser pulses.

VI. CONCLUSIONS

Cationic ground state of the HQW complex was studied using ZEKE photoelectron spectroscopy in the jet cooled molecular beam via various intermediate vibrational levels in the S_1 state. The observed differences in the Franck-Condon activity of the normal modes 15, 9b, and 6b were used to categorically assign the observed transitions in the S_1 - S_0 REMPI spectrum to the respective conformers of the complexes. Mode 15 which was FC active in the *cis*-HYQ was observed in the HQW-I ZEKE spectra, whereas modes 9b and 6b which were active only in *trans*-HYQ were observed in the HQW-II ZEKE spectra. Hence, HQW-I complex which has band origin at $33\,175\text{ cm}^{-1}$ was assigned as the *cis*-hydroquinone-water complex and HQW-II which has band origin at $33\,209\text{ cm}^{-1}$ was assigned as the *trans*-hydroquinone-water complex. This is opposite to the previous assignments of the REMPI spectrum. With these new assignments the BO redshifts in the S_1 - S_0 excitation of the *cis* and *trans* complexes become 365 and 299 cm^{-1} , respectively, relative to the respective monomers. The adiabatic ionization energies of the *cis* and *trans* complexes were determined as $60\,024 \pm 4$ and $60\,071 \pm 4\text{ cm}^{-1}$, respectively, which are about 4000 cm^{-1} redshifted compared to the monomer ionization energies. *Ab initio* computed binding energies of the complexes in the cationic ground state show a large increase in the relative stability, which is consistent with the reduction in the IP values of the complexes; this has been attributed to the increased partial positive charge on the proton in cationic state. The increase in the relative stability is also evident from the observed blueshift in the intermolecular stretching mode in the cationic state ($\sim 224\text{ cm}^{-1}$) compared to that in the S_1 state ($\sim 156\text{ cm}^{-1}$). The computed potential energy surfaces along the intermolecular stretching

normal coordinate show a substantial shift in the cationic state compared to both the S_0 and S_1 states and explains the observed long progression in the stretching mode.

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