# Spatial Isolation of Conformational Isomers of Hydroquinone and Its Water Cluster Using the Stark Deflector

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S *Supporting Information*

ABSTRACT: Conformational isomers of hydroquinone and their 1:1 clusters with water have been spatially separated using a Stark deflector in a supersonic jet. *trans*-Hydroquinone (HyQ) conformer with zero dipole moment is little influenced by inhomogeneous electric fields, whereas *cis* conformer with nonzero dipole moment (2.38 D) is significantly deflected from the molecular beam axis into the direction along which the strong field gradient is applied. Resonant two photon ionization carried out by shifting the laser position perpendicular to the molecular beam axis after the Stark deflector then gives an exclusive S_1−S_0 excitation spectrum of the *cis* conformer only, making possible immaculate conformer-specific spectroscopy and dynamics. As the spatial separation is apparently proportional to the effective dipole moment strength, conformational assignment could be absolute in the Stark deflector, which contrasts with the hole-burning spectroscopic technique where identification of a conformational isomer is intrinsically not unambiguous. *trans*- and *cis*-HyQ−H_2O clusters have also been spatially separated according to their distinct effective dipole moment strengths to give absolute spectroscopic identification of each cluster isomer, nailing down the otherwise disputable conformational assignment. This is the first report for the spatial separation of conformational cluster isomers.

$\partial E/ \partial x \approx 0$
$\partial E/ \partial y \neq 0$
$\partial E/ \partial z \approx 0$

$\mu \sim 4.64$ D
$\mu \sim 3.13$ D

Stark Deflector
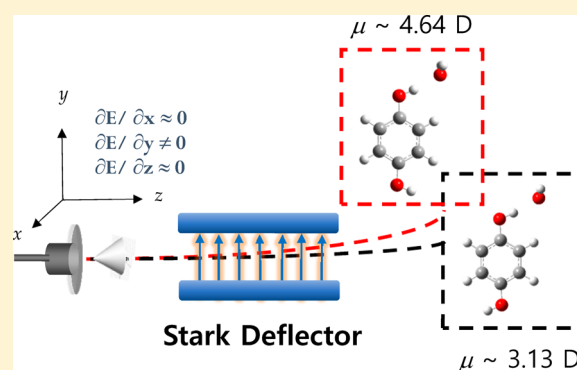
INTRODUCTION

Nature seems to utilize subtle structural differences of molecular conformational isomers quite wisely in its evolution. Actually, in some catalytic organic or biological reactions, reactants and/or intermediates are structurally driven by chemical environments using hydrogen bonding with adjacent functional groups as a tool into specific conformational geometries for expediting or impeding relevant chemical processes.[1−3] However, even though it is widely conceived that chemical reactivity would heavily depend on conformational structures of molecules involved in chemical reactions, understanding of the structure−function relationship at the molecular level seems to be still in its infancy because of the lack of relevant experimental data to date. This is mainly because conformational isomers are hardly separable in most circumstances and thus only the average properties of many possible conformers could be invoked in most chemical reactions at ambient conditions.[4−6] At the same time it should be emphasized, though, that there have been indeed many successes in this endeavor in terms of separation of conformers especially in the gas phase in recent decades. For charged species, ion mobility mass spectrometry has been extremely successful and widely used as conformers with different molecular shapes could be separated according to their different drift times along a specially designed collisional cell.[7,8] For neutral or charged species, spectroscopic separation using conformer-specific vibronic transitions turns out to be very

efficient and single conformer species in the supersonically cooled molecular beam could be exclusively chosen if spectroscopic identification of a specific conformational isomer could be unambiguously done.[9−12] Notably, based on these methods, it has been demonstrated that one of two distinct reaction pathways could be specifically chosen by spectroscopic ionization of a specific conformational isomer only at a time.[13−20]

More recently, another method for conformational separation of neutral species using an electrostatic (or Stark) deflector has been developed and found to be very promising.[21−27] Techniques of manipulation of atoms or molecules using external electric or magnetic fields have been enormously advanced since the first seminal deflection experiment by Stern in 1922.[28] Nowadays, it seems to be basically possible to align, orient, accelerate, decelerate, focus, disperse, or even trap neutral atoms or molecules in space by applying well-designed electric and/or magnetic external fields.[24,29−32] Application of an electrostatic field for the purpose of conformer separation, on the other hand, was first demonstrated by Filsinger et al. in 2008.[22] Furthermore, they could separate *cis* and *trans* conformers of 3-aminophenol[23] distinctly in space using a Stark deflector employing a simple two-wire field model.[33] For

large molecules, most quantum states belong to strong-field seeker in inhomogeneous fields given by the Stark deflector. Thus, even though actual molecular trajectory calculation is somewhat elaborated, it is quite straightforward that a conformer with the larger dipole moment/mass ratio should be more deflected as its associated Stark interaction energy is manifested by the larger translational energy in the transverse direction to the molecular beam. Accordingly, one can spatially separate conformational isomers according to their dipole moment strengths. For 3-aminophenol, the dipole moment of the *cis* conformer is much larger than that of the *trans* conformer. This leads to almost complete spatial separation of two conformers, allowing for the experimental observation of remarkable conformer specificity in an ion−molecule bimolecular reaction for the first time as reported by Chang et al.[26] The Stark deflector, through a number of pioneering experiments recently by the Küpper group,[21] seems to be now firmly demonstrated to be very useful not only for separation of conformational isomers but also for specific quantum state selection of small molecules.[24]

Herein, we have adopted the original two-wire Stark deflector in our setup but combined it with a more conventional pulsed valve (General valve series 9). Although conformer separation was not quite efficient as that achieved with the much colder molecular beam generated from an Even−Lavie pulsed valve,[34] complete separation of the *cis* conformer of 3-aminophenol has been possible in our setup by varying carrier gases and electric field strengths. In this work, conformational isomers of hydroquinone (HyQ) and their 1:1 clusters with water have been successfully separated. We would like to emphasize a great advantage of the Stark deflector in terms of conformer-specific spectroscopic assignment as one can identify specific conformers from the extent of deflection of each conformer.[23] Specifically, this allows us to put an end to the dispute about spectral assignment of *trans*-HyQ−H_2O or *cis*-HyQ−H_2O cluster, which was not unambiguously identified by hole-burning spectroscopic or conformer-specific photoionization studies of the same system.[35,36] Even though separation of molecular cluster from monomer in the Stark deflector had been previously demonstrated,[25] we believe that this is the first report for the spatial separation of conformational isomers for molecular clusters.

■ METHODS

A supersonically cooled molecular beam was generated from a pulsed valve (ϕ = 0.5 mm; series 9 from General valve), skimmed through a skimmer (ϕ = 1.0 mm; Beam dynamics), and collimated by a slit with 1 mm width placed ∼31 cm downstream from the nozzle orifice before entering a 15 cm long Stark deflector (Figure 1). A two-wire field model for the Stark deflector was adopted from the original report by Filsinger et al.[23,24] The spatial gap between two curved electrodes across the molecular beam axis was 1.4 mm in the center, and electric voltage in the range 3−11.4 kV was applied. Inhomogeneous electric fields are given along the perpendicular direction to the molecular beam axis so that strong-field (or weak-field) seekers are deflected upward (or downward) from the main stream of molecular beam. The molecular beam passed through a 1 mm exit slit before it was overlapped with the laser pulse ∼28 cm downstream from the Stark deflector exit for ionization in the extraction region of a linear time-of-flight mass spectrometer. The ultraviolet laser pulse obtained via frequency doubling of a dye laser output pumped by a
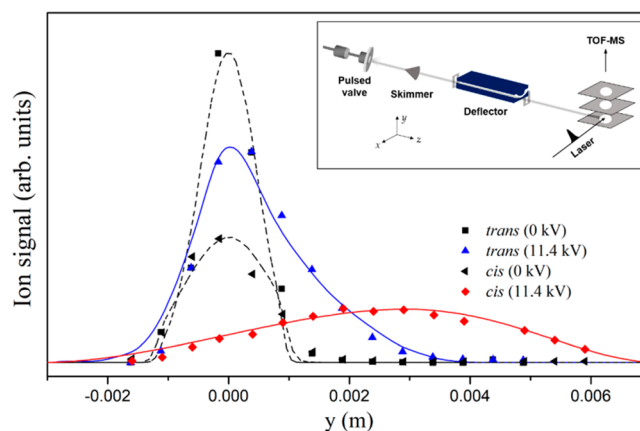

Figure 1. Deflection profiles of *trans*-3-AP and *cis*-3-AP conformers seeded in Ar at the deflector voltage of 11.4 kV taken by monitoring the S_1−S_0 origin signal intensities at 34 477 and 34 118 cm^{-1}, respectively.[23] Symbols are experiment, whereas lines represent simulations. (inset) Experimental setup consisting of the supersonically cooled molecular beam, skimmer, the 15 cm long Stark deflector, slits, and ionization region of the time-of-flight mass spectrometer.

Nd:YAG laser (Continuum, Surelite II) was focused by a spherical plano-convex lens (nominal focal length = 20 cm) mounted on a translational stage to adjust the vertical position of the laser pulse with respect to the molecular beam axis. Ions generated by the laser−molecule interaction were then repelled, accelerated, and drifted in the field-free region to be separated according their mass/charge ratios and detected by a multichannel plate (MCP). 3-Aminophenol (98%, Aldrich) or hydroquinone (>99%, TCI) was purchased and heated to 140 or 145 °C, respectively, before it was mixed with a carrier gas of Ne or Ar. Water clusters were generated by a water bubbler placed between the carrier gas and sample reservoirs. The sample was then expanded into a vacuum with a backing pressure of ∼3 atm. Density functional theory (DFT) calculations were carried out for minimum energy structures and their associated dipole moments using the Gaussian 09 program package.[37]

Simulation has been carried out to reproduce the Stark deflection profiles here. Details of the simulation method were described quite well in other previous works.[21,24,38−40] Briefly, Stark energetic shifts of target molecules were calculated using rotational constants and electric dipole moments obtained from spectroscopic data in the literature[41−44] or DFT calculations (Table S1). Rotational quantum states of each molecule below J = 40 were taken into account in the Stark simulation to include all quantum states (J, M, K_a, K_c) significantly populated below T_{rot} = 10 K. Trajectory of a particle in a single rotational quantum state at a specific Stark voltage was calculated by solving an equation of motion with the time interval of 1 μs to give its deflected position along the y-coordinate in the ionization region (Figure 1). At least 800 particles with different positions and momenta of which the distribution resembles the experiment were simulated for a single (J, M, K_a, K_c) state. Simulations for deflection profiles start to converge when the number of particles is more than 200 for each state. The total deflection profile was then generated by summing all the deflection profiles calculated for individual quantum states after consideration of their Boltzmann factors and nuclear spin statistical weights. Simulated profiles were normalized and fitted to the experiment with varying the rotational temperature.

Table 1. Averaged Experimental Deflection Positions along the y-Axis and Simulated Molecular Beam Rotational Temperatures (T_{rot}) for 3-AP, HyQ, and HyQ–H$_2$O Conformational Isomers at Various Carrier Gases and Applied Voltages

| | average deflection position (mm) | | | | | | | | simul T_{rot} [a] (K) | |
| | Ne | | | | Ar | | | | | |
system	3 kV	6 kV	9 kV	11.4 kV	3 kV	6 kV	9 kV	11.4 kV	Ne	Ar
trans-3-AP[b]	0	0.1	0.1	0.2	0	0.1	0.3	0.5	6.0	3.0
cis-3-AP	0	0.2	0.4	0.6	0.3	1.1	1.9	2.5	8.0	2.0
cis-HyQ		0.3		0.9		0.9		1.8	5.0	2.0
trans-HyQ–H$_2$O		0.5		1.4					3.0	
cis-HyQ–H$_2$O		1.1		2.7					3.0	

[a]The average of simulated T_{rot} for different voltages applied to the deflector is given. [b]The deflection position is measured to be 1.0 mm when Xe carrier gas is used at $V = 11.4$ kV.
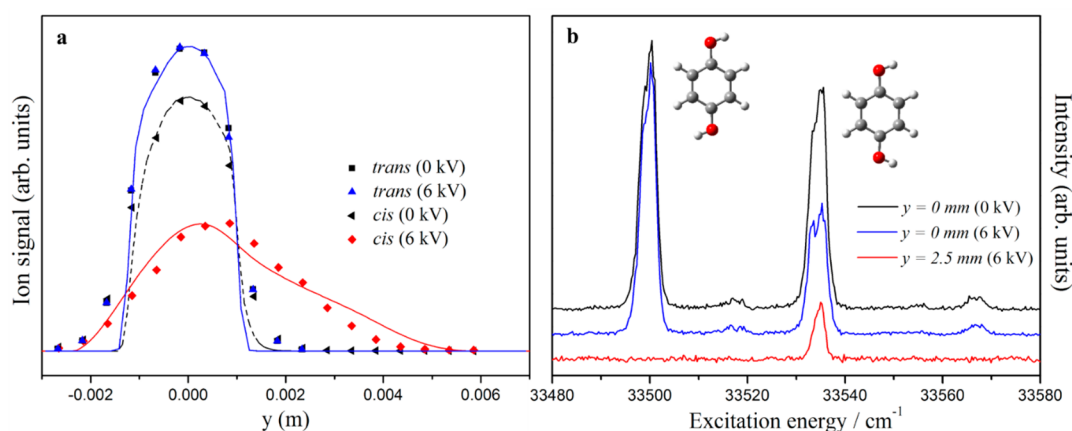

Figure 2. (a) Deflection profiles of *trans*-HyQ and *cis*-HyQ conformers seeded in Ar at the deflector voltage of 0 or 6 kV taken by monitoring the corresponding R2PI origin band intensities at 33 500 and 33 535 cm^{-1}, respectively. Experiment (symbols) is well reproduced by simulation (lines). (b) Stark−R2PI spectra showing well-separated S$_1$−S$_0$ origin bands of *trans*-HyQ (33 500 cm^{-1}) and *cis*-HyQ (33 535 cm^{-1}) at specific deflected regions and voltages.

■ RESULTS AND DISCUSSION

The performance of our experimental setup has been tested with 3-aminophenol (3-AP) as dipole moments of its *cis* and *trans* conformational isomers are quite distinct and were accurately measured to be 2.33 and 0.77 D, respectively.[41] Besides, it is an ideal system for testing the robustness of the current setup compared to the original one reported by Filsinger et al.[23] All eigenstates of 3-aminophenol belong to strong-field seekers, and thus *cis*-3-AP, because of its larger effective dipole moment (μ_{eff}), deflects more significantly compared to *trans*-3-AP. Deflection profiles are obtained by detecting the resonant two photon ionization (R2PI) signal intensity of the S$_1$−S$_0$ origin band of *cis* or *trans* conformational isomer as a function of the vertical displacement position of the laser focal point with respect to the molecular beam axis at the position of ∼28 cm downstream from the Stark deflector (Figure 1). As expected, deflection becomes more efficient for the higher voltage and heavier (slower) carrier gas (Figure S1).[27] The most probable position of the deflection profile is estimated to be just 0.3 mm upward from the molecular beam axis when the applied voltage to the Stark deflector is 3 kV for *cis*-3AP seeded in Ar carrier gas. Yet it is found to increase sharply to 1.1, 1.9, or 2.5 mm as the applied voltage increases to 6.0, 9.0, or 11.4 kV, respectively. The carrier gas effect is also quite significant, giving the vertical deflection position of 0.6 or 2.5 mm for the *cis* conformer when seeded in Ne or Ar carrier gas, respectively, at $V = 11.4$ kV. It is interesting to note that it is even possible to deflect *trans*-3-AP by ∼1 mm when the

molecular beam is much slowed down by Xe carrier gas at $V = 11.4$ kV while the deflected position of the *trans* conformer is measured to be only 0.2 or 0.5 mm when Ne or Ar carrier gas is used at the same voltage (Figure S2). Average deflection positions obtained for various carrier gases with changing the applied voltage are summarized in Table 1. Although the rotational temperature of the jet from the more conventional General valve in the current setup is relatively high compared to that from the Even−Lavie valve used in ref 23, complete spatial separation of *cis*-3-AP from the conformational mixture could be achieved at the vertical position of $y > 4$ mm using the Ar carrier gas at $V = 11.4$ kV. At the same condition, interestingly, *trans*-3-AP could be isolated at the purity of ∼90% at $y = 0$ mm as most of *cis*-3-AP is being deflected out from the center of the molecular beam. Trajectory simulations explain measured deflection profiles quite well. It is noteworthy that the spectral width of the S$_1$−S$_0$ origin band becomes decreased for the deflected species (Figure S3). This is consistent with the intrinsic property of the Stark deflector where molecular species with the lowest rotational angular momentum number are most deflected.

Now, two conformational isomers of hydroquinone in the jet are separated in the Stark deflector described above. It is quite interesting that *trans*-HyQ in the ground electronic state has obviously zero dipole moment whereas the dipole moment of *cis*-HyQ has been measured to be 2.38 D from previous microwave spectroscopy.[42] Deflection profiles taken by monitoring the S$_1$−S$_0$ origin band of *trans* or *cis* conformer
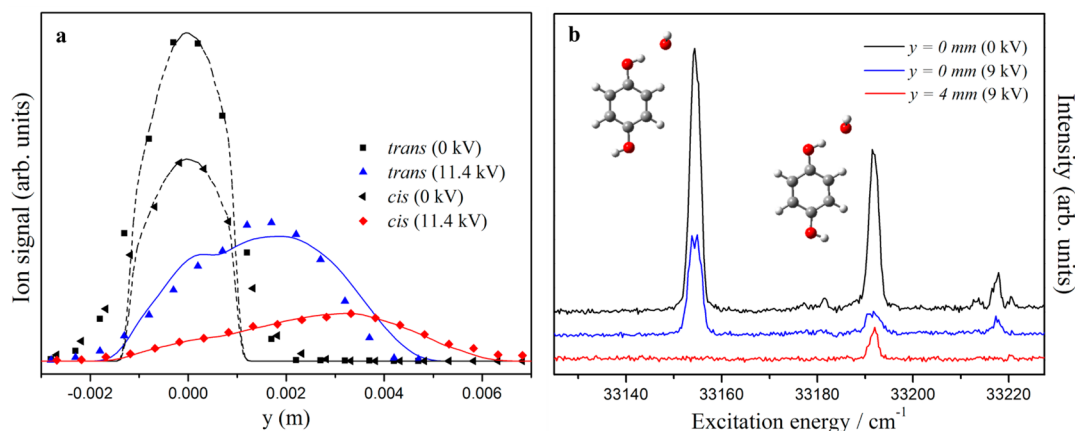
Figure 3. (a) Experiment (symbols) and simulation (lines) of deflection profiles taken by the S_1–S_0 origin band at 33 155 or 33 192 cm^{-1} for *trans*-HyQ–H$_2$O or cis-HyQ–H$_2$O cluster in the molecular beam seeded in Ne, respectively. (b) Stark–R2PI spectra clearly show conformer-specific vibronic structures of two distinct conformational cluster isomers.

clearly show their distinct behaviors in the Stark deflector. When the voltage of 6 kV is applied for the molecular beam containing both conformers seeded in Ar, it has been found that *trans*-HyQ is not deflected and remains in the original molecular beam, confirming that *trans*-HyQ has a symmetry of inversion. On the other hand, *cis*-HyQ deflects quite significantly in the same condition and it is possible to separate out completely pure *cis*-HyQ from the mainstream of the molecular beam at the vertical position of $y > \sim$2.3 mm (Figure 2). As *trans*-HyQ is little influenced by inhomogeneous electric fields, spatial separation of the *cis* conformer is easily attainable even in mild conditions of low voltages and light carrier gases. R2PI spectra taken at different vertical positions after the Stark deflector then give rise to vibronic excitation spectra enriched with either *cis* or *trans* conformer, making possible unambiguous spectral identification of each conformer. This combined Stark–R2PI spectroscopy has great advantage in terms of conformational identification of vibronic transitions compared to the more conventional hole-burning[9−11] or IR-dip spectroscopic technique[12] as one can easily identify the conformational isomer simply by inspecting the molecular geometry alone. The relative population of *trans*-HyQ and *cis*-HyQ in the jet is found to be comparable and our conformational assignment is consistent with previous spectroscopic reports,[44,45] giving the S_1–S_0 origin bands of *trans*-HyQ and *cis*-HyQ at 33 500 and 33 535 cm^{-1}, respectively. Small intensity peaks observed at 33 517 and 33 567 cm^{-1} behave like the origin band of *trans*-HyQ in the Stark deflector and are attributed to its vibrational hot bands as intensities of these bands are influenced by the carrier gas.

In contrast to the case of monomer, spectral assignment for two different conformational isomers of the HyQ–H$_2$O cluster has been controversial. It is spectroscopically well-known that either *trans*- or *cis*-HyQ interacts with water to give *trans*-HyQ–H$_2$O or *cis*-HyQ–H$_2$O cluster in the molecular beam, respectively. Two strongly observed bands at 33 155 and 33 192 cm^{-1} in the mass-resolved R2PI spectrum had been ascribed to S_1–S_0 origins of *trans*-HyQ–H$_2$O and *cis*-HyQ–H$_2$O clusters, respectively, by the Wategaonkar group[35] based on their relative band intensities and similarity of the spectral shift of each cluster isomer with respect to its associated monomeric conformer as well as theoretical calculations. Later, however, from conformer-specific zero-electron kinetic energy

(ZEKE) spectroscopic study of the same system combined with Franck–Condon analyses, the conformational assignment was reversed by the same research group, and thus 33 155 and 33 192 cm^{-1} bands were assigned as S_1–S_0 origins of *cis*-HyQ–H$_2$O and *trans*-HyQ–H$_2$O clusters, respectively.[36] This controversy stems from the fact that electrostatic differences of two cluster conformational isomers in the ground and excited states are quite subtle for theoretical calculations to be decisive.

Deflection profiles obtained after the Stark deflector at 11.4 kV for the molecular beam seeded in Ne now show quite distinct behaviors of the 33 155 and 33 192 cm^{-1} bands, giving the most probable deflection positions of 1.4 and 2.7 mm, respectively (Figure 3). This indicates right away that the 33 192 cm^{-1} band should be associated with the cluster with the larger effective dipole moment whereas the cluster with the relatively smaller dipole moment is associated with the 33 155 cm^{-1} band. According to our DFT calculations (B3LYP/6-311++G(3df,3pd)), the dipole moment of the *cis*-HyQ–H$_2$O cluster is predicted to be larger than that of the *trans*-HyQ–H$_2$O cluster, giving their dipole moments of 4.64 and 3.13 D, respectively. This calculated result is quite consistent with chemical intuition[41] that one can obtain just from different geometrical arrangements of two cluster conformational isomers, considering that the local dipole moment of the hydroxyl group on the *para* position with respect to the clustering hydroxyl moiety adds up to increase the total dipole moment of the *cis*-HyQ–H$_2$O cluster while it cancels out in the *trans*-HyQ–H$_2$O cluster. Our simulations of deflection profiles based on these calculated dipole moments explain the experiment quite well. Therefore, it is quite certain that the 33 192 cm^{-1} band is the origin band of the *cis*-HyQ–H$_2$O cluster whereas the 33 155 cm^{-1} band should be due to the *trans*-HyQ–H$_2$O cluster according to our Stark–R2PI spectroscopy. This is consistent with the assignment from ref 35 rather than that from ref 36 even though the latter is more recently reported. Furthermore, low-frequency van der Waals modes associated with the specific conformational cluster isomer could be also identified. Conformational identification in spectroscopy[41] is so essential for investigation of the structure–function relationship at the molecular level, and our Stark–R2PI spectroscopy is found to be invaluable for that purpose.

■ CONCLUSION

In this report, two geometrically distinct conformational isomers of hydroquinone and their 1:1 clusters with water have been successfully separated in inhomogeneous electric fields given by a simple two-wire Stark deflector in the supersonic jet generated from the more conventional General pulsed valve. R2PI combined with the Stark deflector gives conformer-selective S_1–S_0 excitation spectra which provide unambiguous conformational identification as well as conformer-specific vibronic structures of excited states. Conformational cluster isomers of *trans*- and *cis*-HyQ–H_2O clusters have also been spatially separated according to their distinct effective dipole moment strengths in the Stark deflector, and we could put an end to a dispute regarding the conformational assignment, giving the first example for the spatial separation of conformational cluster isomers in the Stark deflector.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b10431.

> Dependence of deflection on voltages and carrier gases, Stark–R2PI spectra and rotational state distributions for deflected 3-AP, Stark energy curves, and molecular parameters used for simulation of deflection profiles (PDF)

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Notes

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■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Schreiner, P. R. Metal-free Organocatalysis through Explicit Hydrogen Bonding Interactions. *Chem. Soc. Rev.* **2003**, *32*, 289–296.

(2) Taylor, M. S.; Jacobsen, E. N. Asymmetric Catalysis by Chiral Hydrogen-Bond Donors. *Angew. Chem., Int. Ed.* **2006**, *45*, 1520–1543.

(3) Prins, L. J.; Reinhoudt, D. N.; Timmerman, P. Noncovalent Synthesis Using Hydrogen Bonding. *Angew. Chem., Int. Ed.* **2001**, *40*, 2382–2426.

(4) Han, S.; Yoo, H. S.; Kim, S. K. Conformer-Specific Ionization Spectroscopy of Bromocyclohexane: Equatorial versus Axial Conformers. *J. Phys. Chem. A* **2010**, *114*, 10005–10010.

(5) Harris, S. J.; Karsili, T. N. V.; Murdock, D.; Oliver, T. A. A.; Wenge, A. M.; Zaouris, D. K.; Ashfold, M. N. R.; Harvey, J. N.; Few, J. D.; Gowrie, S.; et al. A Multipronged Comparative Study of the Ultraviolet Photochemistry of 2-, 3-, and 4-Chlorophenol in the Gas Phase. *J. Phys. Chem. A* **2015**, *119*, 6045–6056.

(6) Ito, F.; Nakanaga, T.; Futami, Y.; Kudoh, S.; Takayanagi, M.; Nakata, M. Isomeric Structures of CH_3I Dimers in a Supersonic Jet Studied by Matrix-Isolation Infrared Spectroscopy and Ab Initio Calculation. *Chem. Phys. Lett.* **2001**, *343*, 185–191.

(7) Lanucara, F.; Holman, S. W.; Gray, C. J.; Eyers, C. E. The Power of Ion Mobility-Mass Spectrometry for Structural Characterization and the Study of Conformational Dynamics. *Nat. Chem.* **2014**, *6*, 281–294.

(8) Czerwinska, I.; Kulesza, A.; Choi, C.; Chirot, F.; Simon, A.-L.; Far, J.; Kune, C.; de Pauw, E.; Dugourd, P. Supramolecular Influence on *Cis-Trans* Isomerization Probed by Ion Mobility Spectrometry. *Phys. Chem. Chem. Phys.* **2016**, *18*, 32331–32336.

(9) Rodrigo, C. P.; Müller, C. W.; Pillsbury, N. R.; James, W. H., III.; Plusquellic, D. F.; Zwier, T. S. Conformer-Specific Vibronic Spectroscopy and Vibronic Coupling in a Flexible Bichromophore: Bis-(4-hydroxyphenyl)methane. *J. Chem. Phys.* **2011**, *134*, 164312.

(10) Mehta-Hurt, D. N.; Korn, J. A.; Navotnaya, P.; Parobek, A. P.; Clayton, R. M.; Zwier, T. S. The Spectroscopy and Photochemistry of Quinioline Structural Isomers: (E)- and (Z)- Phenylvinylnitrile. *J. Chem. Phys.* **2015**, *143*, 074304.

(11) Lee, J.; Kim, S.-Y.; Kim, S. K. Spectroscopic Separation of the Methyl Internal-Rotational Isomers of Thioanisole Isotopomers ($C_6H_5S-CH_2D$ and $C_6H_5S-CHD_2$). *J. Phys. Chem. A* **2014**, *118*, 1850–1857.

(12) Schmitt, M.; Spiering, F.; Zhaunerchyk, V.; Jongma, R. T.; Jaeqx, S.; Rijs, A. M.; van der Zande, W. J. Far-Infrared Spectra of the Tryptamine A Conformer by IR-UV Ion Gain Spectroscopy. *Phys. Chem. Chem. Phys.* **2016**, *18*, 32116–32124.

(13) Park, S. T.; Kim, S. K.; Kim, M. S. Observation of Conformation-Specific Pathways in the Photodissociation of 1-Iodopropane Ions. *Nature* **2002**, *415*, 306–308.

(14) Choi, K.-W.; Ahn, D.-S.; Lee, J.-H.; Kim, S. K. A Highly Conformationally Specific α- and β-Ala$^+$ Decarboxylation Pathway. *Chem. Commun.* **2007**, *0*, 1041–1043.

(15) Kim, S.-Y.; Lee, J.; Kim, S. K. Conformer Specific Nonadiabatic Reaction Dynamics in the Photodissociation of Partially Deuterated Thioanisoles ($C_6H_5S-CH_2D$ and $C_6H_5S-CHD_2$). *Phys. Chem. Chem. Phys.* **2017**, *19*, 18902–18912.

(16) Kim, M. H.; Shen, L.; Tao, H.; Martinez, T. J.; Suits, A. G. Conformationally Controlled Chemistry: Excited-State Dynamics Dictate Ground-State Reaction. *Science* **2007**, *315*, 1561–1565.

(17) Stearns, J. A.; Mercier, S.; Seaiby, C.; Guidi, M.; Boyarkin, O. V.; Rizzo, T. R. Conformation-Specific Spectroscopy and Photodissociation of Cold, Protonated Tyrosine and Phenylalanine. *J. Am. Chem. Soc.* **2007**, *129*, 11814–11820.

(18) Zhang, L.; Pan, Y.; Guo, H.; Zhang, T.; Sheng, L.; Qi, F.; Lo, P.-K.; Lau, K.-C. Conformation-Specific Pathways of β-Alanine: A Vacuum Ultraviolet Photoionization and Theoretical Study. *J. Phys. Chem. A* **2009**, *113*, 5838–5845.

(19) Oliver, T. A. A.; King, G. A.; Ashfold, M. N. R. The Conformer Resolved Ultraviolet Photodissociation of Morpholine. *Chem. Sci.* **2010**, *1*, 89–96.

(20) Zaouris, D. K.; Wenge, A. M.; Murdock, D.; Oliver, T. A. A.; Richmond, G.; Ritchie, G. A. D.; Dixon, R. N.; Ashfold, M. N. R. Conformer Specific Dissociation Dynamics of Iodocyclohexane Studied by Velocity Map Imaging. *J. Chem. Phys.* **2011**, *135*, 094312.

(21) Chang, Y.-P.; Horke, D. A.; Trippel, S.; Küpper, J. Spatially-Controlled Complex Molecules and Their Applications. *Int. Rev. Phys. Chem.* **2015**, *34*, 557–590.

(22) Filsinger, F.; Erlekam, U.; von Helden, G.; Küpper, J.; Meijer, G. Selector for Structural Isomers of Neutral Molecules. *Phys. Rev. Lett.* **2008**, *100*, 133003.

(23) Filsinger, F.; Küpper, J.; Meijer, G.; Hansen, J. L.; Maurer, J.; Nielsen, J. H.; Holmegaard, L.; Stapelfeldt, H. Pure Samples of Individual Conformers: The Separation of Stereoisomers of Complex Molecules Using Electric Fields. *Angew. Chem., Int. Ed.* **2009**, *48*, 6900–6902.

(24) Filsinger, F.; Küpper, J.; Meijer, G.; Holmegaard, L.; Nielsen, J. H.; Nevo, I.; Hansen, J. L.; Stapelfeldt, H. Quantum-State Selection,

Alignment, and Orientation of Large Molecules Using Static Electric and Laser Fields. *J. Chem. Phys.* **2009**, *131*, 064309.

(25) Trippel, S.; Chang, Y.-P.; Stern, S.; Mullins, T.; Holmegaard, L.; Küpper, J. Spatial Separation of State- and Size-Selected Neutral Clusters. *Phys. Rev. A: At., Mol, Opt. Phys.* **2012**, *86*, 033202.

(26) Chang, Y.-P.; Długołęcki, K.; Küpper, J.; Rösch, D.; Wild, D.; Willitsch, S. Specific Chemical Reactivities of Spatially Separated 3-Aminophenol Conformers with Cold Ca^+ Ions. *Science* **2013**, *342*, 98−101.

(27) Kierspel, T.; Horke, D. A.; Chang, Y.-P.; Küpper, J. Spatially Separated Polar Samples of the *Cis* and *Trans* Conformers of 3-Fluorophenol. *Chem. Phys. Lett.* **2014**, *591*, 130−132.

(28) Gerlach, W.; Stern, O. Der experimentelle Nachweis der Richtungsquantelung im Magnetfeld. *Eur. Phys. J. A* **1922**, *9*, 349−352.

(29) Stapelfeldt, H.; Seideman, T. *Colloquium*: Aligning Molecules with Strong Laser Pulses. *Rev. Mod. Phys.* **2003**, *75*, 543−557.

(30) Bethlem, H. L.; van Roij, A. J. A.; Jongma, R. T.; Meijer, G. Alternate Gradient Focusing and Deceleration of a Molecular Beam. *Phys. Rev. Lett.* **2002**, *88*, 133003.

(31) Parker, D. H.; Bernstein, R. B. Oriented Molecule Beams via the Electrostatic Hexapole: Preparation, Characterization, and Reactive Scattering. *Annu. Rev. Phys. Chem.* **1989**, *40*, 561−595.

(32) Compagnon, I.; Hagemeister, F. C.; Antoine, R.; Rayane, D.; Broyer, M.; Dugourd, P.; Hudgins, R. R.; Jarrold, M. F. Permanent Electic Dipole and Conformation of Unsolvated Tryptophan. *J. Am. Chem. Soc.* **2001**, *123*, 8440−8441.

(33) Ramsay, N. *Molecular Beams*; Oxford University Press: Oxford, U.K., 1956.

(34) Even, U.; Jortner, J.; Noy, D.; Lavie, N.; Cossart-Magos, C. Cooling of Large Molecules below 1 K and He Clusters Formation. *J. Chem. Phys.* **2000**, *112*, 8068.

(35) Meenakshi, P. S.; Biswas, N.; Wategaonkar, S. Gas Phase Spectroscopic Studies on Hydroquinone-Water Complex. *Phys. Chem. Chem. Phys.* **2003**, *5*, 294−299.

(36) Chakraborty, S.; Misra, P.; Wategaonkar, S. Zero Kinetic Energy Spectroscopy of Hydroquinone-Water (1:1) Complex: A Probe for Conformer Assignment. *J. Chem. Phys.* **2007**, *127*, 124317.

(37) Frisch, M. J.; et al. *Gaussian 09*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.

(38) Chang, Y.-P.; Filsinger, F.; Sartakov, B. G.; Küpper, J. CMI_{STARK}: Python Package for the Stark-Effect Calculation and Symmetry Classification of Linear, Symmetric and Asymmetric Top Wave-functions in DC Electric fields. *Comput. Phys. Commun.* **2014**, *185*, 339−349.

(39) Moro, R.; Bulthuis, J.; Heinrich, J.; Kresin, V. V. Electrostatic Deflection of the Water Molecule: A Fundamental Asymmetric Rotor. *Phys. Rev. A: At., Mol., Opt. Phys.* **2007**, *75*, 013415.

(40) Abd El Rahim, M.; Antoine, R.; Broyer, M.; Rayane, D.; Dugourd, P. Asymmetric Top Rotors in Electric Fields: Influence of Chaos and Collision in Molecular Beam Deflection Experiments. *J. Phys. Chem. A* **2005**, *109*, 8507−8514.

(41) Filsinger, F.; Wohlfart, K.; Schnell, M.; Grabow, J.-U.; Küpper, J. Precise Dipole Moments and Quadrupole Coupling Constants of the *Cis* and *Trans* Conformers of 3-Aminophenol: Determination of the Absolute Conformation. *Phys. Chem. Chem. Phys.* **2008**, *10*, 666−673.

(42) Caminati, W.; Melandri, S.; Favero, L. B. Microwave Spectroscopy of Hydroquinone: the Rotational Spectrum of the *Cis* conformer. *J. Chem. Phys.* **1994**, *100*, 8569.

(43) Patwari, G. N.; Doraiswamy, S.; Wategaonkar, S. Hole-Burning Spectroscopy of Jet-Cooled Hydroquinone. *Chem. Phys. Lett.* **1998**, *289*, 8−12.

(44) Humphrey, S. J.; Pratt, D. W. High Resolution $S_1 \leftarrow S_0$ Fluorescence Excitation Spectra of Hydroquinone. Distinguishing the *Cis* and *Trans* Rotamers by Their Nuclear Spin Statistical Weights. *J. Chem. Phys.* **1993**, *99*, 5078.

(45) Tzeng, W. B.; Narayanan, K.; Hsieh, C. Y.; Tung, C. C. A Study of the Excited State Structure and Vibrations of Hydroquinone by Ab Initio Calculations and Resonant Two-Photon Ionization Spectroscopy. *Spectrochim. Acta, Part A* **1997**, *53*, 2595−2604.