Supporting Information

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

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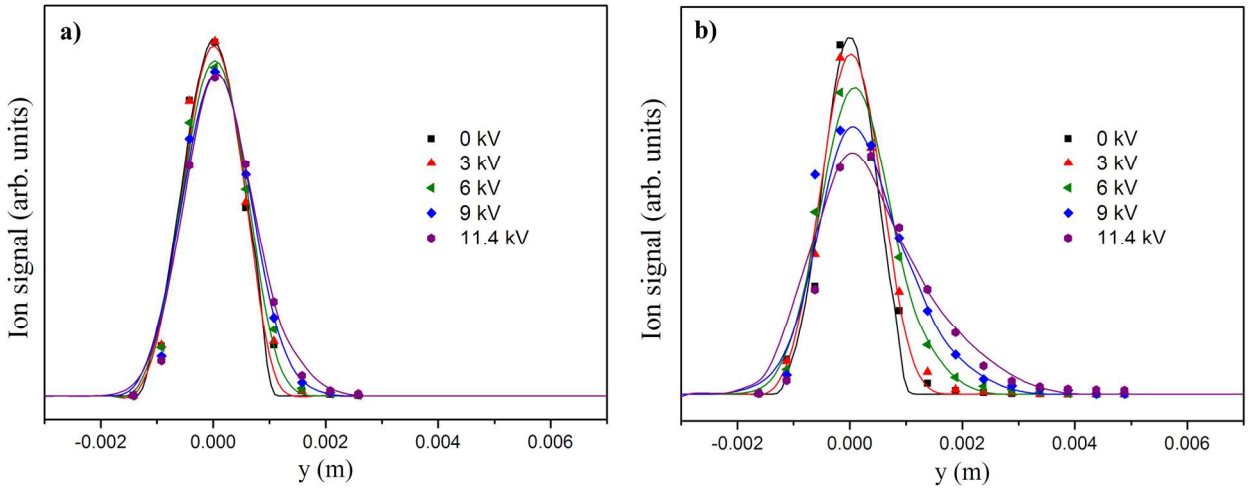
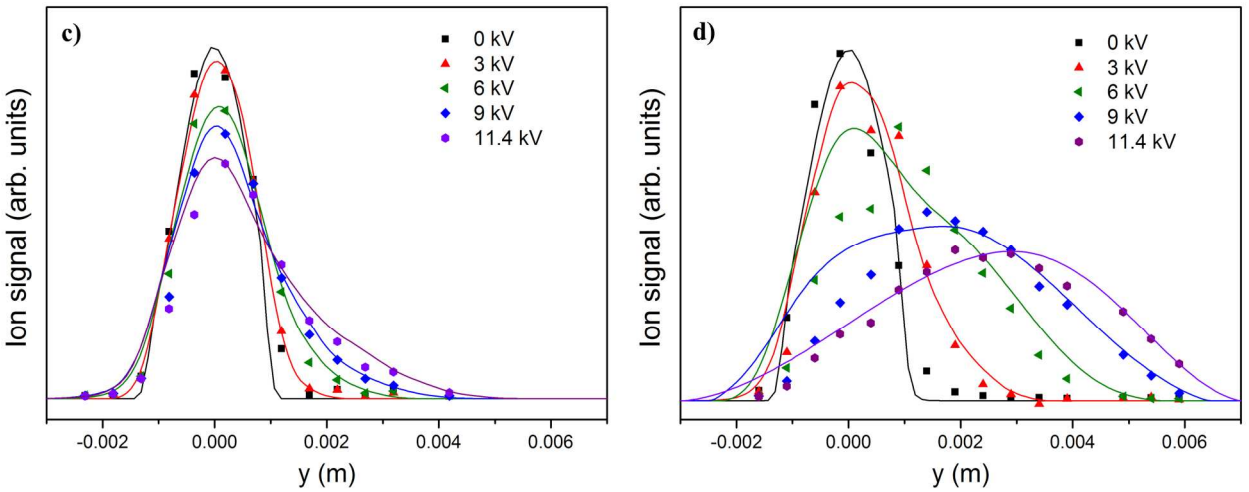
1. Dependence of deflection on voltages and carrier gas of 3-AP conformers.



- *Trans*-3-AP



- *Cis*-3-AP

Figure S1. Deflection profiles of *trans*, *cis*-3-AP seeded in (a, c) Ne and (b, d) Ar at the voltages from 0 kV to 11.4 kV. Symbols represent experiment and lines are simulations.

2. Deflection profiles of trans-3-AP seeded in Xen-on.

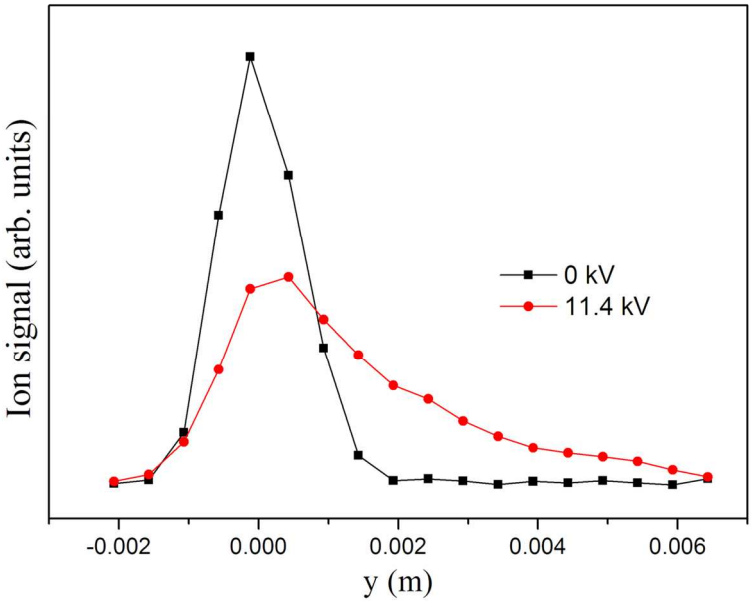
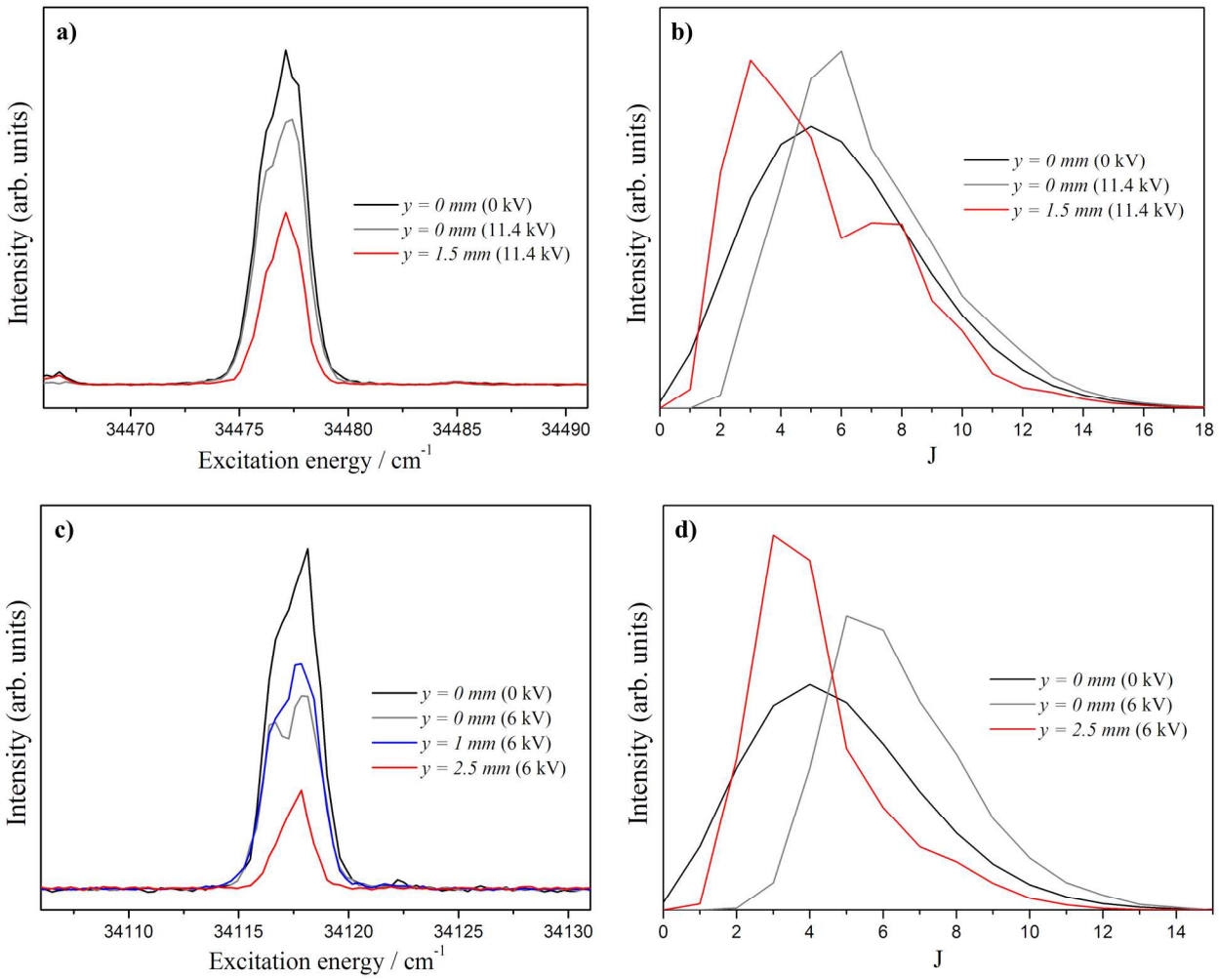


Figure S2. Experimental deflection profiles of *trans*-3-AP seeded in Xe at the deflector voltage of 11.4 kV taken by monitoring the S_1-S_0 origin signal intensity. The average deflection position is estimated to be ~ 1 mm.

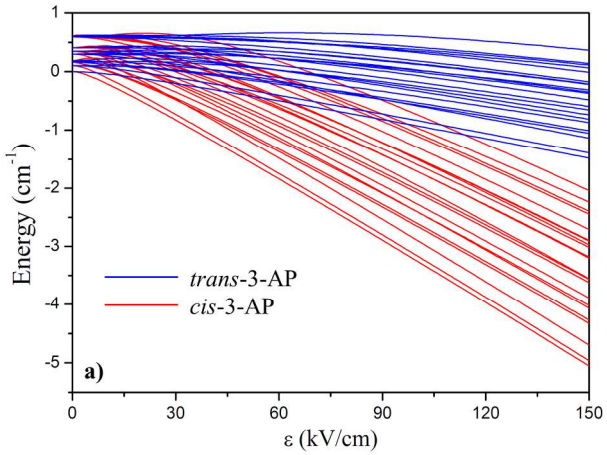


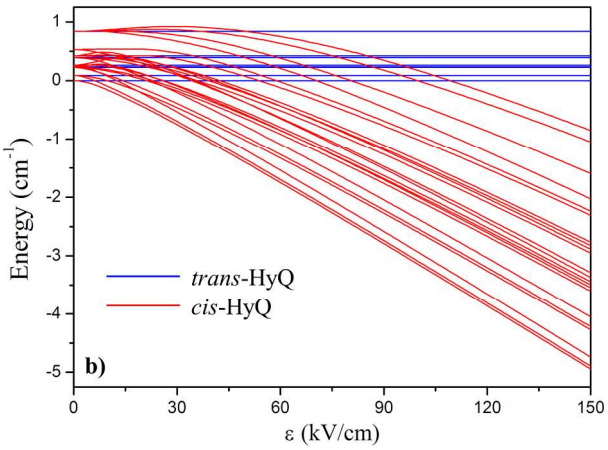
3. Stark-R2PI spectra and rotational state distributions at deflected regions of 3-AP.

Figure S3. Stark-R2PI spectra of (a) *trans*-3-AP and (c) *cis*-3-AP seeded in Ar at the origin band and corresponding normalized rotational state distributions (b, d) populated at specific deflected regions in the deflection profiles at simulated T_{rot} (Table 1). Since rotational states with lowest J's deflect most, relative population of low J's stands out in the deflected region. Accordingly,

full width at half maximum (FWHM) of the origin peak of *cis*(*trans*)-3-AP becomes shortened from 2.5 (2.4) cm^{-1} to 1.7 (2.0) cm^{-1}, respectively.

4. Stark energy curves for (*trans*, *cis*)-3-AP, HyQ, and HyQ-H_2O conformers.





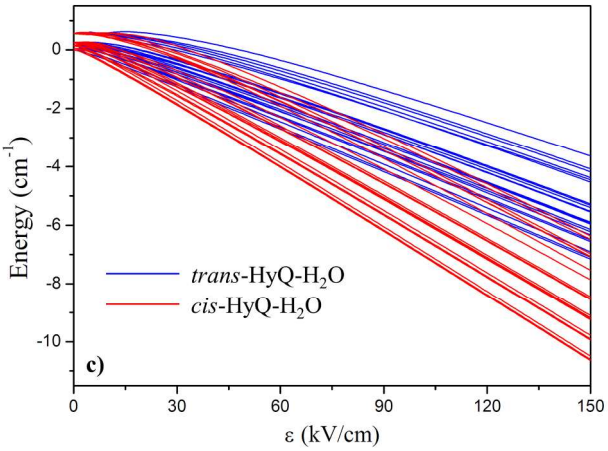


Figure S4. Stark energy shifts of 3-AP, HyQ and HyQ-H_2O conformational isomers for the lowest rotational quantum states (J≤2) as a function of applied electric field strengths.[1,2]

5. Molecular parameters for simulation of deflection profile

Table S1. Molecular mass, rotational constants, and electric dipole moments along the principal axis.

	cis(*trans*)-3-AP[a]	*cis*[b](*trans*[c])-HyQ	*cis*(*trans*)-HyQ-H_2O[d]
	Molecular mass		
Mass (g/mol)	109.13	110.11	128.13
	Rotational Constants		
A (MHz)	3734.93 (3730.17)	5614.14 (5615.1)	3844.31 (3820.5)
B (MHz)	1823.21 (1828.26)	1481.59 (1481.7)	757.35 (760.58)
C (MHz)	1226.49 (1228.19)	1172.67 (1172.8)	634.59 (636.20)
	Electric dipole moments		
μ_A (D)	1.772 (0.5563)	0 (0)	-2.8280 (-2.6244)
μ_B (D)	1.517 (0.5375)	2.38 (0)	3.6821 (1.7094)
μ_C (D)	0 (0)	0 (0)	0 (0)
μ_{Total} (D)	2.33 (0.77)	2.38 (0)	4.64 (3.13)

[a] The values from ref. *Phys. Chem. Chem. Phys.*, 10, 666-673 (2008).[3]
[b] The values from ref. *J. Chem. Phys.*, 100, 8569 (1994).[4]
[c] The values from ref. *J. Chem. Phys.*, 99, 5078 (1993).[5]
[d] Calculated values from B3LYP/6-311++G(3df,3pd).

Supporting References

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

(2) 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.

(3) 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.

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

(5) 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.