Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Excited State Dipole Moments and Lifetimes of 2-Cyanoindole from Rotationally Resolved Electronic Stark Spectroscopy.

Marie-Luise Hebestreit*,[1] Hilda Lartian,[1] Christian Henrichs,[1] Ralf Kühnemuth,[2] W. Leo Meerts,[3] and Michael Schmitt[1]

[1]*Heinrich-Heine-Universität, Institut für Physikalische Chemie I, D-40225 Düsseldorf, Germany*
[2]*Heinrich-Heine-Universität, Lehrstuhl für Molekulare Physikalische Chemie, D-40225 Düsseldorf, Germany*
[3]*Radboud University, Institute for Molecules and Materials,*
Felix Laboratory, Toernooiveld 7c, 6525 ED Nijmegen, The Netherlands.

---

[1] * *Corresponding author; Tel: +49 211 81 13219; E-mail: Marie-Luise.Hebestreit@uni-duesseldorf.de*

ELECTRONIC SUPPORTING INFORMATION

The supporting online material contains:

- A figure, containing the rotationally resolved electronic spectrum of the electronic origin of 1-deuterated 2-cyanoindole.
- A table, containing the experimental molecular parameters of 2-cyanoindole and 1-deuterated 2-cyanoindole.
- A table, containing the comparison of the changes of the inertial defects of 2-cyanoindole and other cyanoindoles upon electronic excitation.
- The description of the results of the Kraitchman analysis.
- A table, containing Cartesian r_s coordinates and center of mass (COM) distances of the H-atoms 1a of 2-cyanoindole in pm from a Kraitchman analysis of the rotational constants of the respective isotopologue.
- A figure, containing changes of the position of the H-Atom in 1-position of the pyrrole ring of 2-cyanoindole from a Kraitchman analysis in respect to the changes of the bond lengths upon electronic excitation.
- A figure, containing the vibronically resolved laser induced fuorescence spectrum of the electronic origin of 2-cyanoindole.
- A figure, containing a steady state absorption and fluorescence spectrum of 2-cyanoindole in ethylacetate.
- A figure, containing the vibronically resolved spectrum of the electronic origin of 2-cyanoindole-water and the fluorescence signal along with the iodine absorption spectrum while trying to record a rovibronically resolved spectrum.
- A table, containing the Cartesian coordinates in Bohr of 2-cyanoindole in the S_0 state from SCS-CC2/cc-pVTZ calculations.
- A table, containing the Cartesian coordinates in Bohr of 2-cyanoindole in the S_1 state from SCS-CC2/cc-pVTZ calculations.

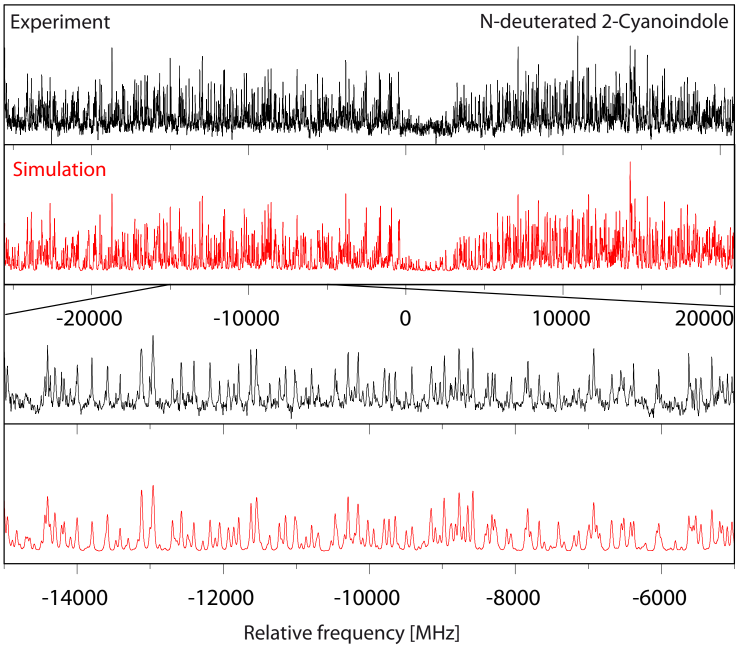

FIG. S1. Rotationally resolved electronic spectrum of the electronic origin of 2-cyanoindole(1-d$_1$), along with a simulation with the best CMA-ES fit parameters.

TABLE S1. Experimental molecular parameters of 2-cyanoindole and 2-cyanoindole(1-d$_1$). Doubly primed parameters belong to the electronic ground and single primed to the excited state. θ is the angle of the the transition dipole moment vector with the main inertial a-axis. A negative sign of this angle means an anti-clockwise rotation of the main inertial a-axis onto the dipole moment vector, shown in Figure 1. For details see text.

	Experiment	
	2-cyanoindole	2-cyanoindole(1-d$_1$)
A'' / MHz	3852.31(3)	3742.82(5)
B'' / MHz	698.76(1)	697.59(1)
C'' / MHz	591.57(1)	588.11(1)
$\Delta I''$ / amuÅ^2	-0.14(2)	-0.16(2)
A' / MHz	3746.10(4)	3643.40(6)
B' / MHz	691.84(2)	690.75(2)
C' / MHz	584.14(2)	580.81(2)
$\Delta I'$ / amuÅ^2	-0.22(3)	-0.23(4)
ΔA / MHz	-106.21(1)	-99.43 (1)
ΔB / MHz	-6.91(1)	-6.84(1)
ΔC / MHz	-7.43(1)	-7.30(1)
$\Delta \nu_{Lorentz}$ / MHz	16.94(1)	15.33(6)
τ / ns	9.40(1)	10.38(8)
θ / $^\circ$	±45.9(20)	45.6(20)
ν_0 / cm^{-1}	33422.63(5)	33426.61(1)

TABLE S2. Comparison of the changes of the inertial defects of 2-cyanoindole and other cyanoindoles upon electronic excitation.

molecule	2-cyanoindole	3-cyanoindole[1]	4-cyanoindole[2]	5-cyanoindole[3]
$\Delta I''$ / amuÅ^2	-0.14	-0.02	-0.02	-0.14
$\Delta I'$ / amuÅ^2	-0.22	-0.08	-0.06	-0.26

Kraitchman analysis

From the rotational constants of 2-cyanoindole and 2-cyanoindole(1-d$_1$), the position of the hydrogen atom in 1-position of the pyrrole ring has been determined on the basis of Kraitchman's equations[4] for planar asymmetric molecules in the ground and the electronically excited states. The $|a|$ and $|b|$ components of the Cartesian coordinates in the coordinate system of the reference isotopologue in the electronic ground and excited states are given in Table S3 along with the center of mass (COM) distances of the respective atom. The $|a|$ component becomes smaller (-2.76 pm) and the $|b|$ component becomes also slightly smaller (-0.90 pm) upon excitation, leading to a decrease of the distance of the H-atom from the center of mass from 224.83 pm to 222.71 pm. This can be understood on the basis of the distortions upon excitation, shown in Figure 5c. Simultaneous lengthening of the C2-N1 bond and shortening of the N1-C8 bond leads to the observed changes of the Cartesian coordinates. This is shown schematically in Figure S2.

TABLE S3. Cartesian r_s coordinates and center of mass (COM) distances of the H-atoms 1a of 2-cyanoindole in pm from a Kraitchman analysis of the rotational constants of the respective isotopologue.

	1-position	
	$|a|$	$|b|$
S$_0$/pm	109.83	196.18
COM /pm	224.83	
S$_1$/pm	107.07	195.28
COM/pm	222.71	

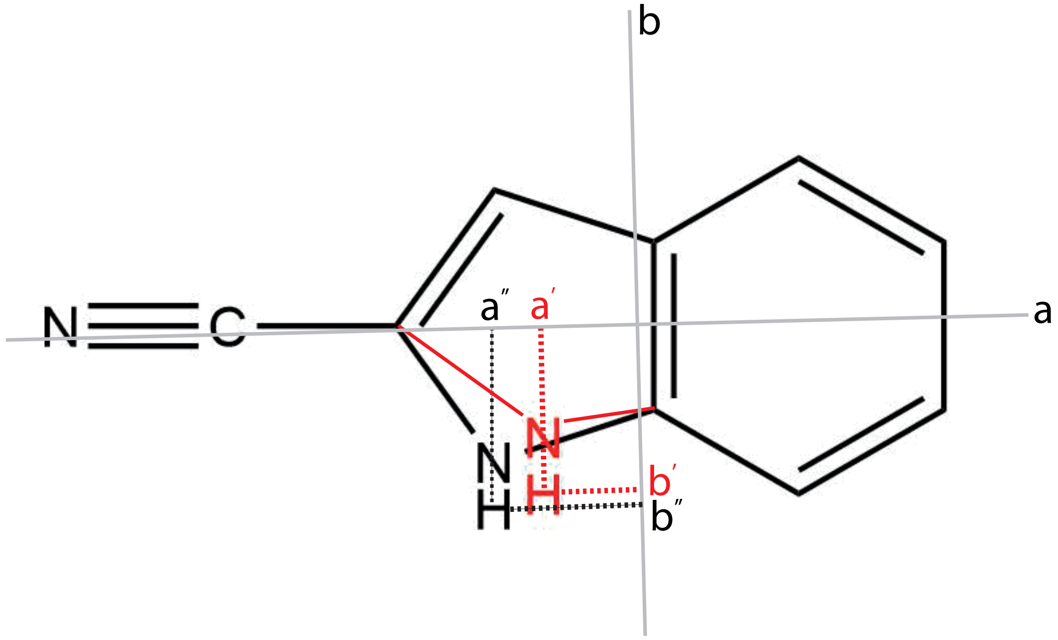

FIG. S2. Changes of the position of the H-Atom in 1-position of the pyrrole ring of 2-cyanoindole from a Kraitchman analysis in respect to the changes of the bond lengths upon electronic excitation. As simplification for the excited state only the N- and H-atom of the pyrrole ring with all involved bondings are shown in red. To clearly emphasize the effect of the changes of the bond lengths they are not represented in true to scale. The black dotted lines lead to the value of the $|a|$ and $|b|$ component in the ground state (a'' and b''). The red dotted lines lead to the value of the $|a|$ and $|b|$ component in the electronic excited state (a' and b').

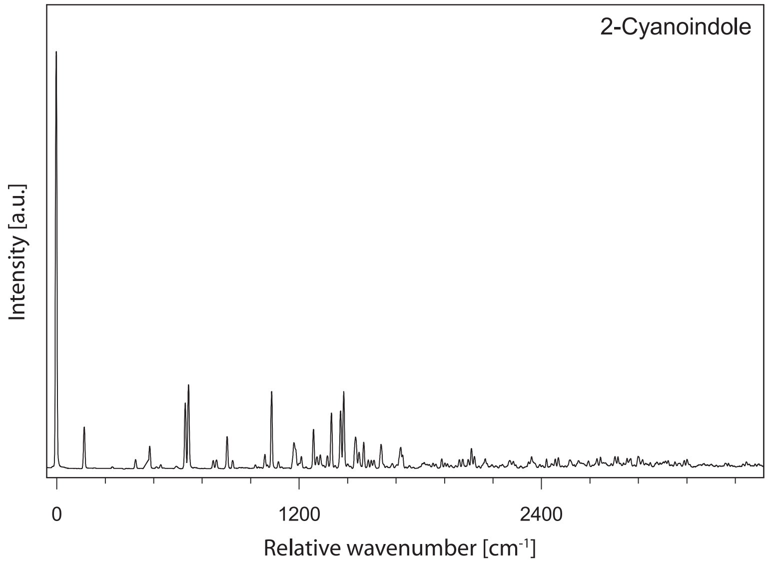

FIG. S3. Vibronically resolved laser induced fluorescence spectrum of the electronic origin of 2-cyanoindole.

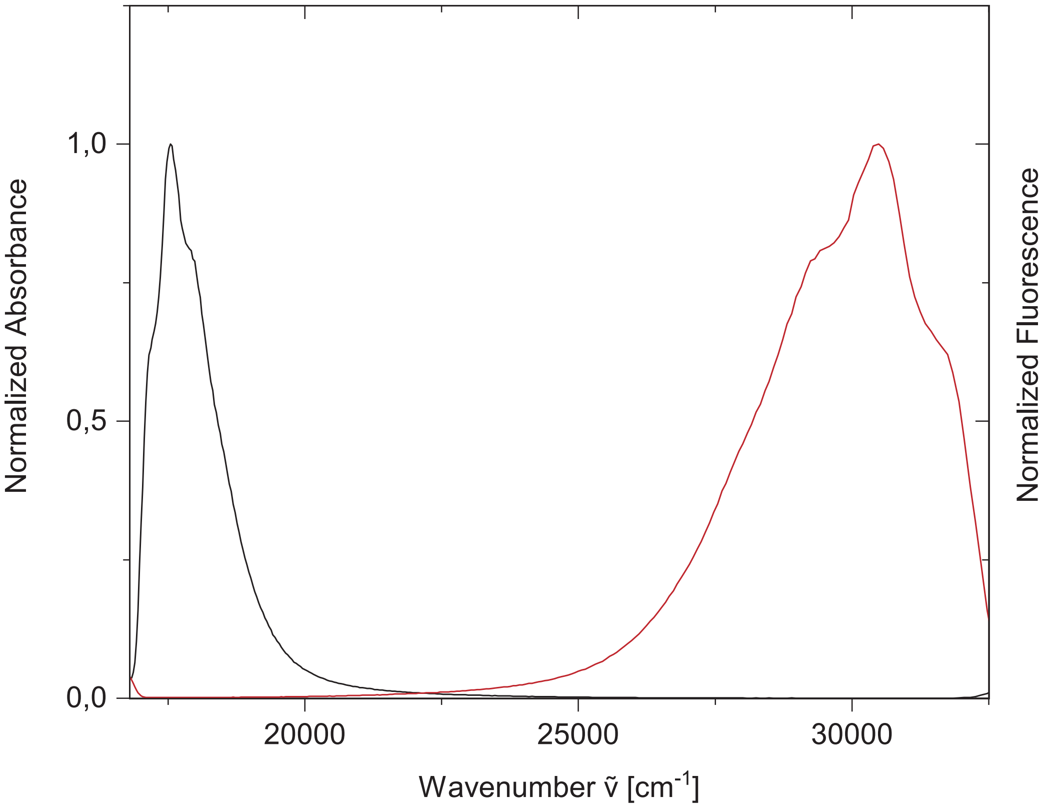

FIG. S4. Steady state absorption and fluorescence spectrum of 2-cyanoindole in ethylacetate.

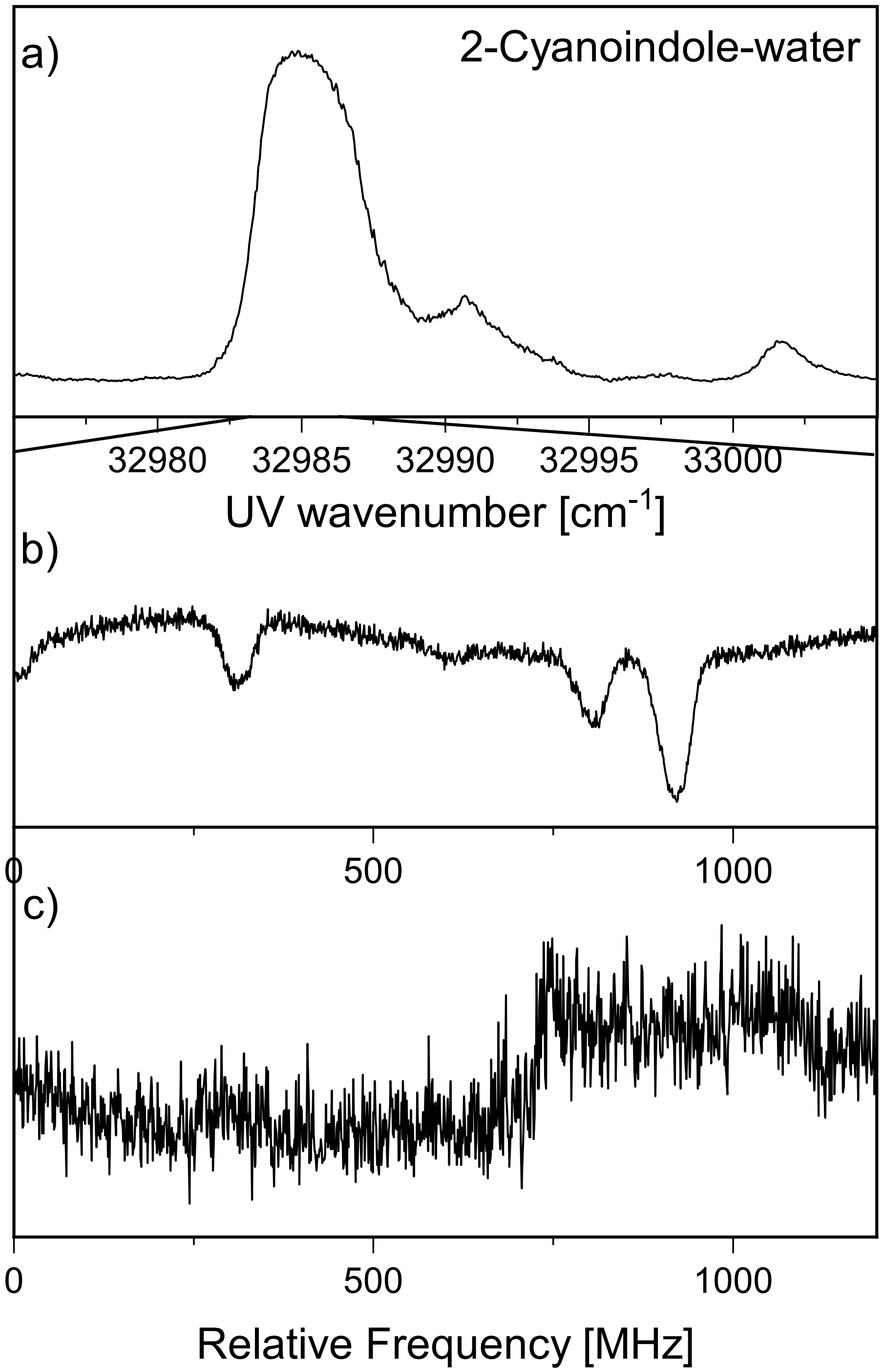

FIG. S5. Overview of the measurements of the 1:1 water cluster of 2-cyanoindole. (a) The origin of the cluster at 32947.5cm^{-1}, red shiftet 438.1cm^{-1} relative to the monomer band in the low resolution laser induced fluorescence spectrum in a free jet with a strong fluorescence signal. (b) Iodine absorption spectrum for obtaining the absolute frequency of the fundamental laser beam at rovibronically resolved measurements by comparing to tabulated lines. (c) Broad onset of fluorescence signal at the position of the 1:1 water cluster of 2-cyanoindole by trying to measure a rotationally resolved laser induced fluorescence spectrum.

TABLE S4. SCS CC2/cc-pVTZ calculated optimized S_0 cartesian coordinates of 2-cyanoindole (in bohr).

c	0.00965109	-0.00000240	-0.00198611
c	0.00227952	0.00002036	2.61618242
c	2.28423702	-0.00006083	4.00954683
c	4.61737681	0.00011409	2.81481571
c	4.61696824	-0.00001119	0.16495783
c	2.35067669	-0.00005505	-1.27373963
c	3.05932230	-0.00013303	-3.87999961
c	5.66879689	-0.00010273	-3.94652258
n	6.61054742	0.00036221	-1.50370261
h	1.84267625	-0.00012365	-5.51235663
h	-1.77683529	-0.00013453	3.62361422
h	2.20733351	-0.00020760	6.05306573
h	6.35955507	0.00029600	3.88646831
c	7.32545773	-0.00041374	-6.06305644
h	-1.74441454	0.00004476	-1.05443043
h	8.45757491	-0.00068733	-1.05500588
n	8.71845132	-0.00078938	-7.79727156

TABLE S5. SCS CC2/cc-pVTZ calculated optimized S_1 cartesian coordinates of 2-cyanoindole (in bohr).

c	-0.00638193	0.00074375	-0.06014177
c	0.02568172	0.00048503	2.65782818
c	2.28255456	-0.00047707	4.09286945
c	4.66183665	-0.00083463	2.84345431
c	4.63536344	-0.00042510	0.18608467
c	2.30756126	0.00042503	-1.33797017
c	3.02605558	0.00053104	-3.92664702
c	5.66479952	-0.00011410	-4.05471004
n	6.57014542	-0.00066410	-1.48500484
h	1.78063181	0.00107702	-5.53849809
h	-1.76792546	0.00096871	3.64216511
h	2.18936694	-0.00073273	6.13148916
h	6.42061035	-0.00136688	3.88509846
c	7.35336138	-0.00047523	-6.08568547
h	-1.78453996	0.00133581	-1.06660896
h	8.42159259	-0.00158840	-1.03017356
n	8.82894109	-0.00077219	-7.77296982

[1] M. Schneider, M.-L. Hebestreit, M. M. Lindic, H. Parsian, A. Y. Torres-Boy, L. Alvarez-Valtierra, W. L. Meerts, R. Kühnemuth and M. Schmitt, *Phys. Chem. Chem. Phys.*, 2018, **20**, 23441–23452.

[2] M.-L. Hebestreit, H. Lartian, M. Schneider, R. Kühnemuth, A. Y. Torres-Boy, S. Romero-Servin, J. A. Ruiz-Santoyo, L. Alvarez-Valtierra, W. L. Meerts and M. Schmitt:, *J. Mol. Struct.*, 2020, **1210**, 127992.

[3] O. Oeltermann, C. Brand, B. Engels, J. Tatchen and M. Schmitt, *Phys. Chem. Chem. Phys.*, 2012, **14**, 10266–10270.

[4] J. Kraitchman, *Am. J. Phys.*, 1953, **21**, 17.