

Investigating Crystal Violet Reactivity and Color with Quantum Theory and Interactive Webpages

John W. Keller and Arianna L. Demmerly

Other Supporting Information

	page
Fig. S1 and Table S1. Worksheet scores and topics	2
Fig. S2. Cyclic OH ⁻ -4-water complexes	3
ORCA input file (Crystal violet)	4,5
Table. Thermodynamic properties of optimized crystal violet react, CVOH, and transition state	6

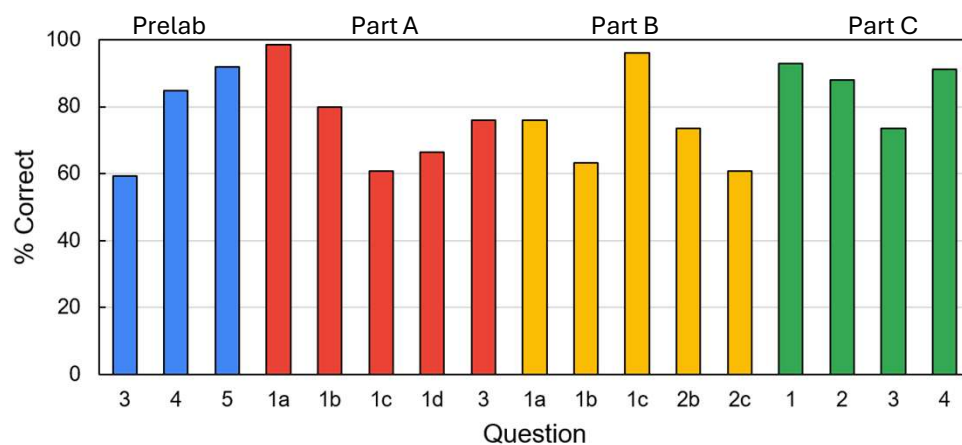
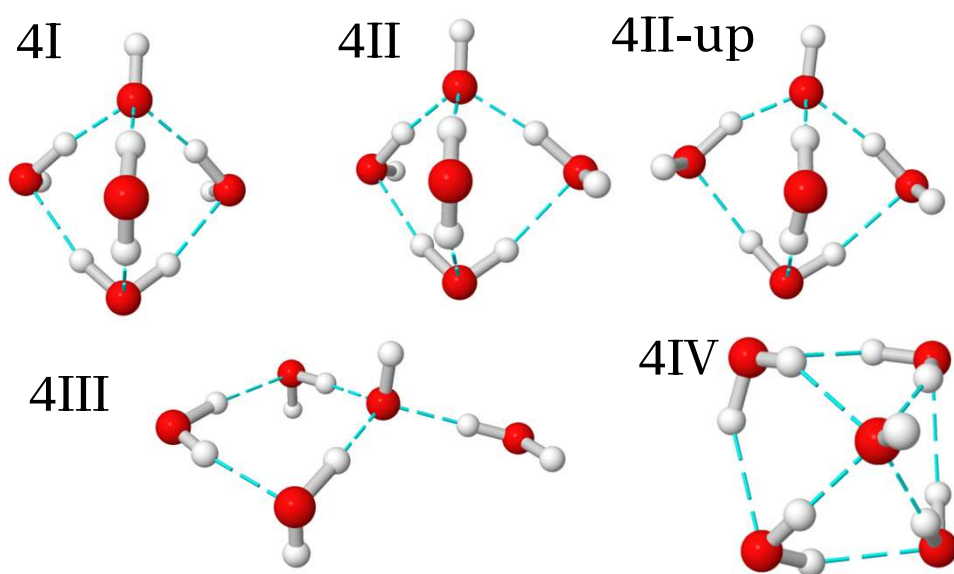


Figure S1. Grading analysis of Spring 2025 Crystal Violet and Quantum Theory prelab and worksheet. Question topics are in Table S1.

Table S1. Worksheet topics

Section	Question	Topic
Prelab	3	HOH..OH. Draw Lewis structure
	4	Write the balanced equation
	5	Calculate ΔE_{rxn}
Part A	1a	Enter partial charges in a table
	1b	Calculate percent total charge
	1c	Complete resonance Lewis structures
	1d	Analyze CV isosurfaces
Part B	3	Analyze three C-N bond lengths
	1a	Calculate ΔE_{rxn} and ΔE_{act}
	1b	Label Energy vs Reaction Progress graph
	1c	Endothermic or exothermic?
	2b	Describe H-bond and C-O changes
Part C	2c	Why does energy first go up, then down?
	1	Calculate two λ_{max} 's using LUMO-HOMO ΔE 's
	2	Compare LUMO's spatial distribution
	3	Guess electromagnetic spectral range
	4	Identify central C in CV's LUMO



Cluster	$E_{\text{B3LYP}} / \text{a.u.}$	Relative Energy / kcal mol^{-1}			
		ΔE_{elec}	$\Delta E_{\text{internal}}$	ΔH	ΔG
4IV	-381.7121341	4.5503	5.2730	5.2730	5.2792
4III	-381.7146916	2.9454	2.2622	2.2628	0.0000
4I	-381.7182986	0.6820	0.1732	0.1732	0.8026
4II	-381.7191093	0.1733	0.0257	0.0264	0.7298
4II-up	-381.7193854	0.0000	0.0000	0.0000	0.8616

Figure S2. Cyclic OH⁻-4 water clusters were optimized in this work at the B3LYP/6-31G(d,p)/SMD level of theory. Isomers 4I-4IV were originally identified by Bankura and Chandra using MP2 or various DFT functionals using the 6-31+G(d) basis set (*Chem. Phys.* **2012**, 400, 154-164). Isomer 4II-up was not identified by Bankura and Chandra, however, it is the most stable of the cyclic clusters at the level of theory used in the crystal violet quantum experiment. The above cluster structures are illustrated with Jmol v 16.3.13.

The cartesian coordinates of these clusters are in the Cartesian-Coordinates file in the Supporting Information.

```

#
# cv-631Gss-b3-sp-smd
#
%pal
nproc 8
End
! B3LYP 6-31G(d,p) CPCM(Water)

% cpcm
smd true
smdsolvent "water"
End
* xyz 1 1

C      0.00000      0.00000      0.00000
N     -0.34080      1.28500     -0.61070
C      0.70560      2.04000     -1.29960
H      0.53090      2.08150     -2.38170
H      0.77050      3.06510     -0.91970

H      1.66450      1.55370     -1.12570
C     -1.62720      1.72880     -0.61120
C     -2.66290      1.00540      0.05130
C     -3.96530      1.45630      0.03610
C     -4.34130      2.66670     -0.60970
C     -3.29880      3.38750     -1.25570
C     -1.99630      2.93700     -1.27350
H     -1.25400      3.50690     -1.81810
H     -3.54070      4.29410     -1.80020
C     -5.70940      3.13560     -0.61460
C     -6.79880      2.18440     -0.61370
C     -8.04140      2.46650      0.01890
C     -9.08080      1.56130      0.03250
C     -8.96260      0.29690     -0.61700
C     -7.72570      0.01030     -1.26700
C     -6.68740      0.91660     -1.24890
H     -5.77630      0.67150     -1.78430
H     -7.59660     -0.92120     -1.80360
N     -9.98760     -0.59820     -0.61570
C    -11.28000     -0.24370     -0.02830
H    -11.70900      0.64320     -0.50870
H    -11.97100     -1.07430     -0.16540
H    -11.19100     -0.04680      1.04620
C     -9.84580     -1.89120     -1.28480
H     -8.98990     -2.44920     -0.89080
H    -10.74400     -2.48070     -1.10750
H     -9.71680     -1.77650     -2.36810

```

H	-9.99000	1.81710	0.56190
H	-8.16320	3.40320	0.55250
C	-5.98780	4.55460	-0.62320
C	-7.13690	5.08960	-1.26880
C	-7.40280	6.44180	-1.29310
C	-6.54070	7.37210	-0.64020
C	-5.39280	6.84440	0.02200
C	-5.12740	5.49190	0.01310
H	-4.26040	5.13030	0.55580
H	-4.72250	7.50520	0.55740
N	-6.80300	8.70710	-0.64940
C	-8.02110	9.21870	-1.27760
H	-8.91920	8.78920	-0.81910
H	-8.05700	10.30000	-1.15140
H	-8.04170	8.99900	-2.35120
C	-5.89910	9.64570	0.01550
H	-4.88370	9.57430	-0.38930
H	-6.25930	10.66000	-0.14870
H	-5.85470	9.46740	1.09670
H	-8.27280	6.79390	-1.83300
H	-7.80270	4.42110	-1.80410
H	-4.71540	0.89120	0.57910
H	-2.43150	0.09590	0.59160
H	-0.21290	-0.00190	1.07500
H	-0.55380	-0.82440	-0.46400
H	1.06480	-0.18450	-0.13540

★

Table. Thermodynamic properties of optimized crystal violet reactants, product, and transition state*

	Final Single Point Energy (Hartrees)	Total thermal energy [‡]	Total Enthalpy	Final entropy	Free Energy	Dipole Moment (Debye)	Vib 1 (cm ⁻¹)	Vib 2 (cm ⁻¹)
CV crystal violet cation	-1134.121206	-1133.591821	-1133.590877	0.084208	-1133.675086	0.155	24.57	30.98
OH-4wat	-381.527714	-381.407464	-381.406520	0.045444	-381.451963	2.2705	56.42	64.99
CV-OH-4wat-TS	-1515.637949	-1514.986310	-1514.985366	0.107387	-1515.092752	15.8989	-303.29	12.06
CV-OH-4wat	-1515.665817	-1515.010911	-1515.009966	0.107431	-1515.117397	11.4044	5.91	16.78
crystal violet alcohol	-1210.038902	-1209.495771	-1209.494827	0.086056	-1209.580883	4.4047	7.62	23.41
$\Delta E_{\text{reaction}}$ (kcal/mol)	-10.6027	-7.2950	-7.8875	-13.9441	6.0566			
$\Delta E_{\text{activation}}$ (kcal/mol)	6.8845	8.1422	7.5497	-13.9717	21.5214			

*ORCA 6.0, B3LYP/6-31G(d,p)/SMD-water [‡]Conditions: 298.15 K, 1.00 atm