Supporting Information: The $\widetilde{A} - \widetilde{X}$ Absorption of Vinoxy Radical Revisited: Normal and Herzberg-Teller Bands Observed via Cavity Ringdown Spectroscopy

Phillip S. Thomas, Rabi Chhantyal-Pun, Neal D. Kline, and Terry A. Miller

Department of Chemistry

The Ohio State University

120 W. 18^{th} Avenue

Columbus Ohio 43210

E-mail: tamiller@chemistry.ohio-state.edu.

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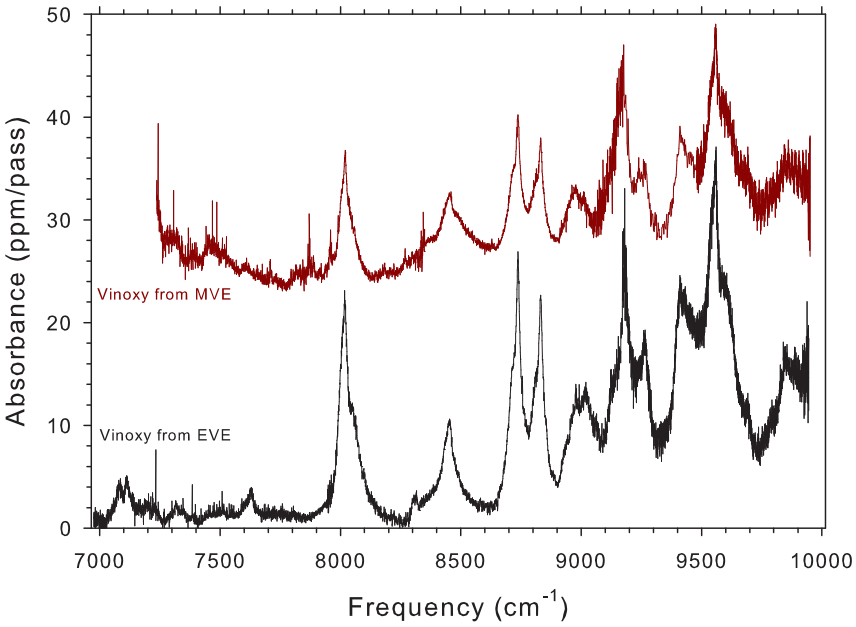

Figure 1: Cavity ringdown spectra of vinoxy radical obtained from 193 nm photolysis of methyl vinyl ether and ethyl vinyl ether. The traces have been vertically offset for clarity.

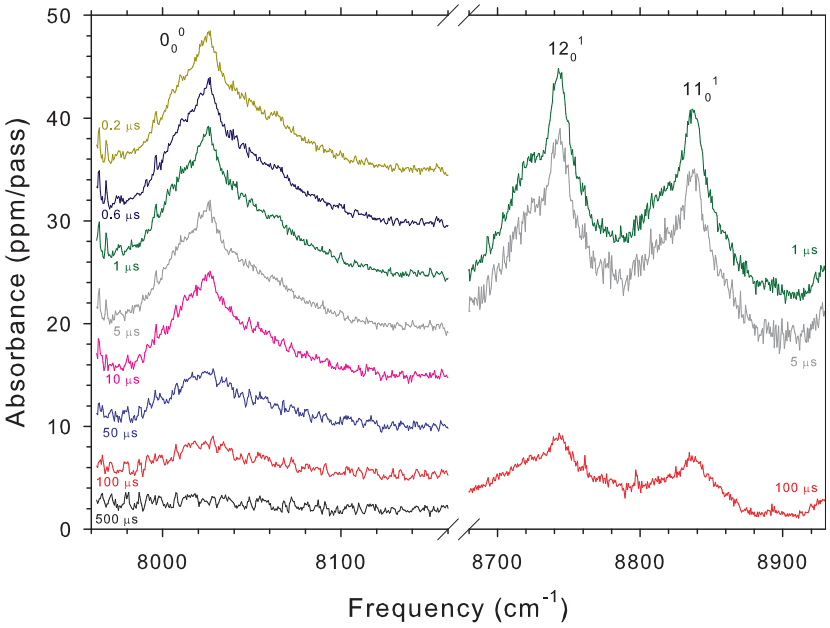

Figure 2: Cavity ringdown spectra of the 0_0^0, 12_0^1, and 11_0^1 bands of vinoxy, obtained at a variety of excimer-probe delay times. Traces taken using different delay times are vertically offset for clarity.

Table 1: Unscaled harmonic and fundamental frequencies calculated at the UB3LYP/aug-cc-pVTZ level, and unscaled harmonic frequencies calculated at the UCCSD/cc-pVDZ level for $\widetilde{X}$ and $\widetilde{A}$ state equilibrium structures of vinoxy. The number in bold at the head of each column is the zero point energy. All values are in cm^{-1}.

UB3LYP/aug-cc-pVTZ				CCSD/cc-pVDZ	
$\widetilde{X}$ state		$\widetilde{A}$ state		$\widetilde{X}$ state	$\widetilde{A}$ state
Harm.	Anharm.	Harm.	Anharm.	Harm.	Harm.
9300.458	**9153.934**	**9349.477**	**9208.499**	**9365.504**	**9549.776**
3253.254	3110.845	3271.782	3122.815	3301.464	3314.785
3142.389	3037.551	3173.002	3011.285	3177.784	3207.411
2944.320	2734.835	2990.651	2802.758	3000.627	3118.580
1544.506	1521.109	1596.294	1483.422	1604.900	1711.401
1474.959	1392.421	1440.181	1411.417	1478.933	1444.244
1397.612	1364.090	1240.630	1207.616	1409.018	1279.028
1160.745	1132.719	1082.818	1062.913	1155.749	1103.286
979.915	959.504	971.444	959.674	973.589	972.002
507.107	500.363	432.295	434.657	499.994	439.959
982.477	955.535	957.023	940.567	978.898	965.165
767.526	718.298	827.052	790.458	709.024	818.422
446.106	421.141	715.781	700.473	441.030	725.271

Table 2: (Squared) values of Duschinsky rotation matrix elements. Rows and columns are indexed by $\widetilde{X}$ and $\widetilde{A}$ state frequencies (cm^{-1}), respectively. Duschinsky matrices have been computed in the harmonic approximation but are indexed by unscaled fundamental frequencies (B3LYP/aug-cc-pVTZ) and unscaled harmonic frequencies (CCSD/cc-pVDZ).

	B3LYP/aug-cc-pVTZ											
$\Downarrow \widetilde{X}/\widetilde{A} \Rightarrow$	3123	3011	2803	1483	1411	1208	1063	960	435	941	790	700
3111	0.981	0.015	0.000	0.001	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000
3038	0.015	0.981	0.000	0.000	0.000	0.000	0.000	0.003	0.001	0.000	0.000	0.000
2735	0.000	0.000	0.995	0.001	0.001	0.003	0.000	0.000	0.000	0.000	0.000	0.000
1521	0.000	0.000	0.003	0.130	0.218	0.247	0.347	0.046	0.007	0.000	0.000	0.000
1392	0.003	0.000	0.000	0.437	0.428	0.093	0.028	0.007	0.003	0.000	0.000	0.000
1364	0.001	0.000	0.001	0.008	0.140	0.316	0.514	0.002	0.017	0.000	0.000	0.000
1133	0.000	0.000	0.000	0.306	0.166	0.338	0.070	0.100	0.019	0.000	0.000	0.000
960	0.000	0.003	0.000	0.114	0.045	0.001	0.001	0.833	0.004	0.000	0.000	0.000
500	0.000	0.001	0.000	0.003	0.000	0.001	0.038	0.009	0.947	0.000	0.000	0.000
956	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.466	0.364	0.169
718	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.434	0.566	0.000
421	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.100	0.070	0.827
	CCSD/cc-pVDZ											
$\Downarrow \widetilde{X}/\widetilde{A} \Rightarrow$	3315	3207	3119	1711	1444	1279	1103	972	440	965	818	725
3301	0.988	0.009	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000
3178	0.009	0.982	0.005	0.001	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000
3001	0.000	0.005	0.989	0.002	0.001	0.003	0.001	0.000	0.000	0.000	0.000	0.000
1605	0.000	0.000	0.002	0.188	0.167	0.246	0.328	0.065	0.003	0.000	0.000	0.000
1479	0.002	0.000	0.001	0.355	0.444	0.109	0.082	0.004	0.004	0.000	0.000	0.000
1409	0.001	0.000	0.003	0.003	0.250	0.223	0.510	0.000	0.011	0.000	0.000	0.000
1156	0.000	0.000	0.000	0.320	0.105	0.415	0.052	0.095	0.013	0.000	0.000	0.000
974	0.000	0.002	0.000	0.129	0.032	0.004	0.002	0.827	0.004	0.000	0.000	0.000
500	0.000	0.001	0.000	0.003	0.000	0.001	0.024	0.007	0.963	0.000	0.000	0.000
979	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.572	0.200	0.226
709	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.340	0.626	0.034
441	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.087	0.174	0.737

Table 3: Electronic energies (a.u.) and cartesian coordinates (Å) for equilibrium and vibrationally averaged structures of vinoxy.

$\widetilde{X}$ state: E (B3LYP/aug-cc-VTZ) = -153.236833306							
Equilibrium geometry				Vibrationally averaged geometry			
H	2.089798	-0.205347	0.000000	H	2.092483	-0.207670	0.000000
C	1.055993	-0.521813	0.000000	C	1.061325	-0.525054	0.000000
H	0.822507	-1.577468	0.000000	H	0.829568	-1.582532	0.000000
C	0.000000	0.426702	0.000000	C	-0.001665	0.428965	0.000000
H	0.284753	1.492346	0.000000	H	0.287066	1.503607	0.000000
O	-1.191627	0.107642	0.000000	O	-1.195138	0.108132	0.000000
$\widetilde{A}$ state: E (B3LYP/aug-cc-VTZ) = -153.202871425							
Equilibrium geometry				Vibrationally averaged geometry			
H	2.071359	0.168304	0.000000	H	2.078285	0.170667	0.000000
C	1.126235	-0.347896	0.000000	C	1.132264	-0.348627	0.000000
H	1.111252	-1.426765	0.000000	H	1.117339	-1.431672	0.000000
C	0.000000	0.366576	0.000000	C	-0.001888	0.364566	0.000000
H	0.020091	1.465201	0.000000	H	0.016169	1.473117	0.000000
O	-1.245014	-0.039853	0.000000	O	-1.248694	-0.038135	0.000000
$\widetilde{X}$ state: E (CCSD/cc-VDZ) = -152.74437557							
Equilibrium geometry							
H	2.112481	-0.250739	0.000000				
C	1.058737	-0.550477	0.000000				
H	0.794016	-1.613521	0.000000				
C	0.000000	0.433565	0.000000				
H	0.319631	1.502946	0.000000				
O	-1.197319	0.132848	0.000000				
$\widetilde{A}$ state: E (CCSD/cc-VDZ) = -152.70931149							
Equilibrium geometry							
H	2.095825	0.183697	0.000000				
C	1.136816	-0.338309	0.000000				
H	1.119154	-1.431802	0.000000				
C	0.000000	0.385470	0.000000				
H	0.003584	1.490875	0.000000				
O	-1.254932	-0.065716	0.000000				

Table 4: Input parameters used for simulations of the rotational contours of vinoxy. Rotational constants were obtained from the anharmonic vibrationally-averaged structures calculated at the UB3LYP/aug-cc-pVTZ level; all spin rotation parameters are set to the $\widetilde{X}$ state values experimentally determined by Endo and Hirota.[1]

Constants		$\widetilde{X}$ state	$\widetilde{A}$ state
A	(cm^{-1})	2.228988	2.539000
B	(cm^{-1})	0.381607	0.364225
C	(cm^{-1})	0.325206	0.317865
ε_{aa}	(cm^{-1})	-0.029987	-0.029987
ε_{bb}	(cm^{-1})	-0.002205	-0.002205
ε_{cc}	(cm^{-1})	-0.000022	-0.000022
$\frac{\varepsilon_{ab}+\varepsilon_{ba}}{2}$	(cm^{-1})	0.002813	0.002813
Control parameters			
T_{00}	(cm^{-1})	8017	
Doppler Linewidth	(cm^{-1})	1	
Natural Linewidth	(cm^{-1})	0.004	
Temperature	(K)	298	
J_{max}		110	
ΔK_{max}		10	

References

[1] Y. Endo and E. Hirota, J. Mol. Spectrosc. **127**, 535 (1988).