Supporting Information Section

Absorption Spectra and Aqueous Photochemistry of β-Hydroxyalkyl Nitrates of Atmospheric Interest

Dian E. Romonosky,[1] Lucas Q. Nguyen,[1] Dorit Shemesh,[2] Tran B. Nguyen,[1] Scott A. Epstein,[1] David B.C. Martin,[1] Christopher D. Vanderwal,[1] R. Benny Gerber,[1,2,*] Sergey A. Nizkorodov[1,*]

[1] *Department of Chemistry, University of California, Irvine, California 92697, USA*
[2] *Fritz Haber Center for Molecular Dynamics, The Hebrew University, Jerusalem 91904, Israel*

*Send correspondence to:
S.A. Nizkorodov (nizkorod@uci.edu), 1-949-824-1262
R.B. Gerber (bgerber@uci.edu), 1-949- 824-6758

Table S1. The lowest electronic excited states of conformer 3 of ethyl nitrate. All parameters are calculated at CC2 level, but the OM2 energies are also provided for comparison. A similar table for conformer 1 is provided in the main text (Table 4).

Electronic State	CC2 energy [eV]	OM2 energy [eV]	Transitions involved	Oscillator strength	Dipole moment [Debye]
Ground	0	0	-	-	2.75
1	5.05	4.41	HOMO-3 → LUMO 65% HOMO-2 → LUMO 32%	3×10^{-6}	2.19
2	6.08	4.69	HOMO-4 → LUMO 26% HOMO-2 → LUMO 24% HOMO-1 → LUMO 24 % HOMO-3 → LUMO 12 %	0.0016	3.31
3	6.49	5.17	HOMO-1 → LUMO 44%	0.076	6.98
4	7.64	5.38	HOMO → LUMO 58%	0.10	1.75
5	8.20	5.78	HOMO-3 → LUMO+5 20% HOMO → LUMO 14%	0.13	1.10

Table S2. Cross-comparison of orbitals of ethyl nitrate and β-hydroxyethyl nitrate.

β-hydroxyethyl nitrate	ethyl nitrate
HOMO-5	HOMO-6
HOMO-4	HOMO-3
HOMO-3	HOMO-1
HOMO-2	HOMO-2
HOMO-1	HOMO
HOMO	---
LUMO	LUMO

Table S3. Henry's law constants used for predicting aqueous partitioning of nitrates examined in this work.

NAME	SMILES	H [atm×m^3/mol]	H [M/atm]	Method
2-hydroxycyclohexyl nitrate (A)	C1(O)C(ON(=O)=O)CCCC1	1.32E-08	7.58E+04	Bond
3-hydroxy-3-methylbutan-2-yl nitrate (B)	C(C)(C)(O)C(C)ON(=O)=O	2.25E-08	4.44E+04	Bond
2-hydroxyhexyl nitrate (C)	C(O)(CCCC)CON(=O)=O	2.99E-08	3.34E+04	Bond
2-hydroxy-2-methyl-5-(prop_1-en-2-yl)cyclohexyl nitrate (D)	C(=C)(C)C1CC(ON(=O)=O)C(C)(O)CC1	3.60E-08	2.78E+04	Bond
2-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-2-yl nitrate (E)	C1(C)(C)C2C(C)(O)C(ON(=O)=O)CC1C2	1.81E-08	5.52E+04	Bond
4-hydroxytetrahydrofuran-3-yl nitrate (F)	C1(O)C(ON(=O)=O)COC1	8.31E-12	1.20E+08	Bond
1-hydroxybut-3-en-2-yl nitrate (G)	C(=C)C(CO)ON(=O)=O	1.26E-08	7.94E+04	Bond
2-hydroxy-1-phenylethyl nitrate (H)	c1(C(CO)ON(=O)=O)ccccc1	7.77E-10	1.29E+06	Bond
2-hydroxy-3-(nitrooxy)propyl methacrylate (I)	C(=O)(C(=C)C)OCC(O)CON(=O)=O	2.52E-11	3.97E+07	Bond
2-ethylhelxyl nitrate (J)	O(N(=O)=O)CC(CCCC)CC	1.44E-03	6.94E-01	Bond
isopropyl nitrate (K)	O=N(=O)OC(C)C	1.61E-03	6.21E-01	Hauff, K et al. (1998)

Hauff, K., R. G. Fischer, and K. Ballschmiter (1998), Determination of C1-C5 alkyl nitrates in rain, snow, white frost, lake, and tap water by a combined codistillation head-space gas chromatography technique. Determination of Henry's law constants by head-space GC, Chemosphere, 37(13), 2599-2615.

Figure S1. Sample FTIR spectrum of compound F (4-hydroxytetrahydrofuran-3-yl nitrate) with bands attributable to the $–ONO_2$ and –OH groups labeled.

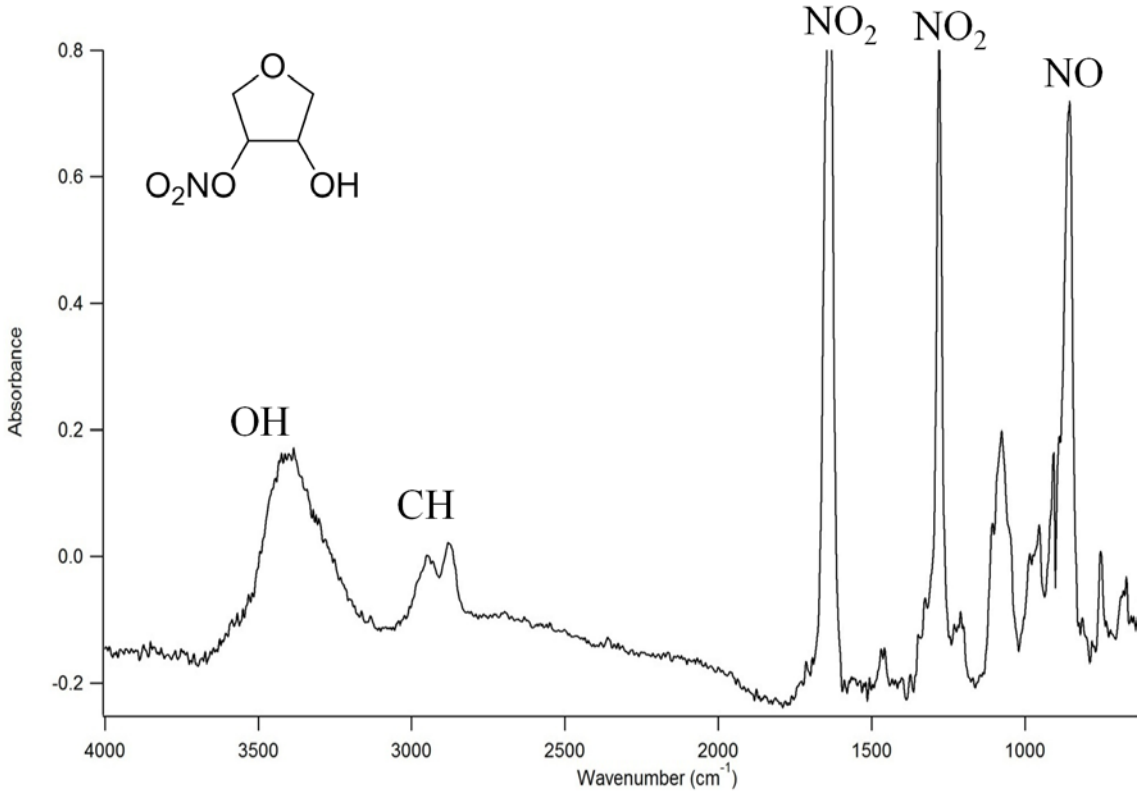

Figure S2. Molecular orbitals (obtained by MP2) involved in electronic transitions of conformer 3 of ethyl nitrate listed in Table S1. A similar figure for conformer 1 is provided in the main text (Figure 3).

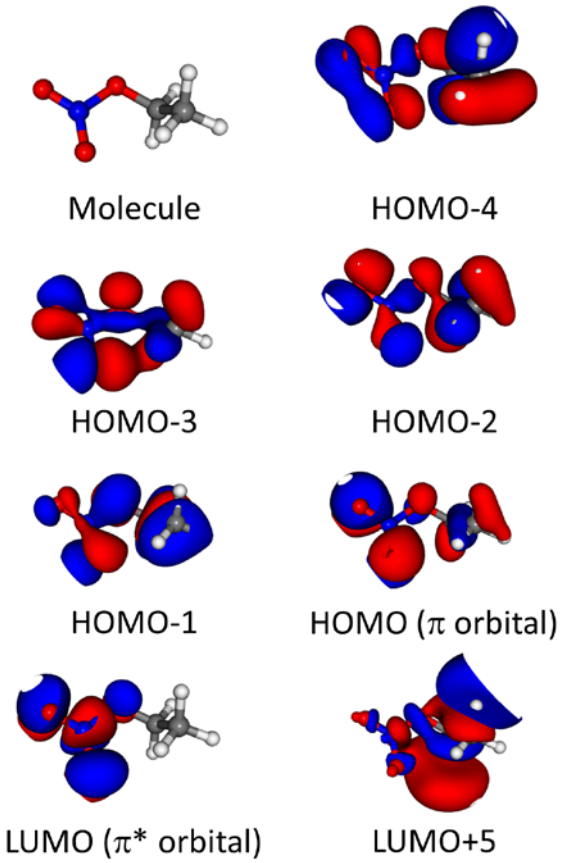

Figure S3. Structures of the conformers of β-hydroxyethyl nitrate as calculated by MP2 listed in Table 5. Same colors around the frame correspond to different rotamers around one bond.

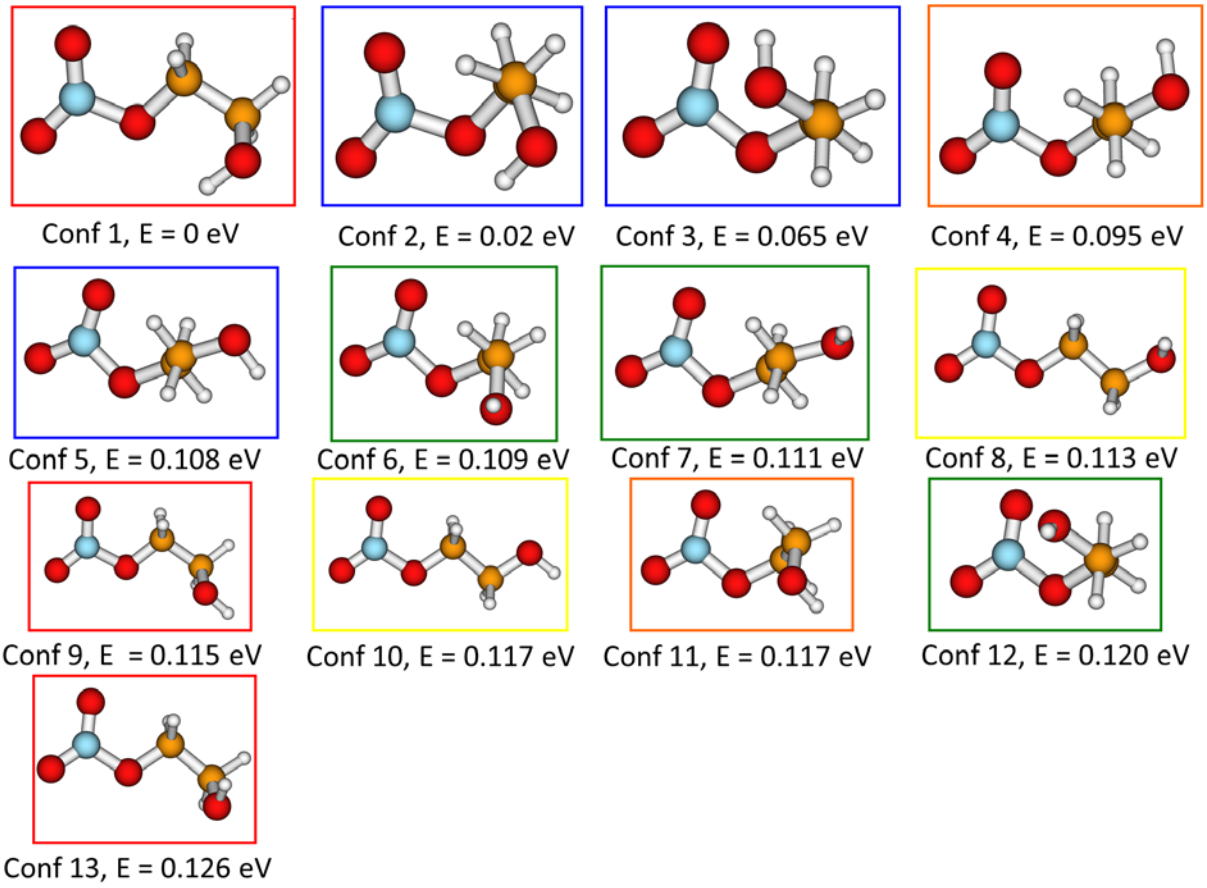

Figure S4. Molecular orbitals as obtained by MP2 involved in electronic transitions of the lowest energy conformer of β-hydroxyethyl nitrate listed in Table 6.

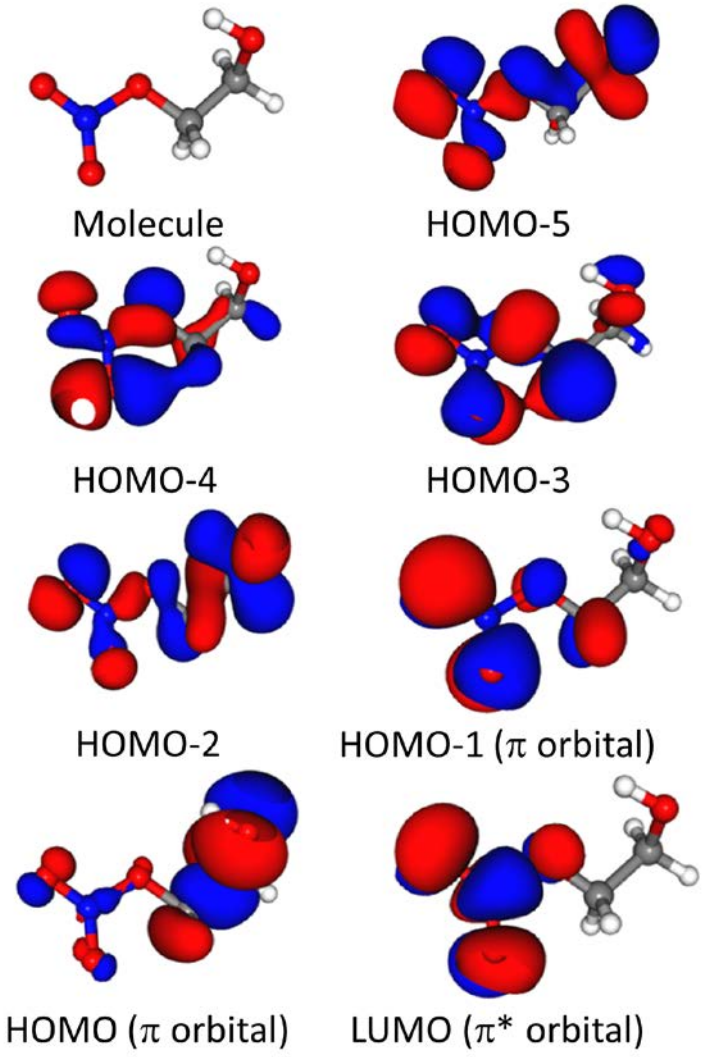

Figure S5. Predicted absorption spectrum of ethyl nitrate calculated by inclusion of one (red trace – labeled nitrate-1) and four (blue trace – labeled nitrate-4) states in the MD simulations. The one-state calculation was scaled down by 50 (to account for the difference in sampling). The shape of the low-energy tail of the spectrum is nearly identical in both cases.