



Theoretical Vibrational Spectra of CWAs: Enabling FTIR Analysis

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Introduction

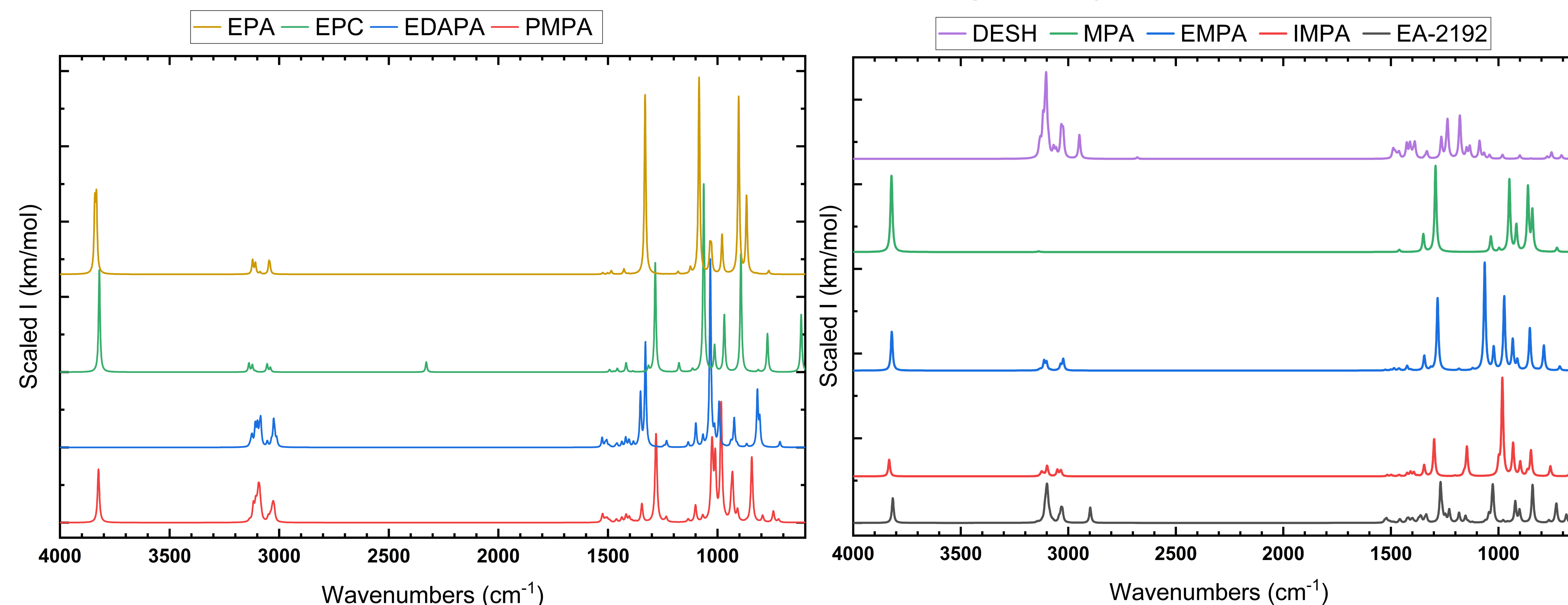
Vibrational spectroscopy is a valuable tool that enables the study of adsorption and reaction of chemical warfare agents and simulants with surfaces of interest. Fourier Transform Infrared Spectroscopy (FTIR) studies have been performed of Chemical Warfare Agents (CWAs) interacting with militarily relevant surfaces; however detailed assignments of vibrational modes have often been based on a qualitative understanding of the spectroscopic results without a strong theoretical base to support conclusions about interaction and reaction of CWAs with surfaces. To assist in bridging this knowledge gap, high level calculations were performed of the lowest energy structure of an isolated molecule in the gas phase and at 0 K.

Theoretical Procedure

Harmonic frequency calculations were performed in Gaussian 09. Revision D.01, at the B3LYP/def2-TZVPPD or other level of theory and basis set. A (200x100) grid of 200 radial shells around each atom and 100 angular points in each shell was used for computing 2-electron integrals, totaling 2*200*100*100 = 4 million points per atom. Very tight quadratic convergence was used for geometry optimization and self-consistent field computation. Calculations were performed utilizing DoD DSRC facilities.

Theoretical results were compared with experimental results to confirm good agreement. It is important to note that $\nu_{a,s}(\text{C-H})$ stretches did not agree well between experiment and theory; this is to be expected due to the failure of the harmonic oscillator approximation to scale for this group compared to heavier atoms. However, this is mitigated by applying a scaling factor based on previous literature results.¹

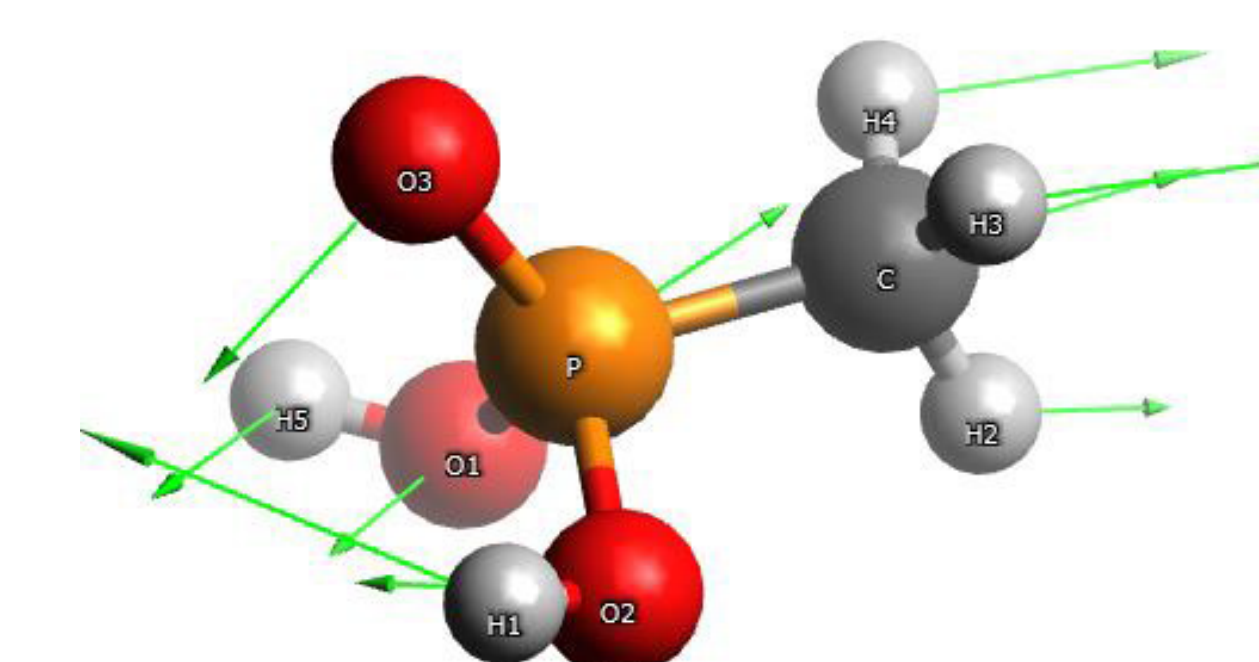
Calculated IR Spectra of Agent Byproducts



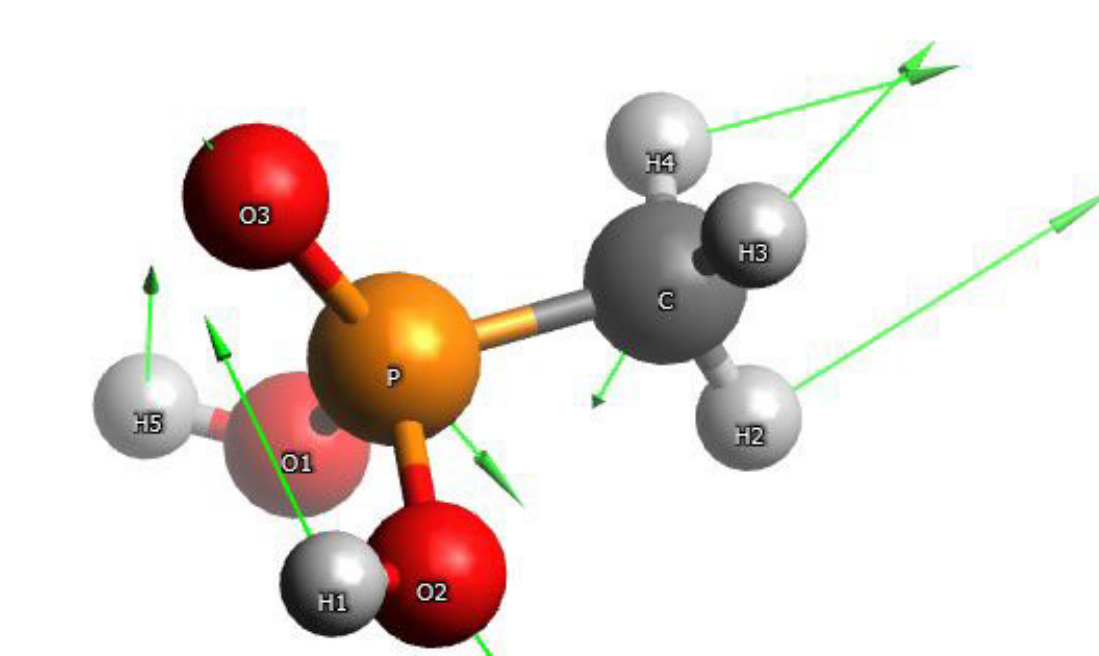
MPA Normal Mode Assignments

#	Peak (cm ⁻¹)	Scaled (cm ⁻¹)	I (km/mol)	Assignments
1	56.8061	54.9088	19.2953	$\rho(\text{OH})$
2	189.3416	183.0176	0.0005	$\tau(\text{CH}_3)$
3	244.7011	236.5281	27.3795	skeletal
4	304.0707	293.9147	15.7183	$\rho(\text{P-CH}_3) + \rho(\text{OH})$
5	325.1429	314.2831	119.4296	$\rho(\text{OH})$
6	374.6420	362.1290	1.8128	$\rho(\text{CH}_3) + \rho(\text{OH})$
7	420.7857	406.7315	75.5788	$\nu(\text{OPO})$ skeletal
8	441.0966	426.3640	42.7028	(PO_3) umbrella
9	727.9159	703.6035	12.3383	$\nu(\text{P-C})$
10	842.2134	814.0835	118.1825	$\nu_s(\text{OPO})$
11	862.8276	834.0092	189.2663	$\nu_a(\text{OPO})$
12	916.6984	886.0807	76.7075	$\rho(\text{CH}_3) + \nu_s(\text{PO}_3)$
13	949.0978	917.3979	212.8417	$\nu_a(\text{OPO}) + \tau(\text{CH}_3)$
14	996.8817	963.5859	9.2823	$\rho(\text{OH})$
15	1035.3211	1000.7414	45.5546	$\delta_s(\text{OH})$
16	1292.5553	1249.3840	254.4209	$\nu(\text{P=O})$
17	1349.2128	1304.1491	51.7509	$\nu(\text{P-C})$
18	1460.6929	1411.9058	4.4386	$\delta(\text{CH}_3)$
19	1462.1899	1413.3528	2.1130	$\delta(\text{CH}_3)$
20	3053.7400	2951.7451	0.0812	$\nu_s(\text{CH}_3)$
21	3135.8750	3031.1368	1.2773	$\nu_a(\text{CH}_3)$
22	3139.8455	3034.9747	1.2300	$\nu_a(\text{CH}_3)$
23	3820.6947	3693.0835	119.2792	$\nu_a(\text{OH})$
24	3823.4647	3695.7610	123.4441	$\nu_s(\text{OH})$

Example Modes



441.0966 cm⁻¹ (PO_3) umbrella



1292.5553 cm⁻¹ $\nu(\text{P=O})$

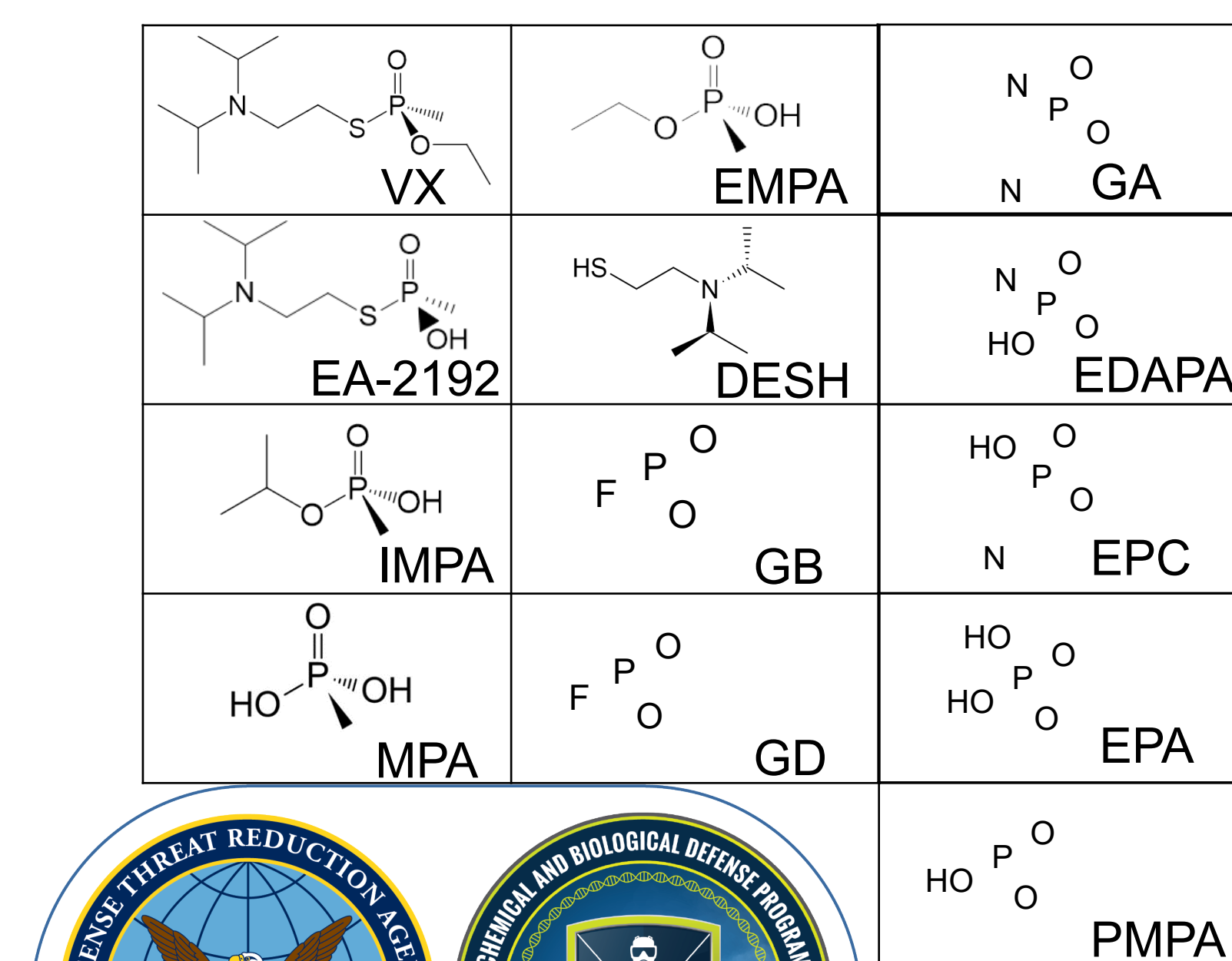
Level of Theory

Chemical	CAS Number	Level of Theory
VX	50782-69-9	B3LYP/def2-TZVPPD
EA-2192	73207-98-4	B3LYP/def2-TZVPPD
IMPA	1832-54-8	B3LYP/def2-QZVPPD
MPA	993-13-5	B3LYP/def2-QZVPPD
EMPA	1832-53-7	B3LYP/def2-QZVPPD
DESH	5842-07-9	B3LYP/def2-SVPD
GB	107-44-8	B3LYP/def2-QZVPPD
GD	96-64-0	B3LYP/def2-QZVPPD
GA	77-81-6	B3LYP/def2-QZVPPD
EDAPA	2632-86-2	B3LYP/def2-SVPD
EPC	117529-17-6	B3LYP/def2-SVPD
EPA	6779-09-5	B3LYP/def2-TZVPPD
PMPA	616-52-4	B3LYP/def2-QZVPPD

Conclusion

The Infrared spectra of CWAs and their hydrolysis products were calculated. Normal mode vibrational assignments have been made for all chemicals. These results will enable future researchers to interpret the complicated infrared spectra collected in advanced studies and may be useful for IR detection algorithms.

Acknowledgements: The authors thank DTRA JSTO for the Single Atom Catalysis Program (CB10832); Wendy Mills, and Dr. Charles Bass for support of this program. Dr. Christopher Karwacki is also acknowledged for supporting this effort. The authors acknowledge the Department of Defense (DoD) High Performance Computing Modernization Program (HPCMP).



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¹ Iron, M. A.; Gropp, J. Cost-effective density functional theory (DFT) calculations of equilibrium isotopic fractionation in large organic molecules. *Physical Chemistry Chemical Physics* **2019** 21 (32) pp. 17555-17570