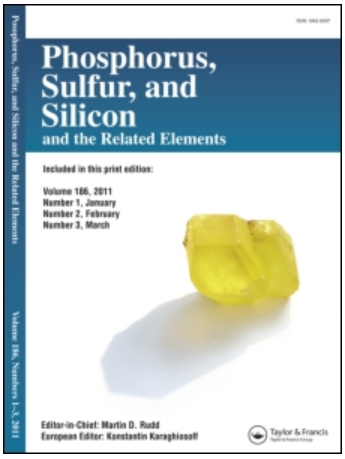

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THEORETICAL PREDICTIONS OF THE STRUCTURE AND VIBRATIONAL INFRARED FREQUENCIES OF 2,2'-DICHLORODIETHYL SULFIDE AND HYDROLYSIS PRODUCTS

William H. Donovan[a]; George R. Famini[a]; James O. Jensen[a]; Hendrik F. Hameka[b]
[a] Development and Engineering Center, U. S. Army Edgewood Research, Aberdeen Proving Ground, MD, U.S.A. [b] Department of Chemistry, University of Pennsylvania, Philadelphia, PA, U.S.A.

To cite this Article Donovan, William H. , Famini, George R. , Jensen, James O. and Hameka, Hendrik F.(1993) 'THEORETICAL PREDICTIONS OF THE STRUCTURE AND VIBRATIONAL INFRARED FREQUENCIES OF 2,2'-DICHLORODIETHYL SULFIDE AND HYDROLYSIS PRODUCTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 80: 1, 47 — 61
To link to this Article: DOI: 10.1080/10426509308036876
URL: http://dx.doi.org/10.1080/10426509308036876

Phosphorus, Sulfur, and Silicon, 1993, Vol. 80, pp. 47–61
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THEORETICAL PREDICTIONS OF THE STRUCTURE AND VIBRATIONAL INFRARED FREQUENCIES OF 2,2′-DICHLORODIETHYL SULFIDE AND HYDROLYSIS PRODUCTS

WILLIAM H. DONOVAN,† GEORGE R. FAMINI and JAMES O. JENSEN
U.S. Army Edgewood Research, Development and Engineering Center, SCBRD-RTC, Aberdeen Proving Ground, MD 21010-5423, U.S.A.

and

HENDRIK F. HAMEKA
Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, U.S.A.

(Received February 1, 1993; in final form March 23, 1993)

We report the computed equilibrium geometries and vibrational infrared frequencies for 2,2′-dichlorodiethyl sulfide and six related hydrolysis products, utilizing the HF/6-311G** and MP2/6-31G* levels of theory. A comparison of the calculated frequencies to the corresponding experimental data yields correction factors for the vibrational modes. In general, we find the use of larger basis sets tends to improve the consistency of the correction factors while inclusion of electron correlation tends to improve their accuracy. The agreement between the experimental and calculated data enables us to make predictions about the major features of the infrared spectra of the hydrolysis species for which no infrared data have been reported.

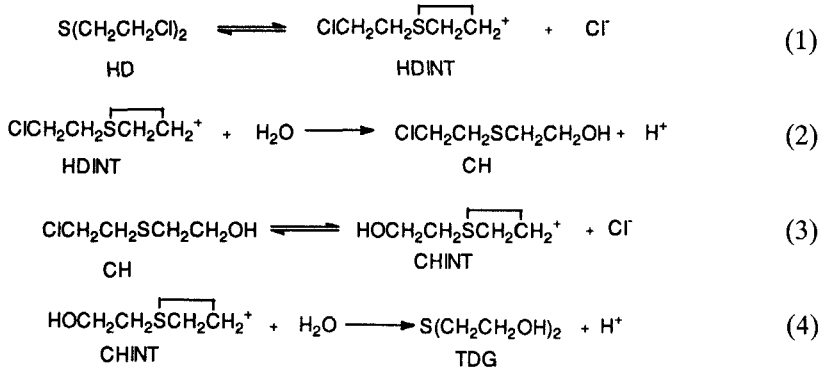
Key words: Spectra; vibrational; infrared; frequencies; intensities; sulfides.

1. INTRODUCTION

The application of ab initio molecular orbital calculations to predict vibrational infrared spectra of sulfur-containing or organophosphorous compounds continues to attract growing interest.[1–9] Previous studies[1,2] have shown that computations on 2,2′-dichlorodiethyl sulfide (sulfur mustard, HD) and related molecules produce reasonable agreement with experimental results when using the HF/3-21G basis set except for modes involving the participation of heavy atoms, such as sulfur and chlorine. Recent advances in computer technology and ab initio programs now make it possible to calculate the vibrational spectra of these compounds using significantly more sophisticated levels of theory. In addition, the recent availability of high quality experimental data[10] of some key compounds now makes it possible to evaluate the performance of the calculations more carefully than before. Thus comparisons can be made to determine if the shortcomings identified earlier[1,2] can be corrected by employing larger basis sets or a simple form of electron correlation.

†Author to whom correspondence should be addressed.

The hydrolysis reactions of HD have received extensive experimental study, revealing considerable complexity.[11–19] However, the initial reactions of primary importance can be summarized by Equations (1)–(4):



where HDINT represents the cyclic chloroethyl ethylene sulfonium ion intermediate, CH is chloroethyl hydroxyethyl sulfide (mustard chlorohydrin), CHINT is the cyclic hydroxyethyl ethylene sulfonium ion intermediate, and TDG is bis(hydroxyethyl) sulfide, (thiodiglycol). The above reactions assume a S_N1 mechanism, fully supported by evidence applicable to the condensed phase.[11–19]

The molecules selected for study in the present paper are of particular interest as they are species likely to be encountered in the hydrolysis reactions of HD. While the vibrational spectra for some of these species are known, no spectra for CH or for the intermediates are available yet. As advances in experimental techniques continue, the spectra of the short-lived intermediates may be identified. In anticipation of this achievement and perhaps to facilitate it, we have included the computational predictions for the cyclic sulfonium ions. In addition, we have also included computational results for $XCH_2CH_2SCH_2CH_3$ (X = Cl, OH) to help establish the reliability of our calculations and for comparison purposes. These compounds, 2-chloroethyl ethyl sulfide (CEES) or the so-called "half-mustard" when X = Cl and its corresponding hydrolysis product 2-hydroxyethyl ethyl sulfide (HEES) when X = OH, are sometimes used as chemical agent simulants as they are less toxic than HD. Experimental IR spectra have been published for these two compounds[10] and HF/3-21G results have appeared for $ClCH_2CH_2SCH_2CH_3$.[2]

In the present paper, we derive scaling factors for the vibrational frequencies rather than for the molecular force constants for the reasons detailed previously.[8] Moreover, we offer commentary about the performance of the two levels of theory employed here in comparison to lower levels of theory applied to similar systems in earlier studies.[1,2]

2. COMPUTATIONAL METHOD

The results reported in this study were obtained using the Gaussian 90 and the Gaussian 92 program packages,[20] running on a Stardent Titan 3000VS and a Convex C3820 computer, respectively. We obtained fully optimized structures for all molecules at the Hartree-Fock level using the dp-polarization 6-311G** basis set (HF/

6-311G**) and at the second-order frozen core Moller-Plesset perturbation theory level using the d-polarization 6-31G* basis set (MP2/6-31G*),[21,22] and subsequently ran frequency calculations on the optimized structures. The resulting frequencies were then compared to existing experimental data. The computed frequencies were obtained analytically, indicating true local minima via all positive frequencies. To ensure reliability of the computed frequencies, structures were optimized using the fopt = tight keyword combination to confirm that none of the variables in our Z-matrices were linearly dependent and to assure the location of precise stationary points through stringent convergence criteria. We assigned normal mode vibrations through inspection of the nuclear displacements listed in the Gaussian frequency calculation output. We made no attempt to identify the particular type of CH_2 bend (wag, rock, twist, or scissor) as this was not important for our analysis. Additionally, no low frequency mode assignments were made because these vibrations often consist of several individual motions and lack experimental data for comparison.

3. RESULTS

Tables I–IV summarize the optimized geometries obtained for all the species examined in this study. The corresponding molecular structures are shown in Figure 1 along with the numbering schemes. Tables V–XI present the calculated frequencies together with experimental data where appropriate. In comparing cal-

TABLE I

Optimized geometries of $S(CH_2CH_2X)_2$[a]

		X = Cl		X = OH	
Bond/Angle	**Type**	**HF/6-311G****	**MP2/6-31G***	**HF/6-311G****	**MP2/6-31G***
1-2	S-C	1.822	1.819	1.818	1.815
2-3	C-C	1.518	1.518	1.518	1.517
3-4	C-X	1.797	1.786	1.402	1.428
2-8	C-H	1.082	1.094	1.083	1.094
3-12	C-H	1.078	1.091	1.088	1.099
4-16	O-H	---	---	0.940	0.972
1-2-3	S-C-C	109.02	108.59	110.37	109.91
2-3-4	C-C-X	110.28	110.20	107.01	105.97
2-1-5	C-S-C	99.33	97.85	99.67	98.07
1-2-8	S-C-H	109.37	109.92	109.48	110.14
2-3-12	C-C-H	111.75	111.21	109.90	110.02
3-4-16	C-O-H	---	---	109.57	107.58
1-2-3-4	S-C-C-X	180.00	180.00	180.00	180.01
3-2-1-5	C-C-S-C	180.00	180.00	180.00	180.03
3-1-5-6	C-S-C-C	180.00	180.00	180.00	179.99
3-1-2-8	C-S-C-H	120.34	120.17	120.42	120.07
3-1-2-9	C-S-C-H	239.66	239.83	239.58	239.93
4-2-3-12	X-C-C-H	118.33	119.06	120.53	120.49
4-2-3-13	X-C-C-H	241.67	240.94	239.47	239.51
2-3-4-16	C-C-O-H	---	---	180.00	180.00
-Energy	**(Hartrees)**	**1472.718310**	**1473.509995**	**704.615519**	**705.496726**

[a] Bond lengths, bond angles, and energies are given in angstroms, degrees, and hartrees, respectively. See Figure 1 for definitions of geometrical parameters.

TABLE II

Optimized geometries of $XCH_2CH_2SCH_2CH_3$[a]

		X = Cl		X = OH	
Bond/Angle	**Type**	**HF/6-311G****	**MP2/6-31G***	**HF/6-311G****	**MP2/6-31G***
1-2	S-C	1.820	1.817	1.817	1.814
2-3	C-C	1.517	1.517	1.518	1.517
3-4	C-X	1.800	1.788	1.403	1.428
1-5	S-C	1.820	1.816	1.819	1.816
5-6	C-C	1.525	1.524	1.524	1.524
6-7	C-H	1.086	1.094	1.086	1.094
2-8	C-H	1.082	1.094	1.083	1.094
5-10	C-H	1.084	1.095	1.084	1.095
3-12	C-H	1.078	1.091	1.088	1.099
3-13	C-H	1.078	1.091	1.088	1.099
6-14	C-H	1.085	1.093	1.085	1.093
4-16	O-H	---	---	0.940	0.972
1-2-3	S-C-C	109.16	108.73	110.45	110.03
2-3-4	C-C-X	110.47	110.42	107.10	106.07
2-1-5	C-S-C	99.91	98.49	100.06	98.58
1-5-6	S-C-C	110.31	109.83	110.48	109.96
5-6-7	C-C-H	109.79	109.94	109.89	110.03
1-2-8	S-C-H	109.50	110.02	109.59	110.22
1-5-10	S-C-H	108.59	109.09	108.62	109.09
2-3-12	C-C-H	111.75	111.20	109.90	110.01
2-3-13	C-C-H	111.79	111.20	109.87	110.01
5-6-14	C-C-H	111.18	111.02	111.17	110.99
1-4-16	C-O-H	---	---	109.55	107.54
1-2-3-4	S-C-C-X	180.07	180.00	179.98	180.01
3-2-1-5	C-C-S-C	179.85	179.99	180.01	180.00
3-1-5-6	C-S-C-C	180.20	180.01	180.06	180.00
1-5-6-7	S-C-C-H	180.00	180.00	180.05	180.00
3-1-2-8	C-S-C-H	120.38	120.21	120.41	120.07
3-1-2-9	C-S-C-H	239.66	239.79	239.61	239.93
6-1-5-10	C-S-C-H	121.15	121.03	121.21	121.10
6-1-5-11	C-S-C-H	238.85	238.97	238.79	238.90
4-2-3-12	X-C-C-H	118.29	119.08	120.58	120.51
4-2-3-13	X-C-C-H	241.65	240.92	239.46	239.49
7-5-6-14	H-C-C-H	119.63	119.70	119.65	119.75
7-5-6-15	H-C-C-H	240.39	240.30	240.33	240.25
2-3-4-16	C-C-O-H	---	---	180.00	180.00
-Energy	**(Hartrees)**	**1013.794867**	**1014.482852**	**629.742982**	**630.475879**

[a] **See Table I, footnote a.**

culated and measured spectra, both the absorption frequencies and intensities should be considered. Thus we present the computed frequencies along with their corresponding intensities in our tables. We matched the computed and experimental absorptions by inspection, placing greater emphasis on the frequencies but using the intensities to assist qualitatively. Factors such as absorption line widths can strongly affect the apparent absorption intensity but are not treated by the calculations.

The local minima identified for compounds $S(CH_2CH_2X)_2$, $XCH_2CH_2SCH_2CH_3$ (where X = Cl, OH) and $ClCH_2CH_2SCH_2CH_2OH$ correspond to the all trans-configuration. This is consistent with precedent from previous HF/3-21G[1,2] and HF/6-31G[23] results and with simple steric considerations. Also, the cyclic species HDINT and CHINT minimize to conformations similar to that reported in a recent 6-31G partial optimization of HDINT.[23] Specifically, the C—S—C angle of the

TABLE III
Optimized geometries of $ClCH_2CH_2SCH_2CH_2OH$[a]

Bond/Angle	Type	HF/6-311G**	MP2/6-31G*
1-2	S-C	1.820	1.818
1-5	S-C	1.818	1.815
2-3	C-C	1.517	1.517
5-6	C-C	1.518	1.518
3-4	C-Cl	1.799	1.787
6-7	C-O	1.401	1.427
6-16	O-H	0.940	0.972
2-8	C-H	1.082	1.094
3-12	C-H	1.078	1.091
6-14	C-H	1.088	1.099
2-1-5	C-S-C	99.46	97.93
1-2-3	S-C-C	109.08	108.66
1-5-6	S-C-C	110.25	109.86
5-6-7	C-C-O	106.85	105.83
6-7-16	C-O-H	109.67	107.64
2-3-4	C-C-Cl	110.40	110.34
3-2-8	C-C-H	110.02	109.85
6-5-10	C-C-H	109.36	108.95
2-3-12	C-C-H	111.77	111.22
5-6-14	C-C-H	109.89	110.04
5-1-2-3	C-S-C-C	180.00	179.99
2-1-5-6	C-S-C-C	180.00	180.02
1-2-3-4	S-C-C-Cl	180.00	180.00
1-5-6-7	S-C-C-O	180.00	180.00
5-6-7-16	C-C-O-H	180.00	180.01
4-3-2-8	Cl-C-C-H	60.00	59.74
7-6-5-10	O-C-C-H	59.58	59.26
1-2-3-12	S-C-C-H	61.69	60.93
1-5-6-14	S-C-C-H	59.47	59.54
-Energy	(Hartrees)	1088.667240	1089.503580

[a] See Table I, footnote a.

three-member cyclic ring in HDINT is found to be 46.5 and 47.1 degrees at the HF/6-311G** and MP2/6-31G* levels, respectively. These values correspond closely to predictions of 46.8 degrees at the HF/6-31G* level[23] and 48.1 degrees for the neutral three-member cyclic thiirane molecule, $S(CH_2)_2$, at the MP2/6-31G* level.[9] In comparing the HF/6-311G** to the MP2/6-31G* geometries, we note only minor differences. The MP2/6-31G* method consistently predicts longer C—H, O—H, and C—O bond lengths by 0.01–0.03 angstroms, and smaller C—S—C and C—O—H bond angles by approximately 1.5–2.0 degrees.

From Tables V and VI, treating the vibrations frequencies of HD and CEES, it is clear that there is close agreement between the computed frequencies at both levels of theory and the experimental results. The MP2/6-31G* frequencies are predicted to be uniformly lower than the corresponding HF/6-311G** frequencies except for the C—Cl stretch modes where they are essentially the same. Even the intensities agree except for some variations in the CH_2 stretch modes. The CH_2 stretch modes also commonly interchange their order between the two levels of theory examined here. In Table VII, reporting the vibrational frequencies of HEES, the situation is complicated somewhat by the C—O stretch mode, which differs by about 85 cm^{-1} between the two levels of theory. The differences in the nearby CH_2 bend modes are closer to 50 cm^{-1}, resulting in some interchange of the order of the modes. In Table VIII (TDG), the C—O stretch modes correspond, but an

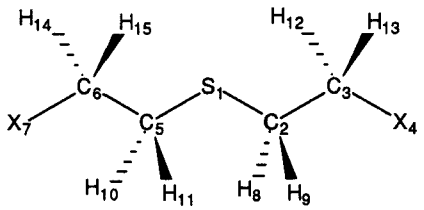
TABLE IV
Optimized geometries of $XCH_2CH_2\overline{SCH_2CH_2}^{-}$ [a]

		X = Cl		X = OH	
Bond/Angle	**Type**	**HF/6-311G****	**MP2/6-31G***	**HF/6-311G****	**MP2/6-31G***
1-2	S-C	1.848	1.840	1.845	1.838
2-3	C-C	1.459	1.471	1.459	1.471
1-4	S-C	1.840	1.830	1.832	1.820
4-5	C-C	1.524	1.524	1.526	1.527
5-6	C-X	1.775	1.769	1.386	1.413
2-7	C-H	1.074	1.087	1.074	1.087
2-8	C-H	1.075	1.087	1.075	1.087
4-11	C-H	1.081	1.093	1.081	1.093
5-13	C-H	1.079	1.092	1.088	1.100
6-15	O-H	----	----	0.942	0.974
1-4-5	C-C-S	110.46	110.13	111.33	111.10
4-5-6	C-C-X	108.23	107.61	103.93	102.43
4-1-2	C-S-C	104.22	102.66	104.23	102.63
4-1-3	C-S-C	104.42	102.46	104.45	102.47
1-2-7	S-C-H	111.10	111.95	111.30	112.06
1-2-8	S-C-H	113.04	113.50	108.78	109.40
1-4-11	S-C-H	108.39	108.82	105.78	106.78
1-4-12	S-C-H	105.37	106.13	112.99	113.38
1-3-9	S-C-H	113.15	113.59	113.06	112.25
1-3-10	S-C-H	111.32	112.15	111.51	113.41
3-2-7	C-C-H	119.66	119.62	119.24	118.93
3-2-8	C-C-H	119.29	118.97	119.61	119.59
2-3-9	C-C-H	119.48	119.43	119.21	118.90
2-3-10	C-C-H	119.24	118.93	119.45	119.43
4-5-13	C-C-H	111.82	111.57	110.32	110.55
4-5-13	C-C-H	111.62	111.51	110.10	110.48
5-6-15	C-O-H	----	----	111.12	109.19
1-4-5-6	S-C-C-X	178.64	179.10	179.37	178.68
5-4-1-2	C-C-S-C	-145.55	-144.25	-145.84	-143.98
5-4-1-3	C-C-S-C	-97.49	-95.90	-97.67	-95.59
5-4-1-11	C-S-C-H	-122.70	-122.40	-122.42	-121.75
5-4-1-12	C-S-C-H	120.35	120.35	120.16	120.27
1-4-5-13	S-C-C-H	62.92	62.05	60.49	58.79
1-4-5-14	S-C-C-H	-60.26	-60.25	-59.07	-61.10
4-5-6-15	C-C-O-H	----	----	175.29	173.56
-Energy	**(Hartrees)**	**1012.929340**	**1013.611448**	**628.887890**	**629.613399**

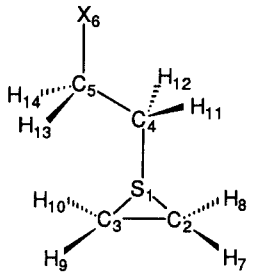
[a] See Table I, footnote a.

OH bend and a CH_2 bend vibration are interchanged. In the case of CH (Table IX), the order of the C—C and C—O stretch frequencies are interchanged as are those of a C—S stretch and a CH_2 bend. Table X (HDINT) is free of any mode interchange between the two levels of theory employed here, but CHINT in Table XI shows interchange between a CH_2 bend and a C—O stretch as well as between two CH_2 bend modes.

The correction factors derived from a comparison of the calculated and experimental spectra of HD, TDG, CEES, and HEES are listed in Table XII. These values represent the quotient between the frequency measured experimentally and the corresponding calculated frequency for a given mode vibration. At the outset, we note that several influences may be responsible for variation in our correction factors. Anharmonicity effects, Fermi resonance, hydrogen bonding, solvent effects, and calibration procedures among others may all contribute variability to these values to some degree.[24,25] Bearing in mind these complications, it is inter-



(A)



(B)

FIGURE 1 (A) Numbering scheme for HD (X_4 = X_7 = Cl), TDG (X_4 = X_7 = OH), CEES (X_4 = Cl, X_7 = H), HEES (X_4 = OH, X_7 = H), and CH (X_4 = Cl, X_7 = OH); (B) numbering scheme for HDINT (X_6 = Cl) and CHINT (X_6 = OH).

esting nevertheless to note the apparent consistency of the derived correction factors, both within each vibrational mode and over all modes. The correction factors derived using the HF/6-311G** basis set vary over a range of less than 3% over all modes if we exclude the OH stretch. While the precise cause of the poor performance of the HF/6-311G** basis set in calculating the OH stretch is not clear, we note that the observed frequency of the OH stretch is known to be sensitive to the extent and nature of hydrogen bonding.[24,25] Hence, the calculations produce an OH stretch for a "free" hydroxyl group where no intermolecular hydrogen bonding occurs. However, the experimental results in neat solution must certainly include intermolecular hydrogen bonding effects, resulting in a shift not accounted for by the calculations. The corresponding factors for the MP2/6-31G* basis set vary over a somewhat greater range (6%), but are more satisfactory from the standpoint of handling the OH stretch mode and being closer to unity.

The σ_{n-1} values listed in Table XII indicate the consistency of the correction factors within a given mode. While most of the σ_{n-1} values listed are based on a limited body of data, the CH_2 stretch and CH_2 bend mode values are likely to be more reliable as they are based on larger data sets. These data indicated a standard deviation of the mean of about 0.01 for these modes.

4. DISCUSSION

In comparing the frequencies calculated by the HF/6-311G** and MP2/6-31G* methods, several general comments are appropriate. Not surprisingly, the MP2

TABLE V
Vibrational frequencies of HD[a]

Mode	HF/6-311G**	INT	MP2/6-31G*	INT	EXP[10]
	37.1	0	31.0	0	
	49.9	0	40.1	0	
	65.8	1	63.8	1	
	118.5	14	122.0	12	
	118.7	0	119.2	0	
	220.6	8	211.6	9	
	231.5	0	226.3	0	
	353.0	1	338.1	1	
	362.0	4	349.9	2	
C-Cl str	764.3	34	768.3	15	690
C-Cl str	783.1	131	783.9	58	702
CH_2 bend	829.6	0	805.5	0	
C-S str	834.0	4	823.7	10	734
CH_2 bend	844.1	8	816.8	7	758
C-S str	873.9	4	855.0	5	
CH_2 bend	1065.7	0	1032.9	0	
CH_2 bend	1089.8	0	1056.9	0	972
C-C str	1107.8	12	1085.9	14	1021
C-C str	1140.7	2	1115.3	2	1037
CH_2 bend	1243.0	0	1193.4	0	
CH_2 bend	1250.7	5	1200.1	3	
CH_2 bend	1352.8	60	1291.6	21	1208
CH_2 bend	1383.7	48	1317.4	33	1216
CH_2 bend	1408.4	0	1343.1	0	
CH_2 bend	1414.2	2	1346.7	2	
CH_2 bend	1467.6	12	1401.2	7	1278
CH_2 bend	1486.3	4	1416.9	4	1295
CH_2 bend	1611.8	12	1548.2	9	1443
CH_2 bend	1616.4	2	1553.6	1	
CH_2 bend	1616.5	2	1553.7	8	
CH_2 bend	1621.3	0	1557.0	1	
CH_2 str	3214.7	3	3129.4	1	
CH_2 str	3215.5	25	3126.6	14	2867
CH_2 str	3256.8	30	3162.1	18	2915
CH_2 str	3256.8	3	3162.2	2	
CH_2 str	3267.6	14	3189.2	6	2933
CH_2 str	3269.0	0	3193.9	0	
CH_2 str	3321.2	17	3232.7	8	2964
CH_2 str	3321.8	0	3233.4	0	

[a] All frequencies and intensities (INT) are listed in cm^{-1} and km/mole, respectively, in order of increasing wavenumber for HF/6-311G** data. The MP2/6-31G* frequencies are arranged to correspond with the HF/6-311G** data and the listed vibrational modes. In some instances, this results in the MP2/6-31G* frequencies deviating from increasing wavenumber. Frequencies measured from experimental data (EXP) were matched based on line position and intensity.

frequency calculations are more demanding computationally than the HF frequency calculations. In addition to requiring more disk space, the MP2 calculations required approximately 1/3 more time for most of the molecules studied here. Clearly, had we chosen to run MP2/6-311G** calculations, the disparities would have been even greater. Hence it is not entirely clear that the additional computational resources required by the MP2 method is justified by the slightly more accurate frequencies produced.

TABLE VI
Vibrational frequencies of CEES[a]

Mode	HF/6-311G**	INT	MP2/6-31G*	INT	EXP[10]
	46.5	0	37.1	1	
	65.3	3	59.3	1	
	102.9	1	99.6	1	
	125.1	6	126.2	5	
	257.9	0	261.4	0	
C-Cl str	266.1	4	259.2	4	
C-S str	292.9	1	281.6	1	
C-S-C bend	392.8	1	377.9	1	
C-S str	741.4	8	731.9	1	653
C-Cl str	775.5	76	777.4	35	701
CH_2 bend	832.6	1	807.9	1	732
CH_2 bend	855.2	7	826.5	7	759
C-S str	857.4	8	841.2	9	770
C-C str	1055.6	4	1037.7	4	927
CH_2 bend	1074.7	0	1041.8	0	971
C-C str	1115.3	8	1089.4	10	1016
CH_3 bend	1143.5	0	1105.4	0	
C-C str	1169.9	1	1130.0	1	
CH_2 bend	1245.3	2	1195.6	1	
CH_3 bend	1363.6	60	1300.7	28	1213
CH_3 bend	1375.7	0	1315.3	0	
CH_2 bend	1410.6	1	1344.3	1	
CH_2 bend	1429.7	31	1366.4	22	1263
CH_2 bend	1477.4	12	1409.7	8	1290
CH_2 bend	1537.8	2	1473.2	5	
CH_2 bend	1609.4	9	1549.2	10	1425
CH_2 bend	1610.0	8	1556.4	8	
CH_2 bend	1615.9	2	1553.6	6	1444
CH_2 bend	1618.5	1	1567.0	3	
CH_2 bend	1621.0	1	1557.9	0	1454
CH_2 str	3170.3	34	3114.2	17	
CH_2 str	3192.6	24	3114.7	25	2871
CH_2 str	3209.9	18	3123.8	6	
CH_2 str	3228.5	0	3170.9	9	
CH_2 str	3234.8	43	3203.4	16	
CH_2 str	3252.3	57	3212.5	18	2928
CH_2 str	3257.3	17	3162.4	10	
CH_2 str	3261.3	6	3186.3	3	
CH_2 str	3321.7	9	3233.1	4	2967

[a] See Table V, footnote a.

The observed trends in the correction factor's variation with basis set are in full accord with precedent from earlier studies.[8,24] Namely, the use of larger basis sets tends to reduce the range of correction factor variation. A previous study[8] reported a difference between the largest and smallest correction factors of about 5% for the HF/6-31G* basis set and 12% for the HF/3-21G basis set. There it was also mentioned that use of larger basis sets yields more consistent correction factors but not necessarily more accurate ones. Here we report that our present findings support the above statements and assert that inclusion of some form of electron correlation (MP2 in this case) delivers more accurate correction factors. Indeed, we are inclined to speculate that more complete treatments of electron correlation would lead to corrector factors closer to unity. The consistency of the correction factors over all modes is important because it allows for the use of a single correction factor for all modes, further simplifying the analysis by removing the need to assign

TABLE VII
Vibrational frequencies of HEES[a]

Mode	HF/6-311G**	INT	MP2/6-31G*	INT	EXP[10]
	50.0	5	39.6	6	
	69.1	5	61.0	3	
	118.7	2	114.7	2	
	135.5	6	131.7	7	
	258.0	1	261.2	2	
O-H bend	276.2	139	271.7	136	
C-S-C bend	309.5	7	294.8	8	
C-S-C bend	322.5	2	313.0	2	
C-C bend	444.6	7	422.9	9	
C-S str	750.8	4	736.8	1	656
CH_2 bend	846.9	3	819.8	3	
C-S str	855.1	25	832.0	17	755
CH_2 bend	872.3	1	841.2	1	782
C-C str	1056.8	3	1038.2	4	941
C-C str	1085.3	12	1057.9	12	
CH_2 bend	1114.9	4	1075.5	2	
CH_2 bend	1146.6	3	1107.9	1	1008
CH_2 bend	1164.4	5	1122.3	2	
C-O str	1183.0	108	1098.4	92	1044
CH_2 bend	1323.5	3	1247.5	1	
OH bend	1330.6	98	1265.4	56	1169
CH_3 bend	1375.7	0	1314.9	0	
OH bend	1407.4	23	1336.2	12	1226
CH_2 bend	1426.1	0	1344.8	1	
CH_2 bend	1441.0	20	1372.9	18	1266
CH_3 bend	1536.8	2	1472.3	4	1337
CH_2 bend	1590.9	2	1499.9	6	1376
CH_2 bend	1609.9	7	1556.4	8	1409
CH_2 bend	1610.9	10	1550.5	15	
CH_2 bend	1619.6	3	1567.5	2	
CH_2 bend	1623.6	6	1558.9	0	1425
CH_2 bend	1658.8	2	1594.2	2	1453
CH_2 str	3155.1	47	3070.0	34	2872
CH_2 str	3168.4	36	3113.2	18	
CH_2 str	3187.1	46	3118.7	38	2927
CH_2 str	3190.1	23	3113.6	27	
CH_2 str	3202.3	37	3123.6	14	
CH_2 str	3225.2	0	3169.1	11	
CH_2 str	3231.8	47	3201.9	17	
CH_2 str	3249.3	68	3211.2	18	2963
CH_2 str	3255.7	23	3188.8	13	
OH str	4184.9	66	3775.9	30	3380

[a] See Table V, footnote a.

vibrational modes. The HF/6-311G** level of theory does particularly well in this regard for the molecules examined in this study. Also noteworthy is the substantial improvement in the ability to handle the vibrational frequencies for the C—S and C—Cl stretches as compared to HF/3-21G results.[1,2,10]

One issue not addressed in the current paper is the importance of contributions of multiple conformers to the experimentally measured spectra. The calculated frequencies we present here are based on the assumption that one conformer represents a global energy minimum and gives rise to the experimentally observed spectra. The presence of multiple similar energy conformers may well lead to discrepancies between the calculated and observed spectra, and this has been shown in some related cases.[10a] Although we were not able to account for every line in

TABLE VIII
Vibrational frequencies of TDG[a]

Mode	HF/6-311G**	INT	MP2/6-31G*	INT	EXP[10]
	42.2	7	34.4	7	
	54.0	0	39.5	0	
	91.3	0	88.0	0	
	127.3	20	124.0	20	
	134.2	0	129.2	0	
	265.2	18	251.7	19	
O-H bend	272.8	0	268.5	0	
O-H bend	274.9	280	270.7	275	
C-S-C bend	292.5	0	284.0	0	
C-S-C bend	415.1	2	393.4	3	
C-S-C bend	453.0	13	431.0	15	
C-S str	841.9	47	823.5	31	727
CH_2 bend	859.6	0	830.4	0	
C-S str	863.7	11	838.1	9	767
CH_2 bend	876.9	0	845.0	0	
C-C str	1075.8	17	1050.3	15	942
C-C str	1106.1	4	1074.6	9	
CH_2 bend	1109.3	0	1070.0	0	
CH_2 bend	1133.7	11	1093.2	6	1010
C-O str	1181.9	161	1097.9	121	1045
C-O str	1186.3	62	1101.9	59	1064
OH bend	1317.3	82	1253.8	29	1161
CH_2 bend	1321.3	0	1245.9	0	
CH_2 bend	1326.2	6	1249.0	3	
OH bend	1343.9	114	1276.1	85	1223
OH bend	1406.0	4	1331.8	4	
CH_2 bend	1424.5	0	1343.3	0	
CH_2 bend	1427.3	0	1345.5	2	
OH bend	1432.0	5	1354.3	5	1285
CH_2 bend	1588.5	2	1497.5	7	1337
CH_2 bend	1594.4	2	1503.0	3	1349
CH_2 bend	1618.0	24	1550.8	18	1408
CH_2 bend	1626.2	1	1559.1	0	
CH_2 bend	1658.8	5	1594.2	3	1465
CH_2 bend	1658.9	0	1594.3	1	
CH_2 str	3154.7	1	3069.6	0	
CH_2 str	3155.1	92	3069.8	68	2875
CH_2 str	3186.9	0	3118.3	0	
CH_2 str	3187.4	96	3118.5	77	2921
CH_2 str	3205.9	5	3129.1	3	
CH_2 str	3207.4	56	3126.3	31	
CH_2 str	3260.2	59	3191.0	25	2950
CH_2 str	3261.9	0	3196.1	0	
OH str	4185.5	127	3776.2	60	3358
OH str	4185.6	8	3776.2	2	

[a] See Table V, footnote a.

the experimental spectra, most of the intense lines were successfully assigned. Hence we suspect that accounting for multiple conformers would significantly increase the labor involved while delivering only relatively minor improvements in spectral matching for molecules of the type studied here. Presently, our computational resources are not sufficient to confirm this at the levels of theory employed in this work. However, others will examine this topic in a separate force constant analysis of some similar molecules based on the HF/4-31G* level of theory.[26]

Besides the multiple conformer issue, some differences can be expected between the calculated gas phase spectra and the experimental condensed phase spectra.

TABLE IX
Vibrational frequencies of CH[a]

Mode	HF/6-311G**	INT	MP2/6-31G*	INT
	39.5	2	32.4	2
	51.8	1	39.5	2
	78.1	0	75.5	0
	119.0	13	120.4	10
	130.1	5	126.5	6
	236.9	12	227.8	13
	262.7	2	254.7	1
O-H bend	273.8	141	270.2	138
CH_2 bend	364.1	0	348.7	0
C-O str	433.0	11	412.5	11
C-Cl str	771.8	75	776.3	34
CH_2 bend	834.8	3	809.5	3
C-S str	837.2	16	821.1	13
C-S str	868.3	29	848.0	19
CH_2 bend	870.3	1	839.3	1
CH_2 bend	1074.6	0	1041.6	0
C-C bend	1084.6	19	1058.5	20
CH_2 bend	1124.8	5	1085.3	3
C-C str	1130.7	0	1106.5	14
C-O str	1186.2	110	1099.0	75
CH_2 bend	1245.7	3	1196.0	2
CH_2 bend	1324.0	3	1247.7	1
OH bend	1327.2	90	1263.2	47
CH_2 bend	1369.1	63	1303.9	38
CH_2 bend	1410.0	1	1343.1	0
OH bend	1419.3	5	1344.6	3
CH_2 bend	1426.7	0	1346.0	2
CH_2 bend	1477.0	8	1409.2	6
CH_2 bend	1591.9	2	1500.5	5
CH_2 bend	1614.5	15	1549.4	12
CH_2 bend	1616.6	1	1553.9	6
CH_2 bend	1624.1	6	1558.1	1
CH_2 bend	1659.4	2	1594.2	2
CH_2 str	3156.0	46	3070.4	33
CH_2 str	3188.7	47	3119.4	37
CH_2 str	3208.4	25	3129.3	3
CH_2 str	3213.8	19	3126.4	21
CH_2 str	3256.9	17	3161.9	10
CH_2 str	3263.7	34	3195.8	6
CH_2 str	3266.3	1	3189.3	10
CH_2 str	3321.5	9	3232.6	4
OH str	4184.8	73	3775.3	34

[a] **See Table V, footnote a.**

Some modes, such as the O—H stretch, will be influenced more strongly by solvation than others. While qualitative estimations of such effects may be possible, quantitative estimations are considerably more difficult. Thus it is possible that comparisons to experimental gas phase spectra, were they available, would deliver closer agreement to the calculated frequencies than what we report here. Despite this, we are pleased to report that relatively good agreement can be achieved between the calculated and the currently available experimental spectra without resorting to extensive manipulations of the raw computed data. This observation implies that the kind of analysis presented here may be conveniently applied to other systems of interest, with expectations for similar levels of success.

TABLE X

Vibrational frequencies of HDINT[a]

Mode	HF/6-311G**	INT	MP2/6-31G*	INT
	60.4	1	60.1	1
	89.1	4	89.7	3
	154.6	4	150.0	4
	259.1	2	257.8	2
	311.0	1	303.6	3
C-S str	328.6	3	323.0	3
C-S str	596.5	57	626.9	19
C-C str	635.9	5	656.5	0
C-S str	732.9	61	734.9	27
CH_2 bend	820.9	3	792.1	3
C-Cl str	852.4	22	838.1	12
CH_2 bend	876.1	1	846.6	1
CH_2 bend	1026.2	1	978.8	0
CH_2 bend	1045.0	0	999.1	1
C-C str	1112.3	4	1068.9	2
C-C str	1118.8	1	1087.3	2
CH_2 bend	1180.6	3	1133.8	8
CH_2 bend	1229.1	26	1158.8	19
CH_2 bend	1253.4	3	1208.1	4
CH_2 bend	1268.5	1	1215.8	0
CH_2 bend	1311.0	1	1243.4	1
CH_2 bend	1382.7	46	1316.5	20
CH_2 bend	1416.4	4	1347.0	4
CH_2 bend	1483.8	6	1408.3	6
CH_2 bend	1578.2	22	1504.5	26
CH_2 bend	1592.3	5	1521.4	4
CH_2 bend	1616.9	3	1545.9	3
CH_2 bend	1626.1	2	1552.1	4
CH_2 str	3238.8	3	3140.2	5
CH_2 str	3248.5	9	3153.0	3
CH_2 str	3297.8	9	3209.1	11
CH_2 str	3298.5	1	3209.5	10
CH_2 str	3302.6	6	3211.7	8
CH_2 str	3318.5	0	3226.8	1
CH_2 str	3398.3	0	3310.2	0
CH_2 str	3410.4	21	3319.9	33

[a] See Table V, footnote a.

TABLE XI

Vibrational frequencies of CHINT[a]

Mode	HF/6-311G**	INT	MP2/6-31G*	INT
	60.4	2	61.6	1
	95.5	13	86.4	17
	173.8	4	169.1	3
	276.7	19	281.4	36
OH bend	286.8	133	261.4	114
S-C str	325.6	2	320.9	3
S-C str	400.4	15	388.3	18
S-C str	606.6	54	633.4	18
C-C str	643.4	5	659.1	0
S-C str	773.8	59	774.4	30
CH_2 bend	846.7	0	812.5	0
CH_2 bend	876.8	1	847.1	2
CH_2 bend	1028.0	1	980.0	0
CH_2 bend	1045.3	4	1000.8	4
C-C str	1090.2	34	1051.0	45
CH_2 bend	1163.5	4	1113.5	5
CH_2 bend	1181.2	4	1134.3	10

TABLE XI (*Continued*)

Mode	HF/6-311G**	INT	MP2/6-31G*	INT
C-O str	1216.1	68	1127.7	39
CH_2 bend	1228.8	24	1158.1	17
C-C str	1253.7	0	1211.6	1
CH_2 bend	1310.8	2	1243.2	1
CH_2 bend	1316.5	26	1239.1	9
OH bend	1339.8	76	1273.0	52
CH_2 bend	1414.5	12	1335.4	13
CH_2 bend	1423.6	1	1340.4	3
CH_2 bend	1577.1	18	1497.5	1
CH_2 bend	1588.2	5	1504.6	29
CH_2 bend	1607.3	15	1521.7	5
CH_2 bend	1625.9	1	1546.0	3
CH_2 bend	1660.0	1	1592.8	0
CH_2 str	3161.0	34	3068.2	26
CH_2 str	3200.5	34	3122.3	23
CH_2 str	3237.9	1	3144.3	2
CH_2 str	3299.0	6	3210.4	12
CH_2 str	3302.5	4	3211.9	11
CH_2 str	3307.1	0	3221.3	3
CH_2 str	3399.3	0	3311.8	0
CH_2 str	3411.4	19	3321.4	30
OH str	4163.5	151	3764.7	105

[a] **See Table V, footnote a.**

TABLE XII

Correction factors for HF/6-311G** and for MP2/6-31G* computed frequencies[a]

Mode	HF/6-311G**	MP2/6-31G*
C-Cl str	0.901 (4) [3]	0.898 (3) [3]
C-S str	0.881 (11) [7]	0.899 (13) [7]
C-C str	0.898 (19) [6]	0.917 (20) [6]
C-O str	0.888 (8) [3]	0.956 (8) [3]
O-H str	0.805 (4) [2]	0.893 (5) [2]
CH_2 str	0.899 (16) [13]	0.925 (9) [13]
CH_2 bend	0.881 (15) [27]	0.918 (12) [27]
O-H bend	0.888 (16) [5]	0.935 (18) [5]
CH_3 bend	0.880 (14) [2]	0.920 (17) [2]

[a] The correction factors listed are computed by dividing the experimentally measured frequency by the computed frequency for a given normal mode vibration. Each number in parenthesis is the standard deviation of the mean, σ_{n-1}, times 10^3. Each number in brackets is the number of data points used to compute the mean correction factor listed and its standard deviation.

4. CONCLUSIONS

The following conclusions emerge from this study:

1. Both the HF/6-311G** and MP2/6-31G* levels of theory are able to satisfactorily estimate the vibrational frequencies for HD and related hydrolysis products, and yield improved values over the HF/3-21G level, particularly for modes involving contributions from heavy atoms.

2. The larger basis sets tend to deliver more consistent correction factors than do the smaller basis sets.

3. Inclusion of electron correlation at the MP2 level appears to improve the accuracy of the calculated frequencies.

4. We predict that application of the appropriate correction factors to the calculated frequencies of the molecules lacking experimental infrared data will produce results closely approximating the actual spectra when they are eventually obtained.

ACKNOWLEDGEMENTS

We express our appreciation to ERDEC, U.S. Army, for financial support of this work.

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