magnetic susceptibility, ESR, and Mössbauer spectra, but unlike other high-spin ferric hemes, this complex is rhombic. The uncommon spectral characteristics of this complex are attributed to the presence of the peroxide ligand. While it is not possible to determine the geometry of the Fe(OEP)O_2^- complex conclusively without a crystal structure, the magnetic spectra suggest that the iron peroxide complex may have a geometry similar to that of the manganese(III) porphyrin peroxide, Mn(TPP)O_2^-, where the metal ion is significantly displaced out of the plane of the porphyrin toward the peroxo ligand. In fact, the EXAFS data measured of the ferric complex, [Na(THF)$_3$][Fe(TPP)O_2], and reported by Friant et al.[13] are consistent with the displacement of the iron from the plane of the porphyrin. Measurements of the rhombicity and the zero-field splitting in Fe(OEP)O_2^- are consistent with the geometry proposed.

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Second-Order Perturbation Theory and Configuration Interaction Theory Applied to Medium-Sized Molecules: Cyclopropane, Ethylenimine, Ethylene Oxide, Fluoroethane, and Acetaldehyde

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Abstract: A systematic comparison of post Hartree–Fock theoretical predictions for molecular structures and vibrational frequencies has been undertaken for the five species identified in the title. Double-ζ plus polarization (DZP) basis sets are used throughout, and for ethylenimine, a significantly larger basis set is used (in addition) to address an inconsistency with respect to experiment. Although good agreement with available experiments is generally reported, a revised assignment of the C_2H_4NH vibrational frequencies is suggested. Theory also allows a clear choice between two existing experimental assignments of the fluoroethane vibrational frequencies.

1. Introduction

It is now increasingly common for ab initio studies on small molecules (defined perhaps as containing two heavy atoms or less) to be considered as worthy of publication only if an attempt has been made to include electron correlation effects. We suggest that the time is quickly approaching when the same situations will hold for medium-sized systems.

There are two commonly used methods for the inclusion of electron correlation that are applicable to the larger systems, compatible with the use of good basis sets. The simplest of these methods, based on second-order perturbation theory, is commonly called MP2.[1] The other approach is based on the variational principle and is called CISD,[2] configuration interaction including all single and double replacements from the self-consistent-field reference function. MP2 has indeed been applied to rather large molecular systems;[3] full geometrical optimizations and force constant analyses have been performed for molecules as large as malonaldehyde.[4] CISD programs are more complicated, and as such there is not yet available the wealth of evidence for this approach. We suspect that the largest molecules (in terms of both the number of atoms and the number of unique geometrical parameters) for which full CISD geometry optimizations and vibrational analyses have been performed are the hydrogen-bonded complex $H_5O_2^+$ [5a] and bicyclobutene, a C_4H_4 isomer.[5b]

Recent advances in gradient theory have enabled our research groups to develop efficient computer programs for the evaluation of MP2 and CISD energies and their gradients.[6] We contend that it is now appropriate to study a series of medium-sized molecules, with good basis sets, by both methods, so that the results may be compared for their reliability.

Let us briefly comment on advantages and disadvantages of these two methods. MP2 has the advantage that it is very simple and also size extensive. It has the disadvantage that it is only applicable to closed-shell systems or open-shell systems, which are well represented by the unrestricted Hartree-Fock (UHF) determinant. Alternatively, CISD is a fully variational procedure, operating in space and spin symmetry, but truncated CI expansions are not size extensive. Both methods are dependent upon the dominance of the reference configuration, but CISD is less so

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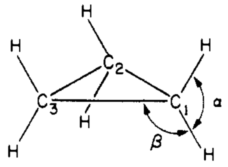
Table I. Energies (E) and Equilibrium Structures for Cyclopropane at the SCF, MP2, and CISD Levels of Theory, with a DZP Basis[a]

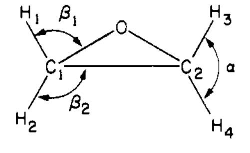


	SCF	MP2	CISD	expt r_o[21]
E	−117.084563	−117.550254	−117.491715	
r_{C-C}	1.503	1.513	1.510	1.512
r_{C-H}	1.076	1.083	1.080	1.083
α	114.4	115.1	114.7	114.0
β	118.0	117.7	117.8	

		SCF ω	MP2 ω	expt ν[22]	mode description
a_1'	ω_1	3313	3239	3038	CH_2 s str
	ω_2	1660	1575	1479	CH_2 scissors
	ω_3	1291	1244	1188	ring str
a_2'	ω_4	1203	1098	1070	CH_2 wag
a_1''	ω_5	1249	1188	1126	CH_2 twist
a_2''	ω_6	3405	3352	3102	CH_2 a str
	ω_7	913	890	854	CH_2 rock
e'	ω_8	3298	3229	3024	CH_2 s str
	ω_9	1591	1515	1438	CH_2 scissors
	ω_{10}	1170	1098	1028	CH_2 wag
	ω_{11}	951	918	868	ring deformn
e''	ω_{12}	3385	3335	3082	CH_2 a str
	ω_{13}	1311	1239	1188	CH_2 twist
	ω_{14}	797	773	739	CH_2 rock

[a] E in hartrees, bond lengths in angstroms, angles in degrees. See figure for description of geometrical parameters. Harmonic frequencies ω_r also reported for SCF and MP2 (cm^{-1}). Fundamentals ν_r taken from reported experimental assignments.

Table II. Equilibrium Geometry and Vibrational Frequencies of Ethylene Oxide (Details as for Table I)



	SCF	MP2	CISD	expt r_s[23]
E	−152.905218	−153.402672	−153.332796	
r_{C-O}	1.404	1.441	1.424	1.431
r_{C-C}	1.459	1.474	1.469	1.466
r_{C-H}	1.078	1.086	1.082	1.085
∠COC	62.6	61.5	62.1	
α	115.5	116.2	115.8	116.6
β_1	115.3	115.0	115.3	
β_2	119.7	119.3	119.4	

		SCF ω	MP2 ω	expt ν[15]	mode description
a_1	ω_1	3296	3202	3024	CH_2 s str
	ω_2	1687	1588	1497	CH_2 scissors
	ω_3	1419	1318	1270	ring stretch
	ω_4	1294	1178	1120[a]	CH_2 wag
	ω_5	986	909	877	ring deformn
a_2	ω_6	3375	3303	3065	CH_2 a str
	ω_7	1274	1200		CH_2 twist
	ω_8	1144	1055	1020	CH_2 rock
b_1	ω_9	3283	3193	2978	CH_2 s str
	ω_{10}	1630	1548	1470	CH_2 scissors
	ω_{11}	1277	1141	1159[a]	CH_2 wag
	ω_{12}	974	858	822	ring deformn
b_2	ω_{13}	3390	3317	3065	CH_2 a str
	ω_{14}	1278	1176	1147	CH_2 twist
	ω_{15}	877	839	808	CH_2 rock

[a] It is hypothesized in the text that these two assignments could conceivably be interchanged.

because in the procedure the excited configurations interact. We base these statement not only on rigorous theoretical analyses of the two methods but also on our experiences with these two methods. The advantages of these methods have allowed us to perform reliable theoretical studies on small systems when these requirements have been well satisfied.

The purpose of this research then is to investigate the reliability of the MP2 and single-reference CISD correlation methods by applying them to a series of experimentally well-understood medium-sized molecules. We did not wish to make this a basis set study as well, and so we have used only one basis. However, it is also evident that there is no point in applying any kind of electron correlation technique without incorporating a relatively large basis set. Thus, we have used a standard double-ζ plus polarization (DZP) basis in conjunction with the MP2 and CISD correlation methods.

If we are able to extrapolate on the basis of results for small systems at the DZP MP2[7] and DZP CISD[8] levels of theory we would expect to obtain equilibrium geometries in good agreement with experiment (i.e., better than ±0.01 Å for bond lengths and ±2° for bond angles).

The molecules selected for our studies are the following: (a) cyclopropane (C_3H_6), 24 e (electrons), 78 bf (basis functions); (b) ethylene oxide (C_2H_4O), 24 e, 68 bf; (c) ethylenimine (C_2H_4NH), 24 e, 73 bf; (d) fluoroethane (C_2H_5F), 26 e, 73 bf; (e) acetaldehyde (CH_3CHO), 24 e, 68 bf. For each of these molecules there are some meaningful geometrical data, so the reliability of each approach can be tested.

In section 2, some further details of the theoretical approach are given. Our results are reported and discussed in section 3, and also given in section 3 are harmonic frequenices at the SCF and MP2 levels of theory to show the considerable improvement that is achieved. Our conclusions are given in section 4.

2. Theoretical Approach

For all of the results presented here, the standard Dunning[9] double-ζ contraction of Huzinaga's[10] primitive sets (9s5p for first-row atoms and 5s for hydrogen) was augmented with one set of polarization functions on every atom to yield the DZP basis. The hydrogen s basis functions were scaled by 1.2. The polarization function Gaussian exponents were $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.80$, $\alpha_d(O) = 0.85$, $\alpha_d(F) = 1.0$, and $\alpha_p(H) = 1.0$.

The SCF and MP2 results were obtained with the Cambridge Analytic Derivatives Package,[11] which has recently been extended to evaluate MP2 closed-shell analytic gradients and second derivatives.[6a,7] These computations were performed on the CRAY-1S. The CISD calculations were performed with the Berkeley implementation of the Graphical Unitary Group Approach,[12] and the structures were optimized with the recently developed theory for the analytic evaluation of CI energy gradients.[6b] The CI calculations were performed in Berkeley on an IBM 3090.

There is one minor lack of comparison in the results. The CADPAC MP2 codes correlate all electrons and all orbitals are active, whereas the CISD expansions were restricted so that the molecular orbitals corresponding to the 1s core electrons were held doubly occupied in all configurations and the corresponding virtual orbitals were deleted from the procedure. We believe that the difference will not significantly affect the results or our discussion.

For ethylenimine only, the vibrational frequencies were determined with the CISD method. Via finite differences of analytic CI gradients, this requires the evaluation of 20 gradients with no elements of point-group symmetry other than the identity (i.e., C_1 symmetry). With the three lowest occupied SCF MO's doubly occupied and the three highest virtual orbitals deleted, there are 137026 configurations for ethylenimine in C_1 symmetry.

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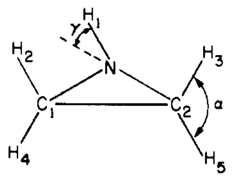
Table III. Equilibrium Geometry and Vibrational Frequencies of Ethylenimine (Details as for Table I)



	SCF (DZP basis)	MP2 (DZP basis)	MP2 (5s3p2d/3s1p)	CISD	expt r_s[24]
E	−133.071 393	−133.561 908	−133.643 134	−133.495 686	
r_{C-N}	1.453	1.481	1.476	1.469	1.475
r_{C-C}	1.478	1.490	1.479	1.486	1.481
$r_{C_1-H_2}$	1.078	1.085	1.079	1.082	1.084
$r_{C_1-H_4}$	1.077	1.083	1.077	1.080	1.083
r_{N-H}	1.000	1.018	1.013	1.011	1.016
∠CCN	59.4	59.8	59.9	59.6	59.9
$\beta_1(H_2C_1N)$	118.5	118.6	118.3	118.6	118.3
$\beta_2(H_4C_1N)$	115.1	114.4	114.3	114.8	114.3
$\beta_3(H_4C_1C_2)$	119.9	119.4	119.5	119.6	119.3
$\beta_4(H_2C_1C_2)$	118.0	117.8	117.8	117.9	117.8
α	114.8	115.4	115.5	115.1	115.7
γ	64.8	67.9	68.0	66.7	67.5[a]

		SCF ω	MP2 ω (DZP basis)	MP2 ω (5s3p2d/3s1p)	CISD	expt ν[20]	mode description
a′	ω_1	3813	3605	3568	3694	3338	NH str
	ω_2	3391	3332	3298	3358	3079	CH_2 a str
	ω_3	3298	3219	3195	3257	3015	CH_2 s str
	ω_4	1668	1576	1560	1614	1482	CH_2 scissors
	ω_5	1390	1318	1311	1348	1211 (1268)[b]	CH_2 twist
	ω_6	1359	1265	1244	1309	1095 (1211)[b]	ring str
	ω_7	1238	1146	1128	1188	1090 (1095)[b]	CH_2 wag
	ω_8	1084	1037	1028	1054	998	NH bend
	ω_9	963	901	880	934	856	ring deformn
	ω_{10}	844	803	797	821	773	CH_2 rock
a″	ω_{11}	3377	3321	3287	3346	3079	CH_2 a str
	ω_{12}	3287	3212	3189	3248	3015	CH_2 s str
	ω_{13}	1620	1539	1530	1569	1463	CH_2 scissors
	ω_{14}	1384	1291	1279	1331	1268 (1237)[b]	CH_2 rock
	ω_{15}	1255	1181	1174	1208	1237 (1131)[b]	CH_2 twist
	ω_{16}	1234	1116	1124	1166	1131 (1090)[b]	CH_2 wag
	ω_{17}	1003	934	930	959	904	ring deformn
	ω_{18}	972	884	854	933	817	CH_2 rock
	$\bar{\chi}$[c]	11.5	5.4	4.3	8.1		
	σ[c]	2.5	1.8	1.6	2.0		

[a] Note that this bond angle is not explicitly reported in the experimental paper[24] and is incorrectly stated to be 61.0° in ref 13a. [b] New assignments, which derive from ref 14 and this work; see text. [c] Average and standard deviations of percent differences between theoretical ω and experimental ν (assuming new assignments).

3. Results

(a) Cyclopropane (CP), (b) Ethylene Oxide (EO), and (c) Ethylenimine (EI). Our results for these saturated three-membered ring systems are reported in Tables I–III. There have been previous theoretical studies of these systems,[13] the best of which appears to be the SCF calculations of Komornicki, Pauzat, and Ellinger,[13] who used a 6-31G[3] basis set. They optimized geometries and evaluated harmonic frequencies. In particular, they examined force fields and critically looked at the reported analyses of infrared and Raman spectra. As is well understood for these strained systems, reliable results will not be obtained unless polarization functions are included in the basis set. We are not aware of any detailed studies of these systems at the correlated level, although ref 3 refers to unpublished calculations by Pople on cyclopropane and ethylene oxide at the MP2, MP3, and MP4 levels, but it is certain that geometries have not been optimized.

There is good experimental information available for the geometrical parameters of these systems; references are given in the tables. As observed by Komornicki et al.,[13] theory correctly predicts the trends in bond lengths as the molecules are compared. For these molecules it appears to hold for these results that, for all quoted bond lengths, eq 1 holds, with the one exception of the

$$r_{AM}^{SCF} < r_{AB}^{CISD} \le r_{AB}^{expt} \le r_{AB}^{MP2} \qquad (1)$$

C–C bond length in ethylenimine. The C–C bond lengths decrease in the order CP → EI → EO due to increased electronegativity of the heteroatom. At the DZP SCF level of theory, the C–C distances are predicted to differ from experiment by −0.009 Å (cyclopropane), −0.003 Å (ethylenimine), and −0.007 Å (ethylene oxide). The comparable differences between theory and experiment with DZP MP2 are +0.001 Å (cyclopropane), +0.009 Å (ethylenimine), and +0.008 Å (ethylene oxide). Finally the DZP CISD carbon–carbon bond distances differ from experiment by −0.002 Å (cyclopropane), + 0.005 Å (ethylenimine), and +0.003 Å (ethylene oxide).

In essence, all three levels of theory are in as good agreement with experiment for these C–C distances as is possible under the circumstances. First, the experimental bond distances are stated as uncertain to within ±0.003 Å. Second, the theoretical predictions are for r_e equilibrium structures, while the experiments refer to r_s (substitution) or r_0 (vibrationally averaged) structures. It is not unusual for r_e structures to differ from r_s or r_0 structures by 0.005 Å or even more. Thus, all three levels of theory presented here succeed in reproducing the experimental C–C distances.

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We would not suggest for one moment that (1) holds for these molecules as the size of the basis set increases. Indeed, we have evidence from large basis set calculations[7] on small molecules that (i) the SCF value gets worse and (ii) the MP2 value often becomes shorter than r_e and has a limit value close to that for CISD for single bonds. For example, for H_2O with a triple-ζ plus double-ζ polarization (TZ2P) type basis, results are the following: SCF, 0.941; MP2, 0.958; CISD, 0.955; experiment, 0.958 Å. Thus, our conclusion so far is that CISD and MP2 improve bond lengths compared to SCF values and they may bracket the experimental value in some cases.

It is more difficult to draw firm conclusions about the bond angles, one reason being that some experimental evidence is missing. For example, if we look at methylene HCH angles best (worst) values are given for CP, SCF(MP2); EO, MP2(SCF); EI, MP2(SCF); but none are in error by more than 1.1°.

Turning now the harmonic frequencies ω_i, which are obtained by diagonalizing the mass-weighted Cartesian second-derivative matrix, we can only compare these values with experimental assignments for the corresponding fundamentals ν_i. The experimental assignments for cyclopropane appear to be most reliable, and Table I shows that MP2 values are all closer to ν than the SCF values. Results from smaller systems[7] suggest that MP2-(DZP) ω_i are within ~4% of "experimental" ω_e if available. The greatest discrepancy between ω_i and ν_i is for the stretching motions, where anharmonic effects are considerable.

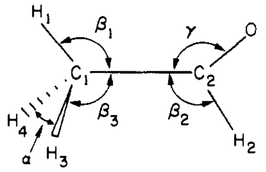
For EI and EO, further discussion is warranted. It is plausible to argue that at least for bond stretching modes

$$\omega_i^{\mathrm{SCF}} > \omega_i^{\mathrm{MP2}} > \nu_i^{\mathrm{expt}} \tag{2}$$

This holds uniformly for cyclopropane but not for EO and EI. Substantial Fermi resonance effects or "floppy" molecule effects are typically necessary for $\omega_i^{\mathrm{MP2}} < \nu_i^{\mathrm{expt}}$. For ω_{15} and ω_{16} of ethylenimine, $\omega_i^{\mathrm{MP2}} < \nu_i^{\mathrm{expt}}$, which suggests that the experimental assignments could conceivably be wrong. Komornicki et al.[13] in their SCF study also suggested that this may be the case by a careful analysis of their normal coordinates and the trends in the three molecules. Komornicki argues that the experimentalists' suppostions that vibrations can be described as CH_2 twist or NH bend may not be entirely correct, because normal coordinates show strong mixing of such motions. Potts[14] obviously had problems with his assignments of EI, and once this remark is made, then it is hardly surprising that assignments and mode descriptions of these larger molecules might be wrong. In Table III, assignments based on our work and that of Komornicki et al.[13] are suggested. The key is that ν_{14} (1268) is misassigned and should be ν_5. It follows that the experimental ν_6 (1095) or ν_7 (1090) should be reassigned as ν_{16}. Supporting evidence is that Potts argues that 1211 cm^{-1} is definitely ring stretch A′; it should now be ν_6, as confirmed by the normal-mode vector.

To confirm these suggestions for ethylenimine, a larger basis set study was performed. A (5s3p/3s) set from Dunning[9] was used, with two sets of d functions (N, α_d = 1.35, 0.45; C, α_d = 1.2, 0.4) and the original set of p functions on H. MP2 geometry optimization and harmonic frequency calculations are reported in Table III for this larger basis. The results for the ring structure show an excellent agreement with experiment. The C–H bonds are shorter than experimental r_s values; there are two reasons for this: (i) MP2-limit values are often shorter than r_e values, and (ii) r_s values are longer than r_e values. For A–H bonds, each of these effects could have an 0.003-Å effect. For the harmonic frequencies ω, we first note that all are in closer agreement with experimental ν (new assignment) than the MP2 (DZP) values for ω. This supports our previous conclusion[7] that the accuracy of MP2 frequencies can be markedly improved with larger basis sets. The new frequencies support the new assignments for ν_5, ν_6, ν_7, ν_{14}, ν_{15}, and ν_{16}. In particular, we note that ω_7 is predicted to be 4 cm^{-1} higher than ω_{16} to be compared with an experimental difference of 5 cm^{-1} for ν_7 and ν_{16} in the new assignment. ω_7 and ω_{16} have comparable predicted infrared intensities, and hence we cannot be dogmatic in the proposed assignment of these two fundamentals. The above is a clear demonstration of the role that the theoretician has to play in spectroscopy; if such theoretical analysis had been available to Potts,[14] he would have had a much easier job in making the vibrational assignments.

Table IV. Equilibrium Geometry and Vibrational Frequencies of Acetaldehyde (Details as for Table I)



	SCF	MP2	CISD	expt[26]
E	−152.953 518	−153.446 283	−153.376 671	
$r_{\mathrm{C-O}}$	1.192	1.227	1.209	1.213 ± 0.01
$r_{\mathrm{C-C}}$	1.506	1.508	1.508	1.504 ± 0.01
$r_{\mathrm{C_1-H_1}}$	1.082	1.089	1.085	1.091 ± 0.005
$r_{\mathrm{C_1-H_3}}$	1.087	1.093	1.090	1.085 ± 0.005
$r_{\mathrm{C_2-H_2}}$	1.097	1.107	1.102	1.106 ± 0.005
α	107.4	107.3	107.4	108.9 ± 0.5
β_1	110.6	110.5	110.5	110.6 ± 0.5
β_2	115.3	115.3	115.3	114.9 ± 1.0
β_3	109.4	109.3	109.3	110.3 ± 0.5
γ	124.6	124.5	124.5	124.0 ± 0.5

		SCF ω	MP2 ω	expt ν^{27}	mode description
a′	ω_1	3323	3268	3014	CH_3 str
	ω_2	3198	3119	2923	CH_3 str
	ω_3	3153	3038		CH str
	ω_4	2016	1785	1746	CO str
	ω_5	1583	1503	1430	CH_3 deformn
	ω_6	1552	1458	1395	CH bend
	ω_7	1514	1420	1353	CH_3 deformn
	ω_8	1227	1163	1114	CC str
	ω_9	962	918	877	CH_3 rock
	ω_{10}	541	506	506	CCO deformn
a″	ω_{11}	3266	3220	2964	CH_3 str
	ω_{12}	1595	1514	1436	CH_3 deformn
	ω_{13}	1253	1153	1107	CH_3 rock
	ω_{14}	848	791	764	CH bend
	ω_{15}	162	159	143	torsion

In light of the questions raised by the MP2 vibrational predictions, it was considered prudent to in addition make DZP CISD predictions. These are included in Table III and are consistent with the assignments suggested in the previous paragraph. In comparison with the new vibrational assignment, DZP CISD provides rather even agreement. Specifically, we find that the CI harmonic frequencies are 6.3% (ω_5), 8.1% (ω_6), 8.5% (ω_7), 7.6% (ω_{14}), 6.8% (ω_{15}), and 7.0% (ω_{16}) higher than the observed fundamentals. The consistency of the agreement is encouraging.

In a similar way Komornicki et al. examined ethylene oxide, but their SCF values were of insufficient accuracy to be really helpful. For ethylene oxide, the only DZP MP2 harmonic vibrational frequency that falls below the observed fundamental is ω_{11} = 1141 (for which ν_{11} = 1159 cm^{-1}). Our results suggest that ν_4 (1120) and ν_{11} (1159) could conceivably be interchanged. Both of these vibrations are described by Potts as CH_2 wag, but examination of the normal coordinates suggest that CH_2 rock and twist have to be included as well. The remainder of the experimental assignments appear reasonable. Nakanaga[15] has reanalyzed the EO spectrum, but the fundamentals he examined (ν_5, ν_{12}, ν_{15}) do not affect our discussion.

It is appropriate to add at this point that much of the improvement in MP2 frequencies over SCF frequencies follows from the improved geometries at the correlated level. The effect of the reference geometry on the calculated frequencies, especially for stretching modes, has been extensively discussed by Fogarasi and Pulay[16] and by Blom et al.[17] in their work on hydrocarbons. It

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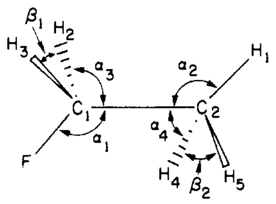
Table V. Equilibrium Geometry and Vibrational Frequencies of Fluoroethane (Details as for Table I)



	SCF	MP2	CISD	expt[26]
E	−178.130048	−178.633641	−178.570623	
r_{C-C}	1.515	1.514	1.514	1.505
r_{C-F}	1.373	1.400	1.389	1.398
$r_{C_1-H_2}$	1.084	1.092	1.089	1.095
$r_{C_2-H_1}$	1.086	1.092	1.089	1.091
$r_{C_2-H_4}$	1.085	1.090	1.088	1.090
α_1	109.9	109.6	109.7	109.7
α_2	109.8	109.7	109.7	109.7
α_3	111.5	111.6	111.5	112.9
α_4	110.6	110.5	110.5	
β_1	108.9	109.2	109.1	108.8
β_2	108.6	108.8	108.8	108.9

		SCF ω	MP2 ω	exptl 1[20,29]	exptl 2[30]	mode description
a′	ω_1 [$\nu_s'(CH_3)$]	3281	3240	3003	2985	CH_3 str
	ω_2 [$\nu_s(CH_2)$]	3243	3152	2941	2930[a]	CH_2 str
	ω_3 [$\nu_s(CH_3)$]	3201	3130	2915	2946[a]	CH_3 str
	ω_4	1654	1567	1479	1485	CH_2 scissors
	ω_5	1622	1544	1449	1470	CH_3 deformn
	ω_6	1572	1477	1395	1402	CH_3 deformn
	ω_7	1524	1438	1365	1397	CH_2 wag
	ω_8	1227	1156	1108	1109	CH_3 rock
	ω_9	1168	1109	1048	1062	CC str
	ω_{10}	962	912	880	881	CF str
	ω_{11}	441	416	415	415	CCF deformn
a″	ω_{12} [$\nu_a(CH_3)$]	3304	3255	3003 (2967)	2999	CH_3 str
	ω_{13} [$\nu_a(CH_2)$]	3280	3222	3003	2964	CH_2 str
	ω_{14}	1599	1521	1449	1449	CH_3 deformn
	ω_{15}	1410	1329	1277	1274	CH_2 twist
	ω_{16}	1297	1220	1048 (1060)	1172	CH_3 rock
	ω_{17}	872	838	810	809	CH_2 rock
	ω_{18}	271	275	243	242	torsion

[a] Assignment is uncertain because of Fermi resonance between ν_2 or ν_3 and $2\nu_4$ or $2\nu_5$.

is clear, however, that the accuracy of the reference geometry does not guarantee accurate harmonic frequencies, and the quality of the wave function certainly plays a very important role. Finally, for the reassignment suggested here, it can be argued that carefully scaled SCF frequencies can sometimes be sufficiently accurate for the critical examination of experimental assignments. We note that for ethylenimine the errors of the DZP SCF frequencies for modes 5–7 and 14–16 are 14.8%, 24.1%, 13.6%, 9.1%, 1.4%, and 9.1%, respectively, when compared to the old assignment but are much more uniform with the new assignment, namely 9.6%, 12.2%, 13.1%, 11.9%, 11.0%, and 13.2%. In fact, Komornicki's[13] scaled SCF/6-31G** frequencies for these modes are very similar to the unscaled CISD results. However, although scaled SCF frequencies could point to a misassignment of the EI spectrum, this is not true for ethylene oxide. For this molecule, the errors of the frequencies for modes 4 and 11 calculated at the DZP/SCF level are 15.5% and 10.2% with respect to the old assignment and 11.6% and 14.0%, respectively, for the new one suggested here. Furthermore, Komornicki's scaled SCF/6-31G** frequencies are 1221 and 1223 cm^{-1} for modes 4 and 11, respectively. Clearly, this sort of accuracy is not sufficient for the critical examination of experimental assignments, and it is only the improved correlated results, which do not depend on empirical scaling factors, that allow us to suggest new assignments.

(d) Acetaldehyde (AA). Our results for acetaldehyde may be found in Table IV. Previous calculations at the SCF and MP level have been referred to by Pople's group.[3] There is an SCF (6-31G*) calculation for the force field and harmonic frequencies by Wiberg, Walters, and Colson.[18]

As is apparent from the observed microwave data, there is some experimental uncertainty. In fact, the experimental error bars are sufficiently large that the relationship (1) is seen to be satisfied for acetaldehyde. The CO doule-bond distance will probably be more reliably predicted by CISD than MP2, and the calculations appear to support this. Again little needs to be said about bond angles since all three levels of theory provide satisfactory agreement with experiment and electron correlation plays a small role.

Wiberg et al.[18] used their SCF results for the force field to present a careful analysis of fundamental assignments. The acetaldehyde vibrational assignments, which appear to be most reliable, are due to Hollenstein et al.;[19] either assignment found in Shimanouchi[20] is clearly imprecise, as evidenced from the earlier

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value of 919 cm^{-1} reported for ν_9. Finally, we observe that the small torsional frequency ω_{15} is little affected by correlation, which is as expected.

The energy difference between the isomers acetaldehyde and ethylene oxide is known to be 26 kcal/mol.[3] It is interesting to observe that our values are 30.2, 27.3, and 27.4 kcal/mol at the SCF, MP2, and CISD levels of theory.

(e) Fluoroethane (FE). There is no outstanding discrepancy between our calculations and the experimental values for the geometrical parameters; we do note that r_{CC}^{expt} at 1.505 Å is slightly shorter than our theoretical predictions. However, it is to be emphasized that inherent differences of 0.005 Å between r_e (as predicted here by theory) and r_o or r_s structures are not uncommon. We are aware of only one other ab initio study on this system where harmonic frequencies were determined.[28] However, these were performed at a much lower level of theory (3-21G/SCF). The difference between the CISD and MP2 geometrical parameters is greatest for r_{C-F} at 0.011 Å.

The case of fluoroethane (Table V) is a very interesting one, because there are two different assignments of the fundamental frequencies. The first one was by Smith,[20b] which was also used by Crowder and Mao.[29] The second one is by Saur et al.[30] They analyzed the spectra of several deuteriated derivatives, and their assignment is in several cases different from the original one. We suggest that this is one of the cases where theory can play an important role in the assignment of vibrational spectra.

We first observe that there is no problem with the low-frequency ν_{10}, ν_{11}, ν_{17}, and ν_{18} and that the DZP MP2 ω's are in excellent agreement with the experimental values. For ν_{16}, our MP2 harmonic frequency is about 160 cm^{-1} higher than the original experimental fundamental. However, Saur et al. observed a band at 1172 cm^{-1} and assigned it to ν_{16}, which is in much better agreement with our DZP MP2 prediction that ω_{16} = 1220 cm^{-1}.

The ν_7 band at 1365 cm^{-1} in ref 19 and 28 was taken from a spectrum in the liquid phase. Saur et al.[30] observe the strongly overlapped ν_6 and ν_7 bands in the 1395–1402-cm^{-1} region. In our analysis, the normal coordinates of our ω_6 and ω_7 also show a strong mixing of the CH_3 s deformation and the CH_2 wag. Saur et al. also observe the 1470-cm^{-1} ν_5 band, which was originally assigned as overlapping with the ν_{14} band at 1449 cm^{-1}. This is again in agreement with our prediction that ω_5 is greater than ω_{14} by about 20 cm^{-1}.

Finally for the C–H stretching modes, Crowder and Mao[29] assign them so that $\nu_a(CH_2) > \nu_a(CH_3)$ and $\nu_s(CH_2) > \nu_s(CH_3)$. Saur et al. give $\nu_a(CH_2) < \nu_a(CH_3)$ and $\nu_s(CH_2) < \nu_s(CH_3)$ but with some uncertainty for the latter, because of a Fermi resonance. We can argue that, for these modes, the anharmonic effect will be similar, and therefore the order of our ω's should be correct within symmetry types. Our result is $\omega_a(CH_2) < \omega_a(cH_3)$ (which favors Saur et al.) and $\omega_s(CH_2) > \omega_s(CH_3)$, which is in agreement with the original assignment.

4. Conclusions

In this paper we have demonstrated the feasibility of performing MP2 and CISD geometry optimizations using DZP basis sets on reasonably sized molecules. The molecules studied were cyclopropane, ethylene oxide, ethylenimine, acetaldehyde, and fluoroethane. We have shown that improvement in bond lengths over SCF is achieved, with MP2 bond lengths being longer and CISD bond distances being shorter than those that are reliably known. For single bonds, the MP2 and CISD bond lengths agree in most cases to better than 0.005 Å. We have argued that if better than DZP basis sets are used, then for single bonds the MP2 and CISD values will both become rather accurate. For multiple bonds, CISD may be the favored procedure, although we have found[7] that MP2 with larger than DZP basis sets also gives good agreement.

Because these calculations were performed in different locations, we cannot directly compare timings. However, the ratio of an MP2 gradient calculation to an SCF gradient calculation on fluoroethane was 1.76 on the CRAY-1S. The ratio of a CISD gradient calculation to an SCF gradient calculation was 3.32 on fluoroethane on the IBM 3090.

We have taken the opportunity to use our results to critically examine available geometrical and spectroscopic data. For ethylenimine, we suspect that some fundamental frequencies may be misassigned. For fluoroethane we favor a more recent vibrational assignment over an older one (with one exception). Perhaps the most important conclusion from this paper is that such calculations are becoming routine and are now available tools for the spectroscopist. We have shown that the accuracy achieved with DZP basis sets for small molecules at the MP2 and CISD levels carries over to medium-sized molecules. Of course, the reader should realize that we have chosen molecules that are well represented by one reference configuration (in all cases $C_0 > 0.9$), but there are of course a very large number of interesting molecules with three, four, or five heavy atoms for which similar theoretical studies can now be carried out.

Note Added in Proof. Attention is drawn to the recent experimental paper on C_3H_6.[31] The new geometrical constants show better agreement with our correlated calculations.

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