Effect of Electron Correlation on Theoretical Vibrational Frequencies

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Theoretical HF/6-31G* (Hartree–Fock, 6-31G* basis set) and MP2/6-31G* (second-order Møller–Plesset, 6-31G* basis set) vibrational frequencies based on complete quadratic force fields have been obtained for a set of 36 one- and two-heavy-atom molecules comprising first-row elements for which experimental spectroscopic data are available. Frequencies calculated at the HF/6-31G* level are an average of 12.6% higher than experimental values. Partial treatment of electron correlation via the perturbation method of Møller and Plesset, terminated at second order, leads to a significant reduction in this error, although theoretical MP2/6-31G* frequencies are still larger than the experimental quantities by 7.3%. Part of the difference may be traced to the restriction of quadratic force fields, as comparison with experimental harmonic frequencies shows deviations of only 9.5% and 4.7% for the two levels, respectively. The calculated frequencies are used in conjunction with the corresponding theoretical equilibrium structures to obtain absolute molecular entropies, which may in turn be used to yield entropies of reaction. These latter quantities are generally in good accord with entropies derived using experimental structures and frequencies.

INTRODUCTION

The last decade has witnessed the successful application of simple levels of *ab initio* molecular orbital theory to the calculation of the equilibrium structures and relative thermochemical stabilities of isolated molecules. Numerous comparisons have been made with available experimental data, and it is now possible to say with a considerable degree of confidence how well a given theoretical level will fare in a particular task. The coming decade will see a furthering of this trend, and in addition will probably witness the application of simple theories to even more challenging chemical problems, in particular to the description of the properties of transition structures and of reaction pathways. In this latter task, attention will need to be focused not only on the characterization of the geometrical structures and relative energies of interesting stationary points on the molecular potential surface, but also on the shape of the surface in the immediate vicinity of these points.

In preface to any significant applications of the theory, detailed comparisons with available experimental data will need to be made wherever possible. For example, experimental vibrational frequencies for stable molecules may, in favorable cases, be decomposed in terms of a set of bond-stretching and angle-bending force constants, which directly describe the relative ease of distortion of a molecular framework away from its equilibrium nuclear arrangement. Force constants may be calculated theoretically and compared directly with values derived from spectroscopic measurements. Alternatively, they may be used in conjunction with a given set of nuclear masses to yield the normal mode vibrational frequencies. Both experimental and theoretical vibrational frequencies may be used along with the corresponding structural data to yield equilibrium thermodynamic properties (e.g., entropies and isotopic partition function ratios) by way of statistical mechanics. The situation may also be turned around, and measured entropies of activation and kinetic isotope effects may, within the framework of the simple transition state theory, be used to provide information about the transition structure itself, a saddle point on the overall potential surface rather than a stable energy minimum.

Numerous applications of nonempirical molecular orbital theory to the calculation of complete quadratic force fields have appeared in the literature. Most of these have utilized single-de-

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terminant (Hartree–Fock) wavefunctions and relatively small (minimal or split-valence) basis sets. Of the results gathered thus far, those obtained at the split-valence level are the most encouraging.[1] Here, deviations between calculated and experimental vibrational frequencies, although sizable, are reasonably constant. This does not appear to be true for calculations at lower (minimal basis set) levels, where the magnitudes of errors vary widely.[2]

Only a relatively few calculations of vibrational frequencies using methods beyond the single-determinant level have appeared in the literature. Meyer and Rosmus[3] compared the results of SCF and both PNO-CI (pseudonatural orbital configuration interaction) and CEPA (coupled electron pair approach) calculations on first- and second-row diatomic hydrides, and in both cases found improvement in the quadratic force constants, particularly with CEPA which gave vibrational frequencies in less than 1% deviation from those derived from experiment. Application of the CEPA method to methane[4] and formaldehyde[5] also gave a marked improvement in the quadratic force constants. CI calculations including single and double excitations have been performed on CH_4,[6] H_2O,[6,7] S_2,[8] HCN,[6,9] H_2CO,[6] and C_2H_2.[10] Here too the calculated force constants were in better agreement with experimental results than those obtained from the underlying Hartree–Fock treatment. MP2 (second-order Møller-Plesset) calculations by Pople and co-workers on ethylene[11] indicate that this method gives greatly improved vibrational frequencies as well. A survey of correlated vibrational frequencies at a uniform level of theory for a wide range of polyatomic molecules has until now not been undertaken.

For the most part the quadratic force fields derived from theoretical calculations have been used only in the evaluation of molecular vibrational frequencies. Calculations of other properties (e.g., entropies) based on theoretically derived force fields have been relatively rare. The one major exception to this has been in the calculation of equilibrium isotope effects.[12] The few studies which have been carried out to date strongly encourage pursuits in this direction.

Our goals at present are threefold. Firstly, we wish to assess the performance of a relatively high level of single-determinant Hartree–Fock theory in the calculation of the vibrational frequencies of polyatomic molecules. Hopefully, the level chosen for exploration will be sufficiently close to the Hartree–Fock limit (at least as far as vibrational frequencies are concerned) that it will be the behavior of the limit itself, and not of some intermediate step toward the limit, which will for all practical purposes be the subject of our attention.

Our second goal is to examine critically the effect of electron correlation on the magnitudes of calculated normal mode frequencies. In this regard, our choice of Hartree–Fock level (basis set) was somewhat restricted. Our previous study, a systematic survey of the effect of electron correlation on calculated equilibrium structures,[13] has clearly shown that correlation treatments need to be constructed on top of relatively large basis set Hartree–Fock calculations.

Finally, we wish to document the potential of both the Hartree–Fock and correlated models with regard to the calculation of thermodynamic properties, in particular, entropies of simple chemical transformations.

The systems dealt with in this work comprise the greater part of the set of one- and two-heavy-atom molecules, the vibrational frequencies for which have been characterized experimentally. Thus, our principal concern at this time is the careful assessment of the theoretical model. Applications to areas where experimental data are incomplete or altogether unavailable, and to which the theory may take on the more valuable predictive role, are deferred.

METHODS

The total energy of a molecule comprising N atoms may be written as

$$E = T + V = \frac{1}{2} \sum_{i=1}^{3N} \dot{q}_i^2 + V_{eq}$$
$$+ \frac{1}{2} \sum_{i=1}^{3N} \sum_{k=1}^{3N} (\partial^2 V/\partial q_i \partial q_k)_{eq} q_i q_k \quad (1)$$

Here, the mass-weighted Cartesian displacements q_i are defined in terms of the location of the nuclei x_i relative to their equilibrium positions $x_{i,eq}$ and their masses M_i.

$$q_i = M_i^{1/2}(x_i - x_{i,eq}) \quad (2)$$

V_{eq} is the potential energy at the equilibrium nuclear configuration, and the expansion of the vibrational energy in terms of a power series is truncated at second order. For such a system, the classical mechanical equations of motion take the following form:

$$\ddot{q}_j = -\sum_{i=1}^{3N} U_{ij} q_i \quad j = 1, 2, \ldots, 3N \quad (3)$$

The U_{ij}, termed quadratic force constants, are the second derivatives of the potential energy with respect to mass-weighted Cartesian displacements, evaluated at the equilibrium nuclear configuration.

$$U_{ij} = (\partial^2 V/\partial q_i \partial q_j)_{eq} \qquad (4)$$

Equations (3) may be solved by obtaining an orthogonal transformation matrix $\mathbf{L}$ such that,

$$\mathbf{L}^t \mathbf{U} \mathbf{L} = \mathbf{\Lambda} \qquad (5)$$

where $\mathbf{\Lambda}$ is diagonal. In terms of a new set of coordinates $\mathbf{q}'$,

$$\mathbf{q}' = \mathbf{L}^t \mathbf{q} \qquad (6)$$

eq. (3) becomes

$$\ddot{q}_j' = -\lambda_j q_j' \quad j = 1, 2, \ldots, 3N \qquad (7)$$

Here, the λ_j are the diagonal elements of $\mathbf{\Lambda}$. Acceptable solutions to eq. (7), the so-called normal modes of vibration, include

$$q_j' = a_j \sin(\lambda_j^{1/2} t + b_j) \quad j = 1, 2, \ldots, 3N \qquad (8)$$

where a_j and b_j are constants defining the amplitude and phase of the vibrational motions, respectively. The corresponding normal vibrational frequencies are given by

$$\nu_j = \lambda_j^{1/2}/2\pi \quad j = 1, 2, \ldots, 3N \qquad (9)$$

In practice six of the solutions (8) (five for linear molecules) will correspond to translation and or rotation of the molecule as a whole. A change of basis to coordinates which are linearly independent of translation and rotation, i.e.,

$$\sum_{i=1}^{N} (\Delta x)_i = 0, \ldots$$
$$\sum_{i=1}^{N} [(\Delta z)_i y_{i,eq} - (\Delta y)_i z_{i,eq}] = 0, \ldots \qquad (10)$$

serves to reduce the order of the matrix of force constants from $3N$ to $3N - 6$ (or $3N - 5$). This new set of coordinates is chosen to be mass independent (i.e., mass weighting is performed after, not before, force constant evaluation) in order that the force constants will be independent of isotopic substitition.

A further change of basis effects factorization of the force constant matrix by symmetry. The back transformation to the force constant matrix in terms of mass-weighted Cartesian coordinates is given by,

$$\mathbf{U} = \mathbf{M}^{-1/2} \mathbf{S}^t \mathbf{F} \mathbf{S} \mathbf{M}^{-1/2} \qquad (11)$$

Here, $\mathbf{S}$ transforms the $3N$ non-mass-weighted Cartesian displacements to $3N - 6$ (or $3N - 5$) "symmetry" coordinates which not only are linearly independent of translation and rigid rotation, but also in terms of which the force constant matrix $\mathbf{F}$ is factored to the maximum extent possible by symmetry. $\mathbf{M}^{-1/2}$ is the diagonal matrix of reciprocal square root masses. Nielsen and Berryman[14] have shown that given any set of coordinates q which span the space of all possible nuclear displacements, a complete set of symmetry coordinates may be generated. Full details have been provided by these authors and will not be repeated here.

Force constants have been evaluated by numerical second differentiation using a two-point approximation. Diagonal force constants are obtained using the relationship:

$$(\partial^2 V/\partial q_i^2)_{eq} \simeq (V^+ + V^- - 2V_{eq})/\delta_i^2 \qquad (12)$$

Here, V^+ and V^- are energies calculated for equilibrium nuclear configurations displaced in the direction of symmetry coordinate q_i by $+\delta$ and $-\delta$, respectively. V_{eq} is the energy corresponding to the equilibrium nuclear arrangement. Off-diagonal force constants are then determined by

$$(\partial^2 V/\partial q_i \partial q_j)_{eq} \simeq [(V^{2+} + V^{2-} - 2V_{eq})$$
$$- (\partial^2 V/\partial q_i^2)_{eq} \delta_i^2 - (\partial^2 V/\partial q_j^2)_{eq} \delta_j^2]/2\delta_i \delta_j \qquad (13)$$

where V^{2+} (V^{2-}) corresponds to the energy of a nuclear configuration simultaneously displaced by $+\delta_i$ ($-\delta_i$) in coordinate q_i and $+\delta_j$ ($-\delta_j$) in coordinate q_j, respectively. The value of δ used is 0.01 Å.

The numerical differentiation techniques employed in the present work are not the most efficient available in our laboratory for dealing with Hartree–Fock wavefunctions. They are, however, the only means available to us at present for obtaining force constants at the second-order Møller–Plesset level. As our present work involves the critical comparison of frequencies calculated at both Hartree–Fock and second-order Møller–Plesset levels, we have opted to perform all calculations using a single differentiation technique.

Two theoretical molecular orbital models are employed in this study. The first utilizes standard single-determinant wavefunctions as derived from the 6-31G* polarization basis set.[15] This particular level has already proven of value in the determination of the equilibrium geometrical structures for a wide variety of polyatomic molecules including many of those dealt with here.[13] The second method is also based on the use of the 6-31G*

Table I. Dependence of calculated vibration frequencies for ethylene on the method of force constant evaluation.

symmetry of mode	description of mode	Calculated Frequency (cm^{-1})[a]		
		numerical second differentiation	numerical differentiation of analytical gradient[b]	analytical second differentiation[c]
a_g	CH_2 s-stretch	3344	3346	3344
a_g	CC stretch	1856	1849	1856
a_g	CH_2 scis.	1496	1494	1497
a_u	CH_2 twist	1149	1157	1155
b_{1g}	CH_2 a-stretch	3338	3390	3394
b_{1g}	CH_2 rock	1369	1349	1353
b_{1u}	CH_2 wag	1094	1095	1095
b_{2g}	CH_2 wag	1094	1100	1099
b_{2u}	CH_2 a-stretch	3418	3421	3420
b_{2u}	CH_2 rock	915	898	897
b_{3u}	CH_2 s-stretch	3321	3322	3321
b_{3u}	CH_2 scis.	1608	1610	1610

[a] HF/6-31G* level.
[b] See ref. 18 for complete description of the numerical procedures employed.
[c] Data from ref. 11.

basis set but takes partial account of the effects of electron correlation by way of Møller–Plesset perturbation theory terminated at second order.[16] This procedure is the same as that used by Pople and co-workers in their study on ethylene.[11] Although more costly than the corresponding Hartree–Fock procedure, it is still simple enough to be routinely applied to the calculation of vibrational frequencies in small (one- and two-heavy-atom) polyatomic molecules.

All calculations have performed using the Gaussian 82/UCI system of programs[17] on a Harris Corporation SLASH 6 digital computer.

RESULTS AND DISCUSSION

Before commencing with a discussion of the performance of the theory with regard to the calculation of molecular vibrational frequencies, it is useful to assess the magnitudes of errors associated both with the numerical differentiation techniques employed and with uncertainties in the selection of equilibrium geometry. Table I lists vibrational frequencies for ethylene calculated at the HF/6-31G* level using three different differentiation techniques. The values in the first column derive from force fields obtained by numerical second

differentiation using symmetry coordinates. The next column of frequencies has been obtained by numerical differencing of gradients obtained analytically. This method, which is also based on the use of symmetry coordinates, will be described in detail elsewhere.[18] Previously reported vibrational frequencies for ethylene,[11] calculated by direct analytical second differentiation, appear in the final column of the table. The only point to be made is that the frequencies derived from all three methods are generally in close accord with each other, with but a single exception (the highest frequency b_{1g} vibration), the largest deviation between any two values being only 18 cm^{-1}. Larger deviations have been noted in some comparisons involving larger polyatomics, although instances in which errors exceed 20 cm^{-1} appear to be relatively infrequent.

The data in Table II illustrate for the single case of the ammonia molecule the changes in vibrational frequencies which might be anticipated due to small errors in the exact choice of equilibrium geometry. A distortion of the equilibrium NH bond length of 0.005 Å leads to changes in the frequencies associated with the symmetric and degenerate stretching modes on the order of 60 cm^{-1}. A smaller (25 cm^{-1}) change in the frequency

Table II. Dependence of calculated vibration frequencies for NH_3 on the choice of equilibrium geometry.

symmetry of mode	Description of mode	Calculated Frequency $(cm^{-1})^a$		
		equilibrium structure[b]	$+0.005\overset{o}{A}$ on $r(NH)$	$+0.5^{o}$ on $\angle(HNH)$
a_1	sym. stretch	3695	3638	3694
a_1	sym. deform	1203	1228	1179
e	deg. stretch	3829	3769	3830
e	deg. deform	1847	1856	1845

[a] HF/6-31G* level.
[b] $r(NH) = 1.002$ Å; $\angle(HNH) = 107.2°$.

associated with the nitrogen inversion motion is noted, due to this slight increase in equilibrium bond length. This particular frequency is also sensitive to slight changes in equilibrium bond angle: an increase of 0.5° leads to a 24-cm^{-1} decrease in frequency. It should be emphasized that the frequency shifts depicted in Table II are due to the anharmonicity of the potential function in the vicinity of the minimum and not to the choice of differentiation method. They also occur if force constants are obtained by either of the direct analytical or mixed numerical–analytical differentiation techniques discussed earlier. They suggest that considerable care must be exercised in obtaining energy optimized structures for use in frequency calculations.

Equilibrium geometries for most of the molecules dealt with in this article have previously appeared in the literature.[13] In all cases calculated bond lengths and angles are within 0.001 Å and 0.1°, respectively, of their true theoretical equilibrium values. Calculated (HF/6-31G* and MP2/6-31G* level) structures for molecules which have previously not been considered, appear in Table III. The bond-length and bond-angle tolerances are the same as stated above. They are compared to experimental structural data where available.

Table IV compares theoretical and experimental vibrational frequencies for H_2 and a selection of one- and two-heavy-atom diatomic molecules. Here, the available experimental data allows for the determination of "harmonic" vibrational

frequencies which are then directly comparable to the theoretically calculated quantities. Note that the experimental harmonic frequencies are considerably smaller than the actual vibrational frequencies. Deviations range from a maximum of 5.6% in the hydrogen molecule to a minimum of 1.2% in CO and N_2. Overall, the mean percentage deviation of harmonic from actual vibrational frequencies is 2.8%. Unfortunately, sufficient experimental spectroscopic data are generally unavailable to enable precise determination of pure harmonic frequencies for any but diatomic, and the simplest polyatomic, species.

With the exception of Li_2, calculated Hartree–Fock level frequencies are larger than the corresponding harmonic experimental quantities. This is consistent with the notion that single-determinant wavefunctions generally lead to an incorrect description of bond dissociation. For example, the best single-determinant description of a partially dissociated H_2 molecule improperly places both electrons at one or the other nuclear positions half of the time, rather than one on each center all of the time. The fact that the calculated dissociation limit is necessarily higher than it should be implies a steeper potential in the vicinity of the equilibrium structure, and hence a harmonic vibrational frequency which is too high.

The mean absolute percentage deviation of the theoretical frequencies from experimental harmonic values $((|\nu_{theory} - \nu_{harmonic}|)/\nu_{harmonic} \times 100)$ is 11%. This deviation is reduced substantially (to 8.6%) if F_2 is eliminated from the comparison. It

Table III. Theoretical and experimental equilibrium geometries.[a]

Molecule	Point Group	Geometrical Parameter	HF/6-31G*	MP2/6-31G*·	Expt.
BeO	$C_{\infty v}$	r(BeO)	1.295	1.361	1.331[b]
BF	$C_{\infty v}$	r(BF)	1.260	1.281	1.262[b]
BH_3	D_{3h}	r(BH)	1.188	1.192	(1.16)[c]
HBNH	$C_{\infty v}$	r(BN)	1.224	1.247	
		r(BH)	1.166	1.171	
		r(NH)	0.982	0.997	
HBO	$C_{\infty v}$	r(BO)	1.185	1.219	(1.19)[d]
		r(BH)	1.167	1.171	(1.17)
H_2CNH	C_s	r(CN)	1.250	1.283	1.273[e]
		$r(CH_{syn})$	1.084	1.097	1.103
		$r(CH_{anti})$	1.080	1.091	1.081
		r(NH)	1.006	1.027	1.023
		$<(H_{syn}CN)$	124.7	125.3	123.4
		$<(H_{anti}CN)$	119.2	118.4	119.7
		$<(HNC)$	111.5	109.8	110.5
HCF	C_s	r(CF)	1.295	1.321	1.314[c]
		r(CH)	1.104	1.120	1.121
		$<(HCF)$	102.8	101.8	101.6

[a] Lengths in angstroms, angles in degrees.
[b] G. Herzberg, *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules*, 2nd ed., Van Nostrand Reinhold, New York, 1950.
[c] D. R. Stull and H. Prophet, *JANAF Thermochemical Tables*, 2nd. ed., Natl. Bur. Stand., Washington, DC, 1971.
[d] M. W. Chase, J. L. Curnett, R. A. McDonald, and A. N. Syverud, *J. Phys. Chem. Ref. Data*, 7, 793 (1978).
[e] M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwendemann, D. A. Ramsay, F. J. Lovas, W. J. Lafferty, and A. G. Maki, *J. Phys. Chem. Ref. Data*, 8, 619 (1979).

has already been commented[13] that the limiting Hartree–Fock bond length in the fluorine molecule is 0.1 Å shorter than the experimental value of 1.417 Å. It is tempting to conclude therefore that the unrealistically tight bonding depicted at the single-determinant level leads to too high a stretching frequency. Large deviations between theoretical Hartree–Fock level and experimental harmonic frequencies also occur for the highly polar lithium fluoride and beryllium oxide molecules and for carbon monoxide and diatomic nitrogen.

Frequencies calculated at the MP2/6-31G* level are generally considerably closer to the experimental harmonic values then are those derived from the Hartree–Fock method using the same basis set. The only exceptions are for the LiH and Li_2 molecules where the performance of both levels of theory is comparable. Overall, the mean absolute percentage deviation of calculated from experimental harmonic frequencies is 4.6%, roughly half that noted for the Hartree–Fock level. The most dramatic individual improvements are for F_2, LiF, BeO, CO, and N_2, the worst cases at the

Table IV. Theoretical and experimental vibrational frequencies for diatomic molecules (cm^{-1}).

Molecule	Theoretical Frequency		Experimental Frequency[a]	
	HF/6-31G*	MP2/6-31G*	Harmonic[b]	Measured
H_2	4647	4528	4395	4160
LiH	1415	1393	1406	1360
BH	2516	2453	2366	2268
FH	4358	4038	4139	3962
Li_2	339	368	351	346
LiF	1033	998	914[b]	898[b]
BeO	1744	1385	1487	1464
BF	1473	1401	1400	1377
CO	2438	2113	2170	2143
N_2	2763	2173	2360	2331
F_2	1245	1008	923[b]	891[b]

[a] Except where otherwise noted, experimental data from Table III, footnote b; tabulated values derived from experimental data through use of the relationship $\nu_{expt} = \omega_e - 2\omega_e x_e + 3.25\omega_e y_e$.

[b] Table III, footnote c.

HF/6-31G* level. In general, frequencies calculated at the MP2/6-31G* level are larger than the corresponding experimental harmonic values. Note, however, that for molecules with multiple bonds (BeO, CO, and N_2), as well as for the highly polar hydrides of lithium and fluorine, this is not the case. Here, the calculated frequencies are smaller than the corresponding experimental quantities. This is consistent with our previous observation[13] that, at the MP2/6-31G* level, calculated bond lengths in these molecules are significantly longer than the corresponding experimental distances. Explorations with higher-order Møller–Plesset perturbation expansions, in particular third order, suggest an improvement in calculated equilibrium structures, especially for molecules incorporating multiple bonds.[19] It remains to be seen whether or not calculations at this level will lead to significantly improved normal mode vibrational frequencies.

A comparison of calculated and experimental vibrational frequencies for the polyatomic one-heavy-atom hydrides is provided in Table V. For three molecules included in the tabulation, CH_4, NH_3, and H_2O, sufficient experimental data are available to enable determination of pure harmonic vibrational frequencies. These have been included in the table. The same general conclusions reached in our discussion of diatomics generally apply here. In particular, the performance of the simple correlated level is generally superior to that of the Hartree–Fock level. The mean absolute percentage deviation of calculated from experimental frequencies is 11.6% and 8.6% for the HF/6-31G* and MP2/6-31G* levels, respectively. Significantly smaller errors (8.0% and 4.4%) are found in comparisons involving the experimental harmonic frequencies of methane, ammonia, and water.

Note that the lower of the two frequencies corresponding to modes of e' symmetry in BH_3 seriously disagrees with the present theoretical value. In light of the high level of agreement between theory and experiment for the remaining molecules in this table and in Table IV, we feel that it is highly likely that this particular assignment is in error.

A comparison of theoretical and experimental frequencies for a much larger set of polyatomic two-heavy-atom hydrides is presented in Table VI.

Table V. Theoretical and experimental vibrational frequencies for one-heavy-atom hydrides (cm⁻¹).

Molecule	Symmetry of Vibration	Description of Mode	Theoretical Frequency		Experimental Frequency[a]	
			HF/6-31G*	MP2/6-31G*	Harmonic	Measured
BH_3	a_1'	sym. stretch	2695	2647	–	2623[b]
	a_2''	out-of-plane stretch	1224	1190	–	1125
	e'	deg. stretch	2815	2789	–	2808
	e'	deg. deform	1304	1256	–	1604
CH_4	a_1	sym. stretch	3196	3115	3137[c]	2917
	e	deg. deform	1715	1649	1567	1534
	f_2	deg. stretch	3305	3257	3158	3019
	f_2	deg. deform	1491	1418	1357	1306
NH_3	a_1	sym. stretch	3695	3504	3506[c]	3337
	a_1	sym. deform	1203	1166	1022	950
	e	deg. stretch	3829	3659	3577	3444
	e	deg. deform	1847	1852	1691	1627
H_2O	a_1	sym. stretch	4076	3772	3832[d]	3657
	a_1	bend	1826	1737	1648	1595
	b_1	antisym. stretch	4194	3916	3943	3756

[a] Except where otherwise noted, experimental data from T. Shimanouchi, *Tables of Molecular Vibrational Frequencies Consolidated. Volume I*, Natl. Bur. Stand., Washington, DC, 1972.

[b] A. Kaldor and R. F.Porter, *J. Am. Chem. Soc.*, **93**, 2140 (1971).

[c] J. L. Duncan and I. M. Mills, *Spectrochim. Acta*, **20**, 523 (1964).

[d] G. Strey, *J. Mol. Spectrosc.*, **24**, 87 (1967).

Table VI. Theoretical and experimental vibrational frequencies for two-heavy-atom hydrides (cm⁻¹).

Molecule	Symmetry of Vibration	Description of mode	Theoretical Frequency		Experimental Frequency[a]
			HF/6-31G*	MP2/6-31G*	
LiOH	σ^+	OH stretch	4258	3964	
	σ^+	OLi stretch	1012	1000	746[b]
	π	bend	376	295	
B_2H_6	a_g	BH_2 s-stretch	2754	2677	2524
	a_g	ring stretch	2305	2312	2104
	a_g	BH_2 scis.	1304	1201	1180
	a_g	ring deform.	829	840	794
	a_u	BH_2 twist	896	811	833
	b_{1g}	ring stretch	1934	1769	1768
	b_{1g}	BH_2 wag	900	956	850
	b_{1u}	BH_2 a-stretch	2843	2767	2612

Table VI *(continued from previous page)*

Molecule	Symmetry of Vibration	Description of mode	Theoretical Frequency		Experimental Frequency	
			HF/6-31G*	MP2/6-31G*		
	b_{1u}	BH_2 rock	1126	899	950	
	b_{1u}	ring puckering	400	334	368	
	b_{2g}	BH_2 a-stretch	2829	2779	2591	
	b_{2g}	BH_2 rock	1001	895	915	
	b_{2u}	ring stretch	2069	2260	1915	
	b_{2u}	BH_2 wag	1072	1186	973	
	b_{3g}	BH_2 a-stretch	1194	1330	1012	
	b_{3u}	BH_2 s-stretch	2735	2698	2525	
	b_{3u}	ring deform.	1837	1746	1602	
	b_{3u}	BH_2 scis.	1287	914	1177	
HBNH	σ^+	NH stretch	4120	3914	3700[c]	
	σ^+	BH stretch	3030	2976	(2800)	
	σ^+	BN stretch	1970	1834	1785	
	π	BH bend	950	816		
	π	NH bend	667	526	460	
HBO	σ^+	BH stretch	3042	2982	(2849)[d]	
	σ^+	BO sretech	2022	1821	1817	
	π	bend	878	799	754	
C_2H_2	σ_g^+	CH stretch	3720	3593	3374	(3497)[e]
	σ_g^+	CC stretch	2250	2006	1974	(2011)
	σ_g^+	CH stretch	3607	3516	3289	(3415)
	π_g	CH bend	795	444	612	(624)
	π_u	CH bend	882	783	730	(747)
C_2H_4	a_g	CH_2 s-stretch	3344	3231	3026	(3153)[f]
	a_g	CC stretch	1856	1724	1623	(1655)
	a_g	CH_2 scis.	1496	1425	1342	(1370)
	a_u	CH_2 twist	1149	1083	1023	(1044)
	b_{1g}	CH_2 a-stretch	3338	3297	3103	(3232)
	b_{1g}	CH_2 rock	1369	1265	1236	(1245)
	b_{1u}	CH_2 wag	1094	980	949	(969)
	b_{2g}	CH_2 wag	1094	931	943	(959)
	b_{2u}	CH_2 a-stretch	3418	3323	3106	(3234)
	b_{2u}	CH_2 rock	915	873	826	(843)
	b_{3u}	CH_2 s-stretch	3321	3222	2989	(3147)
	b_{3u}	CH_2 scis.	1608	1523	1444	(1473)
C_2H_6	a_{1g}	CH_3 s-stretch	3201	3086	2954	(3043)[g]
	a_{1g}	CH_3 s-deform	1584	1493	1388	(1449)
	a_{1g}	CC stretch	1063	1040	995	(1016)
	a_{1u}	torsion	331	452	289	(303)

Table VI *(continued from previous page)*

Molecule	Symmetry of Vibration	Description of mode	Theoretical Frequency HF/6-31G*	Theoretical Frequency MP2/6-31G*	Experimental Frequency	
	a$_{2u}$	CH$_3$ s-stretch	3194	3104	2986	(3061)
	a$_{2u}$	CH$_3$ s-deform	1546	1494	1379	(1438)
	e$_g$	CH$_3$ d-stretch	3242	3228	2969	(3175)
	e$_g$	CH$_3$ d-deform	1646	1520	1468	(1552)
	e$_g$	CH$_3$ rock	1338	1264	1190	(1246)
	e$_u$	CH$_3$ d-stretch	3271	3215	2985	(3140)
	e$_u$	CH$_3$ d-deform	1652	1604	1469	(1526)
	e$_u$	CH$_3$ rock	894	783	822	(822)
HCN	σ^+	CH stretch	3676	3517	3311[h]	(3442)[i]
	σ^+	CN stretch	2442	2038	2097	(2129)
	π	bend	904	702	712	(727)
HNC	σ^+	NH stretch	4092	3844	3620[j]	(3842)[k]
	σ^+	NC stretch	2311	2038	2029	(2067)
	π	bend	519	389	477	(490)
CH$_2$NH	a'	NH stretch	3719	3463	(3297)[l]	
	a'	CH$_2$ s-stretch	3347	3254	3036	
	a'	CH$_2$ a-stretch	3254	3116	2924	
	a'	CN stretch	1901	1724	1640	
	a'	CH$_2$ scis.	1628	1542	1453	
	a'	NH deform	1496	1412	1347	
	a'	CH$_2$ rock	1164	1100	1059	
	a"	torsion	1270	1159	1123	
	a"	CH$_2$ wag	1223	1107	1063	
CH$_3$NH$_2$	a'	NH$_2$ s-stretch	3737	3508	3361	
	a'	CH$_3$ d-stretch	3246	3155	2961	
	a'	CH$_3$ s-stretch	3157	3063	2820	
	a'	NH$_2$ scis.	1838	1745	1623	
	a'	CH$_3$ d-deform	1649	1539	1473	
	a'	CH$_3$ s-deform	1608	1469	1430	
	a'	CH$_3$ rock	1291	1237	1130	
	a'	CN stretch	1151	1113	1044	
	a'	NH$_2$ wag	946	941	780	
	a"	NH$_2$ a-stretch	3820	3641	3427	
	a"	CH$_3$ d-stretch	3283	3228	2985	
	a"	CH$_3$ d-deform	1666	1596	1485	
	a"	NH$_2$ twist	1481	1405	1419	
	a"	CH$_3$ rock	1047	915	1195	
	a"	torsion	355	351	268	
H$_2$CO	a$_1$	CH$_2$ s-stretch	3159	3019	2783	(2944)[m]
	a$_1$	CO stretch	2032	1786	1746	(1764)

Table VI (*continued from previous page*)

Molecule	Symmetry of Vibration	Description of mode	Theoretical Frequency		Experimental Frequency	
			HF/6-31G*	MP2/6-31G*		
	a_1	CH_2 scis.	1675	1567	1500	(1563)
	b_1	CH_2 a-stretch	3226	3064	2843	(3009)
	b_1	CH_2 rock	1362	1249	1249	(1287)
	b_2	CH_2 wag	1332	1194	1167	(1191)
CH_3OH	a'	OH stretch	4123	3785	3681	
	a'	CH_3 d-stretch	3306	3201	3000	
	a'	CH_3 s-stretch	3186	3065	2844	
	a'	CH_3 d-deform	1664	1552	1477	
	a'	CH_3 s-deform	1638	1542	1455	
	a'	OH bend	1508	1424	1345	
	a'	CH_3 rock	1191	1120	1060	
	a'	CO stretch	1161	1082	1033	
	a"	CH_3 d-stretch	3299	3140	2960	
	a"	CH_3 d-deform	1651	1562	1477	
	a"	CH_3 rock	1288	1160	1165	
	a"	torsion	321	250	295	
HCF	a'	CH stretch	3056	2906	(3000)[h]	
	a'	bend	1571	1498	1403	
	a'	CF stretch	1333	1257	1182	
CH_3F	a_1	CH_3 s-stretch	3233	3110	2930	(3031)[n]
	a_1	CH_3 s-deform	1653	1549	1464	(1490)
	a_1	CF stretch	1189	1102	1049	(1059)
	e	CH_3 d-stretch	3286	3205	3006	(3132)
	e	CH_3 d-deform	1547	1556	1467	(1498)
	e	CH_3 rock	1268	1213	1182	(1206)
$transN_2H_2$	a_g	NH s-stretch	3578	3386	3128[o]	
	a_g	NH bend	1911	1749	1583	
	a_g	NN stretch	1763	1523	1529	
	a_u	torsion	1472	1328	1359[p]	
	b_u	NH a-stretch	3613	3334	3131	
	b_u	NH bend	1472	1308	1286	
N_2H_4	a	NH stretch	3827	3621	3325[q]	
	a	NH stretch	3726	3500	3280	
	a	NH bend	1869	1755	1587	
	a	NH bend	1468	1382	1275	
	a	NN stretch	1226	1161	1098	
	a	NN stretch	975	910	780	
	a	torsion	447	426	377[h]	
	b	NH stretch	3832	3630	3350	
	b	NH stretch	3713	3477	3314	

Table VI (continued from previous page)

Molecule	Symmetry of Vibration	Description of mode	Theoretical Frequency HF/6-31G	Theoretical Frequency MP2/6-31G	Experimental Frequency	
	b	NH bend	1858	1755	1628	
	b	NH bend	1435	1363	1275	
	b	NH bend	1108	1069	966	
HNO	a'	NH stretch	3551	2999	3039[r]	(3039)[r]
	a'	bend	1979	1586	1593	(1505)
	a'	NO stretch	1733	1479	1566	(1564)
transNH$_2$OH	a'	OH stretch	4126	3787	3656[s]	
	a'	NH stretch	3718	3470	3297	
	a'	NH$_2$ bend	1855	1723	1605	
	a'	OH bend	1556	1439	1357	
	a'	NH$_2$ wag	1276	1200	1120	
	a'	NO stretch	1122	957	895	
	a"	NH stretch	3810	3585	3350	
	a"	NH$_2$ rock	1482	1336	t	
	a"	torsion	434	286	430	
H$_2$O$_2$	a	OH stretch	4091	3710	3599[u]	
	a	OH bend	1630	1390	1402	
	a	OO stretch	1161	926	877	
	a	torsion	397	329	371	
	b	OH stretch	4095	3731	3608	
	b	OH bend	1494	1294	1266	
HOF	a'	OH stretch	4069	3710	3537[u]	
	a'	OF stretch	1592	1407	1393	
	a'	bend	1176	986	886	

[a] Except where otherwise noted, experimental data from Table V, footnote a.
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Harmonic values are available in several cases and are included in the table in parentheses following the directly measured frequencies.

Broadly speaking, the same general conclusions apply to these comparisons as to those in Tables IV and V. In particular, HF/6-31G* frequencies are consistently larger than experimental values. Most, but not all, of the frequencies calculated using the MP2/6-31G* model are also larger than the corresponding experimental quantities. Overall, mean standard percentage deviations of theoretical frequencies from experimental values are 12.6% and 7.2% for the HF/6-31G* and MP2/6-31G* methods, respectively, nearly the same as the errors associated with the diatomics and the one-heavy-atom hydrides. These errors would be significantly reduced were the data available to correct all the measured frequencies for anharmonicity effects. Considering only the eight molecules (C_2H_2, C_2H_4, C_2H_6, HCN, HNC, H_2CO, CH_3F, and HNO) for which a complete harmonic analysis has been performed, the mean absolute percentage deviations in calculated frequencies from measured (uncorrected) values are 12.8% and 7.1% for the HF/6-31G* and MP2/6-31G* methods, respectively. These errors are diminished to 9.6% and 4.8% for the two theoretical levels when compared to corrected (harmonic) frequencies.

The approximate treatment of correlation has its greatest effect in dealing with molecules incorporating multiple bonds. This parallels the behavior of the HF/6-31G* and MP2/6-31G* methods with regard to the calculation of equilibrium structures,[13] and our previous experience with diatomic molecules.

Calculated and spectroscopic absolute entropies are displayed in Table VII. These have been derived from the statistical mechanical relationships[20]:

$$S = S_{tr} + S_{rot} + S_{vib} + S_{el} - nR\left[\ln\left(nN_o\right) - 1\right] \quad (14)$$

$$S_{tr} = nR\left\{\frac{3}{2} + \ln\left[\left(\frac{2\pi MkT}{h^2}\right)^{3/2}\left(\frac{nRT}{P}\right)\right]\right\} \quad (15)$$

$$S_{rot} = nR$$
$$\times\left\{1 + \ln\left[v\left(1 + \frac{1}{3v} + \frac{1}{15v^2} + \frac{4}{315v^3}\right)/s\right]\right\}$$
$$\text{(if linear)} \quad (16)$$

$$S_{rot} = nR\left\{\frac{3}{2} + \ln\left[(\pi v_A v_B v_C)^{1/2}/s\right]\right\}$$
$$\text{(if nonlinear)} \quad (17)$$

$$S_{vib} = nR\sum_i\left[u_i(e^{u_i} - 1)^{-1} - \ln\left(1 - e^{-u_i}\right)\right] \quad (18)$$

$$S_{el} = nR\ln\omega_{el} \quad (19)$$

where

n	moles of molecules
R	gas constant
N_o	Avogadro's number
M	mass of molecule
k	Boltzmann constant
T	temperature
h	Planck constant
P	pressure
v	$h^2/(8\pi^2IkT)$
I, I_A, I_B, I_C	principal moments of inertia
s	symmetry number
u_i	hv_i/kT
v_i	vibrational frequencies
ω_{el}	electronic ground state degeneracy

Here the appropriate experimental or theoretical

Table VII. Theoretical and experimental entropies at 300 K (e.u.).

Molecule	Theoretical Entropy		Experimental Entropy
	HF/6-31G*	MP2/6-31G*	
H_2	31.28	31.32	31.34
LiH	40.93	40.94	40.84
BH	41.08	41.10	41.09
FH	41.52	41.61	41.54
Li_2	47.29	47.13	47.06
LiF	47.78	47.83	47.86
BeO	47.09	47.30	47.21

Table VII (continued from previous page)

Molecule	Theoretical Entropy		Experimental Entropy
	HF/6-31G*	MP2/6-31G*	
BF	47.91	47.98	47.92
CO	47.17	47.30	47.22
N_2	45.70	45.89	45.78
F_2	48.13	48.40	48.45
BH_3	44.96	45.00	44.80
CH_4	44.41	44.47	44.48
NH_3	45.87	45.97	46.02
H_2O	45.00	45.15	45.10
LiOH	49.96	50.77	
B_2H_6	53.70	54.19	54.17
HBNH	49.13	49.86	
HBO	48.25	48.46	48.64
C_2H_2	47.28	48.73	48.02
C_2H_4	52.10	52.27	52.42
C_2H_6	54.13	53.89	54.57
HCN	47.85	48.29	48.22
HNC	48.78	49.67	49.03
CH_2NH	54.10	54.30	54.31
CH_3NH_2	57.03	57.20	57.73
H_2CO	52.12	52.28	52.29
CH_3OH	56.72	57.30	57.05
HCF	53.24	53.37	53.37
CH_3F	53.08	53.24	53.24
trans N_2H_2	51.96	52.21	52.15
N_2H_4	54.80	55.04	55.46
HNO	52.56	52.85	52.77
trans NH_2OH	55.76	56.67	
H_2O_2	53.99	54.66	54.72
HOF	53.85	54.17	54.18

(HF/6-31G* and MP2/6-31G* levels) equilibrium structures and normal mode vibration frequencies are employed. In all cases directly measured frequencies, rather than corrected harmonic values, have been employed in the calculation of the experimental entropies. Entropies obtained using harmonic vibrational frequencies in lieu of directly measured values differ from the tabulated values by less than 1%. Therefore, they have not been tabulated. The spectroscopically determined entropies do differ from the true experimental entropies due to the neglect of residual (orientational) entropy present at 0 K in the crystal.[20] Nevertheless, we make use of them here both because they are more readily available and because they may be directly compared with the theoreti-

Table VIII. Theoretical and experimental entropies of hydrogenation reactions at 300 K (e.u.).

Hydrogenation Reaction	Theoretical Entropy		Experimental Entropy
	HF/6-31G*	MP2/6-31G*	
$Li_2 + H_2 \rightarrow 2LiH$	3.3	3.4	3.3
$LiF + H_2 \rightarrow LiH + HF$	3.4	3.4	3.2
$BF + H_2 \rightarrow BH + HF$	3.4	3.4	3.4
$CH_3CH_3 + H_2 \rightarrow 2CH_4$	3.4	3.7	3.1
$CH_3NH_2 + H_2 \rightarrow CH_4 + NH_3$	2.0	1.9	1.4
$CH_3OH + H_2 \rightarrow CH_4 + H_2O$	1.4	1.0	1.2
$CH_3F + H_2 \rightarrow CH_4 + HF$	1.6	1.5	1.4
$NH_2NH_2 + H_2 \rightarrow 2NH_3$	5.7	5.6	5.2
$NH_2OH + H_2 \rightarrow NH_3 + H_2O$	3.8	3.1	
$HOOH + H_2 \rightarrow 2H_2O$	4.7	4.3	4.1
$HOF + H_2 \rightarrow H_2O + HF$	1.4	1.3	1.1
$F_2 + H_2 \rightarrow 2HF$	3.6	3.5	3.3

cally calculated values. We will not comment on these data as such, but rather employ them to evaluate both calculated and experimental entropy changes for a variety of simple reactions.

Results for the first of these reactions, involving the change in entropy accompanying complete hydrogenation of two-heavy-atom molecules, are presented in Table VIII. The Hartree–Fock and correlated methods perform equally well, mean absolute deviations of the calculated entropy changes from experiment being 0.3 e.u. for both levels, or on the order of 10%. This level of error appears to us to be small enough as to make either theoretical method of potential use as a predictive tool.

Table IX compares calculated and experimental entropy changes for reactions in which methane is added to a number of two-heavy-atom molecules. The mean absolute deviations in calculated entropy changes from experimentally determined values (0.2 and 0.3 e.u. for the HF/6-31G* and MP2/6-31G* models, respectively) are essentially the same as those for hydrogenation reactions. However, here individual errors of up to 0.8 e.u. are noted for entropy changes calculated using the MP2/6-31G* level, far larger than any encountered with the hydrogenation processes.

Calculated entropies for two kinds of disproportionation reactions are compared to experi-

mental values in Tables X and XI. The first involves disproportionation of molecules with double bonds into the corresponding species with single and triple linkages; the second, disproportionation of molecules incorporating single linkages X–Y, into compounds incorporating X–X and Y–Y bonds. As in the previous examples, both theoretical models are moderately successful in reproducing the experimental entropy changes.

CONCLUSIONS

The following general conclusions follow from the work reported in this article.

(1) Single-determinant Hartree–Fock theory using the 6-31G* polarization basis set is moderately successful in reproducing the measured normal mode vibrational frequencies of simple polyatomic molecules. Although deviations of calculated from measured frequencies are sizable, the errors are relatively constant allowing systematic corrections to be made.

(2) Electron correlation has a significant effect on calculated normal mode frequencies. At the MP2/6-31G* level, the mean absolute deviation of calculated from experimental frequencies is roughly one-half of that obtained at the corresponding Hartree–Fock level.

(3) Both HF/6-31G* and MP2/6-31G* level

Table IX. Theoretical and experimental entropies of methane addition reactions at 300 K (e.u.).

Methane Addition Reaction	Theoretical Entropy		Experimental Entropy
	HF/6-31G*	MP2/6-31G*	
LiOH + CH$_4$ → CH$_3$OH + LiH	3.3	3.0	
LiF + CH$_4$ → CH$_3$F + LiH	1.8	1.9	1.7
HB=O + CH$_4$ → H$_2$C=O + BH$_3$	4.4	4.4	4.0
BF + CH$_4$ → CH$_3$F + BH	2.0	1.9	1.9
HC≡N + CH$_4$ → HC≡CH + NH$_3$	0.9	1.9	1.3
H$_2$C=NH + CH$_4$ → H$_2$C=CH$_2$ + NH$_3$	-0.5	-0.5	-0.4
CH$_3$NH$_2$ + CH$_4$ → CH$_3$CH$_3$ + NH$_3$	-1.4	-1.8	-1.6
C≡O + CH$_4$ → HC≡CH + H$_2$O	0.7	2.1	1.4
H$_2$C=O + CH$_4$ → H$_2$C=CH$_2$ + H$_2$O	0.6	0.7	0.8
CH$_3$OH + CH$_4$ → CH$_3$CH$_3$ + H$_2$O	-2.0	-2.7	-1.9
CH$_3$F + CH$_4$ → CH$_3$CH$_3$ + HF	-1.8	-2.2	-1.6
N≡N + CH$_4$ → HC≡N + NH$_3$	3.6	3.9	4.0
HN=NH + CH$_4$ → H$_2$C=NH + NH$_3$	3.6	3.6	3.7
NH$_2$NH$_2$ + CH$_4$ → CH$_3$NH$_2$ + NH$_3$	3.7	3.7	3.8
HN=O + CH$_4$ → H$_2$C=O + NH$_3$	1.0	0.9	1.1
HN=O + CH$_4$ → H$_2$C=NH + H$_2$O	2.1	2.1	2.2
NH$_2$OH + CH$_4$ → CH$_3$OH + NH$_3$	2.4	2.1	
NH$_2$OH + CH$_4$ → CH$_3$NH$_2$ + H$_2$O	1.9	1.2	
HOOH + CH$_4$ → CH$_3$OH + H$_2$O	3.3	3.3	3.0
HOF + CH$_4$ → CH$_3$F + H$_2$O	-0.2	-0.3	-0.3
HOF + CH$_4$ → CH$_3$OH + HF	0.0	0.3	-0.1
F$_2$ + CH$_4$ → CH$_3$F + HF	2.1	2.0	1.9

frequencies are in better accord with experimental "harmonic" values than with directly measured frequencies. In the case of correlated level calcu-lations, the mean percentage deviation of calcu-lated from experimental frequencies is reduced by one-third. This suggests that corrections for an-

Table X. Theoretical and experimental entropies of double bond disproportionation reactions (e.u.).

Disproportionation Reaction	Theoretical Entropy		Experimental Entropy
	HF/6-31G*	MP2/6-31G*	
2H$_2$C=CH$_2$ → HC≡CH + CH$_3$CH$_3$	-2.8	-1.9	-2.3
2H$_2$C=NH → H$_2$C=CH$_2$ + HN=NH	-4.1	-4.1	-4.0
2H$_2$C=O → C≡O + CH$_3$OH	-0.3	0.0	-0.3
2HN=NH → N≡N + NH$_2$NH$_2$	-3.4	-3.5	-3.1

Table XI. Theoretical and experimental entropies of single bond disproportionation reactions (e.u.).

Reaction	Theoretical Entropy		Experimental Entropy
	HF/6-31G*	MP2/6-31G*	
$2LiOH \rightarrow Li_2 + HOOH$	1.4	0.2	
$2LiF \rightarrow Li_2 + F_2$	-0.1	-0.1	-0.2
$2CH_3NH_2 \rightarrow CH_3CH_3 + NH_2NH_2$	-5.1	-5.5	-5.4
$2CH_3OH \rightarrow CH_3CH_3 + HOOH$	-5.3	-6.1	-4.8
$2CH_3F \rightarrow CH_3CH_3 + F_2$	-3.9	-4.2	-3.5
$2NH_2OH \rightarrow NH_2NH_2 + HOOH$	-2.7	-3.6	
$2HOF \rightarrow HOOH + F_2$	-5.6	-5.3	-5.2

harmonicity are apt to prove a valuable next step if the theory is to be useful as a predictive tool.

(4) Reaction entropies calculated from theoretical equilibrium structures and normal mode frequencies are in good agreement with values obtained from the corresponding spectroscopic data for both HF/6-31G* and MP2/6-31G* models.

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