

Molecular Orbital Studies of Vibrational Frequencies

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Abstract

Molecular orbital techniques for the *ab initio* computation of harmonic force constants are reviewed. Extensive applications with the split-valence 3-21G basis are described and a systematic comparison between theoretical and experimental frequencies is undertaken. The 3-21G force constants are permanently stored on a disk file and may be used to predict frequencies for isotopically substituted species. Applications are made to some deuterated molecules.

1. Introduction

The computation of polyatomic vibration frequencies, using *ab initio* molecular orbital theory, has become a viable technique in recent years. Most such studies to date have been based on the direct analytic evaluation of forces on the nuclei for structures slightly displaced from the equilibrium configuration, a technique introduced by Pulay [1]. Given a Hartree-Fock (HF) wavefunction, it is possible to compute these forces in times comparable to those required for the energy and wavefunction, so that extraction of a complete harmonic force field is possible by considering a small number of displaced structures. Using intermediate basis sets of the double-zeta or split-valence type, quite good results have been obtained, mostly too large by about 10–15% when compared with experimental fundamental frequencies [2–4]. Part of this difference can be attributed to the fact that experimental frequencies come from anharmonic surfaces; if corrected for anharmonicity in cases where the data is available, the experimental harmonic frequencies are larger than the uncorrected ones and are closer to the theoretical values. At the same time, evidence has been presented that corrections for correlation *decrease* the computed harmonic constants, further improving the agreement with experiment [5–7].

More recently, computational techniques have been developed which involve direct analytical second differentiation of the Hartree-Fock energy with respect to the nuclear coordinates [8,9]. For molecules with a larger number of atoms, such techniques are more efficient than numerical differentiation of first derivatives and permit application to somewhat larger molecules. In particular,

use of the simple split-valence basis 3-21G [10] is inexpensive enough for computation of complete Hartree-Fock harmonic potentials for most molecules for which all fundamental frequencies have been identified. The principal objective of this article is to present and evaluate such HF/3-21G force fields for a well-defined set of such molecules. This is the subset of those tabulated by Shimanouchi [11] which contain (1) only atoms H, C, N, O, and F, (2) have no more than ten atoms, and (3) have no more than four nonhydrogen atoms. This set of 37 molecules contains most of the parents for the standard bonds of organic chemistry (e.g., formaldehyde, methylamine . . .). The force constants are used to calculate the harmonic frequencies using principal isotopes, and a full statistical comparison is made between the calculated values and those tabulated by Shimanouchi [11].

The same techniques can be applied with a larger basis set, including polarization functions. To evaluate the role of *d* functions on nonhydrogen atoms, the 6-31G* basis set [12] is used to obtain HF/6-31G* force fields and frequencies for the subset of the Shimanouchi data with (1) only H, C, N, O, F, and (2) no more than two nonhydrogen atoms.

2. Theoretical Methods

As indicated in the introductory section, force constants are calculated at the Hartree-Fock level using either the 3-21G [10] or the 6-31G* [12] basis. If there are *N* nuclei, the energy *E* is calculated as a function of the 3*N* nuclear coordinates *X*₁, *Y*₁, *Z*₁, *X*₂ . . . *Z*_{*N*}. We shall denote these coordinates by *R*_{*i*} (*i* = 1, . . . 3*N*). In addition, programs have been developed to calculate the energy derivatives,

$$f_i = \partial E / \partial R_i \quad (1)$$

$$f_{ij} = \partial^2 E / \partial R_i \partial R_j \quad (2)$$

by direct analytic methods [9]. The procedure followed is first to determine the equilibrium structures by finding a minimum of the function *E*, using the first derivatives *f*_{*i*} to facilitate the search. At the minimum, *f*_{*i*} = 0 (*i* = 1, . . . 3*N*). A single calculation of the second derivatives *f*_{*ij*} is then carried out. These are the cartesian force constants and are then available for study of nuclear motion.

Let *m*_{*i*} be the mass associated with the coordinate *R*_{*i*} (so that *m*₁ = *m*₂ = *m*₃ is the mass of the first nucleus, *m*₄ = *m*₅ = *m*₆ the mass of the second nucleus, etc.). Then if *r*_{*i*} is a small displacement of *R*_{*i*}, the classical equations of motion are

$$m_i \ddot{r}_i = - \sum_j f_{ij} r_j \quad (3)$$

These equations may be treated by standard methods [13]. Mass-weighted force-constants are defined by

$$f'_{ij} = f_{ij} m_i^{-1/2} m_j^{-1/2} \quad (4)$$

and normal-mode displacements have the form

$$r_i = a_i \exp(2\pi\nu it) \quad (5)$$

where

$$\sum_j f'_{ij} a_j = 4\pi^2\nu^2 a_i. \quad (6)$$

Thus the eigenvalues of the matrix f'_{ij} are $4\pi^2\nu^2$ where ν are the harmonic frequencies. The corresponding eigenvectors give the amplitudes of the normal coordinates. Six of the $3N$ frequencies (five for linear molecules) will be zero, corresponding to translational and rotational degrees of freedom.

In practical terms, it should be possible to diagonalize the $3N \times 3N$ matrix f'_{ij} directly and confirm the existence of six zero eigenvalues. The remaining $3N-6$ eigenvalues would then correspond to the internal vibrations. When this procedure is carried out, it is found that the three eigenvalues corresponding to translation are very close to zero but that the rotational degrees of freedom give nonzero values (up to 50 cm^{-1}) unless the stationary point on the potential surface is determined very precisely. For large molecules, with true low-frequency vibrations, this can lead to confusion. These difficulties are avoided by orthogonalizing the coordinates r_i to the known normal coordinates for translation and rotation and then transforming the matrix f'_{ij} to a $(3N-6) \times (3N-6)$ matrix for the remaining set of coordinates. Eigenvalues of this matrix then give the $(3N-6)$ harmonic frequencies directly.

3. Evaluation of Theoretical Harmonic Frequencies

The complete set of experimental, HF/3-21G and HF/6-31G* frequencies is listed in Table I. If degenerate modes are multiply counted, there are 486 frequencies at 3-21G and 83 at 6-31G*.

Comparison between theory and experiment can be carried out in a number of ways. Figure 1 shows a histogram of the 3-21G errors (theory-experiment). This demonstrates that calculated harmonic 3-21G frequencies are consistently too large by up to 400 cm^{-1} . Very few frequencies have errors outside of the range -100 to 400 cm^{-1} . The mean difference, $\nu(3-21G) - \nu(\text{expt.})$, is 179 cm^{-1} for the full sample.

Errors tend to be larger for the larger frequencies, suggesting that a comparison of the ratios $\nu(3-21G)/\nu(\text{expt.})$ might be appropriate. The mean of this ratio for the 486 frequencies is 1.123, implying that the HF/3-21G frequencies are about 12% too large. If such theoretical harmonic frequencies are used for predictive purposes, a multiplicative factor of 0.89 (inverse of 1.123) is recommended.

The 83 frequencies calculated at the HF/6-31G* level can be evaluated in a similar manner. The mean difference, $\nu(6-31G^*) - \nu(\text{expt.})$, is 226 cm^{-1} , somewhat larger than the mean error at the 3-21G level. However, this is due in part to the fact that the 6-31G* sample contains smaller molecules which have

TABLE I. Experimental and theoretical vibrational frequencies.

Sym	Expt	3-21G	6-31G*	Sym	Expt	3-21G	6-31G*	Sym	Expt	3-21G	6-31G*
NNO, C_{∞v}				CF₄, T_d				a¹			
σ	1	2224	2409	a ₁	1	909	971	10	3427	3773	3813
π	2	589	532	e	2	435	454	11	2925	3264	3281
σ	3	1285	816	t ₂	3	1281	1513	12	1485	1702	1665
					4	632	654	13	1419	1456	1479
								14	1195	1047	1052
								15	268	317	341
H₂O, C_{2v}				CH₃F, C_{3v}				CHCH, D_{∞h}			
a ₁	1	3657	3814	a ₁	1	2930	3228	σ _g	1	3374	3719
	2	1595	1800		2	1464	1663		2	1974	2234
b ₂	3	3756	3947		3	1049	1143	σ _u	3	3289	3596
					4	3006	3293	π _g	4	612	918
					5	1467	1686	π _u	5	730	902
					6	1182	1278				883
F₂O, C_{2v}				CHF₃, C_{3v}				CHCF, C_{∞v}			
a ₁	1	926	1167	a ₁	1	3036	3423	σ	1	3355	3697
	2	461	480		2	1117	1218		2	2255	2538
b ₂	3	631	1227		3	700	716	π	3	1055	1159
					4	1372	1590		4	578	887
					5	1152	1331		5	367	528
					6	507	523				
NH₃, C_{3v}				HCOOH, C_s				CH₂CH₂, D_{2h}			
a ₁	1	3337	3646	a ₁	1	3570	3858	a _g	1	3026	3238
	2	950	854		2	2943	3330		2	1623	1842
e	3	3444	3802		3	1770	1940	a _u	3	1342	1522
	4	1627	1858		4	1387	1552	b _{3g}	4	1023	1165
					5	1229	1422		5	3103	3371
					6	1105	1178	b _{3u}	6	1236	1387
					7	625	669		7	949	1115
					8	1033	1193	b _{2g}	8	943	1157
					9	638	677		9	3106	3403
								b _{2u}	10	826	944
									11	2969	3305
								b _{1u}	12	1444	1640
											1610
NF₃, C_{3v}				CH₃OH, C_s				CHFCHF, C_{2h}			
a ₁	1	1032	1086	a ₁	1	3681	3868	a ₁	1	3135	3472
	2	647	627		2	3000	3294		2	1715	1964
e	3	907	1135		3	2844	3177		3	1266	1435
	4	492	483		4	1477	1698		4	1014	1091
					5	1455	1638		5	255	248
					6	1345	1479	a ₂	6	866	1107
					7	1060	1152		7	482	555
					8	1033	1092	b ₂	8	3135	3441
					9	2960	3217		9	1376	1564
					10	1477	1686		10	1127	1216
					11	1165	1254		11	768	811
					12 (250)	360	348	b ₁	12	756	929
CO₂, D_{∞h}				CH₃NH₂, C_s				CH₃CN, C_{3v}			
σ _g	1	1333	1427	a ₁	1	3361	3677	a ₁	1	2954	3218
π _u	2	667	659		2	2961	3230		2	2267	2595
σ _u	3	2349	2463		3	2820	3135		3	1385	1599
					4	1623	1851		4	920	961
					5	1473	1680	e	5	3009	3286
					6	1430	1614		6	1448	1650
					7	1130	1256		7	1041	1224
					8	1044	1095		8	362	493
					9	780	757				
HCN, C_{∞v}				CH₄, T_d							
σ	1	3311	3691	a ₁	1	2917	3187				
π	2	712	990	e	2	1534	1740				
σ	3	2097	2395	t ₂	3	3019	3280				
					4	1306	1520				
H₂CO, C_{2v}											
a ₁	1	2783	3162								
	2	1746	1916								
	3	1500	1692								
b ₂	4	2843	3233								
	5	1249	1378								
b ₁	6	1167	1337								

fewer low-frequency torsion-type modes. The mean value of the ratio $\nu(6-31G^*)/\nu(\text{expt.})$ is 1.130, again showing slightly poorer agreement with experiment than with the 3-21G basis.

The small set of HF/6-31G* calculations partly overlaps the study of Hout, Levi, and Hehre [7]. They considered diatomics as well as a different set of

TABLE I. (Continued from previous page.)

Sym	Expt	3-21G	6-31G*	Sym	Expt	3-21G	6-31G*	Sym	Expt	3-21G	6-31G*	
CH₃NC, C_{3v}				CH₃CH₂F, C_s				CH₃COOH, C_s				
a ₁	1	2966	3223	a'	1	3003	3281	a'	1	3583	3869	
	2	2166	2407		2	2941	3244		2	3051	3333	
	3	1429	1609		3	2915	3215		3	2944	3228	
	4	945	969		4	1479	1708		4	1788	1971	
e	5	3014	3294		5	1449	1673		5	1430	1632	
	6	1467	1671		6	1395	1582		6	1382	1571	
	7	1129	1276		7	1365	1565		7	1264	1477	
	8	263	339		8	1108	1242		8	1182	1284	
					9	1048	1130		9	989	1104	
					10	880	953		10	847	898	
					11	415	409		11	657	616	
				a'	12	3003	3298		12	581	435	
					13	3003	3270		a'	13	2996	3284
					14	1449	1655			14	1430	1645
					15	1277	1434			15	1048	1206
					16	1048	1297			16	642	698
					17	810	908			17	534	581
					18	243	261			18	93	126
C₂H₄O, C_{2v}				C₂H₄NH, C_s				CH₃OCH₃, C_{2v}				
a ₁	1	3006	3328	a'	1	3338	3372	a ₁	1	2996	3292	
	2	1498	1681		2	3079	3416		2	2817	3174	
	3	1271	1326		3	3015	3318		3	1464	1702	
	4	1120	1249		4	1482	1666		4	1452	1652	
	5	877	887		5	1211	1376		5	1244	1358	
a ₂	6	3063	3406		6	1095	1280	a ₂	6	928	963	
	7	1300	1297		7	1090	1198		7	418	419	
	8	860	1096		8	998	1059		8	2952	3206	
b ₂	9	3006	3314		9	856	912		9	1464	1670	
	10	1472	1655		10	773	802		10	1150	1255	
	11	1151	1268		11	3079	3399		11	203	231	
	12	892	891		12	3015	3307	b ₂	12	2996	3289	
b ₁	13	3065	3424		13	1463	1644		13	2817	3164	
	14	1142	1220		14	1268	1387		14	1464	1687	
	15	822	908		15	1237	1275		15	1452	1607	
					16	1131	1257		16	1227	1282	
					17	904	992		17	1102	1186	
					18	817	894	b ₁	18	2925	3210	
									19	1464	1679	
									20	1179	1285	
									21	242	246	
CH₃CHO, C_s				HCOOCH₃, C_s				CH₂CCH₂, D_{2d}				
a'	1	3005	3307	a'	1	3045	3347	a ₁	2	3015	3309	
	2	2917	3200		2	2969	3310		2	1443	1644	
	3	2822	3159		3	2943	3238		3	1073	1198	
	4	1743	1926		4	1754	1914	b ₁	4	865	969	
	5	1441	1628		5	1454	1679	b ₂	5	3007	3307	
	6	1400	1565		6	1445	1622		6	1957	2224	
	7	1352	1555		7	1371	1538	e	7	1398	1594	
	8	1113	1222		8	1207	1330		8	3086	3381	
	9	919	939		9	1166	1287		9	999	1170	
	10	509	531		10	925	963		10	841	1050	
a''	11	2967	3248		11	767	826		11	355	412	
	12	1420	1645		12	318	298					
	13	867	1271		13	3012	3306					
	14	763	889		14	1443	1669					
	14	150	162		15	1168	1278					
					16	1032	1183					
					17	332	331					
					18	130	122					
C₂H₆, D_{3d}				CH₃CCH, C_{3v}								
a _{1g}	1	2954	3200	a ₁	1	3334	3661					
	2	1388	1571		2	2918	3202					
	3	995	1004		3	2142	2408					
	4	289	314		4	1362	1586					
a _{1u}	5	2896	3196									
a _{2u}	6	1379	1580									
e _g	7	2969	3241									
	8	1468	1677									
	9	1190	1351									
e _u	10	2985	3268									
	11	1469	1678									
	12	822	921									

polyatomics and concluded that HF/6-31G* frequencies are 10-15% higher than experimental values. They also used the correlated MP2/6-31G* method and obtained improved results (5-10% higher than experiment). From the present viewpoint, the most important conclusion of our study is that the HF/3-21G frequencies are of comparable accuracy to the HF/6-31G* values.

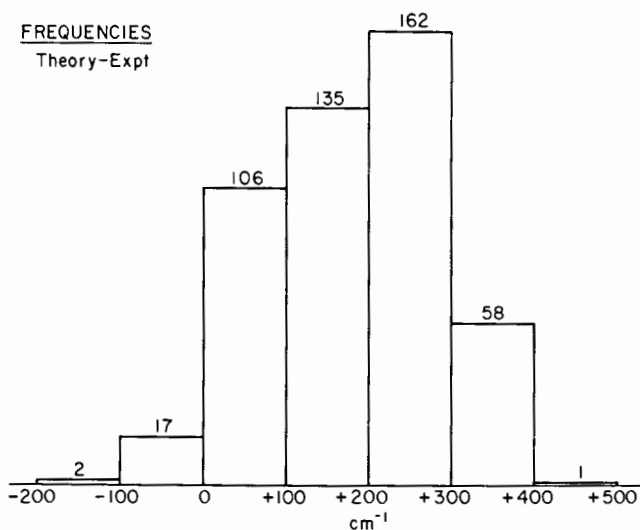


Figure 1. Histograms of differences $\nu(\text{theory}) - \nu(\text{expt})$ for the HF/3-21G theoretical model (units are in cm^{-1}).

low by theory; on the other hand, ν_3 for F_2O is 396 cm^{-1} too high. The origin of these large differences is not clear at the present time.

For some of the larger molecules, the theory is giving a more detailed description of the vibrational frequencies than has been extracted from the experimental data. For dimethylether, for example, several of the symmetric (a_1 symmetry) and antisymmetric (b_2 symmetry) methyl group vibrations have not been resolved into separate components, whereas theory predicts some significant splitting between such levels.

4. Archival Storage of Structures and Force Constants

The information underlying the computed frequencies of Table I is the set of quadratic force constants f_{ij} [Eq. (2)]. The corresponding rotational constants (or moments of inertia) could be computed from the equilibrium structural parameters (bond lengths and bond angles). This data is likely to be of value in applications other than the computation of harmonic frequencies with principal isotopes as discussed in the previous section. For example, the same set of quadratic force constants can be used to predict harmonic frequencies for any other isotopic form of any of the molecules; this would be valuable in studies of isotope effects on equilibrium constants. Another range of applications of the same data would be the study of various empirical force fields of the valence-field type (bond stretching constants, bond angle bending constants, torsional constants etc.). Such force fields could be fitted to the complete sets of cartesian force constants f_{ij} produced by the HF/3-21G calculations.

Since more than 7000 Cartesian force constants were evaluated in this study, publication of the data in tabular form, as part of the manuscript, is impractical. Even if printed tables were distributed, some transcription errors in copying

numbers are inevitable. To eliminate such errors and aid in the application of the data, the complete set of structures and force constants have been incorporated in the Carnegie-Mellon Quantum Chemistry Archive (CMQCA) [14]. This is a computer-based set of data files stored permanently on a disk and available for direct reading by a remote terminal and/or transfer to a remote computer. In effect, these CMQCA files constitute an appendix to this manuscript.

The CMQCA data files have some interactive character. In frequency studies, for example, the (remote terminal) reader is given the option of selecting the nuclear isotopes to be used in association with the stored cartesian force constants. Thus predicted frequencies for any isotopically substituted molecule in the set of 37 is available to supplement Table I. In the following section, we give an example of such an application.

5. Isolated CH Frequencies

The CH stretching frequencies of organic molecules have been extensively studied and correlated with other molecular properties [15, 16]. For CH₂ and CH₃ groups, the vibrational level structure is complicated by bond-bond interactions and by effects of Fermi resonance. Since the properties of individual CH bonds are of greatest interest for theoretical interpretation, such complications

TABLE II. Isolated CH frequencies (cm⁻¹).

Molecule	Expt ^a	3-21G	Molecule	Expt	3-21G
HGN	3312	3691	CH ₃ CN	2979	3265
H ₂ CO	2813	3200	CH ₃ <u>CHO</u>	2770	3161
CH ₄	2992	3259	C ₂ H ₆	2950	3237
CH ₃ F	2976	3272	<u>HCOOCH</u> ₃	2943	3310
CHF ₃	2990	3423	CH ₃ OCH ₃	2984	3284
HCOOH	2943	3331		2884	3193 ^c
CH ₃ OH	2979	3289 ^b	CH ₂ CCH ₂	3049	3347
	2920	3201 ^c	CH ₃ CCH	2958	3244
CH ₃ NH ₂	2880	3140 ^b	CH ₃ <u>CCH</u>	3334	3661
	2955	3245 ^c	c-C ₃ H ₆	3056	3367
CHCH	3336	3666	CH ₃ COCH ₃	3000	3293 ^b
CHCF	3355	3697		2946	3237 ^c
CH ₂ CH ₂	3060	3354	HCCCCH	3326	3655

^a From reference.

^b CH in symmetry plane.

^c CH out of symmetry plane.

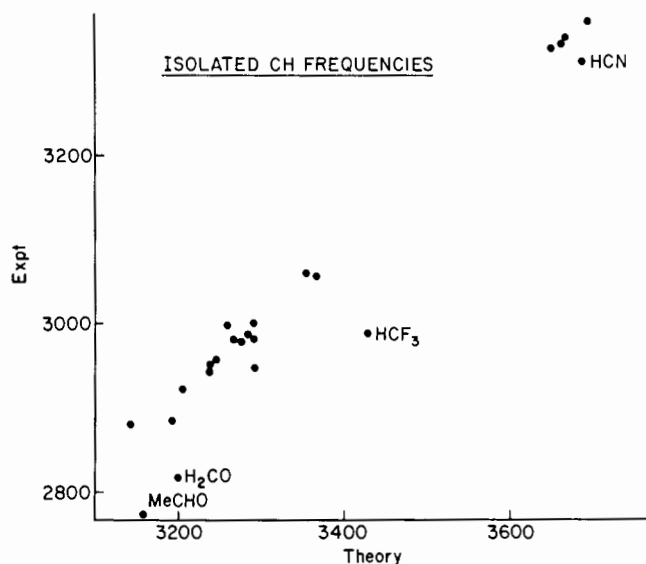


Figure 2. Comparison of theoretical (3-21G) and experimental isolated CH frequencies (units are in cm^{-1}).

should be avoided. This has been done experimentally by the "isolated CH frequency" technique, in which the molecules are completely deuterated except for a single proton [16]. This eliminates interaction effects and usually permits easy identification of frequencies associated with particular CH bonds.

The isolated CH frequencies for the molecules listed in Table I are easily obtained from the interactive CMQCA files described in Sec. 5. These may be compared directly with experimental data, as displayed in Table II and Figure 2. Although the theoretical values are all too large, like those in Table I, the variations of $\nu(\text{CH})$ from compound to compound are quite well reproduced. For some of the molecules, there are two inequivalent positions within a methyl group. In methanol for example, the CH *trans* to OH has a different isolated frequency to the other two CH bonds *gauche* to OH. Both appear in experimental spectra. The differences are quite well reproduced by the theory. For example, in dimethylether, the two CH bonds in the symmetry plane have isolated frequencies 100 cm^{-1} higher than the remaining CH bonds. Theory gives 109 cm^{-1} for this separation.

6. Conclusions

The following conclusions may be drawn from this work:

(1) Computation of all Cartesian quadratic force constants at the HF/3-21G level of theory is practical for molecules of moderate size, containing up to ten atoms.

(2) Harmonic frequencies calculated at this level exceed anharmonic observed fundamental frequencies by an average of 180 cm^{-1} or about 12%.

(3) Expansion of the basis set to 6-31G* (including *d* functions on nonhydrogen atoms) does not produce a significant improvement in the level of agreement with experiment.

(4) Archival storage of the structures and force constants facilitates applications to isotopically substituted molecules. In particular, isolated CH frequencies (from molecules with only one proton) have been studied and experimental trends are well reproduced.

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