JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 99, NUMBER 6 MARCH 16, 1977

Ground States of Molecules. 37.[1] MINDO/3 Calculations of Molecular Vibration Frequencies

Michael J. S. Dewar* and George P. Ford

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received July 13, 1976*

Abstract: MINDO/3 calculations of molecular vibration frequencies are reported for 34 molecules for which detailed experimental data are available. The agreement is satisfactory, becoming good if allowance is made for systematic deviations for specific types of vibration.

The primary goal of the studies reported in this series of papers is the development of theoretical procedures accurate enough and reliable enough to provide useful information concerning the mechanisms of chemical reactions and the properties of transient intermediates in them. Extensive tests of our latest procedure (MINDO/3[2]) have given encouraging results[3] for a wide variety of molecular properties, including heats of formation,[2] geometries,[2] dipole moments,[2] first ionization potentials,[2] polarizabilities,[4] hyperpolarizabilities,[5] nuclear quadrupole coupling constants,[6] ESCA chemical shifts,[7] and the electronic band structure of polymers.[8] The mechanisms predicted for nearly 200 reactions have also been consistent with the available experimental data.[3,9] There is, however, an inevitable uncertainty concerning predictions based on calculations by an empirical procedure outside the areas where it has been thoroughly tested. Since most of the available experimental data refer to stable species represented by local minima on the potential surface, most of the tests of MINDO/3 refer to stable species. The only tests so far carried out for the intermediate sections of potential surfaces have been comparisons of calculated and observed activation energies for reactions. It would greatly strengthen confidence in MINDO/3 predictions for these regions if additional tests could be applied.

The major sources of experimental data in this connection refer to molecular vibration frequencies (indicating the form of potential surfaces in the vicinity of minima), activation parameters (in particular entropies of activation), and kinetic isotope effects. All these quantities, other than enthalpies of activation, are related and can be calculated via the partition function if the vibration frequencies are known.

Procedures for calculating molecular vibration frequencies by MO methods are well established and such calculations have been carried out for several small polyatomic molecules by the EHT,[10] CNDO/2,[11] INDO,[12] MINDO/2,[11,12,13] and RH[14] (Roothaan[15]-Hall[16]) methods and also for several hydrocarbons by MINDO/3.[17] Here we report the results of a detailed MINDO/3 study of 34 polyatomic molecules for which apparently reliable experimental vibration frequencies and vibrational assignments are available. Since these data encompass 54 different types of vibration and over 500 individual frequencies, comparison of our results with experiment should provide a good test of MINDO/3 in this connection.

It may be noted that calculations of force constants for normal modes of vibration have been carried out routinely for some time in these laboratories in applying the McIver-Komornicki[18] criterion to putative transition states.

Computational Procedure

The calculations were carried out by the method used by McIver and Komornicki[18,19] for MINDO/2 calculations of vibration frequencies. Using Cartesian coordinates, first derivatives of the energy are found analytically and second derivatives by finite difference. The matrix of second derivatives (Hessian matrix) is then weighted and used with the standard GF formalism[20] to obtain the frequencies and normal modes. In the case of compounds containing third-row elements (S, Cl), both first and second derivatives of the energy were found by finite difference.

In order to ensure sufficient accuracy in the calculations of derivatives, a relatively small displacement (0.005 Å) and a correspondingly more stringent criterion of SCF convergence were used in each case. Under these conditions the six vibration frequencies corresponding to translation or rotation, while never zero, were usually less than 10 cm^{-1} and only rarely greater than 30 cm^{-1}, the method using analytical derivatives being marginally better in this respect. The magnitude of these spurious frequencies could be further reduced by using a still more stringent SCF criterion. This was not done since previous studies had indicated that it leads to no significant change in the real frequencies.

Results

The calculated and observed frequencies are presented in Table I and compared graphically in Figure 1. The calculated values for ethane, ethylene, acetylene, and benzene are those

Table I. Comparison of Calculated (MINDO/3) and Observed Molecular Vibration Frequencies

Molecule and point group		Assignment	Freq, cm^{-1}		Ref
			Exptl	MINDO/ 3^a	
$H_2O; C_{2v}$	a_1	s stretch	3657	4022	*b*
		Bend	1595	1537	
	b_1	a stretch	3756	4021	
$H_2S; C_{2v}$	a_1	s stretch	2615	2638	*b*
		Bend	1183	897	
	b_1	a stretch	2626	2651	
$NH_3; C_{3v}$	a_1	s stretch	3337	3555	*b*
		s deform	950	1114	
	e	d stretch	3444	3577	
		d deform	1627	1517	
$CO_2; D_{\infty h}$	Σ^+g	s stretch	1333^c	1443	*b*
	Π_u	Bend	667	575	
	Σ_u^+	a stretch	2349	2337	
$CS_2; D_{\infty h}$	Σ^+g	s stretch	658	621	*b*
	Π_u	Bend	397	330	
	Σ_u^+	a stretch	1535	1425	
$HCN; C_{\infty v}$	Σ^+	CH stretch	3311	3536	*b*
	Π	Bend	712	769	
	Σ^+	C≡N stretch	2097	2268	
$CH_2O; C_{2v}$	a_1	CH_2 s stretch	2783	3332	
		C=O stretch	1746	2006	
		CH_2 s cis	1500	1374	
	b_1	CH_2 a stretch	2843	3301	
		CH_2 rock	1249	1046	
	b_2	CH_2 wag	1167	1076	
$HCOOH; C_s$	a′	OH stretch	3570	3942	*b*
		CH stretch	2943	3222	
		C=O stretch	1770	1941	
		OH bend	1387	1334	
		CH bend	1229	1274	
		C–O stretch	1105	1000	
		OCO deform	625	575	
	a″	CH bend	1033	936	
		Torsion	638	529	
$H_2C{=}N^+{=}N^-; C_{2v}$	a_1	CH_2 s stretch	3077	3513	*d*
		NN stretch	2102	2357	
		CH_2 s cis	1414^e	1490	
		CN stretch	1170^e	1233	
		CH_2 a stretch	3188	3554	
		CH_2 rock	1109	950	
		Deform	421	428	
		Deform	564	514	
		CH_2 wag	406	271	
$CH_3Cl; C_{3v}$	a_1	CH_3 s stretch	2937^c	3496	*b*
		CH_3 s deform	1355	1237	
		C–Cl stretch	732	809	
	e	CH_3 d stretch	3039^c	3540	
		CH_3 d deform	1452	1286	
		CH_3 rock	1017	784	
$CH_4; T_d$	a_1	s stretch	2917	3505	*b*
	e	d deform	1534	1326	
	f_2	d stretch	3019	3551	
		d deform	1306	1270	
$CH_3OH; C_s$	a′	OH stretch	3681	3960	*b*
		CH_3 d stretch	3000	3404	
		CH s stretch	2844	3348	
		CH_3 d deform	1477	1330	
		CH_3 s deform	1455	1466	
		OH bend	1345	1304	
		CH_3 rock	1060	1243	
		CO stretch	1033	927	
	a″	CH_3 d stretch	2960	3337	
		CH_3 d deform	1477	1289	
		CH_3 rock	1165	1082	
		Torsion	295^f	275	
$CH_3SH; C_s$	a′	CH_3 d stretch	3015	3509	*g*
		CH_3 s stretch	2948	3479	
		SH stretch	2605	2602	
		CH_3 d deform	1453	1306	
		CH_3 s deform	1332	1253	
		CH_3 rock	1072	837	
		SH bend	802	801	
		CS stretch	710	576	
	a′	CH_3 d stretch	3012	3494	
		CH_3 d deform	1444	1295	
		CH_3 rock	956	759	
		Torsion	200^f	160	
$CH_3NH_2; C_s$	a′	NH_2 s stretch	3361	3577	*b*
		CH_3 d stretch	2961	3309	
		CH_3 s stretch	2820	3398	
		NH_2 s cis	1623	1496	
		CH_3 d deform	1473	1297	
		CH_3 s deform	1430	1414	
		CH_3 rock	1130	1009	
		CN stretch	1044	1250	
		NH_2 wag	780	650	
	a″	NH_2 a stretch	3427	3574	
		CH_3 d stretch	2985	3403	
		CH_3 d deform	1485	1311	
		NH_2 twist	1335^h	1170	
		CH_3 rock	980^h	841	
		Torsion	268	220	
$HC{\equiv}CH; D_{\infty h}$	Σ_g^+	CH stretch	3374	3827	
		C≡C stretch	1974	2237	*b*
	Σ_u^+	CH stretch	3289^c	3770	
	Π_g	CH bend	612	488	
	Π_u	CH bend	730	885	
$H_2C{=}C{=}O; C_{2v}$	a_1	CH_2 s stretch	3071	3599	
		CO stretch	2152	2328	
		Torsion	1388	1407	
		CC stretch	1118	1180	
	b_1	CH_2 a stretch	3166	3639	
		CH_2 rock	979	850	
		Deform	438	385	
	b_2	Deform	588	585	
		CH_2 wag	528	383	
$H_3CCN; C_{3v}$	a_1	CH_3 s stretch	2954	3461	
		CN stretch	2267	2383	
		CH_3 s deform	1385^i	1367	
		CC stretch	920	1079	
	e	CH_3 d stretch	3009	3466	
		CH_3 d deform	1448^o	1298	
		CH_3 rock	1041	911	
		CCN deform	362	377	
$H_2C{=}CHCl; C_s$	a′	CH stretch	3125	3572	*j*
		CH stretch	3086	3540	
		CH stretch	3037	3521	
		CC stretch	1610	1832	
		CH bend	1374	1272	
		CH bend	1281	1086	
		CH bend	1036	863	
		CCl stretch	724	717	
		CCl bend	396	294	
	a″	CH twist	943	913	
		CH_2 wag	897	757	
		CCl bend	621	542	
$H_2C{=}CH_2; D_{2h}$	a_g	CH_2 stretch	3026	3544	*b*
		CC stretch	1623^c	1835	
		CH_2 s cis	1342	1296	
	a_u	CH_2 twist	1023^i	886	
	b_{1g}	CH_2 a stretch	3103	3538	
		CH_2 rock	1236	1024	
	b_{1u}	CH_2 wag	949	979	
	b_{2g}	CH_2 wag	943	811	
	b_{2u}	CH_2 a stretch	3106	3557	
		CH_2 rock	826	697	
	b_{3u}	CH_2 s stretch	2989	3527	
		CH_2 s cis	1444	1306	
; C_{2v}	a_1	CH_2 s stretch	3006	3428	*b*
		CH_2 s cis	1498	1335	
		Ring stretch	1271	1716	
		CH_2 wag	1120	1206	
		Ring deform	877	982	

Table I (*Continued*)

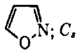
Molecule and point group		Assignment	Freq, cm^{-1} Exptl	MINDO/3[a]	Ref
	a$_2$	CH$_2$ a stretch	3063	3408	
		CH$_2$ twist	1300	1040	
		CH$_2$ rock	860	889	
	b$_1$	CH$_2$ s stretch	3006	3423	
		CH$_2$ s cis	1472	1360	
		CH$_2$ wag	1151	1090	
		Ring deform	892	955	
	b$_2$	CH$_2$ a stretch	3065	3430	
		CH$_2$ twist	1142	1048	
		CH$_2$ rock	822	684	
 S; C_{2v}	a$_1$	CH$_2$ s stretch	3017	3500	*k*
		CH$_2$ s cis	1471	1260	
		CH$_2$ wag	1107	937	
		Ring stretch	1040	1522	
		Ring deform	626	710	
	a$_2$	CH$_2$ a stretch	3089	3497	
		CH$_2$ twist	971	1011	
		CH$_2$ rock	660	761	
	b$_1$	CH$_2$ s stretch	3017	3496	
		CH$_2$ s cis	1440	1314	
		CH$_2$ wag	1050	915	
		Ring deform	685	645	
	b$_2$	CH$_2$ a stretch	3089	3515	
		CH$_2$ twist	945	733	
		CH$_2$ rock	825	708	
 NH; C_s	a′	NH stretch	3346	3465	*b*
		CH$_2$ a stretch	3079	3424	
		CH$_2$ s stretch	3015	3442	
		CH$_2$ s cis	1483	1317	
		Ring stretch	1210	1616	
		NH bend	1096	1159	
		CH$_2$ twist	1090	1075	
		CH$_2$ wag	998	957	
		Ring deform	856	812	
		CH$_2$ rock	772	681	
	a″	CH$_2$ a stretch	3079	3416	
		CH$_2$ s stretch	3003	3434	
		CH$_2$ s cis	1462	1350	
		Ring deform	1268	1100	
		CH$_2$ twist	1237	972	
		CH$_2$ wag	1131	999	
		NH bend	904	935	
		CH$_2$ rock	820	793	
C_2H_6; D_{3d}	a$_{1g}$	CH$_3$ s stretch	2954	3460	*b*
		CH$_3$ s deform	1388	1466	
		CC stretch	995	1196	
	a$_{1u}$	Torsion	289	180	
	a$_{2u}$	CH$_3$ s stretch	2896	3456	
		CH$_3$ s deform	1379	1328	
	e$_g$	CH$_3$ d stretch	2969	3452	
		CH$_3$ d deform	1468	1308	
		CH$_3$ rock	1190[l]	1056	
	e$_u$	CH$_3$ d stretch	2985	3466	
		CH$_3$ d deform	1469[c]	1314	
		CH$_3$ rock	822	759	
CH_3OCH_3; C_{2v}	a$_1$	CH$_3$ d stretch	2996	3389	*b*
		CH$_3$ s stretch	2817	3354	
		CH$_3$ d deform	1464	1447	
		CH$_3$ s deform	1452	1312	
		CH$_3$ rock	1244	1191	
		CO stretch	928	1078	
		COC deform	418	319	
	a$_2$	CH$_3$ d stretch	2952	3335	
		CH$_3$ d deform	1464[l]	1281	
		CH$_3$ rock	1150	1071	
		Torsion	203[l]	114	
	b$_1$	CH$_3$ d stretch	2996	3386	
		CH$_3$ s stretch	2817	3338	
		CH$_3$ d deform	1464	1500	
		CH$_3$ s deform	1452	1363	
		CH$_3$ rock	1227	1305	
		CC stretch	1102	1039	
	b$_2$	CH$_3$ d stretch	2925	3343	
		CH$_3$ d deform	1464	1286	
		CH$_3$ rock	1179	1076	
		Torsion	242	148	
CH_3SCH_3; C_{2v}	a$_1$	CH$_3$ d stretch	2991	3507	*m*
		CH$_3$ s stretch	2916	3479	
		CH$_3$ d deform	1456	1306	
		CH$_3$ s deform	1317	1264	
		CH$_3$ rock	1028	816	
		CS stretch	691	731	
		CSC deform	282	204	
	a$_2$	CH$_3$ d stretch	3013[l]	3493	
		CH$_3$ d deform	1446[l]	1292	
		CH$_3$ rock	963[l]	755	
		Torsion	173[l]	86	
	b$_1$	CH$_3$ d stretch	2991	3506	
		CH$_3$ s stretch	2852	3474	
		CH$_3$ d deform	1440	1306	
		CH$_3$ s deform	1317	1233	
		CH$_3$ rock	972	825	
		CS stretch	741	710	
	b$_2$	CH$_3$ d stretch	2991	3496	
		CH$_3$ d deform	1434	1294	
		CH$_3$ rock	1005	754	
		Torsion	182	95	
 ; C_s	a'	CH stretch	3160	3582	*n*
		CH stretch	3128	3489	
		CH stretch	3086	3486	
		i.p. ring I	1560	1659	
		i.p. ring II	1432	1525	
		i.p. ring III	1373	1437	
		i.p. ring IV	1260	1317	
		CH bend	1217	1173	
		CH bend	1128	1072	
		i.p. ring V	1089	1024	
		i.p. ring VI	1021	984	
		i.p. ring VII	917	729	
		i.p. ring VIII	840	714	
	a''	CH bend	898	816	
		CH bend	792	781	
		CH bend	763	689	
		o.p. ring I	630	526	
		o.p. ring II	588	495	
$H_2C{=}C{=}CH_2$; D_{2d}	a$_1$	CH$_2$ s stretch	3015	3531	*b*
		CH$_2$ s cis	1443	1437	
		CC stretch	1073	1178	
	b$_1$	CH$_2$ twist	865	748	
	b$_2$	CH$_2$ s stretch	3007	3537	
		CC stretch	1957	2208	
		CH$_2$ s cis	1398	1290	
	e	CH$_2$ a stretch	3086	3549	
		CH$_2$ rock	999	902	
		CH$_2$ wag	841	794	
		CCC bend	355	329	
$HC{\equiv}CCH_3$; C_{3v}	a$_1$	CH stretch	3334	3797	*b*
		CH$_3$ s stretch	2918[e]	3457	
		C≡C stretch	2142	2366	
		CH$_3$ s deform	1382	1381	
		C–C stretch	931	1116	
	e	CH$_3$ d stretch	3008	3457	
		CH$_3$ d deform	1452	1301	
		CH$_3$ rock	1053	947	
		CH bend	633	680	
		CCC bend	328	317	
 ; D_{3h}	a$_1$	CH$_2$ s stretch	3038	3491	*b*
		CH$_2$ s cis	1479[e]	1291	
		Ring stretch	1188	1645	
	a''	CH$_2$ twist	1126	961	
	a$_2$'	CH$_2$ wag	1070[i]	1010	
	a$_2$''	CH$_2$ a stretch	3103	3509	
		CH$_2$ rock	854	748	
	e'	CH$_2$ s stretch	3025	3486	
		CH$_2$ s cis	1438	1338	
		CH$_2$ wag	1029	968	
		Ring deform	866	1091	

Table I (*Continued*)

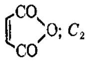
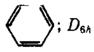
Molecule and point group		Assignment	Freq, cm^{-1} Exptl	Freq, cm^{-1} MINDO/3^a	Ref
	e''	CH_2 a stretch	3082	3484	
		CH_2 twist	1188	1041	
		CH_2 rock	793	692	
$H_2C{=}CHCH_3$; C_s	a'	CH_2 a stretch	3091	3545	*o*
		CH stretch	3017^l	3530	
		CH_2 s stretch	2991	3459	
		CH_3 d stretch	2973	3452	
		CH_3 s stretch	2932	3429	
		C=C stretch	1653	1872	
		CH_3 d deform	1459	1400	
		CH_2 s cis	1419^l	1317	
		CH_3 s deform	1378	1306	
		CH bend	1298	1209	
		CH_2 rock	1174	1158	
		CH_3 rock	945^l	951	
		C—C stretch	914^l	840	
		CCC bend	428	373	
	a''	CH_3 d stretch	2953	3450	
		CH_3 d deform	1443	1309	
		CH_3 rock	1045	973	
		CH_2 twist	990	900	
		CH_2 wag	912	853	
		CH bend	575	510	
		Torsion	188	101	
CH_3COCH_3; C_{2v}	a_1	CH_3 d stretch	3019	3481	*b*
		CH_3 s stretch	2937	3463	
		CO stretch	1731	1947	
		CH_3 d deform	1435	1355	
		CH_3 s deform	1364	1291	
		CH_3 rock	1066	986	
		CC stretch	777	941	
		CCC bend	385	357	
	a_2	CH_3 d stretch	2963^l	3465	
		CH_3 d deform	1426^l	1299	
		CH_3 rock	877^l	791	
	b_1	CH_3 d stretch	3019	3480	
		CH_3 s stretch	2937	3460	
		CH_3 d deform	1410	1444	
		CH_3 s deform	1364	1300	
		CC stretch	1216	1258	
		CH_3 rock	891	875	
		CO bend	530	480	
	b_2	CH_3 d stretch	2972	3468	
		CH_3 d deform	1454	1304	
		CH_3 rock	1091	972	
		CO bend	484	485	
		Torsion	109	66	
C_3H_8; C_{2v}	a_1	CH_3 d stretch	2977	3462	*b*
		CH_3 s stretch	2962	3457	
		CH_2 s stretch	2887	3377	
		CH_3 d deform	1476	1393	
		CH_2 s cis	1462	1321	
		CH_3 s deform	1392	1311	
		CH_3 rock	1158	1135	
		CC stretch	869	944	
		CCC bend	369	354	
	a_2	CH_3 d stretch	2967	3454	
		CH_3 d deform	1451	1313	
		CH_2 twist	1278	1126	
		CH_3 rock	940	840	
		Torsion	216^f	132	
	b_1	CH_3 d stretch	2968	3460	
		CH_3 s stretch	2887	3452	
		CH_3 d deform	1464	1502	
		CH_3 s deform	1378	1318	
		CH_2 wag	1338	1307	
		CC stretch	1054	1169	
		CH_3 rock	922	871	
	b_2	CH_3 d stretch	2973	3459	
		CH_2 a stretch	2968	3361	
		CH_3 d deform	1472	1316	
		CH_3 rock	1192	1050	
		CH_2 rock	748	668	
		Torsion	268^f	164	
 ; C_{2v}	a_1	CH stretch	3117	3536	*p*
		C=O stretch	1852	1941	
		C=C stretch	1592	1749	
		CH bend	1235	1283	
		C–O stretch	1060	1041	
		C–C stretch	864	998	
		i.p. ring II	632	554	
		C=O bend	403	359	
	a_2	CH bend	959	871	
		o.p. ring I	768	696	
		o.p. ring II	275	226	
	b_1	CH stretch	3117	3520	
		C=O stretch	1782	2006	
		C–O stretch	1305	1280	
		CH bend	1054	1176	
		C–C stretch	889	988	
		i.p. ring II	697	601	
		C=O bend	557	504	
	b_2	CH bend	839	833	
		C=O bend	642	590	
		C=O bend	173	111	
 ; C_{2v}	a_1	CH stretch	3154	3577	*b*
		CH stretch	3140	3504	
		i.p. ring II	1491	1594	
		i.p. ring III	1384	1432	
		i.p. ring IV	1140	1291	
		CH bend	1066	1078	
		CH bend	995	1007	
		i.p. ring VII	871	701	
	a_2	CH bend	863^i	777	
		CH bend	728	623	
		o.p. ring I	613	504	
	b_1	CH stretch	3161	3565	
		CH stretch	3129	3502	
		i.p. ring II	1556	1670	
		CH bend	1267	1352	
		CH bend	1180	1108	
		i.p. ring V	1040	1039	
		i.p. ring VI	873	713	
	b_2	CH bend	838	775	
		CH bend	745	706	
		o.p. ring II	603	484	
 ; C_{2v}	a_1	CH stretch	3126	3561	*b*
		CH stretch	3098	3501	
		i.p. ring II	1409	1677	
		i.p. ring III	1360	1348	
		CH bend	1083	1058	
		CH bend	1036	988	
		i.p. ring IV	839	778	
		i.p. ring VII	608	460	
	a_2	CH bend	903	802	
		CH bend	688	712	
		o.p. ring I	567	435	
	b_1	CH stretch	3125	3558	
		CH stretch	3086	3490	
		i.p. ring I	1504	1729	
		CH bend	1256	1100	
		CH bend	1085	970	
		i.p. ring V	872	774	
		i.p. ring VI	751	605	
	b_2	CH bend	867^i	795	
		CH bend	712	699	
		o.p. ring II	452	315	
 ; C_2	a_1	NH stretch	3408	3652	*q*
		CH stretch	3136	3563	
		CH stretch	3114	3514	
		i.p. ring II	1472	1503	
		i.p. ring IV	1384	1460	
		CH bend	1240	1311	
		i.p. ring V	1148	1067	
		CH bend	1078	1027	
		i.p. ring VI	883	715	
	a_2	CH bend	842	759	

Table I (*Continued*)

Molecule and point group		Assignment	Freq, cm^{-1} Exptl	Freq, cm^{-1} MINDO/3^a	Ref
		CH bend	712	647	
		o.p. ring II	615	511	
	b_1	CH stretch	3105	3550	
		CH stretch	3136	3511	
		i.p. ring I	1529	1610	
		i.p. ring III	1416	1437	
		NH bend	1143	1194	
		CH bend	1050	1109	
		CH bend	1015	1049	
		i.p. ring VII	870	708	
	b_2	CH bend	840	752	
		o.p. ring I	649	733	
		CH bend	734	650	
		NH bend	558	472	
; D_{6h}	a_{1g}	CH stretch	3062	3507	*b*
		Ring stretch	992	1189	
	a_{2g}	CH bend	1326	1192	
	a_{2u}	CH bend	673	665	
	b_{1u}	CH stretch	3068	3474	
		Ring deform	1010	843	
	b_{2g}	CH bend	995^i	877	
		Ring deform	703^i	590	
	b_{2u}	Ring stretch	1310	1191	
		CH bend	1150	1078	
	e_{1g}	CH bend	849	820	
	e_{1u}	CH stretch	3063^c	3494	
		Ring deform	1486	1484	
		CH bend	1038	1064	
	e_{2g}	CH stretch	3047	3482	
		Ring stretch	1596^o	1689	
		CH bend	1178	1113	
		Ring deform	606	553	
	e_{2u}	CH bend	975	868	
		Ring deform	410	389	

[a] Calculated frequencies from this work except for $CH_2{=}CH_2$, CH_3CH_3, $CH{\equiv}CH$, and C_6H_6 from ref 17 and $CH_3C{\equiv}CH$, $CH_2{=}C{=}CH_2$, and $CH_3CH_2CH_3$ from unpublished work by M. J. S. Dewar and A. Komornicki. [b] Data from ref 21. [c] Band position uncertain due to Fermi resonance. [d] W. H. Fletcher and W. T. Thomson, *J. Mol. Spectrosc.*, 25, 240 (1968). [e] These assignments have been reversed on the basis of the present calculations. [f] Torsion frequency calculated from microwave spectral data. [g] I. W. May and E. L. Pace, *Spectrochim. Acta, Part A*, 24, 1605 (1968). [h] Estimated by H. Wolff and H. Ludwig, *J. Chem. Phys.*, 56, 5278 (1972); see discussion in ref 14. [i] Frequency estimated from an overtone or combination band. [j] M. Z. El-Sabban and B. J. Zwolinski, *J. Mol. Spectrosc.*, 27, 1 (1968). [k] O. P. Strausz, I. Safarik, W. B. O'Callaghan, and H. E. Gunning, *J. Am. Chem. Soc.*, 94, 1828 (1972); K. Venkateswarlu and P. A. Joseph, *J. Mol. Struct.*, 6, 145 (1970). [l] Result of a normal coordinate calculation. [m] Y. Shiro, M. Ohsaku, M. Hayashi, and H. Murata, *Bull. Chem. Soc. Jpn.*, 43, 609 (1970). [n] C. Pouchan, S. Senez, J. Raymond, and H. Sauvaitre, *J. Chim. Phys., Phys.-Chim. Biol.*, 71, 525 (1974). [o] B. Silvi, P. Labarbe, and J. P. Perchard, *Spectrochim. Acta, Part A*, 29, 263 (1973). [p] A. Rogstad, P. Klaboe, H. Baranska, E. Bjarnov, D. Christensen, F. Nicolaisen, O. F. Nielsen, B. N. Cyvin, and S. J. Cyvin, *J. Mol. Struct.*, 20, 403 (1974); C. DiLauro, S. Califano, and G. Adembri, *ibid.*, 2, 173 (1968); P. Misone and P. Chiorboli, *Spectrochim. Acta, Part A*, 18, 1425 (1962). [q] A. Lautié and A. Novak, *J. Chim. Phys., Phys.-Chim. Biol.*, 69, 1332 (1972).

reported previously.[17] Where possible, the experimental frequencies and assignments are taken from the compilation by Shimanouchi.[21] Those from more recent sources were adapted to Shimanouchi's formalism.

Discussion

The points in Figure 1 are more or less randomly scattered about the line of unit slope, except for the CH stretches which are systematically overestimated by ca. 450 cm^{-1}. Regression analysis, excluding CH stretches, gave a line of slope 0.89 ± 0.02 (99% confidence limits) while that for the CH stretches was 0.92 ± 0.18. The percentage standard deviation for the first category was 9.5%. That for the CH stretches was 15.2%, but fell to 2.1% after systematic correction of the MINDO/3 frequencies by −455 cm^{-1}.

Table II shows a detailed breakdown of these results into various categories of vibrational types. The MINDO/3 values show systematic deviations for each type of vibration (cf. CH stretches). When an appropriate correction (indicated in the fifth column of Table II) is applied, the percentage standard deviation is greatly decreased (compare the last two columns of Table II). The corrections ($\delta\nu$) were calculated from the following expression.

$$\delta\nu = n^{-1} \sum_i (\nu_i^{\text{obsd}} - \nu_i^{\text{calcd}}) \qquad (1)$$

where the sum is over the *n* vibrations of a given type.

The various types of vibration will now be discussed individually.

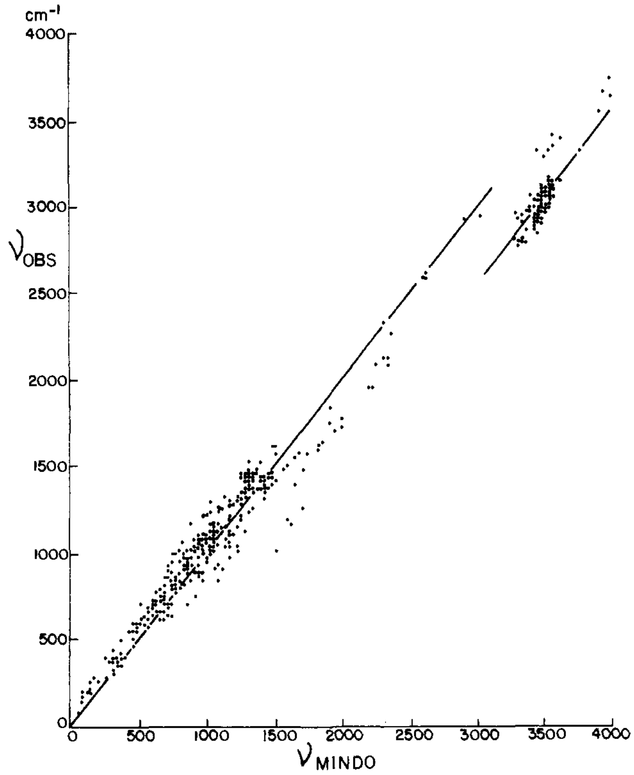


Figure 1. Plot of observed against calculated vibrational frequencies.

CH Stretching Vibrations. As noted above CH stretching modes are systematically overestimated, the exact magnitude of this error varying somewhat with the type of mode involved. Thus the analysis of 119 frequencies encompassing five different types led to an average error of 455 cm^{-1} or 15.2% which, upon application of this correction, led to frequencies in error by only 2.1% and to much less than this when the corrections were calculated for each type of mode individually.

Despite the systematic overestimation of these frequencies, almost all the major qualitative trends are well reproduced by the calculations. Thus the ordering $\nu_{\text{CH}_3\,\text{s stretch}} < \nu_{\text{CH}_3\,\text{d stretch}} < \nu_{\text{CH}_2\,\text{s stretch}} < \nu_{\text{CH}_2\,\text{a stretch}} < \nu_{\text{CH stretch}}$ is correctly repro-

Table II. Analysis of Group Vibrational Frequencies Calculated by MINDO/3

Type of vibration	No.	Obsd Mean value, cm^{-1}	MINDO/3 Mean value	Correction[a]	% error[b]	% error[c] (corrected)
All CH modes	119	3027	3482	−455	15.2	2.1
CH stretch	32	3125	3539	−415	13.4	1.8
CH_2 s stretch	18	3000	3478	−478	16.0	1.4
CH_2 a stretch	18	3076	3487	−411	13.4	1.5
CH_3 s stretch	17	2902	3439	−537	18.6	1.2
CH_3 d stretch	34	2988	3450	−462	15.5	1.5
OH stretch	4	3666	3986	−320	8.8	1.5
NH stretch[d]	4	3386	3567	−181	5.6	1.7
SH stretch	3	2615	2630	−15	0.8	0.6
CH bend	60	952	915	37	9.0	8.0
CH_2 wag	19	974	899	75	10.1	6.6
CH_2 s cis	17	1447	1337	110	8.9	4.7
CH_2 twist	13	1103	968	135	14.4	7.8
CH_2 rock	13	825	918	93	13.0	8.3
CH_3 d deform	34	1456	1329	127	9.9	4.3
CH_3 s deform	17	1384	1330	54	5.3	3.8
CH_3 rock	34	1044	939	105	13.2	8.6
NH bend	4	925	940	−15	6.6	7.4
OH bend	3	1442	1392	51	3.6	0.6
C–C stretch	10	943	1053	−110	14.3	8.6
C=C stretch	7	1518	1693	−175	12.3	4.6
C≡C stretch	2	2058	2302	−244	10.7	*e*
C–N stretch	2	1107	1242	−135	10.9	*e*
C≡N stretch	2	2182	2326	−144	6.5	*e*
C–O stretch	6	1089	1061	28	8.4	8.7
C=O stretch	8	1839	1994	−154	9.5	4.8
C–S stretch	3	714	672	42	11.6	12.3
C=S stretch	2	1097	1023	64	5.8	*e*
C–Cl stretch	2	728	763	−35	7.5	*e*
CCC deform	7	364	339	25	7.8	4.2
Other Deformations[f]	8	462	423	39	11.8	8.9
3-ring deform	8	867	923	−56	16.1	15.1
3-ring stretch	4	1177	1625	−448	38.1	2.7
5-ring stretch + deform	41	1000	970	30	11.7	11.5
6-ring stretch + deform	12	1018	1004	14	9.7	10.1
CC torsion	5	214	129	85	41.4	12.2
CO torsion	4	345	267	78	24.7	11.5
CS torsion	3	185	114	71	40.4	14.7

[a] Correction = $1/n \sum_i (\nu_i^{obsd} - \nu_i^{calcd})$. [b] $100[1/n \sum_i (\nu_i^{obsd} - \nu_i^{calcd})^2]^{1/2}/\bar{\nu}_{obsd}$. [c] $100[1/n - 1 \sum_i (\nu_i^{obsd} - \nu_i^{calcd} + \text{correction})^2]^{1/2}/\bar{\nu}_{obsd}$. [d] Includes data for NH stretch, NH_2 s stretch, and NH_2 a stretch. [e] Error not calculated for less than three data points. [f] Includes data for OCO, CNN, COC, CSC, CCO, and CCN deformations.

duced. In particular MINDO correctly predicts the antisymmetric vibrations to be higher than their symmetric counterparts although quantitatively this difference is somewhat underestimated. The trends in a particular vibration type are also correctly predicted. For example, the ordering among the CH stretch vibrations (acetylenic > 5 ring > 6 ring) is reproduced by MINDO/3.

Other X–H Stretching Modes. Like the CH stretching vibrations the OH and NH modes also seem to be systematically overestimated, in the case of the former by 320 cm^{-1} and the latter by 179 cm^{-1}. Unfortunately the relationship between the symmetric and antisymmetric modes in these cases is not well accounted for. Thus the symmetric and antisymmetric OH stretching modes in water are calculated to be almost degenerate whereas experimentally the latter is found almost 100 cm^{-1} higher. A similar degeneracy is calculated for the symmetric and antisymmetric NH_2 stretching modes in methylamine whereas the latter is observed to be 66 cm^{-1} higher. In contrast the SH stretch is calculated almost precisely, the average error in the three frequencies considered being 15 cm^{-1} or 0.8%. Furthermore, the observed symmetric, antisymmetric SH stretch separation in H_2S is almost exactly reproduced (obsd 11 cm^{-1}; calcd 13 cm^{-1}).

CH Bending Vibrations. The errors among the eight vibration types in this category (CH bend, CH_2 wag, CH_2 s-cis, CH_2 twist, CH_2 rock, CH_3 d deform, CH_3 s deform and CH_3 rock) fall in the range typical of the calculations as a whole, lying between 5.3% for the CH_3 s deform and 14.4% for the CH_2 twist. In contrast to the stretching vibrations, the calculations tend to underestimate these frequencies, although the error is not particularly systematic. The acetylenic CH bend was calculated less well (error 15.6%) than the same vibration in five- (6.2%) and six- (5.4%) membered rings in line with the known[1] tendency of MINDO/3 to fare less well with compounds containing a triple bond. A number of the larger deviations occurred in the CH_2 wag and CH_2 s-cis vibrations of three-membered rings which can almost certainly be attributed to coupling with adjacent ring stretching modes which MINDO seriously overestimates (see below).

Other X–H Bending Vibrations. The small number of results available for NH and OH bending vibrations suggests that these vibrations are calculated satisfactorily.

CX Stretching Vibrations. Vibrations in this group were typically overestimated. The exception for which we had reasonably extensive data was the C–O stretch. These results largely parallel the tendency of MINDO/3 to overestimate the strengths of these bonds as shown by their calculated lengths. The particular stability of the C≡C bond in MINDO/3 has already been noted.[2] One of the few precise linear relationships encountered in this work was found for the 7 C=C stretching frequencies for which a correlation coefficient of 0.998 with the observed frequencies was obtained. This is probably due to the predominance of a single force constant (f_{cc}) in determining these frequencies.

CCC Deformation. These deformations are calculated with excellent precision, the average error being only 25 cm^{-1}; the largest deviation found was 55 cm^{-1} for propene. Examination of the other deformations reveals comparable behavior.

Ring Stretching and Deformation Modes. The stretching vibration for three-membered rings is systematically overestimated by almost 500 cm^{-1} in the MINDO/3 calculation. This is not altogether unexpected as three-membered rings are known to be too stable in the MINDO approximation and in agreement with this rationalization the ring deformation modes are predicted satisfactorily. The five- and six-membered ring stretch/deformations are calculated satisfactorily with average errors of 30 and 14 cm^{-1}, respectively.

Torsions. Since the single bond rotational barriers[1] calculated in the MINDO/3 approximation are too low, it is not surprising that the corresponding torsional vibrational frequencies are similarly underestimated.

Conclusions

The overall agreement between the uncorrected MINDO/3 frequencies and experiment is satisfactory, given that the calculated values are based on harmonic force constants and given that similar RH calculations, close to the Hartree–Fock limit, commonly lead to vibration frequencies in error by ±10%. The errors in the MINDO/3 values are moreover mostly systematic, similar deviations occurring for a given type of vibration in different molecules. When appropriate corrections are applied, the agreement with experiment becomes quite good (Table II). Since calculations of this kind can be carried out without difficulty and at little expense for quite large molecules,[22] the results may be of practical value in assigning observed vibronic transitions and in helping to identify unknown species. We are currently studying in this way several transient molecules which have been observed only in matrices and whose identity is consequently uncertain, for example, the species claimed by Chapman et al.[23] to be benzocyclobutadiene.

Since the vibrational contribution to entropies of molecules becomes important only at very high temperatures, it seems likely that the accuracy attained here may be sufficient for the calculation of entropies of reaction and activation and for the estimation of other related quantities, e.g., specific heats and isotope effects. These problems will be considered in later papers of this series.

Acknowledgments. This work was supported by the Air Force Office of Scientific Research (Grant AFOSR 75-2749) and the Robert A. Welch Foundation (Grant F-126). The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center.

References and Notes

(1) Part 36: *J. Am. Chem. Soc.*, in press.

(2) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1294, 1302, 1307, (1975); M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *ibid.*, **97**, 1311 (1975).

(3) See M. J. S. Dewar, *Chem. Br.*, **11**, 97 (1975).

(4) M. J. S. Dewar, R. C. Haddon, and S. H. Suck, *J. Chem. Soc., Chem. Commun.*, 611 (1974).

(5) J. G. Bergman, M. J. S. Dewar, S. H. Suck, and P. K. Weiner, *Chem. Phys. Lett.*, **38**, 226, 228 (1976).

(6) M. J. S. Dewar, H. W. Kollmar, and S. H. Suck, *J. Am. Chem. Soc.*, **97**, 5590 (1975).

(7) M. J. S. Dewar and D. H. Lo, *Chem. Phys. Lett.*, **33**, 298 (1975).

(8) M. J. S. Dewar, S. H. Suck, and P. K. Weiner, *Chem. Phys. Lett.*, **29**, 220 (1974).

(9) (a) M. J. S. Dewar and S. Kirschner, *J. Am. Chem. Soc.*, **96**, 5244, 5246, 6809, 7578 (1974); **97**, 2931, 2932 (1975); *J. Chem. Soc., Chem. Commun.*, 463 (1975); (b) M. J. S. Dewar and C. A. Ramsden, *J. Chem. Soc., Perkin Trans. 1*, 1839 (1974); (c) M. J. S. Dewar, A. C. Griffin, and S. Kirschner, *J. Am. Chem. Soc.*, **96**, 6225 (1974); (d) R. S. Case, M. J. S. Dewar, S. Kirschner, R. Pettit, and W. Slegeir, *ibid.*, **96**, 7581 (1974); (e) M. J. S. Dewar and H. W. Kollmar, *ibid.*, **97**, 2933 (1975); (f) M. J. S. Dewar and W. Thiel, *ibid.*, **97**, 3978 (1975); (g) M. J. S. Dewar, A. C. Griffin, W. Thiel, and I. J. Turchi, *ibid.*, **97**, 4439 (1975); (h) P. K. Bischoff and M. J. S. Dewar, *Ibid.*, **97**, 2278 (1975); (i) M. J. S. Dewar and I. J. Turchi, *J. Chem. Soc., Perkin Trans. 2*, in press; (j) M. J. S. Dewar and D. Landman, *J. Am. Chem. Soc.*, **99**, 372 (1977); (k) M. J. S. Dewar, R. C. Haddon, A. Komornicki, and H. S. Rzepa, *ibid.*, in press; (l) unpublished work by S. B. Brown, F. Carrion, G. Ford, S. Kirschner, A. Komornicki, D. Landman, M. L. McKee, S. Olivella, and H. S. Rzepa.

(10) W. L. Bloemer and B. L. Bruner, *J. Mol. Spectrosc.*, **43**, 452 (1972).

(11) K. Kozmutza and P. Pulay, *Theor. Chim. Acta*, **37**, 67 (1975).

(12) B. Nelander and G. Ribbegård, *J. Mol. Struct.*, **20**, 325 (1974).

(13) J. T. Gleghorn and R. W. McConkey, *J. Mol. Struct.*, **29**, 133 (1975).

(14) P. Pulay and F. Török, *J. Mol. Struct.*, **29**, 239 (1975) and papers cited there.

(15) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(16) G. G. Hall, *Proc. R. Soc. London, Ser. A*, **205**, 541 (1951).

(17) M. J. S. Dewar and A. Komornicki, *J. Am. Chem. Soc.*, in press.

(18) J. W. McIver and A. Komornicki, *J. Am. Chem. Soc.*, **94**, 2625 (1972).

(19) J. W. McIver and A. Komornicki, *Chem. Phys. Lett.*, **10**, 303 (1971).

(20) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, N.Y., 1955.

(21) T. Shimanouchi, "Tables of Molecular Vibrational Frequencies", National Standard Reference Data Series, National Bureau of Standards, Washington, D.C., 1972.

(22) The time required for a complete vibrational calculation for CH_3CN on our CDC 6600 computer was 90 s.

(23) O. L. Chapman, C. C. Chang, and N. R. Rosenquist, *J. Am. Chem. Soc.*, **98**, 261 (1976).