Force Constants of Triatomic Molecules and Radicals

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Résumé: *Les analyses en coordonnées normales d'une série de molécules triatomiques ont été réalisées à l'aide d'un programme de calcul modifié. Les constantes de force dérivées des nombres d'onde expérimentaux sont données dans les cas suivants: HCO et HNO (trois états électroniques) et HBO, HOO, HOF, HOCl, HOBr, HOI, HCN, HCP, HNC, HNSi, HNGe. On compare les principales constantes de force en tenant compte de la position des atomes considérés, dans le tableau périodique.*

Abstract: *Using a modified computational method, we have made normal coordinate analyses for a collection of triatomic molecules. Force constants obtained from observed vibrational wavenumbers are presented for HBO, HCO (three electronic states), HNO (three electronic states), HOO, HOF, HOCl, HOBr, HOI, HCN, HCP, HNC, HNSi and HNGe. The principal force constants are compared in relation to periodic properties, and the significance of the results is discussed.*

Introduction

While we can consider rotational constants and vibrational wavenumbers to be fairly direct observables, the mass-independent parameters which are really properties of a molecule in a particular electronic state, as governed by electronic motions, are the internuclear distances and the force constants. Sets of these derived parameters determine the geometrical and vibrational structures respectively. Where rotational fine structure is observable and resolvable, lines are usually sufficiently abundant to permit corrections for centrifugal distortion etc., hence to make it possible to deduce the rotational constants (A_0, B_0, C_0) and thence the internuclear separations. On the other hand, vibrational transitions are generally sparse, especially for unstable or reactive molecules obtainable in only small amounts. In these circumstances, few, if any, extra vibrational wavenumbers, beyond the fundamentals, are available to enable corrections for anharmonicity or other secondary vibrational effects. Force field parameters estimated without correction for anharmonicity can be expected to be in absolute error of the order of five per cent, but no real alternative to the harmonic approximation generally exists. The minimum criterion for these approximate parameters, which will be called force constants, to be acceptable is that they should reasonably well regenerate the vibrational wavenumbers for the isotopic molecules from which they were derived, and as well have some predictive capacity for further isotopic molecules. In addition, these approximate force constants should also predict inertial defects, centrifugal distortion constants, mean vibrational amplitudes, kinetic isotope effects etc. Often these properties are rather insensitive to the force constants, and for most molecules this information is not available to provide assistance in defining the force field; to the contrary, these properties are frequently computed from the force field parameters.

In this article, we present results of normal coordinate analyses of some HXY molecules belonging to $C_{\infty v}$ or C_s point groups. Their number includes free radicals and other reactive species observed in argon matrices at cryogenic temperatures, with other related molecules for purposes of comparison.

Method

As the method of computation of force constants that we use here is a modification of previous methods[1,2], we will outline it briefly.

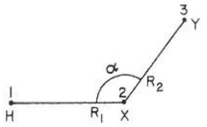

Figure 1. Definition of structural parameters for triatomic molecules.

The potential energy function for vibration is defined according to the general valence force field:

$$\begin{aligned} 2V &= f_1\,(\delta R_1)^2 + f_2\,(\delta R_2)^2 + f_\alpha\,(\ell\delta\alpha)^2 \\ &\quad + 2f_{12}\,(\delta R_1)\,(\delta R_2) + 2f_{1\alpha}\,(\delta R_1)\,(\ell\delta\alpha) \\ &\quad + 2f_{2\alpha}\,(\delta R_2)\,(\ell\delta\alpha). \end{aligned}$$

In this equation, δ implies displacement of the structural parameters R_1, R_2 and α, defined in Figure 1, from their equilibrium values; ℓ is a unit length, 100 pm, the same for all molecules, such both that all the coefficients f_i have the same dimensions (force per unit length) and that force constants f_i which are coefficients of angular changes are directly comparable in different molecules. Only quadratic terms in the potential function are retained according to the harmonic approximation. To facilitate mathematical operations, matrix methods are used. An $\underset{\approx}{F}$ matrix,

$$\underset{\approx}{F} = \begin{pmatrix} F_{11} & F_{12} & F_{13} \\ & F_{22} & F_{23} \\ & & F_{33} \end{pmatrix}$$

symmetric about the principal diagonal, can be formed such that $F_{11} = f_1, F_{12} = F_{21} = f_{12}, F_{22} = f_2, F_{13} = F_{31} = f_{1\alpha}$, etc. An inverse kinetic energy matrix G is also usually formed. For these triatomic molecules, it is also a square matrix of rank three, and symmetric. We form the $\underset{\approx}{G}$ matrix such that all elements have the same dimensions, inverse mass: $G_{11} = \mu_1 + \mu_2$; $G_{12} = G_{21} = \mu_2 \cos\alpha$; $G_{13} = G_{31} = -R_1\mu_2 \sin\alpha/R_2$; $G_{22} = \mu_2 + \mu_3$; $G_{23} = G_{32} = -R_2\mu_2 \sin\alpha/R_1$; $G_{33} = R_2\mu_1/R_1 + R_1\mu_3/R_2 + \mu_2\ (R_1/R_2 + R_2/R_1 - 2\cos\alpha)$. Here μ_i is the reciprocal of the mass of atom i (H or D atoms are always numbered atom 1). The product of $\underset{\approx}{F}$ and $\underset{\approx}{G}$ matrices, in either order, is the $\underset{\approx}{H}$ matrix of which the eigenvalues are proportional to the squares of vibrational wavenumbers. With mass in atomic mass units, wavenumbers in reciprocal centimetres, and force constants in Newtons per metre, according to the fundamental (SI) physical constants of 1969[3] the proportionality constant is $5.89180175 \times 10^{-5}$. As the inverse vibrational problem, determination of force constants from transition wavenumbers, is directly soluble only in special circumstances, regression methods based on trial initial parameters are employed. To accomplish this, computer programmes originally developed by Schachtschneider and Snyder[4] have been modified for this investigation.

Because of the large wavenumber shift of X-H stretching vibrations when deuterium replaces a hydrogen atom, anharmonicity effects are particularly noticeable, even though they are really not proportionately much larger than for non-hydride vibrations. Earlier a simple correction[5] was suggested to lead to a significantly improved fitting of the harmonic force field to the observed transitions. According to this method, wavenumbers of X-H (X-D) stretching vibrations (only) are multiplied by a factor of 1.0456 (1.0331) at the beginning of computations; at the end, the factor is removed from calculated wavenumbers. Because of the general insensitivity to this change of force constants other than f_1, the notable effect is to increase f_1 by $\sim 10\%$. In the tables of results which follow, force constants and wavenumbers computed without this correction are enclosed in parentheses.

Exact atomic masses[6] were used in most cases, but, where appropriate because of unsolved isotopic splitting, weighted averages corresponding to chemical atomic masses were used instead. The atomic mass numbers (i.e., nucleon numbers) are used in the tables to specify the isotopic molecules except where chemical atomic weights were used.

The numbering of vibrations follows convention: v_1 of HXY molecules applies to the HX vibration and v_3 to the XY vibration; the bending vibration is always called v_2.

For comparison with other published force constants, the following equations relate the consistent set of this work to another common basis (primed quantities): $f_1 = f'_1$; $f_2 = f'_2$; $f_{12} = f'_{12}$; $f_\alpha = f'_\alpha/R_1R_2$; $f_{1\alpha} = f'_{1\alpha}/R_1$; $f_{2\alpha} = f'_{2\alpha}/R_2$.

Results

Three groups of monohydride molecules have been studied: (1) the reactive molecules or radicals HBO, HCO, HNO, HOO and some of their electronically excited states; (2) the complete (non-radioactive) set of hydrogen hypohalites; and (3) some linear imino and methylideno compounds.

Table I.—Observed [7] and calculated wavenumbers, (cm^{-1}), geometry[a] and force constants[b] of boron hydride oxide (HBO X $^1\Sigma^+$).

Mass numbers:	1, 10, 16	1, 11, 16	2, 10, 16	2, 11, 16
ν_1 (obs.)			2303	2259
ν_2	764	754	617	606
ν_3	1855	1817	1663	1648
ν_1 (calc.)	2834	2810	2306	2256
ν_1	(2867)	(2845)	(2307)	(2256)
ν_2	764	755	617	606
ν_2	(764)	(755)	(617)	(606)
ν_3	1855	1817	1662	1649
ν_3	(1856)	(1816)	(1662)	(1649)

[a] R_1, R_2, α: 116, 122 pm, 180°
[b] $f_1 = 449.43$ (425.82); $f_2 = 1394.58$ (1378.89); $f_\alpha = 22.89$ (22.89); $f_{12} = -13.37$ (8.50) Nm^{-1}.

(1a) The boron hydride oxide molecule, presumably in a $^1\Sigma^+$ ground state, has been observed in argon matrices[8]. The force constants and computed wavenumbers in Table I have been calculated with bond lengths slightly different from those previously suggested, but the present set is believed to be more appropriate on the basis of spectra-structure correlations. In any case, the results are insensitive to the values selected.

(1b) The formyl radical is characterised in three electronic states. Results for the non-linear states are gathered in Table I. Wavenumbers for the X $^2A'$ state were taken from a consistent set[8], but these are in agreement with earlier work which included the best estimate of the structure[5]. For the B $^2A'$ state[8,9], the v_1 wavenumber of HCO is inserted on the basis of a wavenumber — bondlength correlation, but force constants other than f_1 are not sensitive to the value selected.

(1c) For nitrosyl hydride, two well characterised states, X $^1A'$ and A $^1A''$, are known. The ground state vibrational wavenumbers have finally been established in matrix isolation experiments[10a] and confirmed by gas phase studies. The apparent signal attributed to v_1 of HNO in modulation spectroscopy experiments[11a] seems to have been either an artefact or the overtone of v_3. Previous assignments of v_1 of HNO and DNO in photolysis experiments, summarized in ref. 5, were in error unless hydrogen bonding drastically increased the wavenumbers. Recent measurements on further isotopic molecules[11b] have indicated that the data for v_2 must be changed from those in ref. 10; these changes are incorporated in Table III. All data for the A $^1A''$ state are taken from ref. 12. For the B $^1A'$ state a tentative analysis of the diffuse bands[13-16] in the region of 50,000 cm^{-1} has permitted rough estimates of the vibrational wavenumbers. Then structural parameters were estimated using relative intensities and the Frank-Condon principle as well as correlations. The rough resulting force constants are intensive to the structural parameters as usual. All results appear in Table III.

(1d) The hydroperoxyl radical is also known in three states, but two of these have yielded only diffuse spectra. The first detection of HO_2 was in early flash photolysis experiments (R. G. W. Norrish, personal communication), but the continuous nature of the absorption coupled with the difficulty of measurement of continua by photographic methods prevented proof of identity at that time. Recently, this same continuum has been accurately measured[17,18]. An exceedingly weak emission spectrum, believed to be associated with a forbidden electronic transition, has been detected in the near infrared[19], but no structural

Table II.—Observed[8] and calculated wavenumbers (cm^{-1}), geometry[5,9] and force constants[b,d] of the formyl radical in non-linear states.

	HCO[a] X $^2A'$				HCO[c] B $^2A'$	
Mass numbers:	1, 12, 16	2, 12, 16	1, 13, 16	1, 12, 18	1, 12, 16	2, 12, 16
ν_1 (obs.)	2483	1926	2477.5	2482	(2475)	
ν_2	1087	850	1080	1082	1375	1150
ν_3	1863	1803	1824	1819	1035	925
ν_1 (calc.)	2484.6	1924.3	2474.4	2484.2	2475	1843
ν_1	(2485.2)	(1923.4)	(2473.8)	(2484.6)	(2475)	(1822)
ν_2	1088.5	833.9	1083.3	1084.6	1373	1173
ν_2	(1089.3)	(825.7)	(1084.9)	(1085.7)	(1378)	(1187)
ν_3	1864.4	1800.8	1824.3	1819.6	1021	902
ν_3	(1864.9)	(1800.0)	(1824.3)	(1819.6)	(1039)	(910)

[a] R_1, R_2, α : 114.5, 117.65 pm. 123.3°
[b] $f_1 = 357.03$ (310.2); $f_2 = 1434.82$ (1435.98); $f_\alpha = 59.62$ (70.48); $f_{12} = 23.4$ (27.09); $f_{1\alpha} = -37.64$ (-59.65); $f_{2\alpha} = 25.52$ (30.08) Nm^{-1}.
R_1, R_2, α: 114.8, 138.5 pm, 110.5°
[d] $f_1 = 366.64$ (335.3); $f_2 = 463.6$ (481.9); $f_2 = 71.6$ (71.8); $f_{12} = 10$ (10) Nm^{-1}

Table III.—Observed [10, 12, 16] and calculated wavenumbers (cm^{-1}), force constants and geometry[12] of nitrosyl hydride in three states.

	HNO^a X A'		HNO^b A A''		HNO^c B A''	
R_1, R_2, α	106.28, 121.16 pm, 108.58°		103.6, 124.11 pm, 116.25°		108, 119pm, 123°	
Mass numbers:	1,14,16	2,14,16	1,14,16	2,14,16	1,14,16	2,14,16
ν_1 (obs.)	2719	2043	2854.17	2176.49	2270	1968
ν_2	1505	1156	981.18	755.31	710	585
ν_3	1564	1547.3	1420.77	1401.28	1710	
ν_1 (calc.)	2720.0	2041.7	2889.8	2140.7	2270	1968
ν_1	(2720.4)	(2039.6)	(2880.9)	(2109.3)	(2270)	(1968)
ν_2	1520.2	1144.9	984.7	748.6	724	555
ν_2	(1513.3)	(1136.7)	(984.7)	(748.5)	(724)	(555)
ν_3	1560.0	1538.3	1417.8	1407.0	1710	1453
ν_3	(1571.4)	(1539.5)	(1417.8)	(1406.7)	(1710)	(1436)

[a] $f_1 = 433.37$ (384.2); $f_2 = 1126.64$ (1143.3); $f_\alpha = 108.8$ (115.3); $f_{12} = -40.73$ (-54.33); $f_{1\alpha} = -34.14$ (-51.0); $f_{2\alpha} = 74.93$ (80.33) Nm^{-1}.
[b] $f_1 = 506.0$ (460.03); $f_2 = 866.35$ (866.35); $f\alpha = 41.75$ (41.75); $f_{12} = 10$ (20) Nm^{-1}.
[c] $f_1 = 275$ (255); $f_2 = 1510$ (1475); $f\alpha = 23.3$ (30); $f_{12} = -109$ (-82) Nm^{-1}.

Table IV.—Observed [10, 21] and calculated wavenumbers (cm^{-1}), force constants[a] and geometry of the hydroperoxyl radical.

HOO X ^{2}A''

R_1, R_2, α: 98.5, 136pm, 106°

Mass numbers:	1,16,16	2,16,16	1,18,18	2,18,18	1,16,18	2,16,18	1,18,16	2,18,16
ν_1 (obs.)	3410.5	2529.7	3402	2515	3414	2530	3402	2515
ν_2	1389.0	1085.3	1380.3		1386		1380.3	
ν_3	1101.0	1020.2	1040.0	1000	1069.5	1006	1040	1016.8
ν_1 (calc.)	3417.1	2518.4	3405.8	2502.5	3417.1	2518.4	3405.8	2502.5
ν_1	(3431.6)	(2499.0)	(3420.3)	(2483.1)	(3431.6)	(2499.0)	(3420.3)	(2483.1)
ν_2	1380.0	1096.9	1378.4	1043.8	1384.5	1074.6	1381.1	1064.3
ν_2	(1388.8)	(1094.7)	(1380.0)	(1045.0)	(1386.3)	(1074.4)	(1382.6)	(1062.5)
ν_3	1101.0	1023.6	1027.9	1003.7	1058.5	1010.7	1060.1	1019.2
ν_3	(1084.1)	(1021.4)	(1022.5)	(998.3)	(1052.8)	(1006.7)	(1054.6)	(1016.7)

[a] $f_1 = 713.44$ (658.17); $f_2 = 578.76$ (571.86); $f_\alpha = 73.55$ (73.67); $f_{1\alpha} = 10$ (10); $f_{1\alpha} = 5.08$ (5.08); $f_{2\alpha} = 29.61$ (28.43) Nm^{-1}.

Table V.—Observed [22-24] and calculated wavenumbers, force constants and geometry [27, 28] of hydrogen hypofluorite and hydrogen hypochlorite.

	HOF^a X ^{1}A'		HOCl^b X ^{1}A'		
R_1, R_2, α;	96.4, 144.2pm, 97.2°		95.9, 168.95pm, 102.5°		
Mass numbers:	1,16,19	2,16,19	1,16,35	2,16,35	1,16,37
ν_1 (obs.)	3578.5	2643.5	3609.2	2666.0	
ν_2	1354.8	1003.9	1239.9	(910)	1237.7
ν_3	889.0	891.1	725.0	725.0	720.2
ν_1 (calc.)	3580.6	2637.9	3607.3	2657.9	3607.2
ν_1	(3590.2)	(2613.3)	(3622.3)	(2639.3)	(3622.3)
ν_2	1355.8	1001.4	1239.9	908.5	1238.2
ν_2	(1357.3)	(997.9)	(1239.8)	(908.0)	(1239.4)
ν_3	892.4	887.7	725.0	719.4	719.5
ν_3	(890.4)	(889.8)	(725.9)	(719.9)	(719.5)

[a] $f_1 = 783.53$ (720.55); $f_2 = 427.27$ (432.76); $f_\alpha = 66.85$ (67.14); $f_{1\alpha} = 10.37$ (10.37); $f_{2\alpha} = 28.88$ (34.67) Nm^{-1}.
[b] $f_1 = 794.83$ (731.77); $f_2 = 368.46$ (362.05); $f_\alpha = 52.12$ (48.54); $f_{1\alpha} = -10.43$ (-10.43); $f_{2\alpha} = 20.51$ (22.75) Nm^{-1}.

parameters have been deduced. After matrix-isolation experiments[5,20] had enabled positive identification of HO_2 by vibrational absorption, a gas-phase vibration-rotation spectrum under low resolution has also been measured[18a,b]. The vibrational wavenumbers and deduced geometry from a recent article[10] have been used here, supplemented by further vibrational data of Milligan and Jacox[21]. The results appear in Table IV.

(2a) Both hydrogen hypofluorite and hydrogen hypochlorite have yielded vibrational absorption spectra in both gas[22,24] and solid (matrix) [25,26] phases. The gas phase data are used here. Both geometrical structures[27,28] are well determined

Table VI.—Observed[26, 29] and calculated wavenumbers, force constants and geometry of hydrogen hypobromite and hydrogen hypoiodite.

	HOBr[a] X $^1A'$				HOI[b] X $^1A'$			
R_1, R_2, α:	95.5, 186 pm, 105°				99, 205 pm, 105°			
Mass numbers:	1,16,79.917	2,16,79.917	1,18,79.917	2,18,79.917	1,16,127	2,16,127	1,18,127	2,18.127
ν_1 (obs.)	3590	2652	3580	2637	3417	2524.2	3406	2507.8 cm^{-1}
ν_2	1164	853.9	1162	848.5	1193	874.5	1191	868
ν_3	626	621.5	597.8	593.8	571.5	566.5	543.1	539.8
ν_1 (calc.)	3593.0	2647.2	3581.2	2630.6	3419.2	2518.1	3408.1	2502.7
ν_1	(3600.2)	(2621.4)	(3588.3)	(2604.9)	(3427.3)	(2498.8)	(3415.5)	(2482.4)
ν_2	1165.4	853.3	1161.6	846.4	1194.4	873.6	1190.4	866.8
ν_2	(1166.9)	(849.8)	(1163.7)	(844.4)	(1195.1)	(871.2)	(1191.5)	(865.1)
ν_3	628.2	619.1	599.3	592.7	573.5	564.0	545.3	538.1
ν_3	(627.0)	(621.0)	(597.8)	(593.6)	(573.6)	(564.9)	(545.3)	(538.8)

[a] $f_1 = 788.73\ (724.02)$; $f_2 = 331.12\ (335.39)$; $f_\alpha = 39.03\ (39.35)$; $f_{12} = (-10)$; $f_{1\alpha} = 10.47\ (10.47)$; $f_{2\alpha} = 17.97\ (21.51)$ Nm^{-1}.

[b] $f_1 = 714.41\ (654.19)$; $f_2 = 295.21\ (299.14)$; $f_3 = 38.83\ (38.89)$; $f_{12}\ (-30)$; $f_{1\alpha}\ 20.20\ (10.10)$; $f_{2\alpha} = 16.10\ (18.05)$ Nm^{-1}.

Table VII.—Observed[30] and calculated wavenumbers (cm^{-1}), force constants and geometry of hydrogen isocyanide, iminosilicon and iminogermanium.

	HCN[a] X $^1\Sigma^+$		HNS[b] X $^1\Sigma^+$		HNGe[c] X $^1\Sigma^+$	
R_1, R_2, α:	100,119pm. 180°		100,154pm, 180°		100.5, 169pm, 180°	
Mass numbers:	1,14,12	2,14,12	1,14,28	2,14,28	1.14,72.59	2,14,72.59
ν_1 (obs.)	3620	2679	3583	2669	3521	
ν_2	477	374	523	395	394	
ν_3	2029	1940	1198	1166	969	
ν_1 (calc.)	3620	2769	3583	2669	3521	2619.7
ν_1	(3620)	(2769)	(3583)	(2669)	(3521)	(2590)
ν_2	477	374.5	523	400.8	394	300
ν_2	(477)	(374.5)	(523)	(400.8)	(394)	(300)
ν_3	2035	1940	1199.2	1166	969	937.8
ν_3	(2059)	(1940)	(1213.7)	(1166)	(969)	(937.2)

[a] $f_1 = 775.1\ (703.1)$; $f_2 = 1668.2\ (1724.1)$; $f_\alpha = 8.71\ (8.71)$; $f_{12} = 38.9\ (-51.03)$ Nm^{-1}.

[b] $f_1 = 773.83\ (692.65)$; $f_2 = 831.66\ (880.83)$; $f_\alpha = 8.71\ (8.71)$; $f_{12} = 3.74\ (-84.43)$ Nm^{-1}.

[c] $f_1 = 747.44\ (683.35)$; $f_2 = 691.2\ (691.53)$; $f_\alpha = 4.61\ (4.61)$ Nm^{-1}.

Table VIII.—Observed[30, 33] and calculated wavenumbers (cm^{-1}), force constants and geometry[30, 32, 33] of hydrogen cyanide, excited formyl radical and methinophosphide.

	HCN[a] X $^1\Sigma^+$		HCO[b] A $^2\pi$		HCP[c] X $^1\Sigma^+$	
R_1, R_2, α:	106.4, 115.6pm, 180°		106.5, 118.2pm, 180°		106.7. 154.2pm, 180°	
Mass numbers:	1,12,14	2,12,14	1,12,16	2,12,16	1,12,31	2,12,31
ν_1 (obs.)	3311.45	2630.30	3316.2	2547.7	3216.903	2419.42
ν_2	711.797	569.046	805.5	641.7	674.63	510
ν_3	2096.855	1925.26	1813.4	(1698.4)[d]	1278.43	(1216.09)[d]
ν_1 (calc.)	3311.45	2630.30	3316.2	2547.7	3216.9	2419.42
ν_1	(3311.45)	(2630.30)	(3316.2)	(2547.7)	(3216.9)	(2419.42)
ν_2	711.979	567.58	806.5	640.74	674.7	523.6
ν_2	(711.979)	(567.58)	(806.5)	(640.74)	(674.7)	(523.6)
ν_3	2097.29	1925.26	1813.4	1718.97	1278.43	1230.81
ν_3	(2122.67)	(1925.26)	(1813.4)	(1698.4)	(1278.43)	(1216.09)

[a] $f_1 = 629.49\ (575.98)$; $f_2 = 1825.29\ (1867.55)$; $f_\alpha = 20.21\ (20.21.)$; $f_{12} = -35.92\ (-18.24)$ Nm^{-1}

[b] $f_1 = 645.23\ (583..58)$; $f_2 = 1418.77\ (1436.03)$; $f_\alpha = 25.69\ (25.69)$; $f_{12} = -7.16\ (-27.32)$ Nm^{-1}.

[c] $f_1 = 616.32\ (552.69)$; $f_2 = 887.44\ (907.6)$; $f_\alpha = 14.89\ (14.89)$; $f_{12} = 15.7\ (-39.66)$ Nm^{-1}

[d] Values calculated using the Teller-Redlich product rule.

by microwave spectroscopy. The results are given in Table V.

(2b) In contrast, both hydrogen hypobromite[26] and hydrogen hypoiodite, recently discovered[29] to complete this quartet, have yielded vibrational absorption spectra only in matrices, in which other than noble gas atoms were adjacent to these molecules. The resulting perturbations of wavenumbers are probably significant, but no other vibrational data are available. The geometry is deduced on the basis of correlations and related molecules. The results are in Table VI.

(3a) Data and discussion for the trio of imino molecules hydrogen isocyanide, iminosilicon and iminogermanium have previously been presented[30]. In the results recomputed in Table VII on the same basis as the preceding molecules, only the f_α force constant is changed on conversion to the new basis.

(3b) The additional trio of linear methylidene molecules hydrogen cyanide[30,31], formyl radical in the $A^2\pi$ state[32] and methinophosphide[33] also included here for comparison purposes. All data are for the gas phase species. The results are listed in Table VIII.

Discussion

The major aspects of the analyses are best presented graphically, in Figures 2 and 3. In these, f_{HX} and f_α (in 2) and f_{XY} (in 3) are plotted for all the molecules studied. The values there indicated are those derived on the basis of the anharmonicity correction, as these force constants generally reproduce the experimental wavenumbers considerably better than the alternative sets. The diameter of the circles enclosing each point indicates the precision of determination of the force constants. In all cases, the values for linear molecules were very precise, experimental wavenumbers being regenerated with a precision less than 0.1%. For the non-linear molecules, the precision was in the range 0.3-0.7%, except for HCO $B\ ^2A'$ and HNO $B\ ^1A'$ for which experimental accuracy of wavenumbers is inferior. These specified precisions apply to computations using unadjusted wavenumbers (i.e., those results in parentheses in Tables I-VIII); application of the anharmonicity correction generally improved precision by a factor of 1.5-2, thereby proving the value of the correction procedure.

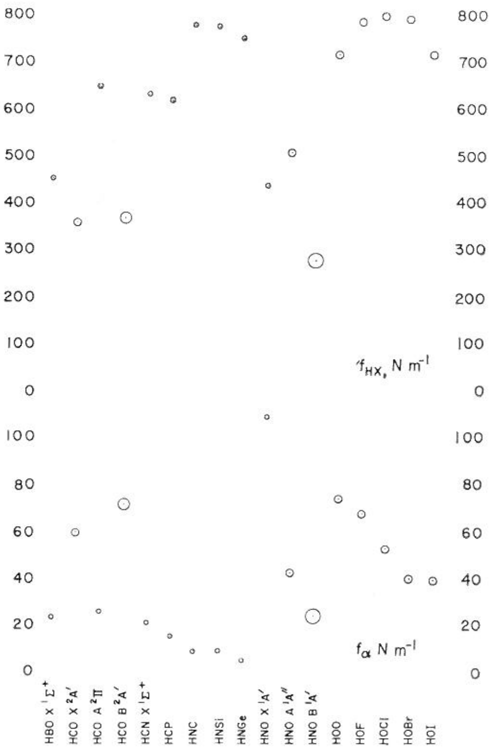

Figure 2. Plot of f_α and f_{HX}, force constants for bending and H-atom stretching vibrations, for various triatomic molecules.

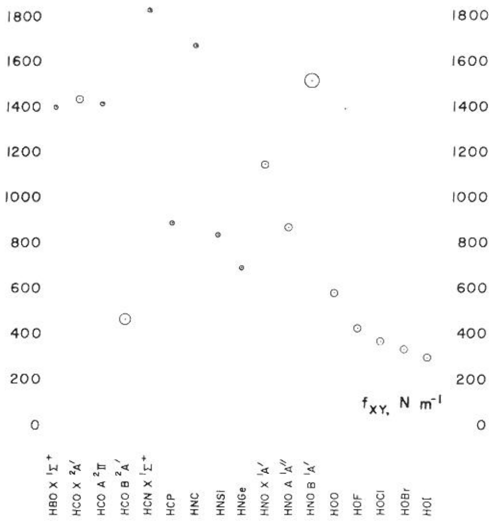

Figure 3. Plot of f_{XY}, force constant for heavy-atom stretching vibration, for various triatomic molecules.

Some obvious trends discernible in the figures relate to the periodic table. For the hypohalites, f_{xy} decreases monotonically in the order of increasing atomic number. A similar decrease for the fourth and fifth groups can be observed in the series of compounds HNC, HNSi and HNGe, and HCN and HCP[30,34]. Differences in the environment of the molecules, either free or under the perturbation of polar neighbours, are unlikely to reverse the trends shown. For the first-row central atoms of the ground-state radicals HBO, HCO, HNO and HOO, f_{xy} gradually decreases, although being very similar for the first two compounds. The changes within the different electronic states of either HCO or HNO are irregular, reflecting the varying nature of dissociation processes. Trends are also evident for the deformation constant f_α, the most obvious being that f_α for linear molecules is generally much smaller than for angular molecules. Also the same kind of decrease of f_α with atoms beyond the first row is notable within appropriate series. For the f_{HX} force constants, trends are less obvious, the variation in values being relatively small within a given series. The interaction force constants, not displayed, in general show no regularities which can be related to periodic properties, but seem merely to indicate, by their magnitude, relative proximity of wavenumbers for normal vibrations of similar transition energies. The physical significance of the values of interaction constants is indeed questionable, despite the fact that observed wavenumbers are far better fitted with their inclusion. The reason for this lack of significance is that changes in calculated wavenumbers, upon deletion of these constants from the potential function, would rarely exceed the inherent error in the harmonic approximation, about five per cent.

Apart from the fundamental interest in force constants as basic structural parameters, these quantities can also be used to test the accuracy of molecular electronic wavefunctions or energy hypersurfaces derived therefrom. In this regard, it is believed that the sets of force constants obtained with anharmonicity corrections will usually be more closely related to the second derivatives of energy with respect to the normal coordinate than the alternative set, because the effect of finite amplitudes of molecular vibrations is lessened in the correction procedure. However, implicit in the use of the same anharmonicity factor of 1.0456 (or 1.0331) for all hydrides (or deuterides) is the assumption of similarity of dissociation energies of HX (or DX) bonds in different compounds. For HNO and HCO ground states, this assumption is demonstrably invalid, as the HN or HC dissociation energies are especially small[10]. Comparison with Dixon's anharmonic force field[35] for HCO X $^2A'$ furnishes proof of the rough approximation of harmonic potential functions. Reflecting the small HC dissociation energy, the appropriate value of the anharmonicity factor for this molecule (in the ground state) is 1.11. Obviously with appropriate anharmonicity corrections applied to all vibrations, the fit of experimental wavenumbers of different isotopic molecules could approach the limit of 0.05% imposed by the Börn Oppenheimer approximation. But the value of the magnitudes 1.0456 and 1.0331 lies in their transferability, and in their justifiable origins[5], as much as in the improvement in fitting experimental wavenumbers gained by their inclusion.

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