447. *Force Constants in Polyatomic Molecules.*

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General solutions have been obtained for the force constants occurring in the potential functions governing the stretching vibrations of the linear triatomic grouping in the molecules HNCO, HNCS, HN_3, and $CH_3{\cdot}CN$. Reasonable sets of force constants are chosen for these molecules, reference molecules whose force constants are known explicitly being used in conjunction with Gordy's relationships.

The nature of chemical bonds and the modification of a particular bond in different environments have been the subject of many investigations. The aim has been to obtain some attribute such as dipole moment or bond energy which represents a partial description of the bond. In this respect force constants are of great value in the study of molecular structure and especially of hybrid linkages. Their particular disadvantage has been the difficulty of obtaining reasonably precise values in cases where isotopic frequencies are unknown. Formerly, the customary practice was to derive relations between the vibration frequencies, on one hand, and the molecular parameters and force constants, on the other [Herzberg, " Molecular Spectra and Molecular Structure," Vol. II (D. Van Nostrand Company Inc., New York, 1945); Wu, " Vibrational Spectra and Structure of Polyatomic Molecules " (Edwards Bros. Inc., Ann Arbor, Michigan, 1946); equations (7), (8), this paper]. Provided the potential function contained fewer force constants than the number of known fundamental frequencies of the molecule, or where a sufficient number of isotopic frequencies were known, assignment of the frequencies to definite modes of vibration enabled the force constants to be determined. In the majority of cases an explicit solution is not possible, and the number of unknown force constants has been reduced by (i) the transfer of values found in related molecules, or (ii) limiting the number of interaction terms in the potential function to those deemed to be the most important.

Both these procedures are somewhat arbitrary and open to criticism. The absolute value of a force constant depends on the environment of the bond or group considered. This varies even in closely related molecules; for instance, Linnett (*J. Chem. Physics*, 1940, **8**, 91) has shown that the stretching force constant of the CH bond, f_{CH}, increases by 6% on passing from methyl fluoride to the iodide. In general, even the relative magnitudes of interaction constants are unknown and the neglect of some such terms as compared with others retained is, in most cases, entirely arbitrary. The usual frequency force-constant relations [equations (7) and (8)] contain terms of the form AF; A is a function of the masses and geometry of the molecule and F contains the interaction constants. Even if F is small, the product AF may not be negligible; it is necessary, then, when omitting interaction terms from potential functions to justify the neglect of the product AF relative to those others, $A'F'$, which are retained.

It is more usual now to include all possible cross-terms in the potential function and to obtain ranges of solution for the force constants (Glockler and Tung, *J. Chem. Physics*, 1945, **13**, 388; Torkington, *ibid.*, 1949, **17**, 357; *Proc. Phys. Soc.*, 1950, *A*, **63**, 804; 1951, *A*, **64**, 32; Thomas, *J. Chem. Physics*, 1951, **19**, 1162). This approach was introduced by Duchesne (*Mem. Soc. roy. Sci. Liége*, 1943, **1**, 429). The range of solutions for the force constants can be conveniently plotted as a function of a parameter p (Torkington, *loc. cit.*; Thomas, *loc. cit.*). From these f–p curves a particular set of force constants can be chosen by reference to one of the bond-lengths used in conjunction with a reference molecule (whose force constants are known explicitly) and, say, Gordy's relationships (*J. Chem. Physics*, 1946, **14**, 305; 1947, **15**, 305). This procedure has led to satisfactory sets of force constants for the molecules ClCN, BrCN, ICN, and OCS (Thomas, *loc. cit.*).

The Solution for the Force Constants.—The notable advances in the solution of secular equations recently made by Torkington (*ibid.*, 1949, **17**, 357, 1026) have made available a powerful technique for obtaining ranges of solutions for the force constants. For an n-atomic molecule, $3n$ Cartesian displacement co-ordinates (x_i) are needed to describe its configuration at any instant. In terms of these, the kinetic energy is

$$2T = \sum_{i=1}^{i=3n} m_i x_i^2$$

where m_i is the mass associated with x_i. It is more convenient to express the potential-energy function in terms of internal co-ordinates (Δ_k) such as changes in bond-lengths, Δr, or bond angles, $\Delta\alpha$.

The internal co-ordinates, Δ_k, may be expressed in terms of the Cartesians (Torkington, *Trans. Faraday Soc.*, 1950, **46**, 27) by linear relations :

$$\Delta_k = \sum_{i=1}^{i=3n} a_{ki}\, x_i \qquad (k = 1, 2, \ldots\ldots . N)$$

where $N = 3n - 6$ represents the number of vibrational degrees of freedom of the molecule. Following Torkington's procedure, if a matrix $[A]$ is defined by the elements

$$A_{kl} = A_{lk} = \sum_{i=1}^{i=3n} a_{ki}\, a_{li}\, M/m_i \qquad (k, l = 1, 2, \ldots . N) \quad . \; . \; . \; . \; . \quad (1)$$

then the secular may be written in matrix form as

$$|dA - \lambda I| = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

In equation (1), m_i is the mass associated with a_{ki} and a_{li}; M is some arbitrary mass introduced so that A_{kl} shall be dimensionless. In equation (2), I is the unit matrix and $\lambda = 4\pi^2 \mathbf{c}^2 \nu^2 M$, ν being a vibration frequency in cm.$^{-1}$ and $\mathbf{c}$ the velocity of light in cm. sec.$^{-1}$; d is the force constant matrix, whose elements, d_{ij}, occur in the general quadratic potential function,

$$2V = \sum_{i=1}^{N} \sum_{j=1}^{N} d_{ij}\, \Delta_i\, \Delta_j \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

Solution of the secular equation gives the values of the roots λ_1 to λ_N in terms of d_{ij} and the elements of $[A]$. Since in general the force constants, d_{ij}, are unknown, the process is reversed in practice and force constants are calculated from the experimentally determined vibration frequencies.

Using certain assumptions, Torkington has achieved a general solution for the secular equation in terms of the force constants. The solution is

$$d_{ij} = \sum_{k=i}^{k=N} (e_{ik}\, e_{jk}/e_{kk}\, h_{kk})\lambda_k \quad (i \geqslant j)$$

in which the subsidiary matrices $[e]$ and $[h]$ have elements defined as follows :

$$e_{ij} = {}^{j}|A|_{ji} \quad (= 0 \text{ for } i > j)$$
$$h_{ij} = \sum_{k=1}^{k=j} A_{ik}\, e_{kj} \quad (= 0 \text{ for } i < j)$$

${}^{j}|A|_{ji}$ is a first minor of element ji, with correct sign, of the jth order determinant ${}^{j}|A|$ derived from the first j rows and columns of $[A]$.

The linear triatomic molecule XYZ (Fig. 1) has two parallel stretching vibrations, ν_1 and ν_2. The higher fundamental frequency, ν_1, can be considered as arising from a pseudo-antisymmetric mode of vibration; the other, ν_2, from a pseudo-symmetric mode.* These stretching vibrations of the XYZ group can be described by the co-ordinates (Thomas, *loc. cit.*)

$$\Delta_1 = \Delta r_1 - p\Delta r_2 \text{ for } \nu_1$$

and

$$\Delta_2 = \Delta r_2 + p\Delta r_1 \text{ for } \nu_2$$

Here p is a variable parameter which takes account of the fact that, although ν_1 is mainly associated with changes in r_1, yet r_2 is also affected to some extent; Δ_1 and Δ_2 are valence-force symmetry co-ordinates for the vibrations ν_1 and ν_2 for all values of p.

FIG. 1. *The stretching vibrations of the linear triatomic molecule* XYZ.

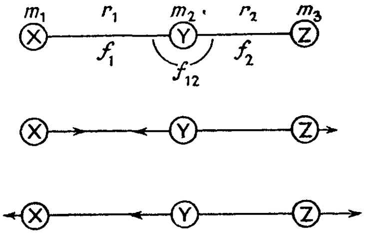
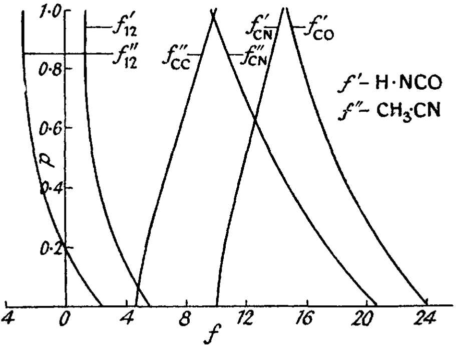


FIG. 2. *Variation of the force constants,* f, *with* p.



The vibrations ν_1 and ν_2 have been shown (Thomas, *loc. cit.*) to be either (i) one pseudo-antisymmetric and the other pseudo-symmetric, or (ii) both pseudo-antisymmetric, the first possibility being the more probable. If r_1 is taken to be the bond primarily associated with the higher pseudo-antisymmetric frequency, then, with $0 \leqslant p \leqslant 1$, the physically plausible range of force constant values is obtained; the matrices for this system have been derived (Thomas, *loc. cit.*) and will not be repeated here.

In terms of the valence-force symmetry co-ordinates the potential function for the system is

$$2V = d_{11}\Delta_1^2 + d_{22}\Delta_2^2 + 2d_{12}\Delta_1\Delta_2 \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The valence-force potential function may be written as

$$2V = f_1\Delta r_1^2 + f_2\Delta r_2^2 + 2f_{12}\Delta r_1\Delta r_2 \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Comparison of (4) and (5) leads to the relations

$$\left.\begin{aligned} f_1 &= d_{11} + p^2 d_{22} + 2\,pd_{12} \\ f_2 &= d_{22} + p^2 d_{11} - 2\,pd_{12} \\ f_{12} &= p(d_{22} - d_{11}) + (1 - p^2)d_{12} \end{aligned}\right\} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

By varying the value of p within the range $0 \leqslant p \leqslant 1$ different sets of values for the valence-force constants, f, are obtained. Curves of f against p may then be drawn, and the most reasonable set of constants chosen. These curves indicate the arbitrariness of many

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* The higher frequency need not necessarily be related to the pseudo-antisymmetric vibration (see Bernstein and Powling, *J. Chem. Physics*, 1950, **18**, 685) and p. 2388.

former force-constant treatments, even for simple molecules, in the absence of isotopic frequencies.

The possible solutions for the force constants are given in Table 2, and typical *f–p* curves in Fig. 2.

Bond Lengths and Frequency Assignment.—The molecules dealt with in this paper are $CH_3{\cdot}CN$, HNCO, HNCS, and HN_3. The motions of the hydrogen atoms, especially the stretching modes, are not coupled to any great extent with those of the rest of the molecule. To a good approximation the methyl group in $CH_3{\cdot}CN$ and the NH groups in the other molecules can be considered as rigid groups; *i.e.*, the molecules are considered as three-particle systems. The three heavy atoms in these molecules are collinear (Herzberg and Reid, *Discuss. Faraday Soc.*, 1950, **9**, 92; Beard and Dailey, *J. Chem. Physics*, 1950, **18**, 1437; Amble and Dailey, *ibid.*, p. 1422).

The bond lengths and frequency assignments are given in Table 1, together with those of certain reference molecules, whose force constants are beyond question.

In the HNCS molecule Reid (*J. Chem. Physics*, 1950, **18**, 1512) assigned a value of 1963 cm.$^{-1}$ to ν_1 and one of 995 cm.$^{-1}$ to ν_2, the pseudo-symmetric stretching vibration. These frequencies give a lower limit of $8{\cdot}55 \times 10^5$ dynes/cm. for the bond-stretching force constant, f_{CS}, of the CS link. This value for f_{CS} is appreciably greater than that found in CS_2 even though the CS bond length is shorter in CS_2 than in HNCS (see Table 1). This may be taken as an indication that Reid's assignment of $\nu_2 = 995$ cm.$^{-1}$ is incorrect, and furthermore that this value is too high.

TABLE 1.

Molecule	Bond	Bond length, Å	Bond stretching frequency, cm.$^{-1}$	Force constant $\times 10^{-5}$, dynes/cm.
CS_2	CS	1·554 [a]	—	7·5 [a]
OCS	CO	1·161 [b]	2064 [i]	15·6
	CS	1·560	859	7·2 [i]
HNCS	CN	1·218 [c]	1963	—
	CS	1·557	860	
HCN	CH	1·059 [d]	3312·9 [a]	5·70 [m]
	CN	1·157	2089·0	18·07
$H_3C{\cdot}CN$	CN	1·158 [e]	2267 [j]	—
	CC	1·460	919·1	
CO_2	CO	1·163 [a]	—	15·5 [a]
HNCO	CO	1·171 [f]	2274 [f]	—
	CN	1·207	1327	
ON_2N_3	N_2N_3	1·126 [g]	2223·5 [k]	17·88 [n]
$HN_1N_2N_3$	N_2N_3	1·134 [h]	2140·4 [l]	—
	N_1N_2	1·240	1269·0	

[a] Herzberg, *loc. cit.* [b] Townes, Holden, and Merritt, *Physical Rev.*, 1948, **74**, 1113. [c] Beard and Dailey, *loc. cit.* [d] Gordy, *Rev. Mod. Phys.*, 1948, **20**, 668. [e] Kessler, Ring, Trambarulo, and Gordy, *Physical Rev.*, 1950, **79**, 54. [f] Herzberg and Reid, *loc. cit.* [g] Coles, Elyasch, and Gorman, *Physical Rev.*, 1947, **72**, 973. [h] Amble and Dailey, *loc. cit.* [i] Callomon, McKean, and Thompson, *Proc. Roy. Soc.*, 1951, *A*, **208**, 341. [j] Venkateswarlu, *J. Chem. Physics*, 1951, **19**, 293. [k] Plyler and Barker, *Physical Rev.*, 1931, **38**, 1827. [l] Davies, *Trans. Faraday Soc.*, 1939, **35**, 1184; Eyster and Gillette, *J. Chem. Physics*, 1940, **8**, 369. [m] Coulson, Duchesne, and Manneback, " Contribution a l'étude de la structure moleculaire," Liége, 1948, p. 33. [n] Richardson and Wilson, *J. Chem. Physics*, 1950, **18**, 694.

If the NH group in *iso*thiocyanic acid is considered as a single particle, HNCS and OCS are isosteric. They are also isoelectronic. On simple grounds, then, it is to be expected that the frequencies ν_1 and ν_2 in these molecules should lie close together in value. This is true for Reid's ν_1. From the values quoted in Table 1, a value of ~860 cm.$^{-1}$ is to be expected for ν_2.

It is possible to get an estimate of ν_2 as follows. Gordy's relationships (*loc. cit.*) connecting bond order, *N*, bond length, *r*, and force constant, *f*, for a link AB are

$$N = a/r^2 + b \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(i)}$$

$$f = 1{\cdot}67N(x_A x_B/r^2)^{\frac{3}{4}} + 0{\cdot}30 \quad . \; . \; . \; . \; . \; . \; . \; . \quad \text{(ii)}$$

where *a* and *b* are constants for a specific bond, *r* is in Ångström units, and *f* in units of 10^5 dynes/cm.

From Table 1 and equation (i) the ratio of the bond orders for the CN links in HNCO and HNCS is

$$N\ (\mathrm{HNCO}) : N\ (\mathrm{HNCS}) = 1 : 0{\cdot}991$$

and in CS_2 and HNCS, for the CS links,

$$N\ (\mathrm{CS_2}) : N\ (\mathrm{HNCS}) = 1 : 0{\cdot}957$$

Gordy's equation (ii) gives N_{CN} (HNCO) = 2·37, when the value of $f_{\mathrm{CN}} = 13{\cdot}98 \times 10^5$ dynes/cm. derived in this paper is used. With the ratio derived above this gives a value of $N_{\mathrm{CN}} = 2{\cdot}35$ in H·NCS which yields a force constant value of $f_{\mathrm{CN}} = 13{\cdot}80 \times 10^5$ dynes/cm. on substitution in relation (ii). Similarly, a value of $6{\cdot}80 \times 10^5$ dynes/cm. is obtained for f_{CS} in H·NCS.

The determinantal secular equation corresponding to the two parallel vibrations of a linear three-particle system yields the equations (Wu, *loc. cit.*, p. 154)

$$\lambda_1 + \lambda_2 = \frac{m_1 + m_2}{m_1 m_2} f_1 + \frac{m_2 + m_3}{m_2 m_3} f_2 - \frac{2}{m_2} f_{12} \quad . \quad . \quad . \quad . \quad (7)$$

$$\lambda_1 \lambda_2 = \frac{m_1 + m_2 + m_3}{m_1 m_2 m_3} (f_1 f_2 - f_{12}{}^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

On substitution of the values given above for f_{CN} (f_1) and f_{CS} (f_2) and the known value for λ_1 solution of these two simultaneous equations in λ_2 and f_{12} ($\Delta r_{\mathrm{CN}}\ \Delta r_{\mathrm{CS}}$) yields the values

$$\nu_2 = 846\ \mathrm{cm.}^{-1} \text{ and } f_{12} = 0{\cdot}98 \times 10^5\ \text{dynes/cm.}$$

These values may be compared with those given in Table 3 for the related molecules CS_2 and OCS. The agreement is excellent. On simple grounds, since r_{CS} (OCS) > r_{CS} (HNCS), it might be expected that ν_2 (OCS) < ν_2 (HNCS), the difference, however, being small.

TABLE 2.

		Value of p				
Molecule	Force constant	0·00	0·25	0·50	0·75	1·00
HNCO	f_{CO}	24·21	20·63	17·89	16·09	14·78
	f_{CN}	10·15	10·78	11·92	13·31	14·50
	f_{12}	5·80	3·23	1·94	1·56	1·44
HNCS	f_{CN}	17·11	14·11	11·88	10·28	9·13
	f_{CS}	6·38	6·95	8·13	9·42	10·64
	f_{12}	3·55	1·23	0·04	−0·51	−0·71
$HN_1N_2N_3$	$f_{\mathrm{N_2N_3}}$	21·21	18·30	15·99	14·30	13·09
	$f_{\mathrm{N_1N_2}}$	9·27	9·85	10·99	12·28	13·41
	f_{12}	4·64	2·29	1·12	0·63	0·51
CH_3·CN	f_{CN}	20·95	16·89	13·83	11·54	9·97
	f_{CC}	4·74	5·51	7·04	8·65	10·12
	f_{12}	2·55	−0·53	−2·00	−2·67	−2·82
OCS	f_{CO}	19·36	15·76	13·11	11·30	9·96
	f_{CS}	6·50	7·16	8·56	9·97	11·36
	f_{12}	3·71	1·05	−0·35	−0·93	−1·15

Simple considerations suggest that, relatively to ν_1, ν_2 would be strong in the Raman spectrum and comparatively weak in the infra-red. Goubeau and Gott's results for HNCS (*Ber.*, 1940, **73**, 127) show the presence of a strong band at 848 cm.$^{-1}$ which has been allocated to ν_2.

The infra-red spectrum of HNCS shows the presence of parallel bands centred at 841 cm.$^{-1}$ and 860 cm.$^{-1}$ (Reid, private communication). The indications are, then, that ν_2 is the parallel band at 860 cm.$^{-1}$, this value being greater than ν_2 in OCS. This fundamental frequency is found in the Raman spectrum at 848 cm.$^{-1}$ in carbon tetrachloride solution owing to a solvent effect. It might be objected that the band found at 860 cm.$^{-1}$ has too low an intensity for a fundamental. For HNCS the ratio of the intensities of ν_1 and ν_2 is ~50 : 1 ; for the corresponding vibrations in HNCO (Herzberg and Reid, *loc. cit.*) the ratio is 200 : 1. It seems, then, that the 860 cm.$^{-1}$ band cannot be ruled out on considerations of intensity alone.

An Empirical Method of determining Force Constants.—The *f–p* curves of Fig. 2 represent an infinite number of sets of force constants. In order to arrive at the most reasonable set of force constants, use may be made of Gordy's equations (*loc. cit.*) in conjunction with reference molecules. From the bond lengths given in Table 1 and relation (i), the ratio of the bond orders for the CO bonds in HNCO and CO_2 is 1 : 1·026. Relation (ii) gives $N = 2{\cdot}24$ for CO_2 on substitution of the known value for the force constant ($15{\cdot}5 \times 10^5$ dynes/cm.; Herzberg, *loc. cit.*). From the known ratio we obtain a value $N_{CO} = 2{\cdot}18$ for the CO bond in HNCO. This value of the bond order yields a force constant value of $f_{CO} = 15{\cdot}00 \times 10^5$ dynes/cm. on substitution in relation (ii). This value for f_{CO} being used, the corresponding values for f_{CN} and f_{12} are obtained from the f–p curves for HNCO. The set of force constants thus obtained is given in Table 3.

Similarly, sets of force constants are obtained for HNCS, HN_3, and $CH_3{\cdot}CN$; OCS, NNO, and HCN, respectively, being used as reference molecules.

The spectrum of OCS has recently been reinvestigated (Callomon, McKean, and Thompson, *loc. cit.*). On using their values for the stretching frequencies and CO_2 as reference molecule, the force constants given in the lower part of Table 3 are obtained. Comparison with the force constants obtained explicitly by using isotopic frequencies (*idem, ibid.*) shows that in the case of OCS, the force constants derived empirically in this paper have an overall accuracy of 2%.

TABLE 3.

Molecule	Reference molecule	Force constant	$f \times 10^{-5}$, dynes/cm.	Molecule	Reference molecule	Force constant	$f \times 10^{-5}$, dynes/cm.
CO_2	—	f_{CO}	15·5	HNCO	CO_2	f_{CO}	15·0
		f_{12}	1·29			f_{CN}	14·3
CS_2	—	f_{CS}	7·5			f_{12}	1·45
		f_{12}	0·60	HNCS	OCS	f_{CN}	13·4
OCS	—	f_{CO}	15·6			f_{CS}	7·3
		f_{CS}	7·2			f_{12}	0·80
		f_{12}	1·0	$HN_1N_2N_3$	ON_2N_3	$f_{N_2N_3}$	17·3
NNO	—	f_{NN}	17·88			$f_{N_1N_2}$	10·3
		f_{NO}	11·39			f_{12}	1·67
		f_{12}	1·36	$CH_3{\cdot}CN$	H·CN	f_{CN}	18·0
HCN	—	f_{CN}	18·07			f_{CC}	5·2
		f_{CH}	5·70			f_{12}	0·2
		f_{12}	−0·30	OCS	CO_2	f_{CO}	15·6
						f_{CS}	7·3
						f_{12}	0·95

Discussion.—The f–p curves of Fig. 2 clearly indicate the most physically plausible range of values for the force constants. The fact that the solutions obtained are reasonable implies that the initial assumption regarding the geometrical form of the parallel vibrations is sound; *viz.*, ν_1, the higher frequency, is pseudo-antisymmetric in character, and ν_2 pseudo-symmetric. The values obtained for the stretching force constants (Table 3) are very reasonable. They fall sensibly into line with the values obtained for similar bonds in related molecules, in those cases where complete quadratic potential functions have been used. The force constants obtained for the CN links in HNCO and in HNCS indicate appreciable double-bond character; in $CH_3{\cdot}CN$ the indications are that the CN bond is almost a pure triple bond. This view is supported by the normal single-bond value for f_{CC} and the small value obtained for f_{12}, which indicates little interaction between the bonds.

There has been considerable discussion about the valency of the nitrogen atoms in compounds such as HN_3 (Samuel, *J. Chem. Physics*, 1944, **12**, 167, 180, 380, 521; 1945, **13**, 251, 572; Wheland, *ibid.*, p. 239). With Gordy's equation (ii) the force-constant values given in Table 3 yield bond orders of 2·40 and 1·61 for the bonds N_2N_3 and N_1N_2, respectively. The total bonding power of the central nitrogen atom is then ~4.

The greatest interest of this work lies in the values obtained for, and the sign of, the length–length interaction constant, f_{12}. It is now becoming clear that, for linear triatomic groupings whose elements occur in the first and the second short period (excluding hydrogen), f_{12} has quite an appreciable positive value centred about 1×10^5 dynes/cm. Linnett and Hoare (*Trans. Faraday Soc.*, 1949, **45**, 844) have given an explanation of the sign of f_{12} in triatomic molecules XYZ. Their ideas are here applied to the linear groupings of the molecules considered. Linnett and Hoare compared the changes in bond length in going from XYZ to the diatomic molecules XY and YZ. They showed that if r_{XY} (XY) > r_{XY} (XYZ), then f_{12} is expected to be negative. They also consider that if f_{XY} (XY) > f_{XY} (XYZ), then f_{12} will be positive. The data necessary for testing these ideas are given in Table 4, which shows that, in the case of the molecules considered here, Linnett and Hoare's criteria lead to the correct sign for f_{12} in all cases, *i.e.*, positive.

TABLE 4.

		r, in Å			$f \times 10^{-5}$, dynes/cm.		
Molecule	Link	r' : XYZ	r'' : XY	$r'' - r'$	f' : XYZ	f'' : XY †	$f'' - f'$
HNCO	CO	1·171	1·13 [a]	−0·04	15·00	18·52	+3·52
	CN	1·207	—	—	—	—	—
HNCS	CS	1·557	1·53 [b]	−0·027	7·3	8·32	+1·02
	CN	1·218	—	—	—	—	—
$HN_1N_2N_3$	N_2N_3	1·134	1·09 [b]	−0·044	17·3	22·40	+5·1
	N_2N_1	1·240	1·15 [a]	−0·09	10·3	15·50	+5·20
OCS	CO	1·161	1·13 [a]	−0·031	15·6	18·52	+2·92
	CS	1·560	1·53 [b]	−0·030	7·2	8·32	+1·12

[a] Herzberg, *loc. cit.* [b] Spöner, " Molekulspektren." † Linnett and Hoare, *loc. cit.*

The actual set of force constants chosen for a particular molecule may be criticised. It should be emphasised that the greatest value of the method lies in providing the possible sets in a convenient graphical form. The most plausible ranges for the various force constants can be seen at a glance, and by reference to the outside limits of one of the stretching force constants the sign of f_{12} is decided in most cases.

Furthermore, the use of Gordy's equations has been found in previous examples to provide an adequate empirical basis for choosing a " best " set of constants which can scarcely be distinguished (within the limits set by neglecting anharmonicity, etc.) from those force constants unequivocably defined, *e.g.*, by isotopic frequencies. At the least, the constants in Table 3 provide strictly comparable sets of parameters for the respective general potential functions. The latter, it may be claimed, provide the most explicit characterisation of the forces defining the equilibrium state of the molecules. Thus, not only is a quantitative measure of the difference in the N–N bonds of HN_3 provided, but the close relation of the latter to those in N_2O is clear. A careful comparison of the constants for HNCO and CO_2, HNCS and CS_2, etc., is justified. Further discussion of these aspects will be undertaken later.

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