The Centrifugal Distortion and the l-Type Doubling Constants in Linear XYZ-Type Molecules. The Determination of Force Field by These Constants

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(Received January 16, 1958)

I

It is usually impossible to determine the set of force constants for a molecule only through vibrational frequencies, unless isotopic substitution is made. Assumptions have frequently been made to reduce the number of unknown constants; one may mention examples of central force field, valence force field(1) or Urey-Bradley field(2). It is, however, possible to use other experimental data than vibrational frequencies for obtaining the force constants. Wilson and Kivelson(3,4) showed that the centrifugal distortion constants of asymmetric top molecules can be used for the determination of the force constants in general force field. However, their results on sulfur dioxide(4) showed a discrepancy with those of infrared absorption spectra(5) based upon the isotopic substitution. An experimental error or other sources might contribute to this discrepancy, so that it is worth while to discuss about these points in a simpler system such as linear XYZ-type molecules.

The linear XYZ-type molecule has three fundamental modes: two of them are stretching vibrations along the molecular axis (parallel vibrations) and the other is a degenerate bending mode (perpendicular one). The force constant for the latter vibration can be determined by the value of frequency alone, but two observed frequencies are insufficient to determine three force constants associated with the former two modes. The centrifugal distortion constant will give additional information about the parallel vibrations. One may, however, note that there is another constant available: the *l*-type doubling constant. The Coriolis force lifts the degeneracy of the bending vibration and the separation between the two resulting energy states can accurately be measured by the microwave spectroscopy(6). Since the centrifugal distortion and the *l*-type doubling constants give independent information, one can test the experimental error or the validity of the underlying assumption made in the theory. A sum rule is found to be useful for such a test.

II

The centrifugal force reduces the effective rotational constant and hence the rotational energy. The quantum mechanical expression for the energy decrease by centrifugal distortion is given by

$$\mathbf{H}_D=(1/2)(\mu_{xx}\mathbf{P}^2{}_x+\mu_{yy}\mathbf{P}^2{}_y)-(1/2)(\mu^e{}_{xx}\mathbf{P}^2{}_x+\mu^e{}_{yy}\mathbf{P}^2{}_y) \qquad (1)$$

where $\mathbf{P}_x$ and $\mathbf{P}_y$ denote angular momentum operators, μ_{xx} and μ_{yy} inverses of moment of inertia, and the superscript e of μ refers to the equilibrium. Now μ_{xx} and μ_{yy} can be expanded as power series of the internal coordinates, $\varDelta R_{XY}$ and $\varDelta R_{YZ}$, but the moment of inertia is usually defined in terms of Cartesian coordinates of individual atoms. The Cartesian coordinates of composing atoms are bound to each other by the complicated Eckart condition, and it is somewhat difficult to obtain the expansion of the moment of inertia in terms of internal coordinates. Hence it is very desirable to derive in general a relation between the normal coordinates and the Cartesian coordinates. The process using the **B**-matrix has already been discussed by the authors.(7) The relation is given by

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1) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, D. Van Nostrand Co., New York, 1949.

2) H. C. Urey and C. A. Bradley, *Phys. Rev.* **38**, 1969 (1931).

3) D. Kivelson and E. B. Wilson, Jr., *J. Chem. Phys.* **20** 1575 (1952); **21**, 1229 (1953).

4) D. Kivelson, ibid. **22**, 904 (1954); L. Pierce, ibid. **24**, 139 (1956).

5) S. Polo and M. K. Wilson, ibid. **22**, 900 (1954).

6) R. G. Shulman and C. H. Townes, *Phys. Rev.* **77**, 421 (1950).

7) Y. Morino and E. Hirota, *J. Chem. Phys.* **23**, 737 (1955).

$$\mathbf{X}=\mathbf{M}^{-1}\mathbf{B}'\mathbf{U}'(\mathfrak{L}^{-1})'\mathbf{Q} \tag{2a}$$

$$=\mathbf{M}^{-1}\mathbf{B}'(\mathbf{L}^{-1})'\mathbf{Q} \tag{2b}$$

where **X** and **Q** denote the Cartesian coordinates and the normal coordinates matrices. $\mathbf{L}^{-1}$ is easily replaced by **L** through the relation $\mathbf{L}\mathbf{L}'=\mathbf{G}$, or $\mathbf{L}^{-1}=\mathbf{L}'\mathbf{G}^{-1}$. [Cf. Eq. 20]

The expression of the **B**-matrix is particularly simple in the present case; then it sufficices to consider only the Cartesian coordinates along the molecular axis (z-axis):

$$\mathbf{B}=\begin{pmatrix}1 & -1 & 0\\ 0 & 1 & -1\end{pmatrix} \tag{3}$$

Hence Eq. 2b becomes

$$\begin{pmatrix}\Delta z_X\\ \Delta z_Y\\ \Delta z_Z\end{pmatrix}=\begin{pmatrix}\dfrac{(m_Y+m_Z)L_{11}+m_ZL_{31}}{m_X+m_Y+m_Z} & \dfrac{(m_Y+m_Z)L_{13}+m_ZL_{33}}{m_X+m_Y+m_Z}\\ \dfrac{-m_XL_{11}+m_ZL_{31}}{m_X+m_Y+m_Z} & \dfrac{-m_XL_{13}+m_ZL_{33}}{m_X+m_Y+m_Z}\\ \dfrac{-m_XL_{11}-(m_X+m_Y)L_{31}}{m_X+m_Y+m_Z} & \dfrac{-m_XL_{13}-(m_X+m_Y)L_{33}}{m_X+m_Y+m_Z}\end{pmatrix}\begin{pmatrix}Q_1\\ Q_3\end{pmatrix} \tag{4}$$

The moment of inertia I_{xx} is given by

$$I_{xx}=\sum_i m_i(y_i^2+z_i^2)\cong\sum_i m_iz_i^{e2}+2\sum_i m_iz^e_i\Delta z_i \tag{5}$$

where $y_i=\Delta y_i$ and $z_i=z^e_i+\Delta z_i$. The same expression holds for I_{yy}. Thus the inverse of the moment of inertia $\mu_{xx}=1/I_{xx}$ becomes

$$\mu_{xx}=(1/I^e_{xx})(1-2\sum_i m_iz^e_i\Delta z_i/I^e_{xx}+\cdots\cdots), \tag{6}$$

where the equilibrium positions of individual atoms z^e_i can readily be calculated

$$z^e_X=[(m_Y+m_Z)R_{XY}+m_ZR_{YZ}]/(m_X+m_Y+m_Z), \tag{7a}$$

$$z^e_Y=[-m_XR_{XY}+m_ZR_{YZ}]/(m_X+m_Y+m_Z), \tag{7b}$$

and

$$z^e_Z=[-m_XR_{XY}-(m_X+m_Y)R_{YZ}]/(m_X+m_Y+m_Z). \tag{7c}$$

If one uses the relations Eqs. 4 and 7 in Eq. 6 the expansion of the inverse of the moment of inertia in normal coordinates is obtained:*

$$\mu_{xx}=\mu_{yy}=(1/I^e_{xx})(1-2(bQ_1+aQ_3)/(I^e_{xx})^{1/2}+\cdots). \tag{8}$$

a and b are constants including the force constants and given by

$$a=\frac{m_X(m_Y+m_Z)R_{XY}+m_Xm_ZR_{YZ}}{(m_X+m_Y+m_Z)(I^e_{xx})^{1/2}}L_{13}+\frac{m_Xm_ZR_{XY}+(m_X+m_Y)m_ZR_{YZ}}{(m_X+m_Y+m_Z)(I^e_{xx})^{1/2}}L_{33}, \tag{9a}$$

and

$$b=\frac{m_X(m_Y+m_Z)R_{XY}+m_Xm_ZR_{YZ}}{(m_X+m_Y+m_Z)(I^e_{xx})^{1/2}}L_{11}+\frac{m_Xm_ZR_{XY}+(m_X+m_Y)m_ZR_{YZ}}{(m_X+m_Y+m_Z)(I^e_{xx})^{1/2}}L_{31}, \tag{9b}$$

and between them there exists a useful relation noted by Nielsen:[8]

$$a^2+b^2=1 \tag{10}$$

When Eq. 8 is inserted into Eq. 1 and terms of the order of Q^2_i are neglected,

$$\mathbf{H}_D=-\frac{bQ_1+aQ_3}{(I^e_{xx})^{3/2}}(\mathbf{P}^2_x+\mathbf{P}^2_y). \tag{11}$$

when the average of this term is taken over the vibrational state (v_1, v^l_2, v_3), the first order energy $(v_1v^l_2v_3|\mathbf{H}_D|v_1v^l_2v_3)$ is equal to zero, but the second order perturbation gives

$$E_D=\frac{|(v_1v^l_2v_3|\mathbf{H}_D|v_1\pm1v^l_2v_3)|^2}{\mp\boldsymbol{h}\nu_1}+\frac{|(v_1v^l_2v_3|\mathbf{H}_D|v_1v^l_2v_3\pm1)|^2}{\mp\boldsymbol{h}\nu_3}$$

$$=-4B^3_e\left[\frac{b^2}{(\boldsymbol{h}\nu_1)^2}+\frac{a^2}{(\boldsymbol{h}\nu_3)^2}\right][J(J+1)-1]^2. \tag{12}$$

Here $B_e=\hbar^2/2I^e_{xx}$ is the equilibrium rotational constant, and ν_1 and ν_3 are vibrational frequencies. Thus the centrifugal distortion constant D_e is given by

$$D_e=4B^3_e\left[\frac{b^2}{(\boldsymbol{h}\nu_1)^2}+\frac{a^2}{(\boldsymbol{h}\nu_3)^2}\right]. \tag{13}$$

The l-type doubling originates from the fact that the Coriolis interaction lifts the degeneracy of the bending vibration. This effect corresponds to an operator:[9]

$$\mathbf{H}_C=-\mathbf{h}_x\mathbf{P}_x-\mathbf{h}_y\mathbf{P}_y, \tag{14}$$

where

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* μ_{xy} is equal to zero. It is to be noted that μ_{xx} and μ_{yy} are independent of the bending coordinates, Q_{2x} and Q_{2y}. (Cf. ref. 9)

[8] H. H. Nielsen, *Revs. Modern Phys.* **23**, 90 (1951).

[9] E. B. Wilson, Jr., and J. B. Howard, *J. Chem. Phys.* **4**, 260 (1936).

$$\mathbf{h}_x=\frac{1}{2}[2\mu_{xx}\mathbf{p}_x+(\mathbf{p}_x\mu_{xx})+\mu_{xx}\mu^{1/2}(\mathbf{p}_x\mu^{-1/2})] \tag{15a}$$

and

$$\mathbf{h}_y=\frac{1}{2}[2\mu_{yy}\mathbf{p}_y+(\mathbf{p}_y\mu_{yy})+\mu_{yy}\mu^{1/2}(\mathbf{p}_y\mu^{-1/2})]. \tag{15b}$$

$\mathbf{p}_x$ and $\mathbf{p}_y$, vibrational angular momenta, are

$$\mathbf{p}_x=aQ_{2y}\mathbf{p}_1+bQ_{2y}\mathbf{p}_3-(aQ_1+bQ_3)\mathbf{p}_{2y} \tag{16a}$$

and

$$\mathbf{p}_y=-aQ_{2x}\mathbf{p}_1-bQ_{2y}\mathbf{p}_3+(aQ_1+bQ_3)\mathbf{p}_{2x}, \tag{16b}$$

respectively. The determinant of (μ_{xx}), μ, is simply $\mu^2{}_{xx}$, because, $\mu_{xx}=\mu_{yy}$ and $\mu_{xy}=0$. Since direct calculation shows that the second and the third term of Eq. 15 cancel each other, Eq. 14 becomes

$$\begin{aligned}\mathbf{H}_C=&\frac{a}{I^e{}_{xx}}(Q_{2x}\mathbf{P}_y-Q_{2y}\mathbf{P}_x)\mathbf{p}_1\\&-\frac{a}{I^e{}_{xx}}(\mathbf{p}_{2x}\mathbf{P}_y-\mathbf{p}_{2y}\mathbf{P}_x)Q_1\\&+\frac{b}{I^e{}_{xx}}(Q_{2x}\mathbf{P}_y-Q_{2y}\mathbf{P}_x)\mathbf{p}_3\\&-\frac{b}{I^e{}_{xx}}(\mathbf{p}_{2x}\mathbf{P}_y-\mathbf{p}_{2y}\mathbf{P}_x)Q_3,\end{aligned} \tag{17}$$

where μ_{xx} is approximated by $(I^e{}_{xx})^{-1}$ [see Eq. 8]. For taking average of Eq. 17, it must be noted that Q_{2x} and Q_{2y} belong to a degenerate state, and hence the perturbation theory for a degenerate case should be applied. Here the first order perturbation energy also vanishes while the second order one is finite. When the two degenerate states are designated by $(v_1 1^{+1} v_3)$ and $(v_1 1^{-1} v_3)$,** according to their positive and negative angular momenta along the molecular axis, only an element $(v_1 1^{+1} v_3 | v_1 1^{-1} v_3)$ plays an essential role for the separation of these states: it is calculated as follows:

$$\sum_{v'_1 v'_2 v'_3}\frac{(v_1 1^{+1} v_3|\mathbf{H}_C|v'_1 v'^{l}_2 v'_3)(v'_1 v'^{l}_2 v'_3|\mathbf{H}_C|v_1 1^{-1} v_3)}{E(v_1 1 v_3)-E(v'_1 v'^{l}_2 v'_3)}=\frac{B^2{}_e}{h\nu_2}\left(1+4a^2\frac{\nu^2{}_2}{\nu^2{}_1-\nu^2{}_2}+4b^2\frac{\nu^2{}_2}{\nu^2{}_3-\nu^2{}_2}\right)J(J+1). \tag{18}$$

Here $v'_1=v_1\pm1$, $v'_3=v_3\pm1$, and $v'^{l}_2=0^0$ and 2^0. Thus the *l*-type doubling constant q_e is given by

$$q_e=\frac{2B^2{}_e}{h\nu_2}\left(1+4a^2\frac{\nu^2{}_2}{\nu^2{}_1-\nu^2{}_2}+4b^2\frac{\nu^2{}_2}{\nu^2{}_3-\nu^2{}_2}\right). \tag{19}$$

Eqs. 13 and 19 for the centrifugal distortion and for the *l*-type doubling constant coincide with those given by Nielsen and others[8,10,11] though they are derived in slightly different manners.

III

Now the force constants to be obtained are implicitly included in the **L**-matrices and accordingly in the constants a^2 and b^2 defined by Eq. 9. On the other hand a^2 and b^2 are connected to each other by the sum rule, Eq. 10, and are given by the two observables, D_e and q_e, through Eqs. 13 and 19. Two of the three equations may be used for determining a^2 and b^2, and the other is available for testing possible errors in D_e and q_e or for confirming the approximation made in deriving Eqs. 13 and 19; that is the harmonic approximation. Table I gives the results of such calculations on several linear molecules of the XYZ-type. Some molecules, such as chlorine cyanide (ClCN) give reasonable values for a^2 and b^2, but others do not. One of the most definite inconsistency is the case of iodine cyanide; its D_e is probably in a considerable error. D_e is really a correction term for the rotational energy and hence it cannot be obtained very accurately. On the other hand the measurement of q_e is easier, particularly in cases when the direct transition is possible to be observed as in hydrogen cyanide (HCN).[6]*** Since in Eq. 19 the second and the third term of q_e are useful in the calculation of the force constants and they are only about twenty percent of the total q_e, the error of q_e is exaggerated about six times in a^2 and b^2.

According to Eq. 9, b^2 (or a^2) thus determined gives a relation between L_{11} and L_{31} (or between L_{13} and L_{33}). In addition to this, another relation $\mathbf{LL}'=\mathbf{G}$, i.e.

$$\begin{aligned}L^2{}_{11}+L^2{}_{13}&=G_{11}=1/m_X+1/m_Y,\\L^2{}_{31}+L^2{}_{33}&=G_{33}=1/m_Y+1/m_Z,\\L_{11}L_{31}+L_{13}L_{33}&=G_{13}=G_{31}=-1/m_Y,\end{aligned} \tag{20}$$

determines the **L**-matrix, which gives the **F**-matrix by the relation $\mathbf{F}=(\mathbf{L}^{-1})'\varLambda\mathbf{L}^{-1}$. Though the signs of the **L**-elements are not fixed in solving Eqs. 20, it does not

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** Only $v_2=1$ state is interested here, so that $l=\pm1$.

10) G. Herzberg, *Revs. Modern Phys.* **14**, 219 (1942)

11) A. H. Nielsen, *J. Chem. Phys.* **11**, 160 (1943).

*** Recently direct *l*-type doubling transitions in ClCN were observed by L. Yarmus, (*Phys. Rev.* **105**, 928 (1957)).

TABLE I

a^2 AND b^2, AND EXPERIMENTAL DATA NECESSARY TO CALCULATE THEM.

Compound	$q+D$			$q+$sum rule		$D+$sum rule	
	b^2	a^2	a^2+b^2	b^2	a^2	b^2	a^2
HCN	0.9984	0.0501	1.0485	$\underline{0.9218}$	0.0782	1.0305	−0.0305
^{35}ClCN	$\underline{0.9246}$	0.0722	0.9968	0.9286	0.0714	0.9242	0.0758
^{79}BrCN	$\underline{0.9511}$	0.0592	1.0103	0.9397	0.0603	0.9519	0.0481
^{127}ICN	1.2668	0.0301	1.2969	0.9613	0.0387	1.2816	−0.2816
OC^{32}S	$\underline{0.9272}$	0.0460	0.9732	0.9576	0.0424	0.9217	0.0783
N_2O	1.0024	0.0398	1.0422	$\underline{0.9436}$	0.0564	1.0235	−0.0235

Compound	(cm^{-1})$^{a)}$			B_0(Mc/s)	q(Mc/s)	D(Mc/s)
	$\tilde{\nu}^0_1$	$\tilde{\nu}^0_2$	$\tilde{\nu}^0_3$			
HCN	2089	712	3312	44315.97$^{c)}$	224.478$^{d)}$	0.09040$^{b)}$
^{35}ClCN	729	397	2201	5970.831$^{b)}$	7.459$^{b)}$	0.001663$^{b)}$
^{79}BrCN	580	368	2187	4120.221$^{b)}$	3.915$^{b)}$	0.0008844$^{b)}$
I^{127}CN	470	321	2158	3255.578$^{c)}$	2.69$^{c)}$	0.00088$^{c)}$
OC^{32}S	859	527	2079	6081.494$^{c)}$	6.39$^{c)}$	0.00127$^{c)}$
N_2O	1285	589	2224	12561.639$^{b)}$	23.736$^{b)}$	0.005359$^{b)}$

a) G. Herzberg, " Molecular Spectra and Molecular Structure ", p. 174.

b) C. A. Burrus and W. Gordy, *Phys. Rev.* **101**, 599 (1956).

c) W. Gordy, W. V. Smith, and R. Trambarulo, " Microwave Spectroscopy ", Table A4.

d) A. Miyahara, H. Hirakawa, and K. Shimoda, *J. Phys. Soc. Japan*, **11**, 335 (1956).

Values of b^2 with underline are used to calculate force constants.

TABLE II

FORCE CONSTANTS. (10^5 dynes/cm)

Compound	b^2	Present result			Herzberg$^{a)}$		Isotopic method$^{b)}$		
		F_{XY}	F_{YZ}	F'	F_{XY}	F_{YZ}	F_{XY}	F_{YZ}	F'
HCN	0.9218	5.90	16.93	0.36	5.8	17.9	6.257	18·68	−0.1907
^{35}ClCN	0.9246	4.74	18.35	1.31	5.2	16.7	4.7∼5.0	16.8∼18.2	0∼1
^{79}BrCN	0.9511	3.96	16.00	0.92	4.2	16.9			
OC^{32}S	0.9272	17.84	6.60	2.34	14.2	8.0			
N_2O	0.9436	18.34	11.06	1.63	13.7	14.6	17.88	11.39	1.36

a) G. Herzberg, " Molecular Spectra and Molecular Structure ", p. 174

b) H. C. Allen, Jr., E. D. Tidwell and E. K. Plyler, *J. Chem. Phys.* **25**, 302 (1956) (HCN); W. S. Richardson and E. B. Wilson, Jr., ibid. **18**, 155, 694 (1950). (ClCN, N_2O).

influence the resulting **F**-matrix, and other solutions than those in Table II are not physically reasonable and can readily be rejected.

It must be noted that in the calculation described above $\tilde{\nu}^0_i$ and B_0 are respectively used instead of the quantities $\tilde{\nu}^e_i$ and B_e which should be used in the rigorous sense.

IV

In Table II the values of the force constants thus determined are compared with those from other sources, so far as available. The constants cited in Herzberg's book[1)] are of central field type, the cross term being ignored. The diagonal terms show a little difference from the present ones. Richardson and Wilson[12)] used isotopic molecules, ^{35}Cl^{13}CN and ^{15}N^{14}NO, to obtain the three force force constants for chlorine cyanide and nitrous oxide. As was stated by them, the cross term F' plays an important role for nitrous oxide molecule: if one uses only two constants, F_{XY} and F_{YZ} to explain the observed $\tilde{\nu}^0_1$ and $\tilde{\nu}^0_3$ (rather than the zeroth order $\tilde{\nu}^e_1$ and $\tilde{\nu}^e_3$), then imaginary constants are resulted. They arrived at well-defined sets of force constants: $F_{XY}=17.88\pm0.7$, $F_{YZ}=11.39\pm0.3$, and $F'=1.36\pm0.3$, which are in close agreement with the values obtained above: $F_{XY}=18.34$, $F_{YZ}=11.06$, and $F'=1.63$. The substitution of ^{13}C for ^{12}C was found to be rather ineffective for determining the force constants of chlorine cyanide, so that only allowed ranges were reported for the three constants: $F_{XY}=4.7\sim5.0$, $F_{YZ}=16.8\sim18.2$, and $F'=0\sim1$, which

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[12)] W. S. Richardson and E. B. Wilson, Jr., *J. Chem. Phys.* **18**, 155, 694 (1950).

are favorably compared with ours: $F_{XY}=4.74$, $F_{YZ}=18.35$, and $F'=1.31$.

For hydrogen cyanide molecules, a rather complete analysis of vibration-rotation interaction was carried out together with that of DCN,[13,14] so that much more accurate values of force constants are available. As the *l*-type splitting is large for this molecule, it is possible to measure by the microwave spectroscopy[15] a direct transition between these doublets. With these data much more reliable values are expected in this molecule than in chlorine cyanide and nitrous oxide. However, the comparison made in Table II shows that the agreement for hydrogen cyanide is not better than those for chlorine cyanide and nitrous oxide. One of the reasons for this discrepancy may be considered to be the use of $\tilde{\nu}^0_i$ rather than $\tilde{\nu}^e_i$ in obtaining b^2. In fact, if $\tilde{\nu}^e_i$ is used ($\tilde{\nu}^e_1=2127.63\,\text{cm}^{-1}$, $\tilde{\nu}^e_3=3442.81\,\text{cm}^{-1}$ for hydrogen cyanide and $\tilde{\nu}^e_1=1953.18\,\text{cm}^{-1}$, $\tilde{\nu}^e_3=2702.94\,\text{cm}^{-1}$ for DCN)[14], b^2 changes to 0.8368 (q_e is used), but $F_{XY}=6.65$, $F_{YZ}=18.22$, and $F'=2.25$, thus the agreement of F' becomes worse.

If conversely the *l*-type doubling constant and the centrifugal distortion constant are calculated by using the force constants given in reference 14, they are 215.68 Mc and 0.08406 Mc, respectively, which are compared with the observed, 224.478 Mc[15] and 0.9040 Mc.[16] These differences (8.80 Mc or 3.9% for the *l*-type doubling constant and 0.00634 Mc or 7.0% for the centrifugal distortion constant) are definitely larger than the errors involved in the observed values. The higher order effects such as anharmonicity of vibrations or higher terms in the expansion of μ_{xx} can produce this order of discrepancy for the two constants. According to the measurement of Douglas and Sharma[13] α/B is about 0.007 and $\omega_e x_e/\omega_e$ about 0.015. Exact expression for the higher order effect has been given only for the centrifugal distortion constant of diatomic molecule, but for polyatomic molecules it would be too complicated to be calculated exactly. One way to avoid the difficulty is to use in Eqs. 13 and 19 B_0 instead of B_e and $\tilde{\nu}^0_i$ for $\tilde{\nu}^e_i$: the *l*-type doubling constant of hydrogen cyanide increases to 221.45 Mc and the centrifugal distortion constant to 0.08722 Mc, though an exact agreement is not obtained.

For molecules including no hydrogen atom these higher order effects are not very critical, α/B and $\omega_e x_e/\omega_e$ being smaller (e.g. α/B of chlorine cyanide is 0.0027). Fairly good coincidence obtained for cases of chlorine cyanide and nitrous oxide can, therefore, be understood.

Note added in proof.

Recently Wilson gave an expression for the centrifugal distortion constant of linear molecules. [E. Bright Wilson, Jr., *J. Chem. Phys.* **27,** 986 (1957)] The result obtained in the present paper [Eq. 13] can be shown to be in complete agreement with his formula, by some minor transformations.

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[13] A. E. Douglas and D. Sharma, ibid. **21**, 448 (1953).

[14] H. C. Allen, Jr., E. D. Tidwell and E. K. Plyler, ibid. **25**, 302 (1956).

[15] See, for example, A. Miyahara, H. Hirakawa and K. Shimoda, *J. Phys. Soc. Japan*, **11**, 335 (1956).

[16] C. A. Burrus and W. Gordy, *Phys. Rev.* **101**, 599 (1956).