VIBRATIONAL-ROTATIONAL SPECTRUM AND POTENTIAL FUNCTION OF A LINEAR ASYMMETRICAL TRIATOMIC MOLECULE

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ABSTRACT

The problem of the vibration-rotational spectrum of the linear asymmetrical triatomic molecule has been worked out, by the perturbation method of wave mechanics, and the expressions for the energy of vibration and the convergence factors of the rotational lines of the bands are obtained in terms of the anharmonic potential constants. The results are applied to the HCN molecule with satisfactory result.

1. *Introduction*

The theoretical method by which the spectra of a polyatomic molecule might be interpreted, thus leading to a determination of the potential constants, has been fully treated by a number of authors.[1-4] Its application to certain molecules has proved successful, and for the CO_2 and H_2O molecules in particular.[5] The treatment of the linear asymmetrical triatomic molecule of the type X-Y-Z has been given by Adel.[6] But his results are not quite correct owing to the fact that a number of errors existed in his calculation and the Hamiltonian of the system employed is not complete. The present paper treats the same problem in an attempt not

1. D. M. Dennison, *Rev. Mod. Phys.* 3, 280 (1931).
2. E. B. Wilson and J. B. Howard, *J. Chem. Phys.* 4, 260 (1936).
3. Ta-You Wu and A. T. Kiang, *J. Chem. Phys.* 7, 178 (1939); and Ta-You Wu, *ibid.* 8, 389 (1940).
4. A. Weinberg and C. Eckart, *J. Chem. Phys.* 5, 517 (1937).
5. A. Adel and Dennison, *Phys. Rev.* 43, 716 (1933) and 44, 99 (1933); Dennison, *Rev. Mod. Phys.* 12, 175 (1940).
6. A. Adel, *Phys. Rev.* 48, 520 (1935).

only to find the correct expressions both for the energy of vibration and the convergence factors of the rotational lines of the bands, but also to apply the result to determine the potential constants of the HCN molecule.

The Hamiltonian for a vibrating and rotating molecule has been given by Wilson and Howard[2], which may be written in the form

$$H = \frac{1}{2}\sum_k \mu^{\frac{1}{4}} p_k \mu_k p_k \mu^{\frac{1}{4}} + \frac{1}{2}\sum_{\alpha,\beta} \mu^{\frac{1}{4}} (M_\alpha - \Lambda_\alpha)\, \mu_{\alpha\beta}\, \mu^{-\frac{1}{2}} (M_\beta - \Lambda_\beta)\, \mu^{\frac{1}{4}} + V. \quad (1)$$

The M_α are the components of the total angular momentum, while Λ_α are the components of the angular momentum arising from the vibration motion along the coordinate axes rotating with the molecule. The p_k are the momenta conjugate to the normal coordinates. $\mu_{\alpha\beta}$ are the cofactors of a determinant μ which contains the moments of inertia which are themselves functions of the normal coordinates. V is the potential function of the system subject to the geometrical symmetry of the molecule. It is assumed that V can be developed as a power series of the normal coordinates.

In the case of the X-Y-Z type molecule, there are three normal modes of vibration, and these are indicated in Fig. 1. We shall use the generalized coordinates[7] which are somewhat different from those defined by Adel. Let q be the relative displacement of the atoms X and Y, z that of atoms Y and Z, while r and φ indicate the polar coordinates of the central atom in a plane perpendicular to the line joining the end atoms.

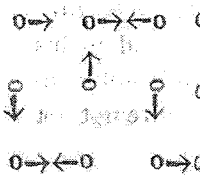

Fig. 1

2. *Zeroth order potential energy of vibration*

We shall first obtain the energy of vibration of the non-rotating molecule, which determines the band centers. Now for the parallel vibrations ω_1 and ω_3, let z_1, z_3, and z_2 indicate the displacements

7 P. E. Bartunek and E. F. Barker, *Phys. Rev.* 48, 520 (1935).

from the equilibrium of X, Y and Z respectively, then $q=z_3-z_1$, $z=z_2-z_3$. The kinetic energy expression

$$T=\tfrac{1}{2}(m_1\dot{z}_1^2+m_2\dot{z}_2^2+m_3\dot{z}_3^2)$$

becomes $$T=\tfrac{1}{2}(\mu_q\dot{q}^2+\mu_z\dot{z}^2+2\mu_{qz}\dot{q}\dot{z}), \qquad (2)$$

where m_1, m_3 and m_2 are the masses of X, Y and Z respectively, and

$$\mu_q=m_1(m_2+m_3)/\Sigma, \qquad \mu_z=m_2(m_1+m_3)/\Sigma,$$
$$\mu_{qz}=m_1m_2/\Sigma, \qquad \Sigma=m_1+m_2+m_3.$$

For the perpendicular vibration ω_2, let (x_1, y_1), (x_3, y_3) and (x_2, y_2) indicate displacements of X, Y and Z respectively in the plane perpendicular to the figure axis. The corresponding kinetic energy is

$$T=\tfrac{1}{2}\{m_1(\dot{x}_1^2+\dot{y}_1^2)+m_2(\dot{x}_2^2+\dot{y}_2^2)+m_3(\dot{x}_3^2+\dot{y}_3^2)\}. \qquad (3)$$

In terms of r and φ, it becomes

$$T=\tfrac{1}{2}\mu_r(\dot{r}^2+r^2\dot{\varphi}^2), \qquad (3')$$

where $$\mu_r=1\Big/\left[\frac{1}{m_1}\left(\frac{s_2}{r_0}\right)^2+\frac{1}{m_2}\left(\frac{s_1}{r_0}\right)^2+\frac{1}{m_3}\right],$$

and $s_1=X-Y$, $s_3=Y-Z$ and $s_1+s_3=r_0=X-Z$, the equilibrium distances between atoms. The symmetry of the molecule imposes the condition that the potential function must be an even function of r. The quadratic terms of V may be written as

$$V_0=\tfrac{1}{2}(k_{11}q^2+k_{22}r^2+k_{33}z^2+2k_{13}qz). \qquad (4)$$

After transforming to the normal forms, T and V_0 become

$$T=\tfrac{1}{2}(\dot{Q}^2+\dot{Z}^2+\dot{R}^2+R^2\dot{\varphi}^2),$$
$$V_0=\tfrac{1}{2}(\lambda_1Q^2+\lambda_3Z^2+\lambda_2R^2), \qquad (5)$$

where $$\lambda_1+\lambda_3=(k_{33}\mu_q+k_{11}\mu_z-2k_{13}\mu_{qz})/M,$$
$$\lambda_1\lambda_3=(k_{11}k_{33}-k_{13}^2)/M, \qquad \lambda_2=k_{22}/\mu_r, \qquad (6)$$

in which Q, R and Z are related to q, r and z by the following:

$$q=c_{11}Q-c_{12}Z, \qquad z=-c_{21}Q+c_{22}Z,$$

and $$r=R/(\mu_r)^{\frac{1}{2}},$$

where
$$\left.\begin{aligned} c_{11} &= c_1(\mu_z\lambda_1 - k_{33})^{\frac{1}{2}}, \\ c_{21} &= c_1(\mu_{qz}\lambda_1 - k_{33})/(\mu_z\lambda_1 - k_{33})^{\frac{1}{2}}, \\ c_{13} &= c_2(\mu_{qz}\lambda_1 - k_{13})/(\mu_q\lambda_3 - k_{11})^{\frac{1}{2}}, \\ c_{23} &= c_2(\mu_q\lambda_3 - k_{11})^{\frac{1}{2}}, \\ c_1^2 &= -c_3^2 = 1/(\lambda_1 - \lambda_3)M, \\ \lambda_i &= (2\pi c\omega_i)^2, \\ M &= \mu_q\mu_z - \mu_{qz}^2. \end{aligned}\right\} \quad (7)$$

By introducing the dimensionless coordinates σ, ξ, ρ, and φ instead of Q, Z, R and φ, which are related to them by $\sigma = 2\pi(\omega_1/h)^{\frac{1}{2}} Q$, $\xi = 2\pi(\omega_3/h)^{\frac{1}{2}} Z$, $\rho = 2\pi(\omega_2/h)^{\frac{1}{2}} R$, and $\varphi = \varphi$, the zeroth order Hamiltonian of the non-rotating molecule takes the form

$$H_0 = (2\pi^2 c/h)(\omega_1 p_\sigma^2 + \omega_2 p_\rho^2 + \omega_3 p_\xi^2 + \omega_2/\rho^2 \cdot p_\varphi^2) + V_0, \quad (8)$$

where $V_0 = \frac{1}{2} hc\,(\omega_1\sigma^2 + \omega_2\rho^2 + \omega_3\xi^2)$.

The zeroth order energy corresponding to this Hamiltonian is

$$W_0 = hc\,(\omega_1(n_1 + \tfrac{1}{2}) + \omega_2(n_2 + 1) + \omega_3(n_3 + \tfrac{1}{2})). \quad (9)$$

3. *Higher order terms in potential energy and terms* $\Lambda_\alpha \mu_{\alpha\beta} \mu^{-\frac{1}{2}} \Lambda_\beta$

The higher power terms of the normal coordinates in the potential function may be written as

$$\lambda V_1 = hc\,(a\sigma^3 + b\sigma\rho^2 + c\sigma\xi^2 + \alpha\xi^3 + \beta\xi\rho^2 + \gamma\xi\sigma^2),$$

$$\lambda^2 V_2 = hc\,(d\sigma^4 + e\rho^4 + f\xi^2 + g\sigma^2\rho^2 + h\sigma^2\xi^2 + i\rho^2\xi^2 + j\sigma\xi^3 + k\sigma\xi^3 + l\sigma\xi\rho^2).$$

The terms depending on Λ_α are $\Lambda_\alpha \mu_{\alpha\beta} \mu^{-\frac{1}{2}} \Lambda_\beta$, which represent the energ of interaction between the parallel and the perpendicular vibrations, and are functions of the vibrational quantum numbers n_1, n_2, and n_3 only. It can be shown that the Λ_α are given by

$$\Lambda_\alpha = s(yp_1 - q_1 p_y^2) + t(yp_2 - q_2 p_x),$$

$$\Lambda_\beta = -s(xp_1 - q_1 p_x) - t(xp_2 - q_2 p_x), \tag{10}$$

and $$\Lambda_\gamma = (xp_y - p_x y),$$

where $x^2 + y^2 = r^2$ etc. and $s = \sqrt{\mu_r}/r_0(-s_2 c_{11} - s_1 c_{21})$,

$$t = \sqrt{\mu_r}/r_0(s_1 c_{22} + s_2 c_{12}), \qquad s^2 + t^2 = 1.$$

λV_1, $\lambda^2 V_2$ and $\Lambda_\alpha \mu_{\alpha\beta} \mu^{-\frac{1}{2}} \Lambda_\beta$ can be treated by means of the familiar perturbation methods. Combining the energy contributed from the zeroth order Hamiltonian, they lead to the following energy expression:

$$W_v/hc = \nu_1 n_1 + \nu_2 n_2 + \nu_3 n_3 + X_{11} n_1^2 + X_{22} n_2^2 + X_{33} n_3^2 + X_{ll} l^2 + X_{12} n_1 n_2 + X_{13} n_1 n_3 + X_{23} n_2 n_3 + \text{const.},$$

where

$$\nu_1 = \omega_1 + 3d/2 + g + h/2 - (3a/\omega_1)(3a/4 + b + c/2) - (\gamma/\omega_2)(3\alpha + \beta + \gamma/2) - (b^2/2)\left(\frac{1}{\omega_1 + 2\omega_2} - \frac{1}{\omega_1 - 2\omega_2}\right) - \frac{c^2}{8}\left(\frac{1}{\omega_1 + 2\omega_2} - \frac{1}{\omega_1 - 2\omega_2}\right) + \frac{\gamma^2}{8}\left(\frac{3}{\omega_2 + 2\omega_1} - \frac{1}{\omega_2 - 2\omega_1}\right),$$

$$\nu_2 = \omega_2 + 3e + g/2 + i/2 - (b/\omega_1)(3a/2 + b + c/2) + (\beta/\omega_2)(3\alpha/2 + \beta + \gamma/2) - \tfrac{1}{2}\left(\frac{b^2}{\omega_1 + 2\omega_2} + \frac{\beta^2}{\omega_2 + 2\omega_2}\right),$$

$$\nu_3 = \omega_3 + 3f/2 + h/2 + i - (c/\omega_1)(3a/2 + b + c/2) - (3\alpha/\omega_2)(3\alpha + \beta + \gamma/2) - (\beta^2/2)\left(\frac{1}{\omega_3 + 2\omega_2} - \frac{1}{\omega_3 - 2\omega_2}\right) - \left(\frac{c^2}{8}\right)\left(\frac{3}{\omega_1 + 3\omega_2} - \frac{1}{\omega_1 - 2\omega_2}\right) - \frac{\gamma^2}{4}\left(\frac{1}{\omega_3 + 2\omega_1} - \frac{1}{\omega_3 - 2\omega_1}\right),$$

$$X_{11} = 3d/2 - 15a^2/4\omega_1 - \gamma^2/2\omega_2 - (\gamma^2/8)\left(\frac{1}{\omega_2 + 2\omega_1} + \frac{1}{\omega_2 - 2\omega_1}\right),$$

$$X_{22} = 3e/2 - \tfrac{1}{2}(b^2/\omega_1 + \beta^2/\omega_2) - (b^2/8)\left(\frac{1}{\omega_1 + 2\omega_2} + \frac{1}{\omega_1 - 2\omega_2}\right) - (\beta^2/8)\left(\frac{1}{\omega_2 + 2\omega_2} + \frac{1}{\omega_2 - 2\omega_2}\right),$$

$$X_{33}=3f/2-15\alpha^2/4\omega_3-c^2/2\omega_1-(c^2/8)\left[\frac{1}{\omega_1+2\omega_3}+\frac{1}{\omega_1-2\omega_3}\right],$$

$$X_{11}=-e/2+\tfrac{1}{8}\left[\frac{b^2}{\omega_1+2\omega_2}+\frac{b^2}{\omega_1-2\omega_2}+\frac{\beta^2}{\omega_3+2\omega_2}+\frac{\beta^2}{\omega_3-2\omega_2}\right],$$

$$X_{12}=g-(3ab/\omega_1-\beta\gamma/\omega_3)-(b^2/2)\left[\frac{1}{\omega_1+2\omega_3}-\frac{1}{\omega_1-2\omega_2}\right],$$

$$X_{13}=h-3(ac/\omega_1+\alpha\gamma/\omega_3)-(c^2/2)\left[\frac{1}{\omega_1+2\omega_3}-\frac{1}{\omega_1-2\omega_3}\right]$$
$$-(\gamma^2/2)\left[\frac{1}{\omega_3+2\omega_1}-\frac{1}{\omega_3-2\omega_1}\right],$$

$$X_{23}=i-(bc/\omega_1+3\alpha\beta/\omega_3)-(\beta^2/2)\left[\frac{1}{\omega_3+2\omega_2}-\frac{1}{\omega_2-2\omega_2}\right] \quad (11)$$

Solving for ω_i, one obtains

$$\omega_1=\nu_1-X_{11}-X_{12}-\tfrac{1}{2}X_{13},$$
$$\omega_2=\nu_2-2X_{22}-\tfrac{1}{2}X_{12}-\tfrac{1}{2}X_{23},$$
$$\omega_3=\nu_3-X_{33}-X_{23}-\tfrac{1}{2}X_{13}.$$

4. *Interaction between vibration and rotation*

Up to here only the eigenvalues for the energy of the non-rotating molecule have been evaluated. We shall consider those terms of the Hamiltonian depending upon the total angular momenta M_α, i. e., the interaction between vibration and rotation. A straightforward application of the method of Wilson and Howard leads to the following two terms:

$$\frac{(M_\alpha^2+M_\beta^2)-2(M_\alpha\Lambda_\alpha+M_\beta\Lambda_\beta)}{2I_e\left[1+(h^{\frac{1}{2}}/2\pi c^{\frac{1}{2}}I_e)(k_1\sigma/\omega_1^{\frac{1}{2}}+k_2\xi/\omega_3^{\frac{1}{2}})+(h/4\pi^2I_e c)\right.}$$

$$\left.\left\{(1-s^2)\frac{\sigma^2}{\omega_1^2}+(1-t^2)\xi^2/\omega_3-2st\,\sigma\xi^2/\omega_1^{\frac{1}{2}}\omega_3^{\frac{1}{2}}\right\}\right. \quad (12)$$

in which I_e is the equilibrium moment of inertia and

$$k_1=2\left[(\mu_q s_1+\mu_{qz}s_2)c_{11}-(\mu_z s_2+\mu_{qz}s_1)c_{21}\right],$$
$$k_2=2\left[-(\mu_q s_1+\mu_{qz}s_2)c_{12}+(\mu_z s_2+\mu_{qz}s_1)c_{22}\right]. \quad (13)$$

In the first approximation, the first term gives the rotational energy of a rigid rotator, namely,

$$\frac{h^2}{8\pi^2 I_0 c\omega}[J(J+1)-l^2]$$

while in the next approximation, it gives the energy change[8]

$$\Delta V_1 = \frac{h^2}{8\pi^2 I_0 c\omega}[J(J+1)-l^2]\left[\left\{\frac{1^2}{I_0}\left(-1+s^2+\frac{k_1^2}{I_0}\right)\right.\right.$$
$$\left.+\left(3k_a\frac{k_1}{\lambda_1 I_0}+k_c\frac{k_2}{\lambda_2 I_0}\right)\right\}\frac{h}{4\pi^2 c\omega_1}\sigma^2+\left(k_e\frac{k_1}{\lambda_1 I_0}\right.$$
$$\left.+k_f\frac{k_2}{\lambda_2 I_0}\right)\frac{h}{4\pi^2 c\omega_2}\rho^2+\left\{\frac{1}{I_0}\left(-1+t^2+\frac{k_2^2}{I_0}\right)\right. \quad (14)$$
$$\left.+\left(3k_b\frac{k_2}{\lambda_2 I_0}+k_d\frac{k_1}{\lambda_1 I_0}\right)\right\}\frac{h}{4\pi^2 c\omega_2}+\left\{\frac{2}{I_0}\left(st+\frac{k_1 k_2}{I_0}\right)\right.$$
$$\left.+2\left(k_c\frac{k_1\omega}{\lambda_1 I_0}+k_d\frac{k_2}{\lambda_2 I_0}\right)\right\}h\sigma\rho/4\pi^2 c\omega_1^{\frac{1}{2}}\omega_2^{\frac{1}{2}}\Big],$$

where $k_a = 8\pi^2\omega_1(\omega_1 c/h)^{-\frac{1}{2}}a$, $k_e = 8\pi^2\omega_2\mu_\gamma(\omega_1 c/h)^{\frac{1}{2}}b$,

$$k_d = 8\pi^2\omega_2(\omega_1 c/h)^{\frac{1}{2}}c, \quad k_b = 8\pi^2\omega_2(\omega_2 c/h)^{\frac{1}{2}}\alpha, \quad (15)$$
$$k_c = 8\pi^2\omega_1(\omega_1 c/h)^{\frac{1}{2}}\gamma, \quad k_f = 8\pi^2\omega_2\mu_\gamma(\omega_2 c/h)^{\frac{1}{2}}\beta.$$

This contributes to the energy an amount

$$\Delta E_1 = (h^2/8\pi^2 I_0 c)[J(J+1)-l^2][(n_1+\tfrac{1}{2})P+(n_2+\tfrac{1}{2})N$$
$$+(n_2+1)M],$$

in which

$$P = \left[\frac{1}{I_0}(s^2+k_1^2/I_0-1)+3k_a\frac{k_1}{\lambda_1 I_0}+k_c\frac{k_2}{\lambda_2 I_0}\right]\frac{h}{4\pi^2 c\omega_1},$$
$$M = \left(k_e\frac{k_1}{\lambda_1\mu_\gamma I_0}+k_f\frac{k_2}{\lambda_2 I_0\mu_\gamma}\right)\frac{h}{4\pi^2 c\omega_2}, \quad (16)$$
$$N = \left[\frac{1}{I_0}(t^2+k_2^2/I_0-1)+3k_b\frac{k_2}{\lambda_2 I_0}+k_d\frac{k_1}{\lambda_1 I_0}\right]\frac{h}{4\pi^2 c\omega_2}.$$

8. For details see T. Y. Wu, *J. Chem. Phys.* 8, 408 (1940).

The energy change due to the contributions of nondiagonal matrix elements M_α Λ_{α_s} up to the second order approximation is

$$\Delta E_2 = \frac{h^2}{8\pi^4 I_0 c}[J(J+1)-l^2]\left[s^2\frac{2(n_1+\frac{1}{2})}{\omega_1-\omega_2}\frac{(n_2+1)}{\omega_1-\omega_2}\right.$$
$$\left.+t^2\frac{2(n_3+\frac{1}{2})}{\omega_3-\omega_2}\frac{(n_2+1)}{\omega_3-\omega_2}\right]\frac{h^2}{8\pi^2 I_0 c}, \tag{17}$$

Thus the total energy change is

$$\Delta E=\Delta E_1+\Delta E_2-(h^2/8\pi^2 I_0 c)[J(J+1)-l^2]\{(n_1+\tfrac{1}{2})\alpha_1$$
$$+(n_2+1)\alpha_2+(n_3+\tfrac{1}{2})\alpha_3\}$$

where

$$\alpha_1=\frac{1}{I_0}\left[(s^2+k_1{}^2/I_0-1)+3k_0\frac{k_1}{\lambda_1 I_0}+k_0\frac{k_3}{\lambda_3 I_0}\right]\frac{h}{4\pi^2\omega_1 c}$$
$$+\frac{s^2 h}{4\pi^2 I_0 c(\omega_1-\omega_2)}, \tag{18}$$
$$\alpha_2=\frac{1}{2I_0}\left[k_0\frac{k_1}{\lambda_1 I_0\mu r}+kI\frac{k_3}{\lambda_3 I_0\mu r}\right]\frac{h}{4\pi^2 c\omega_2}$$
$$-\frac{h}{8\pi^2 I_0 c}\left(\frac{s^2}{\omega_1-\omega_2}+\frac{t^2}{\omega_3-\omega_2}\right),$$
$$\alpha_3=\frac{1}{I_0}\left[(t^2+k_2{}^2/I_0-1)+3k_0\frac{k_2}{\lambda_3 I_0}+k_0\frac{k_1}{\lambda_1 I_0}\right]\frac{h}{4\pi^2 c\omega_3}$$
$$+\frac{t^2 h}{4\pi^2 c I_0(\omega_3-\omega_1)}.$$

The frequencies of the vibration-rotational lines arising from transitions from the normal state to the n_1, n_2, n_3, l states are then given by

$$\nu=\nu_0\pm B_0[2+(n_1+1)\alpha_1+(n_2+2)\alpha_2+(n_3+1)\alpha_3]N$$
$$+B_0(n_1\alpha_1+n_2\alpha_2+n_3\alpha_3)N^2, \tag{19}$$

where $B_0=h/8\pi^2 I_0 c$, and N is the ordinal number of the rotational lines.

5. *Calculation of potential constants of HCN*

The experimental data of the HCN molecule are more accurately given by Lindholm [9], namely,

9. E. Lindholm, *Zeits. f. Phys.* **108**, 454 (1938); also see T. Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (University Press, The National University of Peking 1939).

$$\begin{aligned}
&\nu_1 = 2041.0, \quad X_{11} = -51.8, \quad X_{12} = -3.7, \\
&\nu_2 = 711.9, \quad X_{22} = -2.85, \quad X_{13} = -14.7, \quad X_{ll} \quad 3.25, \\
&\nu_3 = 3368.6, \quad X_{33} = -55.48, \quad X_{23} = -19.6, \quad X_{333} \quad 0.77,
\end{aligned} \tag{20}$$

and the zeroth order frequencies and potential constants[10] are

$$\begin{aligned}
&\omega_1 = 1999.5, \quad \omega_2 = 729.4, \quad \omega_3 = 3450.0 \text{ cm}^{-1}; \\
&k_{11} \quad 6.23 \cdot 10^5, \quad k_{33} = 16.54, \text{ for } k_{13} = -0.25 \text{ to be assumed;} \\
&I_0 = 18.93 \cdot 10 \text{ gr-cm}^2.
\end{aligned} \tag{21}$$

With these values, the transformation coefficients c_{ij}'s and the quantities $k_1, k_2, k_a, \ldots\ldots, k_f$ can be calculated,

$$\begin{aligned}
&c_{11} = -1.018 \cdot 10^{11}, \quad c_{22} -1.004 \cdot 10^{11}, \quad c_1 = 1.102 \cdot 10^8, \\
&c_{21} = 2.975 \cdot 10^{11}, \quad c_{12} = 7.963 \cdot 10^{11}, \quad c_2 = 1.102 \cdot 10^8, \\
&s^2 = 0.034, \quad t^2 \quad 0.966, \quad s^2 + t^2 = 1, \\
&k_1 = -8.814 \cdot 10^{-20}, \quad k_2 = -1.528 \cdot 10^{-20}, \\
&k_a = 4.250 \cdot 10^{46} \alpha, \quad k_e = 1.550 \cdot 10^{46} \mu_r b, \quad k_d = 7.331 \cdot 10^{46} c, \\
&k_b = 9.628 \cdot 10^{46} \alpha, \quad k_f = 2.037 \cdot 10^{46} \mu_r \beta, \quad k_c = 5.581 \cdot 10^{46} \gamma.
\end{aligned} \tag{22}$$

The convergence factors $B_1 - B_{0_0}$ can be obtained from the resolved bands given in Table I[9],

n_1	$n_2 l$	n_3	μ cm^{-1}	B_1 obs.	B_1 calc.	$B_1 - B_{0_0}$ obs.
0	0_0	5	15552.04	1.423	1.42	- 0.0549
1	0_0	4	14670.70	1.423	1.425	- 0.0549
0	0	4	12635.89	1.4343	1.4343	- 0.0436
1	0_0	3	11674.38	1.4366	1.4366	- 0.0413
0	1_1	4	12557.48	1.435	1.435	- 0.0429
1	1_1	3	11613.50	1.436	1.437	- 0.0419
0	0_0	3	9627.22	1.4458	1.4458	- 0.0321
0	1_1	3	9568.53	1.4467	1.4464	- 0.0312
1	0_0	2	8585.60	1.4471	1.4477	- 0.0308
0	1_1	0	712.28	1.4775	1.4775	0.0000

Table I

9. Lindholm, *Zeits. f. Phys.* 103, 434 (1938); also see T. Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (University Press, the National University of Peking, 1939).

10. Here the values of force constants and that of I slightly differ from those given in (9) and (7) because the physical constants $h = 6.624 \times 10^{-27}$ erg. sec. & $m = 1.6734 \times 10^{-24}$ gr. are used.

The convergence of 5 ν_3 gives $B_0\,\alpha_3 = -0.01098$, that of 4 ν_3 yields $B_0\,\alpha_3 = -0.01090$, while from 3 ν_3 one finds $B_0\,\alpha = -0.01070$. The average of these values is

$$B_0\,\alpha = -0.01086. \tag{24}$$

The fundamental ν_2 serves to evaluate α_2 and we find

$$B_0\,\alpha_2 = 0. \tag{24}$$

The difference of $B_1 - B_0$ of $\nu_1 + 4\nu_3$ and $4\nu_3$ gives $B_0\alpha_1 = -0.0113$, that of $\nu_1 + 3\nu_3$ and ν_3 gives $B_0\alpha_1 = -0.0092$, that of $\nu_1 + \nu_{21} + 3\nu_3$ and $\nu_{21} + 3\nu_3$ gives -0.0107, while from the convergence of $\nu_1 + 2\nu_3$ and the constant α_3. one finds $B_0\alpha_1 = -0.0091$. The average of these values is

$$B_0\,\alpha_1 = -0.0101. \tag{25}$$

Substitution of the values of equations (22) (25) into (18) gives

$$1.168a + 0.0306\gamma = 111.9, \tag{26a}$$

$$0.0917\alpha + 0.389c = 82.16, \tag{26b}$$

$$0.389b + 0.0306\beta = -5.69. \tag{26c}$$

Combining (26c) with the relations $X_{22} = -2.85$, $X_{11} = 3.25$, one finds[11]

$$b = -60.0, \quad \beta = 576.8, \quad e = 63.4\ \text{cm}^{-1}. \tag{27}$$

The other constants can not be evaluated from (26a) and (26b) and the other relations of X_{ij} in (11), since there are only seven relations connecting nine unknowns a, c, ..., α, γ. We shall obtain two more relations of these constants from an analysis of the observed bands of DCN molecule. To the zeroth order approximation, the expressions for the fundamentals for DCN are

$$\lambda_1' + \lambda_3' = (k_{11}'\mu_z' + k_{33}'\mu_q' + 2k_{13}'\mu_{qz}')/M',$$

$$\lambda_1'\lambda_3' = (k_{11}'k_{33}' - k_{13}'^2)/M', \tag{28}$$

where $M' = \mu_q'\mu_z' - \mu_{qz}'^2$.

11. The expressions for α_i and hence α_i' differing from those given in (18) will appear, if we follow Dennison's calculation in the case of

These and equation (6) yield the following relations between the fundamentials of HCN and DCN, i. e.,

$$\omega_1/\omega_1' = (\mu_1/\mu_1')^{\frac{1}{2}},\quad \omega_2/\omega_2' = (\mu_2/\mu_2')^{\frac{1}{2}},\quad \omega_3/\omega_3' = (\mu_3/\mu_3')^{\frac{1}{2}}, \tag{29}$$

in which $\mu_1/\mu_1' = 0.867$, $\mu_2/\mu_2' = 0.632$, $\mu_3/\mu_3' = 0.598$

After the substitution of the numerical values of the reduced masses and the force constants of both molecules, the constants k_1', k_2' and c_{ij}'s etc. for DCN thus calculated are

$$\begin{aligned}
&c_{11}' = 2.187\cdot10^{11} \quad c_{33}' = 1.872\cdot10^{11} \quad c_1' = 1.163\cdot10^{8}\\
&c_{21}' = 2.403\cdot10^{11} \quad c_{12}' = 5.440\cdot10^{11} \quad c_2' = 1.163\cdot10^{8}\\
&s'^2 = 0.003 \quad t'^2 = 0.997 \quad s'^2 + t'^2 = 1\\
&k_1' = -9.225\cdot10^{30} \quad k_2' = 0.0308\cdot10^{30}\\
&k_a' = 3.430\cdot10^{46}\alpha \quad k_e' = 0.914\cdot10^{46}\mu_r'b \quad k_d' = 4.075\cdot10^{46}c\\
&k_b' = 4.442\cdot10^{46}\alpha \quad k_f' = 1.167\cdot0^{46}\mu_r'\beta \quad k_c' = 3.739\cdot10^{46}\gamma.
\end{aligned} \tag{30}$$

The expressions for ν_1', ν_2', X_{11}' and X_{33}' are respectively

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CO_2 molecule, *Rev. Mod. Phys.* 12, 175 (1940), for instance,

$$\alpha_2' = \left[k_e\frac{k_1}{\lambda_1 I_0\mu_r} + k_f\frac{k_2}{\lambda_3 I_0\mu_r}\right]\frac{h}{4\pi^2 c\omega_2} + \frac{h}{8\pi^2 I_0 c}\left[s^2\frac{(\omega_1^2+3\omega_2^2)}{\omega_2(\omega_2^2-\omega_1^2)} + t^2\frac{(\omega_3^2+3\omega_2^2)}{\omega_2(\omega_2^2-\omega_3^2)}\right],$$

$$\alpha_2' = \left[k_e'\frac{k_1'}{\lambda_1' I_0'\mu_r'\omega} + k_f'\frac{k_2'}{\lambda_3' I_0'\mu_r'}\right]\frac{h}{4\pi^2 c\omega_2'} + \frac{h}{8\pi^2 I_0' c}\left[s'^2\frac{(\omega_1'^2+3\omega_2'^2)}{\omega_2'(\omega_2'^2-\omega_1'^2)} + t'^2\frac{(\omega_3'^2+3\omega_2'^2)}{\omega_2'(\omega_2'^2-\omega_3'^2)}\right],$$

With the values given in (22), the former will give two sets of values for b and β, namely,

$$b = -16.2, \quad \text{or} \quad -102.3;$$
$$\beta = -590.5; \quad 503.8.$$

Substitution in the latter expression α_2' gives the convergence factor for ν_2' -0.0026, if $b = -16.2$ and $\beta = -590.5$ is chosen, while it would give 0.00054 if $b = -102.3$ and $\beta = 503.8$ is chosen. Both values differ even in the order of magnitude from the empirical data, 0.0015.

$$\nu_1' = \omega_1\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}} + 3\left(\frac{d}{2}\right)\left(\frac{\mu_1}{\mu_1'}\right) + g\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}} + \left(\frac{h}{2}\right)\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}}$$
$$-\left(\frac{15a^2}{4\omega_1}\right)\left(\frac{\mu_1}{\mu_1'}\right) - \left(\frac{3ab}{\omega_1}\right)\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}} - \left(\frac{3ac}{2\omega_1}\right)\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}}$$
$$-\left(\frac{3\alpha\gamma}{2\omega_3}\right)\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}} - \left(\frac{\beta\gamma}{\omega_3}\right)\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}} - \left(\frac{\gamma^2}{2\omega_3}\right)\left(\frac{\mu_1}{\mu_1'}\right)$$
$$-\left(\frac{b^2}{2}\right)\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_2}{\mu_2'}\right)\left[\frac{1}{\omega_1'+2\omega_2'} - \frac{1}{\omega_1'-2\omega_2'}\right]$$
$$-\left(\frac{c^2}{4}\right)\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)\left[\frac{1}{\omega_1'+2\omega_3'} - \frac{1}{\omega_1'-2\omega_3'}\right]$$
$$-\left(\frac{\gamma^2}{8}\right)\left(\frac{\mu_1}{\mu_1'}\right)\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}}\left[\frac{3}{\omega_3'+2\omega_1'} - \frac{1}{\omega_3'-2\omega_1'}\right]$$
$$+t'^2\left(\frac{h}{8\pi^2 I_0' c}\right)\left(\frac{\omega_1'}{\omega_2'}+\frac{\omega_2'}{\omega_1'}\right),$$

$$\nu_3' = \omega_3\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}} + \left(\frac{3f}{2}\right)\left(\frac{\mu_3}{\mu_3'}\right) + \left(\frac{h}{2}\right)\left(\frac{\mu_1}{\mu_3'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}} + \left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}}$$
$$-\left(\frac{3ac}{2\omega_1}\right)\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}} - \left(\frac{bc}{\omega_1}\right)\left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}} - \left(\frac{c^2}{2\omega_1}\right)\left(\frac{\mu_3}{\mu_3'}\right)$$
$$-\left(\frac{15\alpha^2}{4\omega_3}\right)\left(\frac{\mu_3}{\mu_3'}\right) - \left(\frac{3\alpha\beta}{\omega_3}\right)\left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}} - \left(\frac{3\alpha\gamma}{2\omega_3}\right)\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}}$$
$$-\left(\frac{b^2}{2}\right)\left(\frac{\mu_2}{\mu_2'}\right)\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}}\left[\frac{1}{\omega_3'+2\omega_2'} - \frac{1}{\omega_3'-2\omega_2'}\right]$$
$$-\left(\frac{c^2}{8}\right)\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)\left[\frac{3}{\omega_1'+2\omega_3'} - \frac{1}{\omega_1'-2\omega_3'}\right]$$
$$-\left(\frac{\gamma^2}{4}\right)\left(\frac{\mu_1}{\mu_1'}\right)\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}}\left[\frac{1}{\omega_3'+2\omega_1'} - \frac{1}{\omega_3'-2\omega_1'}\right]$$
$$+t'^2\left(\frac{h}{8\pi^2 I_0' c}\right)\left(\frac{\omega_3'}{\omega_2'}+\frac{\omega_2'}{\omega_3'}\right),$$

$$X_{11}' = -\left(\frac{3a}{2}\right)\left(\frac{\mu_1}{\mu_1'}\right) - \left(\frac{15a^2}{4\omega_1}\right)\left(\frac{\mu_1}{\mu_1'}\right) - \left(\frac{\gamma^2}{2\omega_3}\right)\left(\frac{\mu_1}{\mu_1'}\right)$$
$$-\left(\frac{\gamma^2}{8}\right)\left(\frac{\mu_1}{\mu_1'}\right)\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}}\left[\frac{1}{\omega_3'+2\omega_1'} + \frac{1}{\omega_3'-2\omega_1'}\right],$$

$$X_{23}' = \left(\frac{3f}{2}\right)\left(\frac{\mu_2}{\mu_2'}\right) - \left(\frac{15\alpha^2}{4\omega_2}\right)\left(\frac{\mu_2}{\mu_2'}\right) - \left(\frac{\alpha c'}{2\omega_1}\right)\left(\frac{\mu_2}{\mu_2'}\right)$$

$$- \left(\frac{c'^2}{8}\right)\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_2}{\mu_2'}\right)\left[\frac{1}{\omega_1'+2\omega_2'} + \frac{1}{\omega_1'-2\omega_2'}\right],$$

and (31)

$$\nu_1'(\text{obs.}) = \nu_1' + X_{11}' = \omega_1\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}} + 2X_{11}\left(\frac{\mu_1}{\mu_1'}\right) + X_{12}\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}}$$

$$+ \tfrac{1}{2}X_{13}\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}} - s^2\left(\frac{h}{8\pi^2 I_0 c}\right)\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}}\left(\frac{\omega_1}{\omega_2} + \frac{\omega_2}{\omega_1}\right)$$

$$+ s'^2\left(\frac{h}{8\pi^2 I_0' c}\right)\left(\frac{\omega_1'}{\omega_2'} + \frac{\omega_2'}{\omega_1'}\right) + \left(\frac{b^2}{2}\right)\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}}\left[\frac{1}{\omega_1+2\omega_2} - \frac{1}{\omega_1-2\omega_2}\right.$$

$$\left. - \left(\frac{\mu_2'}{\mu_2}\right)^{\frac{1}{2}}\left(\frac{1}{\omega_1'+2\omega_2'} - \frac{1}{\omega_1'-2\omega_2'}\right)\right]$$

$$+ \left(\frac{c_2^2}{4}\right)\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}}\left[\frac{1}{\omega_1+2\omega_2} - \frac{1}{\omega_1-2\omega_2} - \left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}}\left(\frac{1}{\omega_1'+2\omega_2'}\right.\right.$$

$$\left.\left. - \frac{1}{\omega_1'-2\omega_2'}\right)\right] + \frac{\gamma^2}{4}\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left[\left(\frac{1}{\omega_2+2\omega_1}\right)\left\{\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}} + \left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}}\right\}\right.$$

$$\left. + \left(\frac{1}{\omega_2-2\omega_1}\right)\left\{\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}} - \left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}}\right\}\right.$$

$$\left. - 2\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}}\left(\frac{1}{\omega_2'+2\omega_1'}\right)\right].$$

$$\nu_2'(\text{obs.}) = \nu_2' + X_{22}' = \omega_2\left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}} + 2X_{22}\left(\frac{\mu_2}{\mu_2'}\right) + \tfrac{1}{2}X_{13}\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}}$$

$$+ X_{23}\left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}} - t^2\left(\frac{h}{8\pi^2 I_0 c}\right)\left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}}\left(\frac{\omega_2}{\omega_3} + \frac{\omega_3}{\omega_2}\right)$$

$$+ t'^2\left(\frac{h}{8\pi^2 I_0' c}\right)\left(\frac{\omega_2'}{\omega_3'} + \frac{\omega_3'}{\omega_2'}\right) + \left(\frac{\beta^2}{2}\right)\left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}}\left[\frac{1}{\omega_2+2\omega_3}\right.$$

$$\left. - \frac{1}{\omega_2-2\omega_3} - \left(\frac{\mu_2}{\mu_2'}\right)^{\frac{1}{2}}\left(\frac{1}{\omega_3'+2\omega_2'} - \frac{1}{\omega_3'-2\omega_2'}\right)\right]$$

$$+ \left(\frac{\gamma^2}{4}\right)\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}}\left[\frac{1}{\omega_3+2\omega_1} - \frac{1}{\omega_3-2\omega_1} - \left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{1}{\omega_3'+2\omega_1'}\right.\right.$$

$$\left.\left. - \frac{1}{\omega_3'-2\omega_1'}\right)\right] + \left(\frac{c^2}{4}\right)\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}}\left[\left(\frac{1}{\omega_1+2\omega_3}\right)\left\{\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}} + \left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\right\}\right.$$

$$\left. + \left(\frac{1}{\omega_1-2\omega_3}\right)\left\{\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}} - \left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\right\}\right.$$

$$\left. - 2\left(\frac{\mu_1}{\mu_1'}\right)^{\frac{1}{2}}\left(\frac{\mu_3}{\mu_3'}\right)^{\frac{1}{2}}\left(\frac{1}{\omega_1'+2\omega_3'}\right)\right].$$

where I_0' is the equilibrium moment of inertia of the molecule. From the Raman spectrum, the value of ν_1' (obs.) $= 1906$ cm^{-1} was identified,[12] while those of ν_3' (obs.) and I_0' obtained by Bartunek and Barker were 2630 cm^{-1} and $23.17 \cdot 10^{-40}$ gr-cm^2 respectively. Substituting the known values into equation (31), we find

$$\begin{aligned} 0.25c^2 \cdot 10^{-3} + 6.61\gamma^2 \cdot 10^{-3} &= 180.0, \\ 0.45c^2 \cdot 10^{-3} + 16.7\gamma^2 \cdot 10^{-3} &= 453.7. \end{aligned} \tag{32}$$

Thus $c = +307.3$, $\gamma = +518.8$ cm^{-1} are obtained, and (26a) and (26b) give $a = +82.2$, $\alpha = -407.6$ cm^{-1}. The value of d, f, g, h, and i can be evaluated from X_{11}, X_{33}, X_{12}, X_{13} and X_{22} with the aid of the calculated value of a, b, c, α, β, γ and the fundamentals. The results of calculation are listed in Table II and expressed in wave number.

a =	82.2	d =	31.2	g =	72.6	α =	-407.6
b =	-60.0	e =	63.4	h =	229.8	β =	576.8
c =	307.3	f =	98.2	i =	-249.6	γ =	518.8

Table II. Potential constants of HCN

The potential constants of HCN molecule has been evaluated. A check of these constants and hence a test of the method of the theory are furnished by the isotope effect. The expression for α_2' will be after a similar calcuation

$$\alpha_2' = \left\{ k_1' \frac{k_1'}{\lambda_1' I_0' \mu_r'} + k_f' \frac{k_2'}{\lambda_2' I_0' \mu_\kappa'} \right\} \frac{h}{4\pi^2 c \omega_2'} + \left(\frac{h}{8\pi^2 I_0' c} \right) \left(\frac{s'^2}{\omega_1' - \omega_2'} + \frac{t'^2}{\omega_3' + \omega_2'} \right).$$

With the values of b and β, and the constants for DCN, one obtains

12. A. Dadieu and H. Kopper, *Wien. Anz.* 92, (1935).

$B_0' \alpha_2 = 0.00136$, where $B_0' = h/8\pi^2 I_0' c$,

which agrees quite well with the convergence factor for ν_2' 0.0013 observed by Bartunek and Barker. Further checks will be obtained, of course, from a study of the harmonics and the combinations of parallel vibrations of DCN and their rotational structure. Unfortunately such data are still lacking.

In conclusion, the writer takes great pleasure in thanking Professor T. Y. Wu for his advice throughout the course of the work.