The Analysis of the Molecular Vibration by the Molecular Orbital Method. I. Application to HCN

Tomoo MIYAZAKI, Masaru IKEDA, and Masayuki SHIBATA

Department of Applied Chemistry, Faculty of Science and Engineering, Waseda University, Nishi-Ohkubo, Shinjuku-ku, Tokyo 160

(Received July 24, 1974)

The approximate self-consistent molecular orbital method has been applied to the analysis of the vibrational spectrum of HCN. The frequencies of the fundamental, overtone, and combination bands in the region from about 700 to 12000 cm^{-1} have been calculated, and their absolute infrared absorption intensities have been estimated, the variational method being used in this calculation. Also, the frequencies and absorption intensities of hot bands, referring to the bending vibration, have been calculated. In comparison with the experimental results, the calculated frequencies were not always appropriate. However, it was found that these results are effective in the analysis of the molecular vibration if the calculated frequencies are discussed along with their infrared absorption intensities.

There have been reports in which the force constant and $\partial\mu_i/\partial S_j$ have been calculated on the basis of the results of molecular orbital calculations, where μ_i is the component of the molecular dipole moment and where S_i is an appropriate vibrational coordinate.[1-18] However, these results are not always desirable in comparison with the values from the experimental results. The main reason for the undesirable results is that the following requirement is hard to put into practice: the semi-empirical molecular orbital method adopted in the estimation of those values has to lead simultaneously to many appropriate values for the molecular constants, such as the bond length, the bond angle, the force constant, the dipole moment, and its derivative $(\partial\mu_i/\partial S_j)$. For example, the CNDO/2 method[1] proposed by Pople *et al.* can obtain reasonable values for the moleculr geometry, the dipole moment, and its derivative, but the calculated stretching force constant tends to be larger than that generally found. The MINDO/2' method[20] proposed by Dewar *et al.* leads to appropriate values for the molecular geometry and the stretching force constant, but adequate values for the bending force constant and the dipole-moment derivative with the bending coordinate cannot be obtained.

In previous papers,[14,15] the present authors discussed the abnormal infrared absorption intensity of the C–H stretching vibration band in chloroform on the basis of the dipole-moment derivative and the potential function calculated from the CNDO/2 method. In these calculations, the mechanical and electrical anharmonicities were considered and the variational method was used to estimate the energy and wave function of the vibrating system. At that time, some substantial modification for the potential function had to be made, although there was a problem to be solved in the method of modification.

In this work, the frequencies of the fundamental, overtone, and combination bands in the vibrational spectrum of HCN in the region from about 700 to 12000 cm^{-1} have been calculated by the use of the potential function obtained by the MINDO/2' method. Moreover, their absolute infrared absorption intensities have been estimated from the dipole-moment derivative calculated by the CNDO/2 method. Also, the frequencies and absorption intensities of the hot bands, referring to the bending vibration, have been calculated. In comparison with the experimental results, the calculated frequencies were not always appropriate. However, it was found that these results are effective in the analysis of the molecular vibration if the calculated frequencies are discussed along with their infrared absorption intensities. Furthermore, the effect of the different level of approximation for the bending coordinate on the calculated results was discussed.

Methods of Calculation

The Potential Energy Function. The total energies of the molecule required to determine the potential energy function for the molecular vibration have been calculated by the MINDO/2' method. In this calculation, the values of the parameters, B_{AB}, in the following approximate equation for the resonance integral, $\beta_{\mu\nu}$, were slightly modified:

$$\beta_{\mu\nu} = B_{AB}(I_\mu + I_\nu)S_{\mu\nu} \quad (1)$$

where I_μ and I_ν are the valence-state ionization potentials of the atomic orbitals, χ_μ and χ_ν, where $S_{\mu\nu}$ is the corresponding overlap integral, and where B_{AB} is a parameter characteristic of the A—B atom pair. The values of B_{CH} and B_{CN} were taken to be 0.3021 and 0.3522 respectively (the original values in the MINDO/2' method: $B_{CH}=0.2823$ and $B_{CN}=0.3453$). The calculated bond lengths of HCN, which is a linear structure, were 1.0445 Å and 1.1739 Å for r_{CH} and r_{CN} respectively (the observed values: $r_{CH}=1.06317$ Å and $r_{CN}=1.15535$ Å). According to the method of least-squares, the potential energy function, V, was obtained by fitting the increase in the total energy calculated for the distorted molecule to the 5th-order function with respect to the internal coordinates, R_i (the 6th order for the bending coordinate), but the 5th-order terms were omitted in the succeeding calculations.

$$V(R) = \sum_{i\leq j} K_{ij}R_iR_j + \sum_{i\leq j\leq k} K_{ijk}R_iR_jR_k + \sum_{i\leq j\leq k\leq l} K_{ijkl}R_iR_jR_kR_l. \quad (2)$$

For the HCN molecule, the internal coordinates are two bond-stretching coordinates, $R_1=\Delta r_{CH}$ and $R_2=$

Δr_{CN}, and two bending coordinates perpendicular to each other, $R_3=\Delta\theta_{(y)}$ and $R_4=\Delta\theta_{(z)}$. Generally, doubly degenerate vibrations, such as the bending coordinates in HCN, are treated as superpositions of these vibrations by the introduction of the polar coordinates. In this work, such a general treatment was avoided because the treatment was inconvenient in calculating collectively, by the variational method, the frequencies of all the vibrations in the molecule in view of the mechanical anharmonicity. In this calculation, the superposed system was described by a product of the wave functions of the doubly degenerate vibrations.

The calculations of the energy-increase arising from the bending deformation were performed for the different cases by the following methods, I and II. In these calculations, it was prescribed that we employ the B matrix, generally used, which is derived from the approximate linear-relation between the internal and the Cartesian coordinates. In Method I, the molecule was distorted according to the rectilinear bending deformation. The conformation of the distorted HCN molecule required to calculate the cross terms between bending and stretching vibrations was decided by the Δr_{CH}, Δr_{CN}, and $\Delta\theta$ values, which are related with one another as is shown in Fig. 1. In

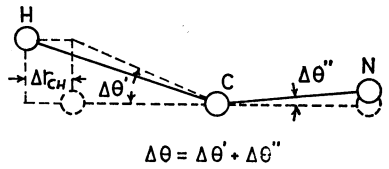


Fig. 1. Conformation of the distorted HCN referring to the C-H stretching and the rectilinear bending coordinates.

Method II, the molecule was distorted according to the curvilinear bending coordinate indicated in the potential surface of HCN, illustrated by Suzuki *et al.*[22] In this treatment, the conformation of the distorted HCN can be determined without trouble by Method I. Finally, the potential energy function represented by the internal coordinates was transformed to a function with the normal coordinates by the use of the L_R matrix elements:

$$V(Q)=\sum_i\frac{1}{2}\lambda_{ii}Q_i^2+\sum_{i\leq j\leq k}g_{ijk}Q_iQ_jQ_k+\sum_{i\leq j\leq k\leq l}h_{ijkl}Q_iQ_jQ_kQ_l. \quad (3)$$

The variational Treatment. The variational method has been used to calculate the energy levels of vibrations in view of the mechanical anharmonicities.

The total wave function, Ψ^{total}, for the molecular vibration is described as a linear combination of ψ's, each of which is written as a product of the harmonic oscillator wave functions, φ's, of all the vibrations in the molecule:

$$\Psi^{\text{total}}=\sum_i C_i\psi_i, \quad (4)$$

$$\psi_i=\varphi_l^1\varphi_m^2\varphi_n^3\varphi_o^4, \quad l,m,n, \text{ and } o=0,1,2,3\cdots\cdots \quad (5)$$

where φ_n^k indicates the n-th harmonic oscillator wave function, referring to the normal coordinate, Q_k (here, n is the principal quantum number of the vibration), and ψ_i is decided by the variety of the combination of the quantum numbers, l, m, n, and o.

The variational treatment of the coefficient, C_i, leads to this equation:

$$\sum_{j=0}^{k}C_j(H_{ij}-E\delta_{ij})=0, \qquad i=0,1,2,3,\cdots\cdots k, \quad (6)$$

$$H_{ij}=\langle\psi_i|\hat{T}+\hat{V}|\psi_j\rangle, \quad (7)$$

where δ_{ij} is the Kronecker delta symbol, $\hat{T}$ is the operator of the kinetic energy, $-\frac{h^2}{8\pi^2}\sum_k\frac{\partial^2}{\partial Q_k^2}$ and $\hat{V}$ is the operator referring to the potential function (3) with the normal coordinates. The energy, E, is the root of the secular equation:

$$|H_{ij}-E\delta_{ij}|=0.$$

Generally, the accuracy of the wave function improved by this treatment is restricted by the maximum values of the quantum numbers, l,m,n, and o. The upper limits of the quantum numbers are determined by the ability of the computer and the other restrictions. On the other hand, in order to obtain the improved wave function in the quantum numbers from 0 to 3, we have to consider the harmonic wave functions in the quantum numbers from 0 to 10 for each vibration in Eq. (5) at least. Therefore, we divided the variational treatment into the following two steps.

The First Step: The wave function of a specified normal vibration (k) was modified in view of the principal terms of the mechanical anharmonicity, without cross terms. In this treatment, the modified wave function, Φ^k, was described by a linear combination of harmonic oscillator wave functions, φ^k's, as follows:

$$\Phi^k=\sum_i C_i^k\varphi_i^k, \qquad i=0 \text{ to } 11. \quad (8)$$

The operator, $\hat{H}'(k)$, used in this calculation was as follows:

$$\hat{H}'(k)=-\frac{h^2}{8\pi^2}\frac{\partial^2}{\partial Q_k^2}+\frac{1}{2}\lambda_{kk}Q_k^2+g_{kkk}Q_k^3+h_{kkkk}Q_k^4. \quad (9)$$

The wave function and their energies can be obtained from the appropriate set of the secular equation and the equation corresponding to Eq. (6).

The Second Step: The total wave function, Ψ^{total}, was described as a linear combination of ψ's, each of which was written as a product the wave functions, Φ's, obtained from the first-step treatment:

$$\Psi^{\text{total}}=\sum_i C_i\psi_i, \quad (10)$$

$$\psi_i=\Phi_l^1\Phi_m^2\Phi_n^3\Phi_o^4, \quad l,m,n, \text{ and } o=0 \text{ to } 4. \quad (11)$$

The variety of combinations in ψ_i was restricted by the condition that $l+m+n+o\leq 4$. The calculations in the subsequent treatment were the same as those described above.

The Dipole Moment and its Expansion. It is desirable for the dipole moment of molecule to be calculated according to the method used to determine

the potential function. However, the values of the dipole-moment derivative with the bending coordinate obtained from the MINDO/2' method which was used to determine the potential function were not desirable in calculating the infrared absorption intensity; the detailed reasons why will be indicated later (see "Discussion"). Therefore, in this work, the component of the dipole moment was expanded by the normal coordinates on the basis of the results of the CNDO/2 calculations for the molecule which was distorted according to the L_x matrix elements, the values of equilibrium distances calculated by the MINDO/2' method being employed. The function of the dipolemoment component, μ_x, was obtained as the 5th-order expansion with the normal coordinates, but the 4th- and 5th-order terms were omitted in the calculation of the absorption intensities:

$$\mu_x = \mu_x{}^0 + \sum_i M_i Q_i + \sum_{i\leq j} M_{ij} Q_i Q_j + \sum_{i\leq j\leq k} M_{ijk} Q_i Q_j Q_k. \quad (12)$$

The Absolute Infrared Absorption Intensity. The method of the calculation of the absolute infrared absorption intensity in [$cm^2 s^{-1}$ $molecule^{-1}$] units was described in detail in a previous paper.[15] Practically, though, there is a difference in the integrals involving the cross terms in comparison with the previous calculation. The equation required to calculate the absolute absorption intensity, A, is as follows:

$$A_{v+n\leftarrow v} = \frac{8\pi^3}{3ch}\left(\frac{N_v}{N_t} - \frac{N_{v+n}}{N_t}\right)\nu_{v+n,v} \sum_{i=x,y,z} |(\mu_i)_v{}^{v+n}|^2, \quad (13)$$

$$N_v = N_0 \exp\left(-(E_v - E_0)\right)/kT, \quad (14)$$

$$N_t = N_0 \sum_{v=0}^{\infty} \exp(-(E_v - E_0))/kT, \quad (15)$$

$$(\mu_i)_v{}^{v+n} = \langle \Psi_v{}^{\text{total}} | \hat{\mu}_i | \Psi_{v+n}{}^{\text{total}} \rangle, \quad (16)$$

where N_0 and N_v are the numbers of the molecules per unit volume in the E_0 and E_v states of the total energies respectively; N_t is the total number of molecules, c is the velocity of light, h is Planck's constant, k is Boltzmann's constant, $\hat{\mu}_i$ is the operator corresponding to the function of the dipole-moment component with the normal coordinates (12), and $\nu_{v+n,v}$ is the transition energy in [s^{-1}] units between the E_v and E_{v+n} states of total energies. In this calculation, the absolute temperature, T, was taken to be 300 K. The absorption intensities of the hot bands, referring to the bending vibration, were also calculated.

Table 1. Coefficients of potential function, $V(R)$, for HCN

	Units	Method I	Method II	Ref.[22]
K_{11}	mdyn/Å	3.00985	3.00908	3.1150
K_{22}	mdyn/Å	9.35171	9.35063	9.3872
K_{33}, K_{44}	mdyn·Å/rad²	0.12100	0.12040	0.1296
K_{12}	mdyn/Å	0.40217	0.40050	−0.2160
K_{111}	mdyn/Å²	−4.39913	−4.39595	−6.0848
K_{222}	mdyn/Å²	−16.34869	−16.28970	−19.2273
K_{112}	mdyn/Å²	−0.15529	−0.21974	−0.3215
K_{122}	mdyn/Å²	0.16522	−0.36209	−1.3345
K_{133}, K_{144}	mdyn/rad²	2.04294	−0.03181	−0.1341
K_{233}, K_{244}	mdyn/rad²	−0.18322	−0.49783	−0.2716
K_{1111}	mdyn/Å³	4.25730	+4.27731	+8.7854
K_{2222}	mdyn/Å³	17.43130	17.39006	17.5164
K_{3333},K_{4444}	mdyn·Å/rad⁴	0.40753	0.00552	0.0029
K_{1122}	mdyn/Å³	2.93309	2.41937	1.1719
K_{1133},K_{1144}	mdyn/Årad²	−7.46997	+0.01205	+0.2008
K_{2233},K_{2244}	mdyn/Årad²	−0.84781	0.16097	−0.1889
K_{3344}	mdyn·Å/rad⁴	0.81506	0.01104	
K_{1112}	mdyn/Å³	0.42934	0.61351	1.0544
K_{1222}	mdyn/Å³	4.56675	2.83037	4.7149
K_{1233},K_{1244}	mdyn/Årad²	0.94222	0.93988	0.1962

Results and Discussion

In this work, trial calculations were performed by the use of several semi-empirical molecular orbital methods, such as the CNDO/2'[11] CNDO/BW,[19] and MINDO/2'[20] methods. We expected that any method would serve the purpose of determining the frequencies and intensities for the infrared absorption bands of HCN. Unfortunately, not every method answered to our expectations.* Elaborate parametrizations in any method would be able to satisfy our requirements, but such treatment is intricate and tedious, for universal validity is required for the values of parameters. For this reason, the MINDO/2' and CNDO/2 methods were used to calculate the total energy and the dipole moment of HCN respectively. *However, it should be emphasized that this treatment is an expediency.* The parameters in the MINDO/2' method were slightly modified in order to obtain agreement between the calculated frequencies and observed ones.

The coefficients of the potential function, $V(R)$, as calculated from Methods I and II, are indicated in Table 1; the values obtained by others[22] are also included. The large values of the cross terms between the stretching and the bending vibrations were obtained by Method I. In view of the level of approximation of the B matrix used in this work, the

* The force constants, k's, calculated by means of the CNDO/2 method were larger than those generally found:

$k_{11}=2K_{11}=12.861$ mdyn/Å, $k_{22}=2K_{22}=41.434$ mdyn/Å,
$k_{12}=K_{12}=0.42583$ mdyn/Å, $k_{33}=k_{44}=2K_{33}=2K_{44}$
$=0.57394$ mdyn·Å/rad².

These values of the force constants led to undesirable results for the calculated frequencies of the absorption bands.

On the other hand, the coefficients, M's, of the $\mu_i(Q)$ function calculated from the MINDO/2' method were as follows:

$$\mu_x(Q): \quad M_{33}=M_{44}=68.969\times10^{20} \text{ esu}/(g\cdot c),$$
$$\mu_y(Q),\ \mu_z(Q): \begin{cases} M_3=M_4=10.020\times10 \text{ esu}/\sqrt{g} \\ M_{333}=M_{444}=-117.43\times10^{40} \text{ esu}/(\sqrt{g^3}c^2). \end{cases}$$

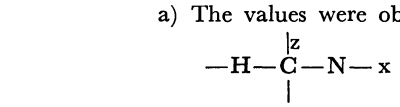
These values led to abnormal absorption intensities of the bending vibration; the intensities of the fundamentals, $A(0001)$ and $A(0010)$, are weak, and the intensity of the first overtone, $A((0002)+(0020))$, is much stronger than that of the former:

$A(0001)=A(0010)=57.379\times10^{-10}$ cm^2 s^{-1} $molecule^{-1}$,
$A((0002)+(0020))=504.38\times10^{-10}$ cm^2 s^{-1} $molecule^{-1}$.

TABLE 2-a. COEFFICIENTS OF $V(Q)$ AND $\mu_x(Q)$ FOR HCN
(V: [erg], μ_x: [esu·cm], Q: [$\sqrt{g}$·cm])

	Units	Coefficients[a]		Units	Coefficients[b,c]
$\frac{1}{2}\lambda_{11}$	$1/s^2$	19.7909×10^{28}	Const.	esu·cm	-2.47862×10^{-18}
$\frac{1}{2}\lambda_{22}$	$1/s^2$	8.20873×10^{28}	M_1	esu/$\sqrt{g}$	-1.42897×10
$\frac{1}{2}\lambda_{33}$, $\frac{1}{2}\lambda_{44}$	$1/s^2$	0.89465×10^{28}	M_2	esu/$\sqrt{g}$	-3.58430×10
			M_{11}	esu/($g\cdot c$)	23.5191×10^{20}
g_{111}	$1/(\sqrt{g}\cdot c\cdot s^2)$	-2.22583×10^{49}	M_{22}	esu/($g\cdot c$)	0.36093×10^{20}
g_{222}	$1/(\sqrt{g}\cdot c\cdot s^2)$	-0.40414×10^{49}	M_{33}, M_{44}	esu/($g\cdot c$)	31.5773×10^{20}
g_{112}	$1/(\sqrt{g}\cdot c\cdot s^2)$	-0.89214×10^{49}	M_{12}	esu/($g\cdot c$)	-55.4788×10^{20}
g_{122}	$1/(\sqrt{g}\cdot c\cdot s^2)$	0.27610×10^{49}	M_{111}	esu/($\sqrt{g^3}\cdot c^2$)	0.60743×10^{40}
g_{133}, g_{244}	$1/(\sqrt{g}\cdot c\cdot s^2)$	0.01609×10^{49}	M_{222}	esu/($\sqrt{g^3}\cdot c^2$)	-11.8450×10^{40}
g_{233}, g_{244}	$1/(\sqrt{g}\cdot c\cdot s^2)$	-0.10941×10^{49}	M_{112}	esu/($\sqrt{g^3}\cdot c^2$)	-23.5586×10^{40}
h_{1111}	$1/(g\cdot c^2\cdot s^2)$	1.73513×10^{69}	M_{122}	esu/($\sqrt{g^3}\cdot c^2$)	45.0192×10^{40}
h_{2222}	$1/(g\cdot c^2\cdot s^2)$	0.13131×10^{69}	M_{133}, M_{144}	esu/($\sqrt{g^3}\cdot c^2$)	-81.5843×10^{40}
h_{3333}, h_{4444}	$1/(g\cdot c^2\cdot s^2)$	0.00305×10^{69}	M_{233}, M_{244}	esu/($\sqrt{g^3}\cdot c^2$)	-7.93415×10^{40}
h_{1122}	$1/(g\cdot c^2\cdot s^2)$	0.29456×10^{69}			
h_{3344}	$1/(g\cdot c^2\cdot s^2)$	0.00609×10^{69}			
h_{1133}, h_{1144}	$1/(g\cdot c^2\cdot s^2)$	-0.04606×10^{69}			
h_{2233}, h_{2244}	$1/(g\cdot c^2\cdot s^2)$	0.02798×10^{69}			
h_{1112}	$1/(g\cdot c^2\cdot s^2)$	0.77069×10^{69}			
h_{1222}	$1/(g\cdot c^2\cdot s^2)$	-0.07116×10^{69}			
h_{1233}, h_{1244}	$1/(g\cdot c^2\cdot s^2)$	0.15097×10^{69}			

a) The values were obtained from the method II. b) Cartesian axis used in this calculation is as follows:



c) Negative dipole corresponds to $^+$(H-C-N)$^-$.

TABLE 2-b. COEFFICIENTS, $M^{(y)}$ AND $M^{(z)}$, FOR $\mu_y(Q)$ AND $\mu_z(Q)$. (μ_y, μ_z: [esu·cm], Q: [$\sqrt{g}$·cm])

$M^{(y)}$	$M^{(z)}$	Units	Coefficients	$M^{(y)}$	$M^{(z)}$	Units	Coefficients
M_3	M_4	esu/$\sqrt{g}$	5.51851×10	M_{113}	M_{114}	esu/($\sqrt{g^3}\cdot c^2$)	27.5416×10^{40}
M_{13}	M_{14}	esu/($g\cdot c$)	-47.2999×10^{20}	M_{223}	M_{224}	esu/($\sqrt{g^3}\cdot c^2$)	7.20507×10^{40}
M_{23}	M_{24}	esu/($g\cdot c$)	29.3334×10^{20}	M_{123}	M_{124}	esu/($\sqrt{g^3}\cdot c^2$)	22.2784×10^{40}
M_{333}	M_{444}	esu/($\sqrt{g^3}\cdot c^2$)	16.0836×10^{40}	M_{344}	M_{334}	esu/($\sqrt{g^3}\cdot c^2$)	16.0836×10^{40}

TABLE 3. ENERGY LEVELS AND WAVE FUNCTIONS OF VIBRATION WITH C-H STRETCHING MODE AS THE MAIN CONSTITUENTS.
(ε_v and $\Phi_v=\sum_i C_{vi}\varphi_i$)

The values were obtained from the method II.

v	0	1	2	3	4
ε[erg]$\times10^{13}$	3.30722	9.84286	16.3074	22.7325	29.1481
C_{v0}	**0.99695**	−0.07500	0.00426	−0.01787	0.01014
C_{v1}	0.07518	**0.97448**	−0.20456	0.02843	−0.03528
C_{v2}	0.00418	0.20544	**0.90684**	−0.35004	0.07883
C_{v3}	0.02013	0.02676	0.35323	**0.77630**	−0.47987
C_{v4}	0.00293	0.04099	0.07313	0.48879	**0.58106**
C_{v5}	−0.00006	0.01244	0.06820	0.14252	0.58408
C_{v6}	0.00078	0.00146	0.03063	0.10312	0.22695
C_{v7}	0.00014	0.00202	0.00670	0.05843	0.14542
C_{v8}	−0.00003	0.00074	0.00440	0.01810	0.09488
C_{v9}	0.00003	0.00003	0.00214	0.00888	0.03717
C_{v10}	0.00001	0.00009	0.00037	0.00483	0.01662
C_{v11}	−0.00000	0.00004	0.00017	0.00121	0.00815

$\Delta\varepsilon_{0,1}=3291.28\ \mathrm{cm}^{-1}$, $\Delta\varepsilon_{0,2}=6546.75\ \mathrm{cm}^{-1}$, $\Delta\varepsilon_{0,3}=9782.35\ \mathrm{cm}^{-1}$, $\Delta\varepsilon_{0,4}=13013.19\ \mathrm{cm}^{-1}$.
The $\Delta\varepsilon_{0,1}$ in the harmonic oscillator model was $3339.76\ \mathrm{cm}^{-1}$.

Table 4. Energy levels and wave functions of vibration with C-N stretching mode as the main constituents.
(ε_v and $\Phi_v=\sum_i C_{vi}\varphi_i$)

The values were obtained from the method II.

v	0	1	2	3	4
ε[erg]$\times 10^{13}$	2.13383	6.38356	10.6117	14.8199	19.0097
C_{v0}	**0.99906**	−0.04184	0.00102	−0.01085	0.00354
C_{v1}	0.04183	**0.99190**	−0.11729	0.00822	−0.02132
C_{v2}	0.00150	0.11722	**0.96923**	0.21138	0.02510
C_{v3}	0.01136	0.00939	0.21113	**0.92178**	−0.31458
C_{v4}	0.00101	0.02303	0.02689	0.31405	**0.84221**
C_{v5}	0.00002	0.00434	0.03760	0.05646	0.41590
C_{v6}	0.00028	0.00041	0.01105	0.05588	0.09900
C_{v7}	0.00003	0.00075	0.00175	0.02219	0.07873
C_{v8}	−0.00000	0.00018	0.00162	0.00493	0.03860
C_{v9}	0.00000	0.00002	0.00056	0.00317	0.01098
C_{v10}	0.00000	0.00003	0.00010	0.00136	0.00586
C_{v11}	−0.00000	0.00001	0.00007	0.00030	0.00267

$\Delta\varepsilon_{0,1}=2140.12\ \mathrm{cm^{-1}}$, $\Delta\varepsilon_{0,2}=4269.37\ \mathrm{cm^{-1}}$, $\Delta\varepsilon_{0,3}=6388.55\ \mathrm{cm^{-1}}$, $\Delta\varepsilon_{0,4}=8498.49\ \mathrm{cm^{-1}}$.
The $\Delta\varepsilon_{0,1}$ in the harmonic oscillator model was $2150.90\ \mathrm{cm^{-1}}$.

Table 5. Energy levels and wave functions of vibration with bending mode as the main constituents.
(ε_v and $\Phi_v=\sum_i C_{vi}\varphi_i$)

The values were obtained from the method II.

v	0	1	2	3	4
ε[erg]$\times 10^{13}$	0.70669	2.12287	3.54463	4.97192	6.40467
C_{v0}	**0.99999**	0	0.00141	0	0.00041
C_{v1}	0	**0.99999**	0	0.00404	0
C_{v2}	−0.00141	0	**0.99997**	0	0.00796
C_{v3}	0	−0.00406	0	**0.99990**	0
C_{v4}	−0.00040	0	−0.00799	0	**0.99977**
C_{v5}	0	−0.00088	0	−0.01321	0
C_{v6}	0.00000	0	−0.00148	0	−0.01968
C_{v7}	0	0.00002	0	−0.00220	0
C_{v8}	0.00000	0	0.00004	0	−0.00299
C_{v9}	0	0.00000	0	0.00007	0
C_{v10}	−0.00000	0	0.00000	0	0.00013
C_{v11}	0	−0.00000	0	0.00001	0

$\Delta\varepsilon_{0,1}=713.17\ \mathrm{cm^{-1}}$, $\Delta\varepsilon_{0,2}=1429.15\ \mathrm{cm^{-1}}$, $\Delta\varepsilon_{0,3}=2147.91\ \mathrm{cm^{-1}}$, $\Delta\varepsilon_{0,4}=2869.42\ \mathrm{cm^{-1}}$.
The $\Delta\varepsilon_{0,1}$ in the harmonic oscillator model was $710.08\ \mathrm{cm^{-1}}$.

Table 6. Wave numbers, $\tilde{\nu}$, and absorption intensities, A, of vibrational spectrum of HCN
($\tilde{\nu}$: [$\mathrm{cm^{-1}}$], A: [$\mathrm{cm^2\ s^{-1}\ molecule^{-1}}$], $T=300$ K)

Method I			Method II			Ref.[21,22]
$\tilde{\nu}$	$A\times 10^{10}$	Vibrational Modes[a] (v^1,v^2,v^3,v^4)[b]	$\tilde{\nu}$	$A\times 10^{10}$	Vibrational Modes[a] (v^1,v^2,v^3,v^4)[b]	$\tilde{\nu}$ (obsd)
738.95	1148.6[c]	(0001)	704.65	1065.7[c]	(0001)	713.74 (001^1)
738.95	1148.6	(0010)	704.65	1065.7	(0010)	
1540.73	0	(0011)	1410.23	70.400	(0002) + (0020)	1411.42 (002^0)
1552.64	221.28	(0002) + (0020)	1411.55	0	(0011)	
1556.89	0	(0002) − (0020)	1411.58	0	(0002) − (0020)	
2147.11	378.48[c]	(0100)	2113.61	4.537	(0003) + *(0021)*	2115.00 (003^1)
2340.14	2.511	(0030) − *(1030)*	2113.61	4.537	(0030) + *(0012)*	
2340.14	2.511	(0003) − *(1003)*	2116.54	0.032	(0012) − *(0030)*	
2473.26	5.500	(0021) − *(1021)*	2116.54	0.032	(0021) − *(0003)*	
2473.26	5.500	(0012) − *(1012)*	2136.24	485.26[c]	(0100)	2096.68 (010)
2919.03	19.666	(0110)	2841.83	10.386	(0110)	2807.06 (011^1)
2919.03	19.666	(0101)	2841.83	10.386	(0101)	
3286.20	76.198[c]	(1000)	2852.85	0.006	(0004) + (0040) + *(0022)*	
3743.36	0	(0111)	2854.24	0	(0004) − (0040)	
3756.94	0.023	(0102) + (0120)	2854.30	0	(0013) + (0031)	

Table 6. (Continued)

Method I			Method II			Ref.[21,22]
$\tilde{\nu}$	$A\times10^{10}$	Vibrational Modes[a] (v^1, v^2, v^3, v^4)[b]	$\tilde{\nu}$	$A\times10^{10}$	Vibrational Modes[a] (v^1, v^2, v^3, v^4)[b]	$\tilde{\nu}$ (obsd)
3759.21	0	(0102) − (0120)	2858.52	0	(0022) − (*0004*) − (*0040*)	
3892.25	3.470	(0022)	2858.55	0	(0013) − (0031)	
3968.86	0	(0013) + (0031) − (*1011*)	3278.82	144.58[c]	(1000)	3311.47 (100)
3994.55	0	(0004) − (0040)	3545.09	0.827	(0120) + (0102)	3504.07 (012^0)
4011.60	2.446	(0004) + (0040)	3545.36	0	(0102) − (0120)	
4037.60	7.671	(1010)	3545.37	0	(0111)	
4037.60	7.671	(1001)	3981.36	31.087	(1001)	4005.64 (101^1)
4041.92	0	(0013) − (0031)	3981.36	31.087	(1010)	
4299.03	1.061	(0200)	4265.53	0.816	(0200)	4173.02 (020)
4963.09	0	(1002) − (1020)	4280.37	0.080	(0103) + (*0121*)	4202.77 (013^1)
4979.27	0.080	(0112) − (*0210*) + (*0130*)	4280.37	0.080	(0130) + (*0112*)	
4979.27	0.080	(0121) − (*0201*) + (*0103*)	4288.03	0	(0112) − (*0130*)	
5026.02	0.051	(0130) − (0112)	4288.03	0	(0121) − (*0103*)	
5026.02	0.051	(0103) − (0121)	4682.12	22.461	(1002) + (1020)	4684.61 (102^0)
5077.55	0	(1011) + (*0013*) + (*0031*)	4682.95	0	(1011)	4705.25 (102^2)
5090.37	4.573	(1002) + (1020) + (*0022*)	4683.06	0	(1002) − (1020)	
5104.86	0.029	(0210) + (*0130*)	4968.20	0.030	(0210)	4879.73 (021^1)
5104.86	0.029	(0201) + (*0103*)	4968.20	0.030	(0201)	
5442.91	16.746	(1100)	5419.36	17.333	(1100)	5393.70 (110)
6136.38	0	(0202) − (0220)	5426.37	0.005	(1003) + (*1021*)	5368.62 (103^1)
6142.34	0.011	(0202) + (0220)	5426.37	0.005	(1030) + (*1012*)	
6144.94	0	(0211)	5428.52	0	(1012) − (*1030*)	
6161.04	0.120	(1021) + (*0021*)	5428.52	0	(1021) − (*1003*)	
6161.04	0.120	(1012) + (*0012*)	5695.67	0.078	(0202) + (0220)	5572.17 (022^0)
6256.26	0.013	(1101) − (*1003*)	5701.50	0	(0202) − (0220)	
6256.26	0.013	(1110) − (*1030*)	5701.54	0	(0211)	
6286.34	1.294	(1003) + (*1101*) + (*0003*)	6119.67	0.478	(1110)	6084.81 (111^1)
6286.34	1.294	(1030) + (*1110*) + (*0030*)	6119.67	0.478	(1101)	
6428.36	0.227	(0300)	6393.20	0.360	(0300)	
6475.71	8.920	(2000)	6521.45	13.911	(2000)	6519.61 (200)
7245.87	0	(1102) − (1120)	6874.74	0.147	(1102) + (1120)	6761.30 (112^0)
7260.38	0	(1111)	6877.89	0	(1102) − (1120)	6781.74 (112^2)
7261.11	0.032	(1102) + (1120)	6877.92	0	(1111)	
7265.98	0.330	(2001) + (*1003*)	7112.88	0.001	(0301)	
7265.98	0.330	(2010) + (*1030*)	7112.88	0.001	(0310)	
7328.52	0.002	(0310)	7218.98	1.153	(2010)	7194.22 (201^1)
7328.52	0.002	(0301)	7218.98	1.153	(2001)	
7590.84	0.773	(1200)	7551.44	0.312	(1200)	
8181.18	0	(2002) − (2020)	7966.51	0.143	(2002) + (2020)	
8192.38	0	(2011) + (*1011*)	7967.18	0	(2011)	
8212.82	0.004	(2002) + (2020)	7967.21	0	(2002) − (2020)	
8437.54	0	(1201)	8308.91	0.001	(1210)	
8437.54	0	(1210)	8308.91	0.001	(1201)	
8602.53	0.056	(0400)	8651.19	0.063	(0400)	
8637.94	0.252	(2100)	8666.64	0.015	(2100)	8585.57 (210)
9435.06	0.055	(2101)	9435.47	0.013	(2101)	9257.56 (211^1)
9435.06	0.055	(2110)	9435.47	0.013	(2110)	
9624.93	0.175	(3000)	9734.39	0.001	(1300)	
9738.53	0.030	(1300)	9747.54	0.390	(3000)	9627.02 (300)
10344.30	1.429	(3001)	10486.50	0.037	(3010)	10282.03 (301^1)
10344.30	1.429	(3010)	10486.50	0.037	(3001)	
10814.66	0.004	(2200)	10884.85	0	(2200)	
11807.75	0.046	(3100)	11948.97	0.003	(3100)	11674.46 (310)
12236.33	0.025	(4000)	12969.68	0.013	(4000)	12635.90 (400)

a) The italics indicate the additional modes. b) The v^k indicates the quantum number of energy level for the molecular vibration k. c) The observed values are as follows:[23] $A(0001)=1140\times10^{-10}$, $A(0100)=7.2\times10^{-10}$, $A(1000)=2700\times10^{-10}$ in unit [$cm^2\,s^{-1}$ molecule^{-1}].

Table 7. Wave numbers, $\tilde{\nu}$ and absorption intensities, A, of hot bands of HCN
The values were calculated by the method II.
($\tilde{\nu}$: [cm^{-1}], A: [cm^2 s^{-1} molecule^{-1}], T=300 K)

$\tilde{\nu}$	$A\times10^{10}$		Vibrational Modes	Ref.[21] $\tilde{\nu}$ (obsd)	$\tilde{\nu}$	$A\times10^{10}$		Vibrational Modes	Ref.[21] $\tilde{\nu}$ (obsd)
	G: $(0001)^z$	G: $(0010)^y$				G: $(0001)^z$	G: $(0010)^y$		
705.57	40.110(z)	40.110(y)	(0002) + (0020)		4723.86		0.001	(1012) − (1030)	
706.89	38.220(y)	38.220(z)	(0011)		4723.86	0.001		(1021) − (1003)	
706.92	38.227(z)	38.227(y)	(0002) − (0020)		4991.02	0.001(z)	0.001(y)	(0202) + (0220)	4858.43 (022^0)
1408.95	4.740		(0003)		4996.84	0.001(z)	0.001(y)	(0202) − (0220)	
1408.95		4.740	(0030)		4996.88	0.001(y)	0.001(z)	(0211)	
1411.88		0.032	(0012)		5415.01		0.480	(1110)	5371.35 (111^1)
1411.88	0.032		(0021)		5415.01	0.480		(1101)	
1431.58	0.013(z)	0.013(y)	(0100)		5688.55	0	0	(0300)	
2137.17		17.794	(0110)		5816.79	0.029(z)	0.029(y)	(2000)	
2137.17	17.794		(0101)		6170.08	0.030(z)	0.030(y)	(1102) + (1120)	6047.56 (112^0)
2148.19	0.393(z)	0.393(y)	(0004) + (0040)		6173.23	0.021(z)	0.021(y)	(1102) − (1120)	6068.00 (112^2)
2149.58	0.298(z)	0.298(y)	(0004) − (0040)		6173.26	0.021(y)	0.021(z)	(1111)	
2149.64	0.286(y)	0.286(z)	(0013) + (0031)		6408.23	0.015		(0301)	
2153.86	0	0	(0022)		6408.23		0.015	(0310)	
2153.89	0	0	(0013) − (0031)		6514.33		0.550	(2010)	6480.76 (201^1)
2574.16	0.701(z)	0.701(y)	(1000)	2598.01 (100)	6514.33	0.550		(2001)	
2840.43	0.271(z)	0.273(y)	(0120) + (0102)	2788.85 (012^0)	6846.78	0	0	(1200)	
2840.70	0.333(z)	0.332(y)	(0102) − (0120)		7261.85	0.034(z)	0.034(y)	(2002) + (2020)	
2840.71	0.333(y)	0.333(z)	(0111)		7262.52	0.038(y)	0.038(z)	(2011)	
3276.70	8.642		(1001)	3292.17 (101^1)	7262.56	0.038(z)	0.038(y)	(2002) − (2020)	
3276.70		8.642	(1010)		7604.25		0.011	(1210)	
3560.87	0.004(z)	0.004(y)	(0200)		7604.25	0.011		(1201)	
3575.71	0.074		(0103)		7946.53	0	0	(0400)	
3575.71		0.074	(0130)		7961.98	0.001(z)	0.001(y)	(2100)	
3583.37		0	(0112)		8730.81	0.002		(2101)	
3583.37	0		(0121)		8730.81		0.002	(2110)	
3977.46	1.003(z)	1.003(y)	(1002) + (1020)	3970.87 (102^0)	9029.73	0	0	(1300)	
3978.30	1.037(y)	1.037(z)	(1011)	3991.51 (102^2)	9042.88	0.001(z)	0.001(y)	(3000)	
3978.40	1.037(z)	1.037(y)	(1002) − (1020)		9781.84		0.019	(3010)	9568.29 (301^1)
4263.54		0.026	(0210)		9781.84	0.019		(3001)	
4263.54	0.026		(0201)		10180.19	0	0	(2200)	
4714.70	0.024(z)	0.024(y)	(1100)		11244.31	0.002(z)	0.002(y)	(3100)	
4721.71	1.566		(1003) + (0121)	4654.88 (103^1)	12265.02	0	0	(4000)	
4721.71		1.566	(1030) + (0112)						

treatment in Method I may be considered to be more reasonable than that in Method II. However, the final result from Method I was undesirable in comparison with the observed values. Therefore, we are especially interested in the treatment of Method II, which brings better results. The results calculated by Method II are mainly indicated in Tables 2 to 5.

The variational treatment was divided into two steps because of the technical counterplan. However, this treatment was effective in obtaining additional information. For example, we thus learned that the wave functions of molecular vibration can be specified in view of the principal terms of anharmonicity, without cross terms, as is indicated in Tables 3,4, and 5.** It is recognized that the mechanical anharmonicity of the C–H vibration is as large as that generally found. Moreover, the effects of cross terms in anharmonicity on the frequencies of the absorption bands can be confirmed. The coefficients of the function of the dipole-moment component with the normal coordinates are indicated in Table 2. In Table 6, the final results involving the frequencies and the absorption intensities of the vibrational spectrum of HCN are indicated, and the principal and additional modes of vibration are clarified. It should be noted that the representation of the vibrational mode is indicated by the quantum number of the energy level of vibration, considering the principal terms of anharmonicity without cross terms. The frequencies and the absorption intensities of the hot bands, referring to the bending vibration, are listed in Table 7. In Tables 6 and 7, the calculated frequencies and the intensities of the absorption bands are not always appropriate. However, it was found that the calculated intensities are effective in clarifying the assignment of the observed absorption bands. In comparison with the results in the references,[21,22] we can make the following statements: the absorption intensities of (1011), (1002)—(1020), (1111), and (1102)—(1120) are equal to zero, and the order of intensities of (0300), (1200), and (2002)+(2020) is 10^{-11} degree in [$cm^2\ s^{-1}$ $molecule^{-1}$] units. The absorption intensity of the degenerate hot band {(0111), (0102)−(0120)} is larger than the intensity of (0102)+(0120), and also {(0211), (0202)—(0220)} is larger than (0202)+(0220).

The results presented above show that the molecular orbital calculations are effective in the analysis of the vibrational specturm if the absorption intensities are slso calculated.

The authors would like to acknowledge the continuing encouragement of Professor K. Higasi. In their calculation, they were helped by the "University Contribution" of UNIVAC Japan, Ltd.

** There remains a further question as to the number of harmonic wave-functions used in Eq. (8). Therefore, the wave numbers, $\tilde{\nu}$, and the absorption intensities, A, were calculated under different restrictions. The results calculated on the basis of the condition (i=0 to 13) are as follows:

$\tilde{\nu}$		$A\times10^{10}$
704.92	(0001)	1065.7
1410.76	(0002) + (0020)	70.400
2114.40	(0003)	4.537
2137.04	(0100)	485.26
2853.91	(0004) + (0040)	0.006
3280.05	(1000)	144.58
4267.12	(0200)	0.816
6395.59	(0300)	0.360
6523.88	(2000)	13.911
8654.41	(0400)	0.063
9751.18	(3000)	0.390
12974.26	(4000)	0.013

($\tilde{\nu}$: cm^{-1}, A: $cm^2\ s^{-1}$ $molecule^{-1}$)

In comparison with the values shown in Table 6, there is no difference in the absorption intensity and the difference in the wave numbers is not a serious problem in this work.

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