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The Raman Spectrum and the Potential Function of Cyanogen

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From investigations on cyanogen, diacetylene and dimethyldiacetylene by electron diffraction Pauling, Springall and Palmer have concluded that the C—C single bond in these compounds has a considerable amount of double bond character [1]. It seems worth while to try these results confirmed from calculation of the potential functions, and in the case of C_2N_2 where Pauling *et al.* find 40 per cent double bond character such have already been carried out on basis of the valence force system [2–4]. However, it is to be expected that this can only give a rough approximation and that a more general type of potential function including "cross terms" should be applied. But even in the simple case of C_2N_2 not enough vibration frequencies can be observed in the infrared and Raman spectra to make a calculation of the complete harmonic potential function possible. This difficulty could be overcome by considering also frequencies from the isotopic molecule $C^{12}C^{13}N_2^{14}$ which constitutes about 2.2 per cent of natural cyanogen. In fact, by taking the Raman spectrum with a spectrograph of high resolving power and dispersion we have been able to detect two frequencies one of which can be ascribed to this molecule. In the following will be given the results of new electron diffraction experiments on cyanogen, and of a reinvestigation of the Raman spectrum including depolarization measurements of the two strongest lines. Finally, using data also from the infrared spectrum obtained by others [4] the force constants in the harmonic potential function are calculated and the nature of the valence force field is discussed.

EXPERIMENTAL

Preparation. The cyanogen used for these experiments was prepared according to Kistiakowsky [5] and A. Klemenc [6] by dripping a concentrated solution of potassium cyanide into a concentrated solution of cupric sulphate under reduced pressure. The gas evolved was purified by repeated distillations and finally dried over P_2O_5.

Electron diffraction *. Electron diffraction photographs were taken of C_2N_2 by the rotating sector method. From the microphotometer traces of four plates the radial distribution function $\frac{\sigma(r)}{r}$ was obtained by a procedure previously described in this journal [7]. This curve had very pronounced maxima at $r = 1.16$ Å, $r = 2.53$ Å and $r = 3.68$ Å corresponding to a linear model with distances: C—C: 1.38 Å, N≡C: 1.15 Å which is in complete agreement with the investigations of Pauling *et al.*[1] The probable error is about ± 0.02 Å.

Raman spectrum. The apparatus and methods for obtaining the Raman spectrum were those usually employed in this laboratory and which have been described elsewhere [8]. The observed frequencies are given in Table 1 together with their visually estimated intensity and comments on the general appearance of some of the Raman lines.

As far as we know the Raman lines 521.4 cm^{-1}, 561.4 cm^{-1}, 841 cm^{-1} and 2 298.4 cm^{-1} have not been observed before [9-11]. On the other hand we have not been able to detect the very weak lines 304 cm^{-1}, 696 cm^{-1}, 1 102 cm^{-1} and 1 386 cm^{-1} found by Reitz and Sabathy in their investigation of cyanogen [11].

A one prism spectrograph of high light-gathering power (camera lens f 1 : 2.5) was used for polarization measurements. The Raman tube was irradiated with approximately parallel light from two Philip's HO 2 000 Hg-lamps. By aid of a Rochon prism the scattered light was split into two beams with the polarization planes at right angles. In this way we got two separated pictures on the slit of the spectrograph and hence two spectra on the photographic plate. On the same plate and with the same set up were

Table 1.

Frequency in cm^{-1}	Intensity	Remarks
c. 240	weak	Broad diffuse
c. 475	very weak	Diffuse
507.2	strong	Somewhat diffuse
521.4	weak	
561.4	very weak	
750	very weak	
841	weak	
850.6	medium	Sharp
1 028.5	weak	Sharp
2 298.4	weak	
2 328.5	very strong	Sharp

* One of us (C. K. M.) is very indebted to Professor O. Hassel and his staff for a stay at the Physical-Chemical Laboratory of the University at Oslo during which this part of the work was done.

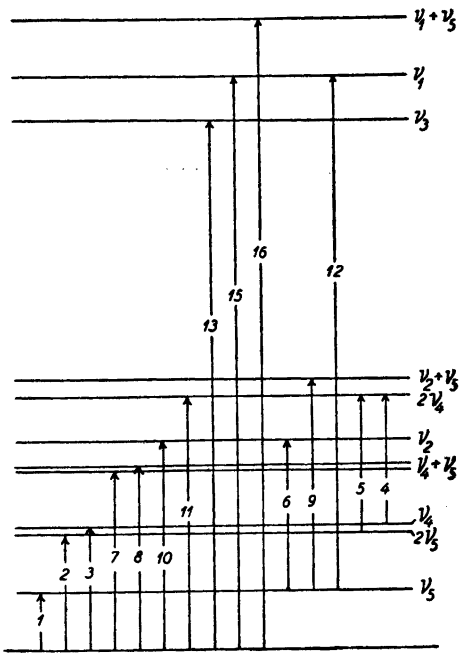

Fig. 1. Vibrational energy level diagram of the cyanogen molecule. The numbering of the different transitions refer to Table 2.

next photographed the two analogous spectra from a very pure CCl_4-sample and finally without the Rochon prism, the continuous spectrum of the hot filament of a small lamp with a Pt-step-filter before the slit. The plates were photometered by aid of a photoelectric microphotometer. The adjacent continuous step spectra photometered at the wave length of the Raman line considered gave the relation between blackening and energy. On basis of this and from the microphotometer traces of the Raman lines apparent depolarization degrees were calculated for C_2N_2 and CCl_4. Finally, using the known values for CCl_4 as standards [12] the true depolarizations were obtained. (It may be added here that the spectrograph slit was so wide that the heights of the maxima of the photometer curves could serve directly as a measure for the energy.) The mean values from four plates gave for:

$$\nu_4 = 507.2 \text{ cm}^{-1}, \quad \varrho = 0.83 \text{ and } \nu_1 = 2\,328.5 \text{ cm}^{-1}, \quad \varrho = 0.33$$

As the error is estimated to about ± 5 per cent it is concluded that ν_4 is depolarized. The line $\nu_2 = 850.6$ cm^{-1} was too weak for quantitative measurements to be made. However, it seemed to be polarized which one would also conclude from the sharpness of this line.

ASSIGNMENT OF FREQUENCIES

From classical stereochemistry as well as from considerations of the elctronic structure the molecule is expected to be linear and symmetric. As mentioned above, this is confirmed by the electron-diffraction measurements.

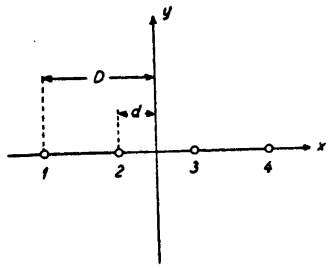

Fig. 2. Cartesian coordinates chosen for the symmetric C_2N_2-molecule. The four atoms placed along the X-axis are numbered from 1 to 4 and the dimensions of the molecule is given by the distances D and d.

Table 2. Raman and infrared frequencies of C_2N_2.

No.	Frequency in cm^{-1}	Activity observed	Remarks	Interpretation	Symmetry	Selection rule activity
1	c. 240	I–R (R)	σ-band	ν_5	E_{1u}	I–R (σ)
2	c. 475	R		$2\nu_5$	A_{1g}, A_{2g}, E_{2g}	R (pol)
3	507.2	R	depol.	ν_4	E_{1g}	R (dep)
4	521.4	R		$2\nu_4-\nu_4$	E_{1g}, E_{3g}	R (dep)
5	561.4	R		$2\nu_4-2\nu_5$	A_{1g}, A_{2g}, E_{2g}	R (pol)
6	618	I–R	σ-band	$\nu_2-\nu_5$	E_{1u}	I–R (σ)
7	732	I–R	π-band	$\nu_4+\nu_5$	A_{1u}, A_{2u}, E_{2u}	I–R (π)
8	750	R				
9	841	R		$(\nu_2+\nu_5)-\nu_5$	A_{1g}, A_{2g}, E_{2g}	R (pol)
10	850.6	R	polarized	ν_2	A_{1g} *	R (pol)
11	1 028.5	R		$2\nu_4$	A_{1g}, A_{2g}, E_{2g}	R (pol)
12	2 092	I–R	σ-band	$\nu_1-\nu_5$	E_{1u}	I–R (σ)
13	2 149	I–R	π-band	ν_3	A_{2u}	I–R (π)
14	2 298.4	R		ν_1 isotope	$C_{\infty h}, A_1$	R (pol)
15	2 328.5	R	(polarized)	ν_1	A_{1g}	R (pol)
16	2 562	I–R	σ-band	$\nu_1+\nu_5$	E_{1u}	I–R (σ)
17	2 662	I–R	σ-band	$\nu_3+\nu_4$	E_{1u}	I–R (σ)

Hence, C_2N_2 has the symmetry $D_{\infty h}$. From group-theoretical considerations [13] it follows that there are 3 non-degenerate fundamental vibrations, two of which are symmetric (A_{1g}) and one antisymmetric (A_{2u}) with respect to the inversion, further 2 degenerate vibrations being respectively symmetric (E_{1g}) and antisymmetric (E_{1u}). The five modes of vibration are shown schematically in Fig. 3. According to selection rules all the antisymmetric fundamentals

* Fermi-resonance between the two A_{1g} components causes an enhanced activity of the overtone, 2 ν_4, which appears as a Raman-line of medium strength.

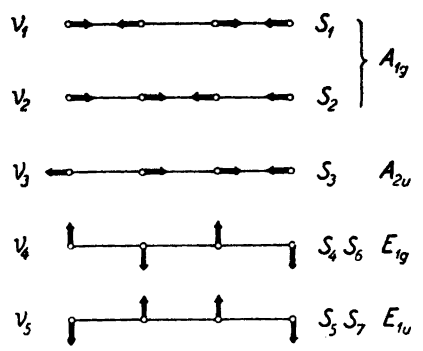

Fig. 3. Vibrational modes of the linear C_2N_2-molecule. The symmetry coordinates as well as the symmetry species are given for each normal vibration. Only one components of the degenerate vibrations is shown.

are infrared active while the symmetric ones are Raman active. Furthermore, A_{1g} vibrations give polarized Raman lines ($\varrho < 6/7$), all others depolarized ($\varrho = 6/7$).

The problem of assigning the observed frequencies to definite modes of vibration has caused some discussion in the literature [2], but must now be considered as settled. We shall therefore not go into any detail here. The assignment given in Table 2 (and Fig. 1) is in essential agreement with that given in Herzberg's book [2]. Two of the new Raman-lines 521.4 and 561.4 cm^{-1} can uncompelled be explained as the difference tones ν_4—$2\nu_4$ and $2\nu_5$—$2\nu_4$. Of the remaining new lines 2 298.4 cm^{-1} is undoubtedly due to ν_1 of the isotopic molecule $N{\equiv}C^{12}{-}C^{13}{\equiv}N$. As well the shift in frequency as the intensity ratio (I (2 328.5)/I(2 298.4)) is of the right order of magnitude. Furthermore, the line is sharp (strongly polarized) as should be expected. The remaining 841 cm^{-1} line is tentatively given the assignment ν_5—($\nu_2 + \nu_5$), because its intensity seems to be too high for interpreting it as an isotopic line. Below we are showing that neither its frequency is compatible with this assignment.

THE POTENTIAL FUNCTION OF THE C_2N_2 MOLECULE

The general harmonic potential function for vibrations belonging to the different symmetry classes may be formulated as:

$$
\begin{aligned}
&A_{1g}\ (\nu_1 \text{ and } \nu_2) && 2V_1 = a_{11}S_1^2 + a_{22}S_2^2 + 2a_{12}S_1S_2\\
&A_{2u}\ (\nu_3) && 2V_2 = a_{33}S_3^2\\
&E_{1g}\ (\nu_4) && 2V_3 = a_{44}S_4^2 + a_{66}S_6^2\\
&E_{1u}\ (\nu_5) && 2V_4 = a_{55}S_5^2 + a_{77}S_7^2
\end{aligned}
$$

where a_{11}, a_{22} . . . . . a_{77} are force constants and S_1, S_2 . . . . . S_7 the geometric symmetry coordinates. These are linear combinations of the atomic displacement coordinates with the property that they form basis for irreducible representations of the symmetry group and are independent of translations and rotations of the molecule. The symmetry coordinates for a simple molecule as C_2N_2 can be found by inspection (Fig. 3). The same coordinates may also be used for any isotopic species of this molecule, because the interatomic distances and the potential function are unchanged.

Linear vibrations (*Symmetry classes* A_{1g} *and* A_{2u}). Numbering the atoms as indicated in Fig. 2. we choose:

$$S_1 = x_1—x_4,\ S_2 = x_2—x_3 \text{ and } S_3 = x_1—x_2—x_3 + x_4$$

In order to exclude translation in the x-direction the following relation must be satisfied:

$$m_1x_1 + m_2x_2 + m_3x_3 + m_4x_4 = 0$$

Here m_i is the mass of the i-th atom. This enables us to express the displacement coordinates as linear combinations of the symmetry coordinates:

$$\begin{aligned}
x_1(2M) &= (m_2 + m_3 + 2m_4)S_1—(m_2—m_3)S_2 + (m_2 + m_3)S_3 \\
x_2(2M) &= —(m_1—m_4)S_1 + (m_1 + 2m_3 + m_4)S_2—(m_1 + m_4)S_3 \\
x_3(2M) &= —(m_1—m_4)S_1—(m_1 + 2m_2 + m_4)S_2—(m_1 + m_4)S_3 \\
x_4(2M) &= —(2m_1 + m_2 + m_3)S_1—(m_2—m_3)S_2 + (m_2 + m_3)S_3 \\
(M &= m_1 + m_2 + m_3 + m_4)
\end{aligned} \tag{1}$$

Lagrange's equations with the symmetry coordinates as generalized coordinates are:

$$\frac{d}{dt}\left(\frac{\partial \Delta T}{\partial \dot{S}}\right) + \frac{\partial \Delta V}{\partial S} = 0$$

where ΔT is the kinetic and ΔV the potential energy. Instead of inserting (1) into the kinetic energy function:

$$2\Delta T = m_1\dot{x}_1^2 + m_2\dot{x}_2^2 + m_3\dot{x}_3^2 + \mathrm{m}_4\dot{x}_4^2$$

we calculate the first member of Lagrange's equation from

$$\frac{\partial \Delta T}{\partial \dot{S}} = \sum_i m_i\dot{x}_i \frac{\partial x_i}{\partial S}$$

By using this procedure it is possible to set up the equations of motion for each symmetry class separately, considering only those symmetry coordinates which belong to that particular symmetry class.

In this case we want to determine the four "linear" force constants: a_{11}, a_{22}, a_{12} and a_{33}. This is possible because we in addition to the three fundamentals (ν_1, ν_2 and ν_3) in C_2N_2 now also know the frequency of one of the fundamentals (ν_1 (isot.)) in $C^{12}C^{13}N_2^{14}$. Because the symmetry of this molecule is lower ($C_{\infty}v$) all the linear fundamentals belong to the same symmetry class (A_1). Hence we cannot separate the variables S_1, S_2 and S_3. We get the following equations of motion:

$$\begin{aligned}
&\{(m_1+m_3)\ (m_1+m_4)+4m_1m_4\}\ddot{S}_1-(m_2-m_3)\ (m_1-m_4)\ddot{S}_2+[(m_1-m_4)\\
&(m_2+m_3)\ \ddot{S}_3+8a_{11}MS_1+8a_{12}S_2=0\\
&-(m_1-m_4)\ (m_2-m_3)\ddot{S}_1+\{(m_1+m_4)\ (m_2+m_3)+4\ m_2m_3\}\ddot{S}_2-[(m_2-m_3)\\
&(m_1+m_4)\ddot{S}_3+8a_{12}MS_1+8a_{22}MS_2=0\\
&(m_2+m_3)\ (m_1-m_4)\ddot{S}_1-(m_1+m_4)\ (m_2-m_3)\ddot{S}_2+(m_1+m_4)\ (m_2+m_3)\ddot{S}_3\\
&+8a_{33}MS_3=0
\end{aligned} \tag{2}$$

Trying solutions of the type $S_i=A_ie^{2\pi i\nu ct}$ and requiring non-trivial solutions we get the secular equation:

$$\begin{vmatrix}
2Ma_{11}-\{(m_1+m_4)(m_2+m_3)+4m_1m_4\}\varkappa & 2Ma_{12}+(m_2-m_3)\ (m_1-m_4)\varkappa & \\
& -(m_1-m_4)(m_2+m_3)\varkappa & \\
2Ma_{12}+(m_1-m_4)(m_2-m_3)\varkappa & 2Ma_{22}-\{(m_1+m_4)(m_2+m_3)+4m_2m_3\}\varkappa & \\
& (m_2-m_3)(m_1+m_4)\varkappa & \\
-(m_1-m_4)(m_2+m_3)\varkappa & (m_1+m_4)(m_2-m_3)\varkappa & \\
& 2Ma_{33}-(m_1+m_4)(m_2+m_3)\varkappa &
\end{vmatrix}=0 \tag{3}$$

where $\varkappa=\pi^2c^2\nu^2$ (c is the velocity of light).

The above equations will of course also be valid for the symmetric molecule $C_2^{12}N_2^{14}$ when the proper values are inserted for the atomic masses. The secular equation (3) then reduces to:

$$\begin{vmatrix}
a_{11}-m_1\varkappa & a_{12} & 0 \\
a_{12} & a_{22}-m_2\varkappa & 0 \\
0 & 0 & a_{33}-\dfrac{2m_1m_2}{M}\varkappa
\end{vmatrix}=0 \tag{4}$$

which splits up into the two equations:

$$(a_{11}a_{22}-a_{12}^2)-\varkappa(m_1a_{22}+m_2a_{11})+\varkappa^2m_1m_2=0 \tag{5}$$

(Two roots, $\varkappa_1$ and $\varkappa_2$, corresponding to ν_1 and ν_2 of symmetry class A_{1g}) and

$$a_{33} \cdot M - 2m_1 m_2 \varkappa_3 = 0 \tag{6}$$

($\varkappa_3$ corresponds to ν_3 of symmetry class A_{2u}).

From (4) we obtain the following relations:

$$a_{11}a_{22} - a_{12}^2 = m_1 m_2 \varkappa_1 \varkappa_2 \tag{7}$$

and

$$a_{11}m_2 + a_{22}m_1 = m_1 m_2 \, (\varkappa_1 + \varkappa_2) \tag{8}$$

Inserting the following numerical values:

$m_1 = m_4 = 14.0075$, $m_2 = 12.0038$, $m_3 = 13.0075$, $M = 53.0263$, $N = 6.0228 \cdot 10^{23}$, $c = 3.10^{10}$, $\nu_1 = 2\,328.5$, $\nu_2 = 850.6$, $\nu_3 = 2\,149$ and ν_1(isot.) $= 2\,298.4$ into (6), (7), (8) and the evaluated determinant (3) we calculate:

$$\begin{aligned} a_{11} &= \ 3.920 \cdot 10^5 \text{ dyne·cm}^{-1} \\ a_{22} &= \ 7.520 \cdot 10^5 \text{ dyne·cm}^{-1} \\ a_{12} &= \pm\ 3.890 \cdot 10^5 \text{ dyne·cm}^{-1} \\ a_{33} &= \ 4.402 \cdot 10^5 \text{ dyne·cm}^{-1} \end{aligned}$$

The ambiguity caused by the $\pm$ sign for a_{12} will be discussed below.

In these calculations we have considered the structure of cyanogen to be $N \equiv C - C \equiv N$. Now, it is a possibility that the carbon and nitrogen atoms should be interchanged (though the isotopic atom should still be a carbon atom): $\overset{-}{C} \equiv \overset{+}{N} - \overset{+}{N} \equiv \overset{-}{C}$. This means that we have to interchange the masses m_1 and m_2, m_3 and m_4 in our calculations. But if we do so it is easily seen from equations (3), (4), (6), (7) and (8) *that we get exactly the same calculations as before, only that a_{11} and a_{22} have been interchanged.*

We might next try whether the observed Raman line $\nu = 841$ cm^{-1} should be an isotope line corresponding to $\nu_2 = 850.6$ cm^{-1}. By introducing the numerical values for the force constants into (3) we calculate:

$$\nu_2(\text{isot.}) = 846 \text{ cm}^{-1}$$

for the isotopic molecule $C^{12}C^{13}N_2^{14}$. The difference between this value and the observed 841 frequency is so large that we believe it to be outside as well experimental error as uncertainty in the calculation. This supports our conclusion, mentioned above that the 841 cm^{-1} line must be assigned to the $C_2^{12}N_2^{14}$ molecule.

Non-linear vibrations. These can be treated in a way quite analogous to the linear vibrations. We shall here only state the results obtained for the symmetric molecule $C_2^{12}N_2^{14}$.

Symmetry class E_{1g}. $\nu_4 = 507.2$ cm^{-1}

$$a_{44} = a_{66} = 4\ \varkappa_4 \frac{m_1 m_2}{m_2 + m_1 \left(\frac{D}{d}\right)}$$

Inserting numerical values, $d = 0.69$ Å and $D = 1.84$ Å (cp. Fig. 2), we calculate:

$$a_{44} = a_{66} = 0.229 \cdot 10^5 \text{ dyne.cm}^{-1}$$

Symmetry class $E_{1u} \cdot \nu_5 = 240$ cm^{-1}

$$a_{55} = a_{77} = 2\ \varkappa_5 \cdot \frac{m_1 m_2}{M}$$

giving

$$a_{55} = a_{77} = 0.055 \cdot 10^5 \text{ dyne·cm}^{-1}$$

DISCUSSION

In order to get a better understanding of what is the physical significance of the potential function it may be helpful to consider the forces called into action when we give the molecule certain deformations. To this purpose we choose the following:

1) atom 1 is given a small displacement, Δx,
2) atoms 1 and 2 are both given the same displacement, Δx, and
3) atom 2 alone is given the displacement Δx,

while all other atoms are kept fixed in their original positions of equilibrium.

For this calculation we express the part of the potential function involving only linear vibrations in cartesian coordinates:

$$\Delta V = (a_{11}+a_{33})(x_1^2+x_4^2) + (a_{22}+a_{33})(x_2^2+x_3^2) + 2(a_{12}-a_{33})(x_1x_2+x_3x_4) - 2(a_{12}+a_{33})(x_1x_3+x_2x_4) + 2(a_{33}-a_{22})x_2x_3 + 2(a_{33}-a_{11})x_1x_4$$

A certain displacement, Δx, from the equilibrium position of one or more of the atoms will produce a force on the i-th atom:

$$K(i) = -\left(\frac{\partial \Delta V(x_j)}{\partial x_i}\right)\left(\frac{\partial \Delta V(x_j)}{\partial x_j}\right)_{x\ =\Delta x}$$

The "restoring coefficients", defined as $dK(i)/dx$, are given in the following Table 3, while the numerical values of the forces are given in Table 4 for the two different models of the molecule and with a_{12} as well negative as positive.

Table 3. Restoring coefficients of the single atoms for special atomic displacements.

Atom	K_1	K_2	K_3
1	$-2(a_{11}+a_{33})$	$-2(a_{11}+a_{12})$	$-2(a_{12}-a_{33})$
2	$-2(a_{12}-a_{33})$	$-2(a_{22}+a_{12})$	$-2(a_{22}+a_{33})$
3	$2(a_{12}+a_{33})$	$2(a_{22}+a_{12})$	$-2(a_{33}-a_{22})$
4	$2(a_{11}-a_{33})$	$2(a_{11}+a_{12})$	$2(a_{12}+a_{33})$

Table 4. Forces acting on single atoms in C_2N_2 for special atomic displacements Δx, unit: 10^5 dyne.

Model	Atom	K_1		K_2		K_3	
		a_{12} neg.	a_{12} pos.	a_{12} neg.	a_{12} pos.	a_{12} neg.	a_{12} pos.
N≡C—C≡N	1	$-16.64\,\Delta x$	$-16.64\,\Delta x$	$-0.06\,\Delta x$	$-15.62\,\Delta x$	$16.58\,\Delta x$	$1.02\,\Delta x$
	2	$16.58\,\Delta x$	$1.02\,\Delta x$	$-7.26\,\Delta x$	$-22.82\,\Delta x$	$-23.84\,\Delta x$	$-23.84\,\Delta x$
	3	$1.02\,\Delta x$	$16.58\,\Delta x$	$7.26\,\Delta x$	$22.82\,\Delta x$	$6.24\,\Delta x$	$6.24\,\Delta x$
	4	$-0.96\,\Delta x$	$-0.96\,\Delta x$	$0.06\,\Delta x$	$15.62\,\Delta x$	$1.02\,\Delta x$	$16.58\,\Delta x$
⁻C≡N⁺—N⁺≡C⁻	1	$-23.84\,\Delta x$	$-23.84\,\Delta x$	$-7.26\,\Delta x$	$22.82\,\Delta x$	$16.58\,\Delta x$	$1.02\,\Delta x$
	2	$16.58\,\Delta x$	$1.02\,\Delta x$	$-0.06\,\Delta x$	$-15.62\,\Delta x$	$-16.64\,\Delta x$	$-16.64\,\Delta x$
	3	$1.02\,\Delta x$	$16.58\,\Delta x$	$0.06\,\Delta x$	$15.62\,\Delta x$	$0.96\,\Delta x$	$0.96\,\Delta x$
	4	$6.24\,\Delta x$	$6.24\,\Delta x$	$7.26\,\Delta x$	$-22.82\,\Delta x$	$1.02\,\Delta x$	$16.58\,\Delta x$

By inspection of the figures in Table 4 it is easily seen that *the only physically reasonable solution is the $N \equiv C—C \equiv N$ model* with a_{12} negative, leading to the values given in column 1, 3 and 5, upper part. However, the other possibilities are also quite interesting, if we try to interpret what they mean physically. With a_{12} negative and the CNNC model we see that there is a strong interaction between the C and N atoms as well as between the C atoms, but none between the N atoms; this must mean that there is a bond between the C atoms from one end of the molecule to the other while the adjacent N atoms are not bonded to one another. Similarly, the change of sign of a_{12}

(from —to+), which is mathematically equivalent to interchanging the atoms 2 and 3, physically must be interpreted as giving a strong interaction corresponding to a triple bond between the atoms 1 and 3 and between 2 and 4. We see, in fact, that the calculations, being performed without paying any attention to the possible distribution of the carbon and nitrogen atoms between the places 1, 2, 3 and 4, *in every case lead to the same dynamical formula for the molecule*. This is because the physical interpretation of the force constants — or the restoring coefficients — is independent of the numbering of the atoms and hence always will show between which atoms there is a single resp. a triple bond or no bonding at all.

Table 4 shows furthermore that there is quite a strong interaction between atom 1 and the atoms 3 and 4 in our selected NCCN model, the restoring coefficients being + resp. — ca. $1 \cdot 10^5$ dyne.cm^{-1}. (Of course, for symmetry reasons, there is a corresponding interaction between 4 and the atoms 1 and 2.) This is, as we will show in a following paper, what is to be expected from the molecular orbital theory.

The restoring coefficients play the rôle of force constants and we may take as characteristic force constant for the C≡N bond: $K_{CN} = K_1\ (2) = 16.6 \cdot 10^5$ dyne.cm^{-1} and for the C—C bond: $K_2\ (2) = 7.26 \cdot 10^5$ dyne.cm^{-1}. However, in the latter value is included a contribution of $1.02 \cdot 10^5$ dyne.cm^{-1} due to interaction between 2 and 4. Hence, if we want to get the force constant for the "pure" C—C bond we must subtract this amount and get

$K_{CC} = K_2\ (2)_{corr.} = 6.24 \cdot 10^5$ dyne.cm^{-1}.

Let us next apply different empirical rules connecting the interatomic distances and the corresponding characteristic force constants:

Badger's rule[15]:	$K(r-a)^3 = 1.86 \cdot 10^5$
Clark's » [3]:	$K \cdot r^6 = 1.266^6$
Linnet-Thompson's rule [3]:	$K \cdot r^6 = 1.31^6$

The two first relations are valid for diatomic molecules while the last should apply to polyatomic molecules. Therefore, one would expect to get best results with the corrected K_{CC} values when using Badger's or Clark's rule while Linnet-Thompson's formula should be applicable to the "raw" uncorrected value. The following Table 5 shows that this is so.

Previous calculations based on the valence force system have given [2] $K_{C\equiv N} = 17.6 \cdot 10^5$ dyne·cm^{-1} and $K_{C-C} = 5.22 \cdot 10^5$ dyne·cm^{-1} although Linnet and Thompson [3] for the same constants find 17.5 and $6.69 \cdot 10^5$ dyne. cm^{-1}. This is more or less what one would expect from consideration of the

"valence structure" of C_2N_2. However, a simple and more exact relation seems to exist between the restoring coefficients as defined above and the bond orders as calculated by the *LCAO*-method. This will be discussed in a following paper.

Table 5. Interatomic distances in Å as calculated from the force constants in 10^5 dyne·cm^{-1} according to different empirical rules.

Interatomic distances	$d_{C\equiv N}$	d_{C-C}	d_{C-C}
Force constant in 10^5 dyne.cm^{-1}	16.6	7.26	6.24
Badger	1.16	1.32	1.35
Clark	1.15	1.33	1.37
Linnet-Thompson	1.17	1.38	1.42
Observed value	1.15	1.38	1.38

SUMMARY

Investigation of C_2N_2 by electron diffraction using the rotating sector method confirms the results obtained by Pauling *et al.* The Raman spectrum has been reinvestigated and four new lines detected, one of which is assigned to the isotopic molecule NCC^{13}N. On the basis of measured Raman frequencies and one frequency taken from the infrared absorption spectrum the complete harmonic potential function has been calculated. An interpretation of the physical significance of the force constants is given. It is thereby shown that the spectroscopic method unambigously leads to the configuration NCCN. Different empirical rules giving the relation between force constants and bond lengths are tested.

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