

ϵ is the difference of energy between the beginning and end states of the nucleus in units mc^2 . A_1 and A_2 are given by (8); they contain the dependence of the process on the energy levels of the intermediate nucleus. It turns out, however, that the values of those energies do not greatly influence the probability. Roughly one can put

$$A_1 + A_2 \approx \left| \frac{H_{nk} H_{km}}{W_k - W_n} \right|^2 \sim \frac{g^4}{m^2 c^4},$$

with g given by (5). Numerical evaluation for $Z=31$ leads to

$$P = 1.15 \times 10^{-35} F(\epsilon - 2) \text{ sec.}^{-1} \\ = 3.6 \times 10^{-28} F(\epsilon - 2) \text{ year}^{-1}. \quad (12)$$

As seen from the general formula (11) P is almost independent of Z .

The value of F for some arguments is given in the following table:

$F(\epsilon+2) =$	$\epsilon = 4$	$\epsilon = 6$	$\epsilon = 8$	$\epsilon = 10$
	0.37×10^2	9.2×10^4	3.4×10^6	4.2×10^7
$P(\epsilon-2) =$	$\epsilon = 12$	$\epsilon = 20$		
	3.3×10^8	1×10^{11}		

The author wishes to express her gratitude to Professor E. Wigner for suggesting this problem, and for the interest taken in it.

The Infrared Absorption Spectra of the Linear Molecules Carbonyl Sulphide and Deuterium Cyanide

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Carbonyl sulphide. The discovery of new vibration-rotation bands in the infrared absorption spectrum of carbonyl sulphide has made it possible to determine the vibrational energy level scheme of the molecule. The agreement between theory and experiment is quite satisfactory. *Deuterium cyanide.* The fundamental bands of deuterium cyanide ω_2 at 570 cm^{-1} and ω_3 at 2630 cm^{-1} have been measured with grating spectrometers. The former has a strong zero branch at 570.16 cm^{-1} , and the fine structure

lines on each side are well separated. From the line spacing the moment of inertia of the molecule is found to be $22.92 \times 10^{-40} \text{ gram cm}^2$. A comparison of this value with the corresponding one for HCN, i.e., $18.72 \times 10^{-40} \text{ gram cm}^2$, permits the calculation of the internuclear distances. From the positions of these two bands, together with those of the observed fundamentals of HCN, the zeroth order quadratic potential energy expression is computed.

THE infrared absorption spectrum of carbonyl sulphide (COS) has been investigated by Cassie and Bailey¹ who found ten unresolved bands in the region $1-20\mu$ using a prism spectrometer. Vegard² has deduced from x-ray measurements that the molecule is linear with interatomic separations C-O of 1.10 Angstrom units and C-S of 1.96 Angstrom units. The calculated moment of inertia is $178 \times 10^{-40} \text{ gram cm}^2$.

The perturbed expression for the vibrational energy is

$$E(\text{vibration}) = \nu_1 V_1 + \nu_2 V_2 + \nu_3 V_3 + X_{11} V_1^2 \\ + X_{22} V_2^2 + X_{33} V_3^2 + X_{12} V_1 V_2 + X_{13} V_1 V_3 \\ + X_{23} V_2 V_3 + X_{ll} l^2 + \text{constant}$$

where the V 's are the vibrational quantum numbers, l is the azimuthal quantum number, and ν_1 to X_{ll} are constants. If ten bands which involve these constants in an independent way are located experimentally the ten constants may be calculated and the energy level system for the molecule determined. This is of fundamental importance because it provides the correlating network and serves to predict new absorption bands.

This problem is similar to that of HCN which has been developed through a number of experimental researches to a fairly complete solution.^{3, 4, 5, 6, 7, 8} Recently Herzberg and Spinks⁹

¹ Bailey and Cassie, Proc. Roy. Soc. A135, 375 (1932).

² Vegard, Zeits. f. Krist. 77, 411 (1931).

³ Burmeister, Verh. d. D. Phys. Ges. 15, 589 (1913).

⁴ Barker, Phys. Rev. 23, 200 (1924).

⁵ Badger and Binder, Phys. Rev. 37, 800 (1931).

⁶ Brackett and Liddel, Smith. Inst. 85, No. 5 (1931).

⁷ Choi and Barker, Phys. Rev. 42, 777 (1932).

⁸ Adel and Barker, Phys. Rev. 45, 277 (1934).

⁹ Herzberg and Spinks, Proc. Roy. Soc. A147, 434 (1934).

have photographed two HCN bands at $\lambda 10,385$ and $\lambda 11,645$ under high resolution. The moment of inertia obtained from the fine structure observed is 18.70×10^{-40} gram cm^2 . By assuming the C-H distance to be the same as in acetylene, i.e., 1.06 Angstrom units, they found the atomic distance C-N to be 1.15 Angstrom units. These dimensions may be determined in a more reliable manner by comparing the spectra of HCN and DCN. We have observed two of the fundamental bands of the latter molecule, and have completely resolved one of them, thus obtaining a precise measure of the moment of inertia.

Adel¹⁰ gives an analysis of vibrational isotope effects in three particle systems showing how the infrared spectra of two or more isotopic molecules can be applied to the analysis of their quadratic potential energy function making the assumption that the molecular force field is invariant under an isotopic change of mass. We are now able to compute these potential constants for HCN and DCN.

Three infrared spectrometers were available. The first, which is equipped with a rocksalt prism and gratings having 2400 and 4800 lines

¹⁰ Adel, Phys. Rev. **46**, 222 (1934).

per inch has been described by Barker and Meyer.¹¹ It was used for the region $1-10\mu$. The second is a recording instrument with a KBr prism set up by Randall and Strong¹² and is particularly adapted for rapid exploration out to 20μ . The third spectrometer has a grating with 1200 lines per inch and a KBr foreprism, the optical system having been described by Hardy.¹³ It was used for analyzing the bands at 17.5μ and 19μ .

Two absorption cells were used. The first is twenty cm in length with KBr windows, and the second is twenty-five cm in length with windows of rocksalt.

Carbonyl sulphide was prepared by treating 50 cm^3 of concentrated water solution of KSCN with a cold mixture of 520 grams of concentrated H_2SO_4 and 400 cm^3 of water. The gas COS is given off at 25°C (contaminated with a few impurities in slight amount namely CO_2 , CS_2 and H_2S) according to the reaction;¹⁴ $\text{KSCN} + \text{H}_2\text{O} + 2\text{H}_2\text{SO}_4 \rightarrow \text{COS} + \text{KHSO}_4 + \text{NH}_4\text{HSO}_4$.

¹¹ Barker and Meyer, Trans. Faraday Soc. **25**, 912 (1929).

¹² Randall and Strong, Rev. Sci. Inst. **2**, 585 (1931).

¹³ Hardy, Phys. Rev. **38**, 2162 (1931).

¹⁴ Mellor, *Comprehensive Treatise in Chemistry*.

TABLE I. Observed bands of carbonyl sulphide.

OBSERVED BY BARKER & BARTUNEK				OBSERVED BY CASSIE & BAILEY					RAMAN LINES OBSERVED BY DADIEU & KOHLRAUSCH			
BAND NO.	(cm^{-1})	BAND NO.	(cm^{-1})	BAND NO.	(cm^{-1})	ASSIGNMENT	BAND NO.	(cm^{-1})	ASSIGNMENT	LINE NO.	(cm^{-1})	ASSIGNMENT
1	4101	9	1558.6	1	4084	$2\omega_3$	9	—	$3\omega_2$	1	2233	$2\omega_1 + \omega_2$
2	3739	10	1530.4	2	3742	$2\omega_1 + \omega_3$	10	—	$\omega_3 - \omega_2$	2	2055	ω_3
3	3096	11	1047.4	3	3095	$2\omega_2 + \omega_3$	11	1051	$2\omega_2$	3	1383	$\omega_1 + \omega_2$
4	2919	12	859.2	4	2904	$\omega_1 + \omega_3$	12	859	ω_1	4	1041	$2\omega_2$
5	2575	13	526.6	5	—	$\omega_2 + \omega_3$	13	—	$1_1 \rightarrow 2_2$	5	859	ω_1
6	2050.5	14	521.5	6	2079	ω_3	14	527	ω_2	6	678	$2\omega_1 - 2\omega_2$
7	1892	15	514.3	7	1898	$2\omega_2 + \omega_1$	15	—	$1_1 \rightarrow 2_0$	7	524	ω_2
8	1710			8	1718	$2\omega_1$						

TABLE II. Carbonyl sulphide bands.

OBSERVED	CALCULATED	ASSIGNMENT	OBSERVED	CALCULATED	ASSIGNMENT
4101*	4101	$2\omega_3$	514.3	516	$1_1 \rightarrow 2_0$
3739	3779	$2\omega_1 + \omega_3$		RAMAN LINES	
3096	3094	$2\omega_2 + \omega_3$	2233	2227	$2\omega_1 + \omega_2$
2919*	2919	$\omega_1 + \omega_3$	2055	2050.5	ω_3
2575*	2575	$\omega_2 + \omega_3$	1383	1380.7	$\omega_1 + \omega_2$
2050.5*	2050.5	ω_3	1041	1037.5	$2\omega_2$
1892*	1892	$2\omega_2 + \omega_1$	859	859.2	ω_1
1710*	1710	$2\omega_1$	678	672.5	$2\omega_1 - 2\omega_2$
1558.6*	1558.6	$3\omega_2$	524	521.5	ω_2
1530.4	1529	$\omega_3 - \omega_2$		CONSTANTS	
1047.4	1037.5	$2\omega_2$	$\nu_1 = 863.4$	$X_{11} = -4.2$	$X_{12} = -2.35$
859.2*	859.2	ω_1	$\nu_2 = 518.95$	$X_{22} = -1.10$	$X_{13} = 9.3$
526.6*	526.6	$1_1 \rightarrow 2_2$	$\nu_3 = 2050.5$	$X_{33} = 0$	$X_{23} = 3.$
521.5*	521.5	ω_2			$X_{11} = 2.65$

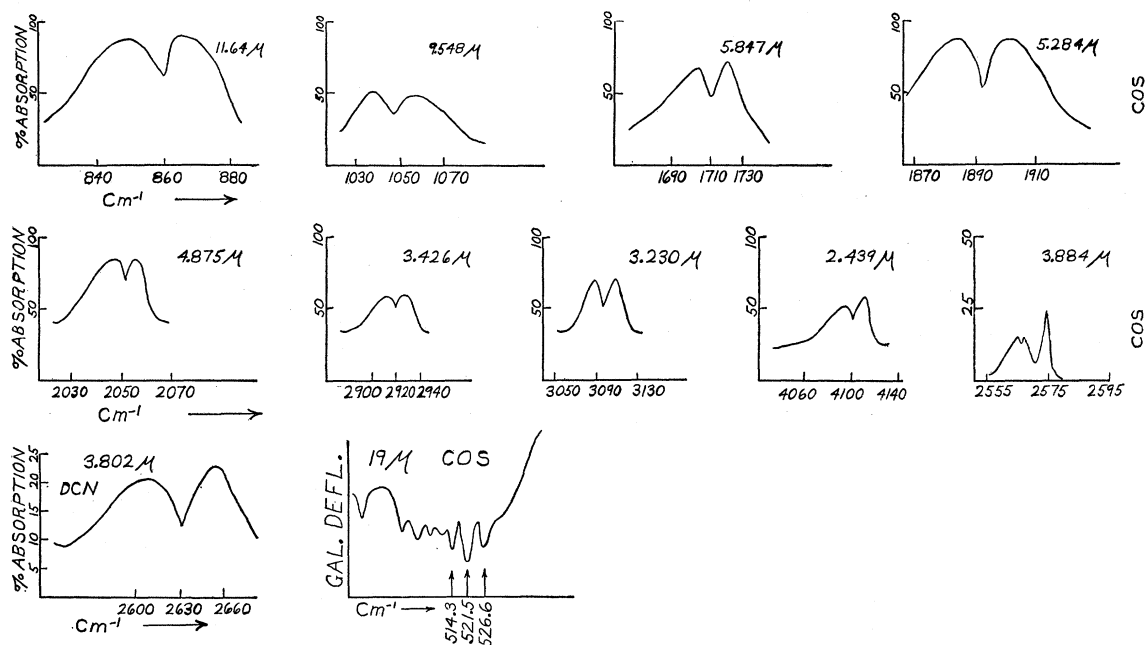


FIG. 1. Carbonyl sulphide bands and the deuterium cyanide band ω^3 .

The products were passed from the generating flask through a trap immersed in a mixture of ice and salt which condenses the greater part of the CS_2 , then through a 33 percent solution of KOH to precipitate CO_2 and H_2S , and finally through traps containing CaCl_2 and P_2O_5 . The dry gas was then condensed with liquid air and stored in a five liter reservoir.

The deuterium cyanide was supplied by the California Isotope Company in a small glass capsule containing a mixture of about 40 percent DCN and 60 percent HCN .

The readings were taken in the usual in and out method for all the bands with the exception of the 17.5μ band of DCN , the 14μ band of HCN and the 19μ region of COS . In these cases the cell was in the beam permanently during the time deflections were taken. It was then removed and the "background" mapped on the same day. Care was always taken of course to insure a pure spectrum. The Nernst glower was used as a source of continuous radiation. The calibration of the spectrometers is in terms of the water vapor lines in the region of 6μ .

The results for carbonyl sulphide are shown in Fig. 1 and Tables I and II. Table I gives the observed bands in terms of wave numbers with

the bands observed by Cassie and Bailey¹ for comparison. At the end of the table the Raman lines observed by Dadiou and Kohlrausch¹⁵ are listed.

The 2.67μ band is not reproduced. It is very irregular due to superposition of the CO_2 and H_2S bands in the same region since it is impossible to remove every trace of these substances from the gas. It is extremely difficult to judge the position of the center but it seems to be at 3739 cm^{-1} . Cassie and Bailey¹ found a band in this region which they list as 3742 cm^{-1} . This band was not used in calculating the constants. The two bands 1558.5 cm^{-1} and 1530 cm^{-1} are also not reproduced. Both have sharp zero branches similar to the 2575 cm^{-1} band. Two of the three zero branches in the 19μ region are upper stage transitions from the first excited state to the second excited states. These are clearly shown on the photographic record, Fig. 1. The proportion of molecules in the first excited state at room temperature is 17 percent which is sufficient to account for the upper stage absorption.

Table II gives the observed and calculated positions of the infrared bands and Raman lines,

¹⁵ Dadiou and Kohlrausch, Physik. Zeits. 33, 165 (1932).

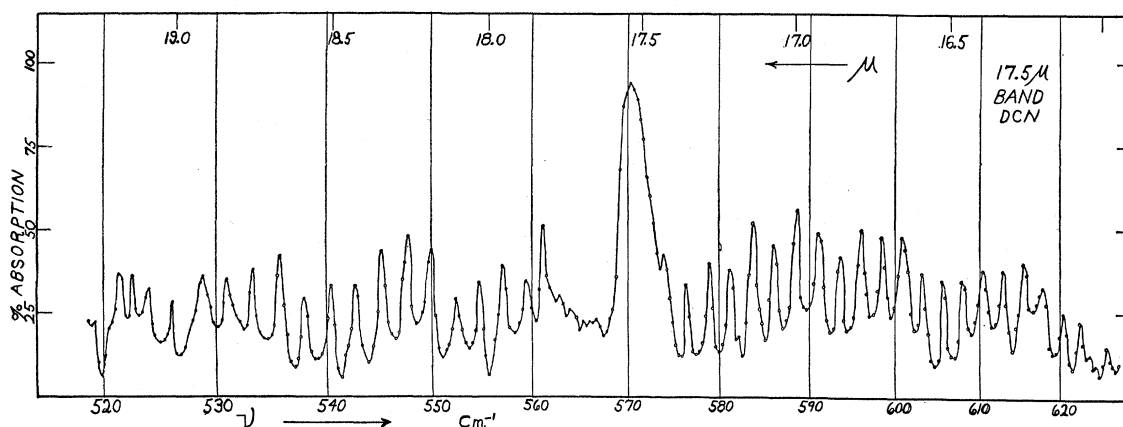


FIG. 2. Rotation lines of the 17.5 μ region of deuterium cyanide.

the calculated values of the ten constants being obtained from the bands marked with asterisks. These constants are given at the end of the table.

The results for deuterium cyanide are shown in Fig. 2 indicating the fine structure of the 17.5 μ region; in Fig. 1 where the fundamental band ω_3 appears; and in Tables III and V. Table III gives the observed and calculated positions of the rotation lines of DCN while Table IV gives similar results for HCN. The

calculated values in these tables were obtained from the formula $\nu = \nu_0 + Am + Bm^2 + Cm^3$ the constants ν_0 , A , B and C being obtained empirically. The ordinal number "m" is counted from the band center. The constants are for DCN $\nu_0 = 569.10$; $A = 2.425$; $B = 0.0013$; $C = -0.00003$ and for HCN $\nu_0 = 712.07$; $A = 2.952$; $B = 0$; $C = 0$.

The part of the band immediately to the low frequency side of the zero branch is somewhat irregular due to the superposition of the upper stage bands of DCN. The rather sharp intense

TABLE III. Rotation lines of the 17.5 μ band of DCN zero branch 570.16 cm^{-1} .

R BRANCH $\Delta J = +1$				P BRANCH $\Delta J = -1$				R BRANCH $\Delta J = +1$				P BRANCH $\Delta J = -1$			
Obs.	Calc.	Res.	m	Obs.	Calc.	Res.	m	Obs.	Calc.	Res.	m	Obs.	Calc.	Res.	m
—	571.53	—	1	—	—	—	—	600.76	600.78	-.02	13	537.86	537.87	-.01	—
573.74	573.96	-.22	2	564.52	564.26	0.26	—	603.17	603.22	-.05	14	535.53	535.48	.05	—
576.28	576.39	-.11	3	561.81	561.83	-.02	—	605.66	605.67	-.01	15	533.17	533.11	.06	—
578.84	578.82	.02	4	559.41	559.42	-.01	—	608.05	608.11	-.06	16	530.83	530.75	.08	—
581.06	581.26	-.20	5	556.98	557.00	-.02	—	610.45	610.54	-.09	17	528.36	528.40	-.04	—
583.67	583.69	-.02	6	554.62	554.61	.01	—	612.94	613.00	-.06	18	526.02	526.04	-.02	—
586.25	586.13	.12	7	552.29	552.19	.10	—	615.60	615.44	.16	19	523.86	523.71	.15	—
588.59	588.56	.03	8	549.98	549.80	.18	—	617.99	617.88	.11	20	521.51	521.36	.15	—
591.15	591.02	.13	9	547.69	547.41	.28	—	620.56	620.32	.24	21	—	—	—	—
593.60	593.45	.15	10	545.10	545.01	.09	—	622.71	622.76	-.05	22	—	—	—	—
595.94	595.90	.04	11	542.59	542.63	-.04	—	624.88	625.21	-.33	23	—	—	—	—
598.31	598.34	-.03	12	540.37	540.24	.13	—	—	—	—	—	—	—	—	—

TABLE IV. Rotation lines of the 14 μ band of HCN zero branch 712.28 cm^{-1} .

R BRANCH $\Delta J = +1$				P BRANCH $\Delta J = -1$				R BRANCH $\Delta J = +1$				P BRANCH $\Delta J = -1$			
Obs.	Calc.	Res.	m	Obs.	Calc.	Res.	m	Obs.	Calc.	Res.	m	Obs.	Calc.	Res.	m
—	715.02	—	1	—	—	—	—	753.35	753.40	-.05	14	670.69	670.74	-.05	—
717.86	717.97	-.11	2	706.33	706.17	0.16	—	756.29	756.35	-.06	15	667.66	667.79	-.13	—
720.81	720.93	-.12	3	703.23	703.21	.02	—	759.25	759.30	-.05	16	664.66	664.84	-.18	—
723.78	723.88	-.10	4	699.60	700.26	-.66	—	762.23	762.25	-.02	17	661.69	661.89	-.20	—
726.77	726.83	-.06	5	697.25	697.31	-.06	—	765.24	765.21	.03	18	658.75	658.93	-.18	—
729.80	729.78	.02	6	694.24	694.36	-.12	—	768.28	768.16	.12	19	656.08	655.98	.10	—
732.85	732.73	.12	7	691.38	691.41	-.03	—	770.99	771.11	-.12	20	653.19	653.03	.16	—
735.93	735.69	.24	8	688.42	688.45	-.03	—	774.07	774.06	.01	21	650.33	650.08	.25	—
738.72	738.64	.08	9	685.48	685.50	-.02	—	777.18	777.01	.17	22	647.02	647.13	-.11	—
741.85	741.59	.26	10	682.57	682.55	.02	—	779.97	779.97	.00	23	—	644.17	—	—
744.69	744.54	.15	11	679.69	679.60	.09	—	782.78	782.92	-.14	24	—	641.22	—	—
747.55	747.49	.06	12	676.57	676.65	-.08	—	785.84	785.87	-.03	25	—	638.27	—	—
750.44	750.45	-.01	13	673.49	673.69	-.20	—	788.81	788.82	-.01	26	—	—	—	—

TABLE V. Average separations of the rotation lines.

DCN 17.5 μ BAND		HCN 14 μ BAND		DCN 17.5 μ BAND		HCN 14 μ BAND	
$\frac{R(m)-P(m)}{2m}$	m	$\frac{R(m)-P(m)}{2m}$	m	$\frac{R(m)-P(m)}{2m}$	m	$\frac{R(m)-P(m)}{2m}$	m
2.305 cm ⁻¹	2	2.883 cm ⁻¹		2.416	14	2.952	
2.412	3	2.930		2.416	15	2.954	
2.429	4	3.023		2.413	16	2.956	
2.408	5	2.952		2.414	17	2.957	
2.421	6	2.973		2.414	18	2.958	
2.426	7	2.962		2.414	19	2.953	
2.413	8	2.969		2.412	20	2.954	
2.414	9	2.958		—	21	2.946	
2.425	10	2.964		—	22	2.958	
2.425	11	2.955		Average 2.414 cm ⁻¹		Average 2.955 cm ⁻¹	
2.414	12	2.958		$I = 22.92 \times 10^{-40}$ g cm ²		$I = 18.72 \times 10^{-40}$ g cm ²	
2.419	13	2.959					

line at 561.07 cm⁻¹ is probably the zero branch of the transition 1₁→2₀ where the subscript indicates the l value. The upper stage transition 1₁→2₂ probably lies somewhere within the zero branch of that from the ground state 0₀→1₁. At room temperature about 14 percent of the molecules are in the first excited state. This is sufficient to account for the presence of upper stage zero branches.

Table V gives the average separations of the lines from which the moment of inertia about the center of gravity is calculated. Values of $(R(m)-P(m))/2m$ are given for both HCN and DCN, with the calculated moments of inertia.

A search was made for the other two fundamentals ω_1 and ω_3 as well as for harmonics. Because of the rather small amount of gas available the only other band observed was ω_3 at 2630 cm⁻¹.

In the case of HCN because of the strong absorption of carbon dioxide in the background, readings could not be taken for a short space as the deflections dropped to zero. Because of the regularity of the lines the missing line was interpolated and found to agree very well with the calculated value.

The expression for the moment of inertia of this linear triatomic molecule about its center of gravity is

$$I = m_1 x^2 + m_2 y^2 - \frac{1}{m_1 + m_2 + m_3} (m_1^2 x^2 + m_2^2 y^2 - 2m_1 m_2 x y)$$

where x is the H-C distance and y is the C-N distance. m_1 , m_2 and m_3 are the masses of the hydrogen, nitrogen and carbon atoms, respectively. Introducing the isotopic masses m_1 and

m_1' and solving the two equations simultaneously we obtain the interatomic separations, $x = 1.06 \times 10^{-8}$ cm and $y = 1.15 \times 10^{-8}$ cm.

The theory of small oscillations may be applied, considering the molecule as a group of uncoupled simple harmonic oscillators of which two are linear and one is plane isotropic in a plane perpendicular to the axis of the molecule. The normal modes of vibration are well known. We shall use coordinates somewhat different from those defined by Adel¹⁰ in order to preserve the same meaning of these coordinates for both isotopes. Let r represent the distance from the central atom to the line joining the end atoms measured parallel to the displacement of the particles in the perpendicular vibration. Let q measure the relative separation of the hydrogen and carbon atoms, and z measure the relative displacement of the carbon and nitrogen atoms. In the perpendicular vibration let y_1 , y_2 and y_3 represent the displacements of the hydrogen, nitrogen and carbon atoms. Then the kinetic energy is

$$T = \frac{1}{2} m_1 \dot{y}_1^2 + \frac{1}{2} m_2 \dot{y}_2^2 + \frac{1}{2} m_3 \dot{y}_3^2.$$

The expression for r in terms of y_1 , y_2 and y_3 and the internuclear distances is

$$r = y_1 y / r_0 + y_2 x / r_0 - y_3 \quad \text{where} \quad r_0 = x + y.$$

Since the momentum is conserved as well as the moments of momenta about any point one has two additional relations

$$m_1 \dot{y}_1 + m_2 \dot{y}_2 + m_3 \dot{y}_3 = 0 \quad \text{and} \quad m_1 \dot{y}_1 x - m_2 \dot{y}_2 y = 0.$$

In terms of r the kinetic energy becomes $T = \frac{1}{2} \mu_r \dot{r}^2$ where

$$\mu_r = 1 / \left[\frac{1}{m_2} \left(\frac{x}{r_0} \right)^2 + \frac{1}{m_1} \left(\frac{y}{r_0} \right)^2 + \frac{1}{m_3} \right].$$

For the longitudinal vibrations x_1, x_2 and x_3 represent the displacements from equilibrium of the hydrogen, nitrogen, and carbon atoms, respectively. Then

$$q = x_3 - x_1; \quad z = x_2 - x_3;$$

and

$$m_1\dot{x}_1 + m_2\dot{x}_2 + m_3\dot{x}_3 = 0.$$

In this case the kinetic energy is $T = \frac{1}{2}m_1\dot{x}_1^2 + \frac{1}{2}m_2\dot{x}_2^2 + \frac{1}{2}m_3\dot{x}_3^2$ or in terms of \dot{q} and \dot{z} , $T = \frac{1}{2}\mu_q\dot{q}^2 + \frac{1}{2}\mu_z\dot{z}^2 + \frac{1}{2} \cdot 2\mu_{qz}\dot{q}\dot{z}$ where

$$\mu_q = \frac{m_1(m_2 + m_3)}{S}; \quad \mu_z = \frac{m_2(m_1 + m_3)}{S}; \quad \mu_{qz} = \frac{m_1m_2}{S}$$

and $S = m_1 + m_2 + m_3$, the total mass of the molecule. The potential energy is subject to the geometric symmetry of the molecule. It may be written $V = \frac{1}{2}(k_{11}q^2 + k_{22}z^2 + 2k_{13}qz + k_{33}z^2)$. The secular determinant of the normal coordinate transformation factors into a linear and a quadratic expression, and yields the following set of equations,

$$\lambda_1 + \lambda_3 = \frac{\mu_q k_{33} + \mu_z k_{11} - 2\mu_{qz} k_{13}}{\mu_q \mu_z - \mu_{qz}^2},$$

$$\lambda_1 \lambda_3 = \frac{k_{11} k_{33} - k_{13}^2}{\mu_q \mu_z - \mu_{qz}^2},$$

$$\lambda_2 = k_{22} / \mu_r.$$

In normal coordinates the kinetic and potential energies assume the forms

$$T = \frac{1}{2}(\dot{Q}^2 + \dot{R}^2 + \dot{Z}^2), \quad V = \frac{1}{2}(\lambda_1 Q^2 + \lambda_2 R^2 + \lambda_3 Z^2).$$

The normal vibrations expressed in wave numbers are $\nu_i = (1/2\pi c)(\lambda_i)^{1/2}$. The constant k_{22} may be computed from ω_2 of HCN and DCN and is nearly the same for both as would be expected. Using the fundamentals ω_1 and ω_3 of HCN and the fundamental ω_3' of DCN the unobserved fundamental ω_1' of DCN can be calculated as well as the other three constants k_{11}, k_{13} and k_{33} . There are two sets of constants because the equations are quadratic. These are

$$\begin{array}{ll} k_{22} = 0.8071 \times 10^6 & k_{22} = 0.8071 \times 10^6 \quad \text{dynes/cm} \\ k_{11} = 5.6987 \quad \text{"} & \text{Or } k_{11} = 5.6981 \quad \text{"} \\ k_{13} = 6.443 \quad \text{"} & k_{13} = -0.30491 \quad \text{"} \\ k_{33} = 25.34 \quad \text{"} & k_{33} = 18.065 \quad \text{"} \end{array}$$

k_{13} represents the interaction between the extreme atoms, and should be small. Hence the second set is the more plausible.

The observed and calculated values of the wave numbers for the fundamental bands of HCN and DCN are as follows:

Observed wave numbers	Calculated wave numbers
$\omega_1 = 2089.0 \text{ cm}^{-1}$	$\omega_1 = 2089.6 \text{ cm}^{-1}$
$\omega_2 = 712.1$	$\omega_2 = 712.8$
$\omega_3 = 3312.9$	$\omega_3 = 3312.3$
$\omega_1' = -$	$\omega_1' = 1896.7$
$\omega_2' = 569.1$	$\omega_2' = 568.6$
$\omega_3' = 2630.0$	$\omega_3' = 2629.5$

Absorption Spectrum of Tin Sulphide

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The absorption spectrum of tin sulphide between 3200A and 4600A has been photographed at moderate dispersion and between 4000A and 4600A at high dispersion. The system in the near ultraviolet may be represented by the formula:

$$\nu = 28,336.2 + 332.77(v' + \frac{1}{2}) - 1.42(v' + \frac{1}{2})^2 - 488.25(v'' + \frac{1}{2}) + 1.47(v'' + \frac{1}{2})^2.$$

This formula is not in agreement with that given by

Butkow and Tschassowenny who seem to have incorrectly assigned the system origin. A new system has been located in the visible which is limited by predissociation to two v'' progressions. These bands are given by the formula:

$$\nu = 23,287.67 + 367.5(v' + \frac{1}{2}) - 488.25(v'' + \frac{1}{2}) + 1.47(v'' + \frac{1}{2})^2.$$

The observed isotope structure of the strong bands in this system confirms their vibrational assignment.