

The Vibrational Energy Level System of the Linear Molecule HCN

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The discovery of new rotation-vibration bands in the infrared absorption spectrum of gaseous HCN has made possible a determination of the vibrational energy level system of the normal molecule. The agreement between theory and experiment is completely satisfactory. The fundamental frequencies of the isotopic molecule H^{13}CN are predicted from those found for H^{12}CN .

INTRODUCTION

ONE of the most important problems entailed in the analysis of the infrared spectrum of a molecule is the accurate determination of the vibrational energy level scheme from the observed absorption centers. In addition to providing the correlating network which serves to classify new absorption regions of the molecule unambiguously, the energy diagram contributes information which is of importance for other problems in physics and chemistry. Thus, the direct calculation of the thermodynamic potentials demands a precise knowledge of the vibrational states of the molecule.¹ Also, the coefficients in the expression for the position of an oscillational level serve to describe the potential function which governs the anharmonic vibrations of the atoms.² In this report it is proposed to set forth the energy level diagram of the linear molecule H-C-N.

ANALYSIS

In proceeding with the analysis, we shall employ the expression:

$$E_{\text{vib}} = \nu_1 V_1 + \nu_2 V_2 + \nu_3 V_3 + x_{11} V_1^2 + x_{22} V_2^2 + x_{33} V_3^2 + x_{1l} l^2 + x_{12} V_1 V_2 + x_{13} V_1 V_3 + x_{23} V_2 V_3,$$

which gives the energy of vibration of the linear triatomic molecule correct through a second order perturbation calculation on the anharmonic potential function. Here, V_1 , V_2 , V_3 and l are the quantum numbers of vibration, and $\nu_1 \cdots x_{23}$

are functions of the harmonic and anharmonic constants of the potential energy of the normal molecule.² Quite clearly, the energy diagram may be constructed as soon as the quantities $\nu_1 \cdots x_{23}$ become available. These, in turn, may be found from the set of ten simultaneous equations founded upon the application of the expression for E_{vib} to the positions of ten vibration levels as deduced from infrared and Raman measurements.

APPLICATION TO HCN

The solution of this problem for the HCN molecule was made possible by the experimental work discussed in the next paragraph, specifically by the determination of the combination bands $\nu_2 + \nu_3$ and $2\nu_1 + \nu_2$.

A metal tube 150 cm long closed with thin glass windows served as the absorption cell. After being evacuated it was filled with saturated vapor of HCN and introduced into the optical

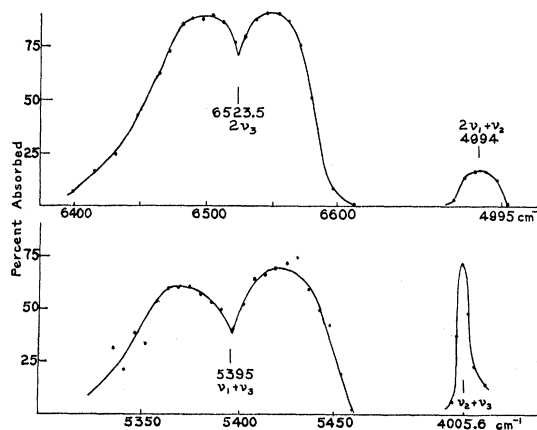


FIG. 1. Near infrared absorption bands of HCN.

¹ L. Kassel, *Phys. Rev.* **43**, 364 (1933).

² Adel and Dennison, *Phys. Rev.* **43**, 716; **44**, 99 (1933).

path of a prism grating spectrometer, the grating having 4800 lines per inch. This gives sufficient resolution to show the band contours clearly, but does not resolve the rotational structure. Fig. 1 shows the four weak bands which have been

TABLE I. Observed and calculated positions of some infrared lines of HCN.

V_1	V_2	V_3	l	Position		Observer
				Calculated	Observed	
0	0	0	0	0.0 cm ⁻¹	0.0 cm ⁻¹	
0	1	0	1	712.3	712.3 *	Choi and Barker ³
0	2	0	0	1412.6	1412.4 *	Choi and Barker ³
0	2	0	2	1425.0		
1	0	0	0	2089.0	2089.0 *	Kastler ⁴
0	3	0	1	2113.3	2117.3	Barker ⁵
1	1	0	1	2801.1	2801.1 *	Choi and Barker ³
0	4	0	0	2802.8	2800.0	Barker ⁵
0	4	0	2	2815.2	2815.0 *	Barker ⁵
0	0	1	0	3312.9	3312.9 *	Adel and Barker
1	2	0	0	3501.2		
1	2	0	2	3513.6		
0	1	1	1	4005.6	4005.6 *	Adel and Barker
1	3	0	1	4201.7		
2	0	0	0	4282.0		
0	2	1	0	4686.3		
0	2	1	2	4698.7		
2	1	0	1	4993.9	4993.9 *	Adel and Barker
0	3	1	1	5367.4		
1	0	1	0	5386.8	5395 (?) †	Adel and Barker
2	2	0	0	5693.8		
2	2	0	2	5706.2		
0	0	2	0	6523.2	6523.5	Adel and Barker
3	0	0	0	6579.0		
1	2	1	0	6759.8		
1	2	1	2	6772.2		
0	1	2	1	7196.3		
3	1	0	1	7290.7		
2	0	1	0	7564.7		
0	2	2	0	7857.4		
0	2	2	2	7869.8		
2	1	1	1	8257.0		
1	0	2	0	8582.0	8591 (?)	Brackett and Liddel ⁶
4	0	0	0	8980.0		
1	1	2	1	9254.9		
0	0	3	0	9630.9	9645 (?)	Brackett and Liddel ⁶
3	0	1	0	9846.6		
1	2	2	2	9928.2		
0	1	3	1	10284.4		
2	0	2	0	10744.8		
0	2	3	2	10938.3		
1	0	3	0	11674.5	11674.5 *	Badger and Binder ⁷
1	1	3	1	12327.9		
0	0	4	0	12635.8	12635.8 *	Badger and Binder ⁷

† The intense water vapor background absorption in this region rendered precise measurements on $\nu_1 + \nu_3$ very difficult.

³ Choi and Barker, Phys. Rev. **43**, 777 (1932).

⁴ C. R. Kastler, Comptes Rendus **194**, 858 (1932).

⁵ E. F. Barker, Phys. Rev. **23**, 200 (1924).

⁶ Brackett and Liddel, Smithsonian Institution **85**, No. 5 (1931).

⁷ Badger and Binder, Phys. Rev. **37**, 800 (1931).

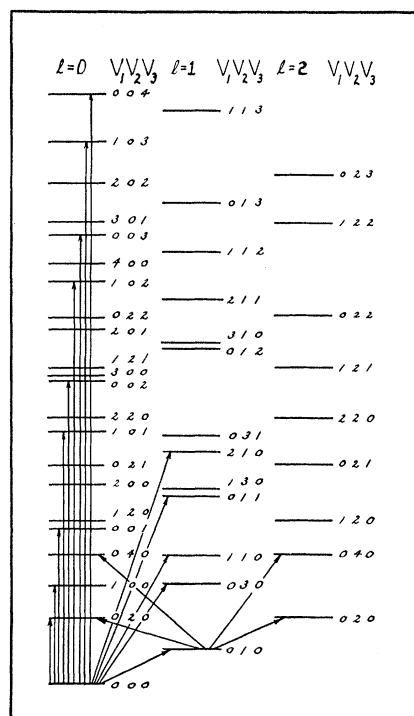


FIG. 2. Diagram of vibrational energy levels for HCN showing transitions which have been observed.

identified. (It seemed desirable at this time to redetermine the band center for ν_3 at 3μ as there is an obvious error in the position indicated in reference 3. The midpoint of the reported maxima lies at 3311 cm^{-1} while the band center is listed at 3289 cm^{-1} . For this measurement a short cell with salt windows was used and just enough gas to give rather weak absorption maxima. The central absorption minimum was found to lie at 3312.9 cm^{-1} .)

In Table I, column III lists the observed infrared and Raman spectra of gaseous HCN. The ten levels marked with asterisks are those used in the solution for the energy constants $\nu_1 \dots x_{23}$ the resulting numerical values being

$$\begin{aligned} \nu_1 &= 2037.0\text{ cm}^{-1}, & x_{11} &= 52.0\text{ cm}^{-1}, & x_{12} &= -0.2\text{ cm}^{-1}, \\ \nu_2 &= 712.1, & x_{22} &= -2.9, & x_{13} &= -15.1, \\ \nu_3 &= 3364.2, & x_{33} &= -51.3, & x_{23} &= -19.6. \\ & & x_{11} &= 3.1, & & \end{aligned}$$

Column II gives some of the more important vibrational levels as computed from these energy constants. From the comparison between observed and computed positions, it would seem of interest to remeasure the band $3\nu_3$.

The computed energy diagram, drawn to scale, and the eighteen transitions which have already been observed are indicated in Fig. 2.

CONCLUSION

We have now completely determined the vibrational energy scheme of the molecule of gaseous HCN, thus making it possible to classify at once new infrared and Raman data. The application of these results to a discussion of the specific heat, free energy and other thermodynamic quantities characteristic of HCN is in progress, and the results should appear in the near future.

NOTE ON THE ISOTOPE MOLECULE H²CN

In conformity with the assumption of valence forces acting within the molecule and with the

second assumption that these forces are invariant for an isotopic change in mass, the data ν_1 , ν_2 and ν_3 of normal HCN suffice for the calculation of the fundamental frequencies of isotopic H²CN. In this manner we find for H²CN: $\nu_1 \cong 1920 \text{ cm}^{-1}$; $\nu_2 \cong 570 \text{ cm}^{-1}$; $\nu_3 \cong 2580 \text{ cm}^{-1}$, probably correct to within five percent.

It is of interest to note that whereas it has been impossible to observe ν_1 in the infrared spectrum of HCN because it lies buried beneath the mass of absorption $3\nu_2$ and $4\nu_2 - \nu_2$, the above calculation indicates that ν_1 and $3\nu_2$ of H²CN may be expected to lie about 100 cm^{-1} apart. An attempt to locate the fundamentals of H²CN is projected in order to obtain data which will contribute to a description of the potential function of the molecule.