

Rotational spectrum and structure of KCN

T. Törring

Freie Universität Berlin, Berlin, Germany

J. P. Bekooy and W. Leo Meerts

Fysisch Laboratorium, Katholieke Universiteit, Nijmegen, The Netherlands

J. Hoeft

Freie Universität Berlin, Berlin, Germany

E. Tiemann

Universität Hannover, Hannover, Germany

A. Dymanus

Fysisch Laboratorium, Katholieke Universiteit, Nijmegen, The Netherlands

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The spectrum of gaseous KCN was measured in the frequency range between 2 and 39 GHz by microwave absorption and by molecular-beam electric-resonance spectroscopy. Combination of the new results with earlier microwave data of KCN in the 100 GHz range made it possible to assign 64 transitions to the ground vibrational state and to fit them to the asymmetric rotor model. The three rotational constants, the five quartic distortion constants, and two sextic distortion coefficients could be determined. Assuming a CN distance of 1.162(10) Å we find $r_{\text{KC}} = 2.6(1)$ Å and $\angle \text{KCN} = 76^\circ(10)$. The molecules thus have a nonlinear, T-shaped structure. The inertial defect gives an estimated value of the lowest vibrational frequency of KCN $\omega_2 = 157 \text{ cm}^{-1}$, which is in reasonable agreement with $\omega_2 = 139 \text{ cm}^{-1}$ from matrix-isolation studies.

I. INTRODUCTION

From all group I cyanides only the structure of hydrogen cyanide is well established by microwave spectroscopy. The molecule is linear and the hydrogen may be attached either to the C atom (cyanide)¹ or to the N atom (isocyanide).² The alkali cyanides are generally assumed to be linear, too, although experimental and theoretical evidence is scarce and contradictory. Therefore in this paper, unless explicitly indicated, these molecules are denoted by LiCN, etc., whatever the structure may be.

Bak *et al.*³ performed a detailed set of quantum mechanical calculations for LiCN. They showed that the equilibrium configuration is the linear isocyanide, with only a very small energy difference of about 0.4 eV between Li-NC and Li-CN. Clementi *et al.*⁴ extended these calculations by mapping the energy surface for the Li⁺ ion around the CN⁻ anion. They found that the lowest energy path from Li-NC to Li-CN will permit the Li⁺ to "orbit" the CN⁻ upon excitation of 0.3–0.4 eV. In this situation there is no preferred structural formula and the bond has been called "polytopic." However, the barrier of 0.3–0.4 eV is high enough to allow many excited vibrational states below the barrier. Another way of interpreting these results is to say that the linear Li-NC undergoes large amplitude bending vibrations. In the limit of highly excited states this motion changes to an orbiting of the Li⁺ around CN⁻. Unfortunately, no calculations for the heavier alkali cyanides have been performed. It may be assumed that the barrier will be lower than in LiCN.⁵

Vibrational frequencies of the alkali cyanides have been measured by Ismail *et al.*⁶ using the matrix-isolation technique. Their results are listed in Table I.

From isotopic effects the isocyanide structure was confirmed for LiCN, but the cyanide structure was preferred for NaCN and KCN. A linear equilibrium configuration was assumed in all cases. The large increase of the bending vibrational frequency from LiCN to NaCN seems to contradict this interpretation and to indicate a more drastic structural change. The matrix results are in complete disagreement with earlier infrared absorption work on KCN vapor by Leroi and Klemperer.⁷ They studied the region above 200 cm⁻¹ and reported two vibrational frequencies. One of them ($\omega = 2158 \text{ cm}^{-1}$) clearly belongs to the C–N stretching mode, the other one ($\omega = 207 \text{ cm}^{-1}$) does not agree with any of the values reported by Ismail *et al.*⁶ The reason for this discrepancy is not clear.

The microwave rotational spectrum of KCN was measured by Kuijpers *et al.*⁸ Altogether 165 lines were found in the frequency region between 85 and 107 GHz. No assignment of vibrational quantum numbers was possible from intensity ratios. This was due to the low signal to noise ratio of the spectrum and the small intensity variations expected from excitation of low frequency vibrations at a temperature of 870 K. From a number of transitions effective rotational constants

TABLE I. Vibrational frequencies in cm⁻¹ for LiCN, NaCN, and KCN from matrix-isolation studies (Ref. 6).

	LiCN	NaCN	KCN
ω_1	681	368	288
ω_2	119	168	139
ω_3	2080	2047	2050

B_{eff} and distortion constants D_{eff} were tentatively fitted. The obtained constants showed clearly that the observed spectrum was inconsistent with that of a linear molecule. Assuming reasonable bond distances rotational constants $B = 3.0(5)$ and $3.4(5)$ GHz are expected for K-CN or K-NC, respectively. The discrepancy with the experimental value of $B_{\text{eff}} = 4.70(15)$ GHz is much larger than any possible errors in the bond length extrapolations. It was concluded that the structure was incompatible with that of a linear or slightly bent molecule.

In the polytopic model the CN^- behaves more or less like one ion (pseudo halogen). The rotational constant is therefore related to the atomic masses and to the average distance \bar{r} between K^+ and the center of mass of the CN^- group. From $B_{\text{eff}} = 4.7$ GHz a value for $\bar{r} = 2.63$ Å was found which compares very well to the internuclear distance of KCl : $r_e = 2.67$ Å. Polytopic bonding was therefore assumed to give the most satisfactory explanation for the overall pattern of the observed spectrum in Ref. 8. In a more refined model one has to solve the rotation-vibration Hamiltonian that allows for large amplitude motions.⁹⁻¹¹ In such a model the KCN molecule is assumed to be composed of a diatomic rigid core (CN^-) and an ion (K^+) which can move in an angle dependent potential around this core. For a reasonably high potential barrier (> 500 cm^{-1}) the average position of the K^+ in the lowest vibrational state of the molecule will be near the minimum of that potential. Some preliminary calculations performed in Nijmegen on KCN using the model discussed by Zhilinskii *et al.*¹¹ with a proper choice for the angle dependent potential ($V \cos^2 \theta$, θ being the angle between K^+ and the CN axis) yielded values for the effective rotational constant close to the experimental value. Unfortunately, it was not possible to test if this model could explain the details of the 100 GHz spectrum without additional information. Assignment of lines was prevented not only by the presence of many lines from excited vibrational states but also by the high J levels involved and the large centrifugal effects expected for these lines.

Two independent studies were undertaken in order to obtain more experimental data on the KCN molecule. In Berlin the microwave absorption technique was used to study the lower rotational transitions around 28 and 38 GHz. The molecular-beam electric-resonance (MBER) spectrometer in Nijmegen was equipped with a supersonic source. This method reduced the internal rotational and vibrational temperatures of the KCN molecules in the beam drastically, thus simplifying the interpretation of the spectrum. The microwave and radiofrequency transitions below 31 GHz were investigated. The two groups were successful in observing many transitions and unraveled the spectrum from the ground vibrational state. The new and old⁸ microwave data were combined with the MBER spectra and the transitions for the ground vibrational state could be selected. The identified ground state spectrum was unambiguously assigned to that of a near prolate asymmetric top molecule.

The derived rotational constants and a reasonable assumption for the CN distance lead to a T -shape struc-

ture for the KCN molecule, where the connecting line between the K nucleus and the center of mass of the C and N nuclei is approximately perpendicular to the CN axis.

II. MICROWAVE ABSORPTION EXPERIMENTS

Observation of low J transitions by microwave absorption was seriously impeded by the outstandingly low intensity of the spectrum. Even in the 100 GHz region most lines were near to the limit of sensitivity of the spectrometer. Fortunately, the reduced absorption coefficients at lower frequencies could be partly compensated by using larger absorption cells and by improving performance of detectors at lower frequencies. A conventional Stark effect spectrometer was used in the present experiment. Several constructions of high temperature absorption cells have been given in Ref. 12. A cell of type III was used with an effective absorption length of about 80 cm at a temperature of 800–900 K. For intensity reasons our efforts were concentrated on the observation of $J = 4 - 3$ and $J = 3 - 2$ transitions. In the expected frequency range from 36 to 39 and from 27 to 29 GHz a total number of 109 lines was found. One line from a $J = 2 - 1$ transition was detected at 19 GHz. The overall pattern of these transitions is very similar to the spectrum in the 100 GHz region. The large number of observed transitions shows that many excited vibrational states contribute to the spectrum.

The measurements confirmed the average effective rotational constant of $B_{\text{eff}} = 4.7$ GHz derived from the measurements around 100 GHz.⁸ Due to the poor signal to noise ratio it was not possible to obtain additional information from Stark effect measurements or to assign vibrational quantum numbers from intensity ratios. It was therefore necessary to use an estimated structural model as a guideline for the analysis of the spectrum. The general pattern of the spectrum with well defined groups of lines for the different rotational transitions clearly indicated that the asymmetry of the molecular rotor could only be very small. Moreover the structure must be consistent with the measured B_{eff} and with reasonable bond distances. These conditions forced us to start our analysis based on a quite unusual T -shaped structure for the KCN molecule. The K nucleus was assumed to be located between the C and N nuclei at a distance of approximately 2.55 Å perpendicular to the C-N internuclear axis.

For this configuration the largest dipole moment component is expected to be μ_a , parallel to the a -axis of the molecule. The strongest rotational transitions of a slightly asymmetric top will then be a -type transitions with selection rules:

$$\Delta J = 1; \quad \Delta K_{-1} = 0; \quad \Delta(J - K_1) = 0. \quad (1)$$

The frequencies of these transitions can be written as

$$\nu = 2B_{\text{eff}}(J + 1) - 4D_{\text{eff}}(J + 1)^3, \quad (2)$$

where B_{eff} and D_{eff} depend only on K_{-1} and $(J - K_1)$ and on the vibrational state of the molecule.¹³ Using this expression we were able to select series of lines from the spectrum with fixed quantum numbers ν , K_{-1} , and J

$-K_1$). The previous microwave data were included in that analysis. If only series including the transition $J=3-2$ are considered, $K_{-1} \leq 2$. This made it possible to determine the quantum numbers K_{-1} and $(J - K_1)$ from the characteristic variation of B_{eff} and D_{eff} , and a clear distinction could be made between series belonging to different vibrational states.

The transitions were then fitted to an asymmetric rotor spectrum using a computer program written by Kirchhoff.¹⁴ Large centrifugal distortion effects were to be expected for lines with higher K_{-1} values. These transitions were therefore calculated step by step and after identification from the spectrum included in the calculation. In the last step 40 microwave transitions with K_{-1} quantum numbers up to 10 were fitted all well within the experimental uncertainties. All assigned lines were a -type transitions with the selection rules given in (1). No strict conclusion was possible about which vibrational state had been assigned. However, the overall intensity and the position of the fitted lines gave a very strong indication that these transitions belong to the ground vibrational state.

III. MOLECULAR-BEAM ELECTRIC-RESONANCE EXPERIMENTS

Several attempts both at Nijmegen¹⁵ and elsewhere (see, e.g., Ref. 16) have been undertaken to observe and analyze MBER spectra of KCN using MBER spectrometers equipped with effusive sources. Weak, many MHz's wide features were observed if high rf powers were applied resulting in saturated and power broadened transitions. Reduction of the rf powers lead to unobservable weak signals. In order to obtain a drastic decrease of the internal temperatures of the KCN molecules we decided to use the seeded beam technique. With this technique a large gain in sensitivity for low J transitions has been realized thanks to rotational cooling ($T_r \sim 40$ K) and improved focusing of the seeded beam with its reduced velocity spread and angular divergence.

The electric resonance spectrometer is basically the one described by van Wachem¹⁷ with a modification on the source chamber to handle the large gas load¹⁸ necessary for the production of the seeded beam. The KCN beam intensity was monitored by a surface ionization detector. An additional enhancement of the signal to noise ratio by a factor of 10 of the KCN spectral lines was obtained by increasing the detection area of the detector. The effective aperture of the detector was 3×3 mm.

The source used in the present experiment (Fig. 1) is essentially identical to the design of Gläser.¹⁹ The stainless steel oven consists of two chambers each indirectly heated by tantalum filaments. The carrier gas enters the supply chamber and the mixture is expanded from the nozzle chamber. The temperature is monitored by two thermocouples located at the bottom of the supply chamber and at the nozzle chamber. The two temperatures can be varied to a large degree independently. The supply chamber was typically held at 1150 K corresponding to an estimated vapor pressure of KCN of about 10 mbar. The temperature of the nozzle

chamber was usually 100 K higher. A skimmer (diameter 2.5 mm) at a distance of 25 mm from the nozzle was slightly heated by radiation from the source. No clogging occurred during a run of a full load of salt lasting for about two weeks.

We expanded through a $150 \mu\text{m}$ nozzle 1% to 2% KCN diluted in argon. The total backing pressure was 0.6 bar. A measurement of the velocity distribution¹⁸ of a pure argon beam under identical conditions yielded a translational temperature $T_t = 30(5)$ K. From the intensities of a large number of $\Delta J = 0$ transitions in the KCN spectrum we estimated the rotational temperature of the KCN molecules in the beam $T_r = 40(10)$ K, which is within the error equal to T_t of the carrier gas argon. We conclude that the rotational relaxation of the KCN molecules in the beam is complete.

Much less can be said about the vibrational relaxation of the KCN molecules in the beam, since until now only a few transitions of excited vibrational states have tentatively been identified. However, since almost all of the strong and most of the weaker MBER transitions in the region between 8 and 26 GHz have been identified as belonging to the ground vibrational state it is felt that the vibrational relaxation of the low frequency vibrational modes is quite strong.

A first attempt was made to observe and analyze the rf spectrum (0–500 MHz). Although many strong well-resolved lines were observed in this region, we were not able to unravel the spectrum at that time. From the previous microwave experiments⁸ the $J=1-0$ transition was expected at 9.4 GHz. Searches have been made first between 9 and 10 GHz and subsequently over the complete frequency region between 1 and 26 GHz. To make scans over such wide frequency ranges feasible within a reasonable sweep time the instrumental line-width (~ 20 kHz) was artificially broadened by frequency modulating the radiation sources [backward wave oscillators (BWO) or klystrons] with white noise.²⁰ In this way

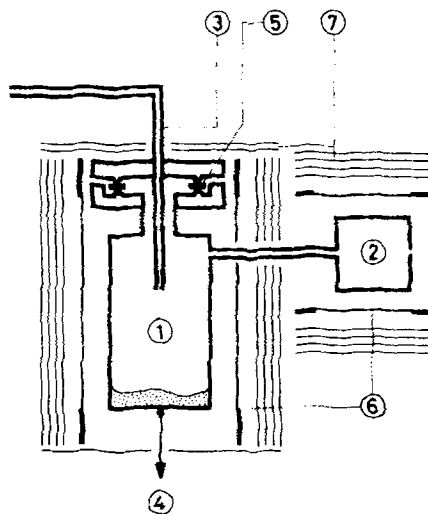


FIG. 1. The supersonic beam source. 1. Supply chamber; 2. Nozzle chamber; 3. Gas line; 4. Thermocouple; 5. Ta-Ni-Ta gasket; 6. Filaments; 7. Radiation shields.

we could scan over a 1 GHz range in 45 min without loss of sensitivity of the spectrometer. Once a line was located roughly from a wide scan detailed measurements were made with the BWO or klystron phase locked to a stable frequency derived from a frequency synthesizer. Many strong transitions were observed with this method. The typical signal to noise ratio was 40 at RC = 1 s. However, the density of transitions above 8 GHz was much lower than in the rf region.

When we started the analysis of the MBER spectrum no assumption on the structure of the KCN molecule was made. The initial identification of the MBER spectrum was based on a pattern recognition of two series of transitions that clearly showed a regularity in the frequency sequence and in their optimum voltages for the state selection fields. The two groups could be identified as transitions between *K*-doublet splittings in a slightly asymmetric prolate top molecule. In first order approximation these splittings are given¹³ for $K_{-1} = 1$ and 2 by $\frac{1}{2}(B - C)J(J + 1)$ and $(B - C)^2(J - 1)J(J + 1)(J + 2)/(16(2A - B - C))$, respectively. After the initial *J* assignment of the *K* doublets all transitions in the observed region were predicted from an exact computer calculation of the MBER spectrum combined in a step by step calculation of the 100 GHz microwave data. The rotational transitions $1_{01} - 0_{00}$, $2_{02} - 1_{01}$, $3_{03} - 2_{02}$, $3_{13} - 4_{04}$, $7_{07} - 6_{16}$ and $16_{1,15} - 15_{2,14}$ could then also be identified; the first three and the *K*-doublet transitions are all *a* type, i. e., associated with μ_a , while the latter three transitions are *b* type. In order to establish the identification of the above given *b*-type transitions and to increase the accuracy of some of the distortion constants we measured another five high *J* *b*-type transitions: $12_{2,11} - 13_{1,12}$, $17_{1,16} - 16_{2,15}$, $22_{3,20} - 23_{2,21}$, $23_{3,21} - 24_{2,22}$, and $27_{2,25} - 26_{3,24}$. A total of 26 MBER transitions has been observed.

IV. FINAL FIT AND STRUCTURE OF KCN

The complementary information obtained from microwave absorption and MBER experiments has led to identical assignments. The observed transition frequencies from Table II were fitted to an asymmetric rotor model.²⁴ The best fit values for the determinable molecular parameters^{21,22} are given in Table III. The *a*-type transitions determine mainly the *B* and *C* rotational constants, whereas the rotational constant *A* can accurately be obtained from the *b*-type lines. Two (H_{JK} , H_{KJ}) sextic distortion coefficients could be fitted from the spectra; the remaining five (H_J , H_K , h_J , h_K , h_{JK}) were set to zero. As can be seen from Table II the agreement between the observed and calculated transition frequencies is excellent. The planarity constraints for the τ 's^{13,14} were not imposed in the fit of the data which resulted in a rather large τ -planarity defect¹⁴ for KCN: $\Delta\tau = -0.86(2)$ kHz. The derived constants assuming planarity are given in Table IV. Due to the large value of $\Delta\tau$ a rather large difference in the calculated centrifugal distortion constants τ_{aabb} and τ_{abab} is obtained if they are derived from $\{\tau_1, \tau_2\}$ or $\{\tau_1, \tau'_{cccc}\}$. The large value of the τ -planarity defect might be caused by the expected nonrigidity of the KCN molecule.

Although the quality of the fit of the data is very good, a precise determination of the structure is difficult. For a triatomic molecule spectroscopic information from at least two different isotopic species is necessary for a unique determination of the three structural parameters. However, very reliable information on the CN distance is available from many molecules. Experimental values for HCN,¹ HNC,² and all the cyanogen halides¹³ as well as the calculated values for LiNC and LiCN are all within $r_{CN} = 1.15 \pm 0.02$ Å. The spread for the experimental values alone is even less $r_{CN}(\text{expt}) = 1.162 \pm 0.010$ Å. At the moment we have no reason to expect large deviations from these values for KCN.

A computer program was written to fit r_{KC} and χ KCN as a function of r_{CN} such that the three experimental rotational constants were calculated as well as possible. The values for *A*, *B*, and *C* were reproduced in this way to within 10 MHz. The calculations show that for $r_{CN} = 1.15$ Å the K nucleus is located exactly on a line perpendicular to CN bond and through the center of mass of the CN group. In that case the CN moment of inertia determines entirely the rotational constant *A*, and there is no fit possible for smaller CN distances. For $r_{CN} > 1.15$ Å two different possible structures are found: the K nucleus is shifted either to the C nucleus (structure A) or to the N nucleus (structure B). From the present measurements no decision can be made which of these structures is the correct one. Figure 2 depicts the variation in the position of the K nucleus expressed in r_{KC} and χ KCN, versus the CN distance. Both r_{KC} and χ KCN depend very critically on r_{CN} . In many cases zero point vibrations are another limiting factor for the accuracy in the determination of effective structural parameters. Although these effects are rather large in KCN, as follows from the inertial defect, they can completely be neglected compared to the uncertainties due to the r_{CN} variation. The best structural parameters we can give for KCN from the present measurements are $r_{CN} = 1.162(10)$ Å, $r_{KC} = 2.6(1)$ Å, and χ KCN = 76°(10). Isotopic substitution is necessary for a more precise structure determination.

Though accurate values for all the τ -distortion constants are obtained a reliable force field calculation has to await the more accurate structure. The lowest vibrational frequency of KCN can be estimated to within 10% to 20% from the inertial defect¹³: $\omega_2 = h/2\pi^2\Delta I$. A value for $\omega_2 = 157$ cm⁻¹ is obtained in this way, which is in good agreement with $\omega_2 = 139$ cm⁻¹ from the matrix-isolation work.⁶

V. CONCLUSIONS AND DISCUSSION OF FURTHER ASPECTS

The present measurements have demonstrated for the first time that high temperature asymmetric molecules can be studied by MBER and microwave spectroscopy. It has been proved without doubt that KCN in the ground vibrational state behaves like an asymmetric rotor with a *T*-shaped structure. Structural parameters may be considerably improved by measuring isotopic species of KCN. This study will be done with the MBER technique in view of the simpler spectrum and the much lower ma-

TABLE II. Frequencies (in MHz) of the observed and calculated rotational transitions of KCN in the ground vibrational state.

J'	K'_{-1}	K'_1	J	K_{-1}	K_1	Type	Observed frequency	Observed-calculated	Reference ^a
3	1	2	3	1	3	a	2 423.00(30)	0.09	MBER
4	1	3	4	1	4	a	4 038.02(20)	0.05	MBER
6	1	5	6	1	6	a	8 478.23(25)	0.01	MBER
7	1	6	7	1	7	a	11 302.87(25)	0.17	MBER
8	1	7	8	1	8	a	14 529.42(25)	0.09	MBER
9	1	8	9	1	9	a	18 157.17(25)	-0.07	MBER
10	1	9	10	1	10	a	22 185.13(25)	-0.12	MBER
16	2	14	16	2	15	a	6 759.36(10)	-0.01	MBER
17	2	15	17	2	16	a	8 500.59(10)	-0.01	MBER
18	2	16	18	2	17	a	10 537.68(10)	0.01	MBER
19	2	17	19	2	18	a	12 893.67(10)	-0.01	MBER
20	2	18	20	2	19	a	15 589.96(10)	0.01	MBER
21	2	19	21	2	20	a	18 645.64(10)	0.02	MBER
22	2	20	22	2	21	a	22 077.46(10)	-0.01	MBER
23	2	21	23	2	22	a	25 899.58(10)	-0.01	MBER
1	0	1	0	0	0	a	9 475.49(10)	0.01	MBER
2	0	2	1	0	1	a	18 948.55(30)	0.	MBER
3	1	3	4	0	4	b	14 443.37(30)	0.03	MBER
7	0	7	6	1	6	b	16 795.78(30)	-0.03	MBER
12	2	11	13	1	12	b	19 359.91(30)	0.04	MBER
16	1	15	15	2	14	b	17 648.34(20)	-0.02	MBER
17	1	16	16	2	15	b	30 303.33(20)	0.01	MBER
22	3	20	23	2	21	b	30 162.39(20)	0.01	MBER
23	3	21	24	2	22	b	17 645.59(20)	-0.01	MBER
27	2	25	26	3	24	b	21 500.65(20)	0.	MBER
3	1	3	2	1	2	a	27 816.57(25)	0.01	mw
3	0	3	2	0	2	a	28 416.80(10)	-0.01	mw, MBER
3	2	1	2	2	0	a	28 425.85(50)	-0.22	mw
3	1	2	2	1	1	a	29 027.89(30)	-0.08	mw
4	1	4	3	1	3	a	37 085.61(10)	0.04	mw
4	0	4	3	0	3	a			
4	3	2	3	3	1	a	37 877.86(50)	0.03	mw
4	3	1	3	3	0	a			
4	2	3	3	2	2	a	37 886.97(20)	-0.01	mw
4	2	2	3	2	1	a	37 909.69(20)	0.	mw
4	1	3	3	1	2	a	38 700.59(15)	-0.03	mw
9	6	3	8	6	2	a			
9	6	4	8	6	3	a	85 034.2(5)	-0.24	8
9	5	5	8	5	4	a			
9	5	4	8	5	3	a	85 111.4(3)	0.15	8
9	4	5	8	4	4	a			
9	4	6	8	4	5	a	85 178.3(3)	-0.10	8
9	2	8	8	2	7	a	85 196.7(3)	-0.08	8
9	2	7	8	2	6	a	85 468.0(4)	-0.11	8
9	1	8	8	1	7	a	87 005.4(2)	-0.03	8
10	1	10	9	1	9	a	92 621.3(5)	0.18	8
10	0	10	9	0	9	a	94 360.1(3)	0.03	8
10	7	3	9	7	2	a			
10	7	4	9	7	3	a	94 382.1(2)	-0.01	8
10	6	5	9	6	4	a			
10	6	4	9	6	3	a	94 480.7(2)	0.11	8
10	5	5	9	5	4	a			
10	5	6	9	5	5	a	94 566.9(2)	-0.06	8
10	4	7	9	4	6	a			
10	4	6	9	4	5	a	94 643.4(2)	-0.02	8
10	2	9	9	2	8	a	94 647.3(3)	0.10	8
10	3	8	9	3	7	a	94 714.8(4)	0.	8
10	3	7	9	3	6	a	94 721.0(4)	-0.07	8
10	2	8	9	2	7	a	95 019.3(2)	0.05	8
10	1	9	9	1	8	a	96 649.2(2)	0.07	8
11	1	11	10	1	10	a	101 858.4(3)	-0.11	8
11	9	3	10	9	2	a			
11	9	2	10	9	1	a	103 556.9(4)	-0.17	8
11	8	3	10	8	2	a			
11	8	4	10	8	3	a	103 694.1(2)	0.06	8

TABLE II (Continued)

J'	K'_{-1}	K'_1	J	K_{-1}	K_1	Type	Observed frequency	Observed-calculated	Reference ^a
11	0	11	10	0	10	a	103 705.8(2)	0.01	8
11	7	5	10	7	4	a ₁	103 817.0(2)	0.02	8
11	7	4	10	7	3	a ₁			
11	6	5	10	6	4	a ₁	103 926.0(3)	-0.08	8
11	6	6	10	6	5	a ₁			
11	5	7	10	5	6	a ₁	104 022.3(2)	0.	8
11	5	6	10	5	5	a ₁			
11	2	10	10	2	9	a	104 092.5(3)	-0.14	8
11	4	7	10	4	6	a ₁	104 108.6(2)	-0.04	8
11	4	8	10	4	7	a ₁			
11	3	9	10	3	8	a	104 190.9(4)	0.15	8
11	3	8	10	3	7	a	104 200.8(5)	-0.13	8
11	2	9	10	2	8	a	104 586.9(2)	0.03	8
11	1	10	10	1	9	a	106 284.9(4)	-0.18	8

^aMBER and mw stand for the results of the present MBER and microwave absorption studies, respectively.

terial consumption in comparison to microwave spectroscopy.

Detailed information about the electronic structure is highly desirable for a better understanding of the unusual bond. Some information may be obtained from measurements of the dipole moment components μ_a and μ_b and from the hyperfine structure. For the low J MBER transitions we were able to resolve the nuclear hyperfine structure associated with the K and N nuclei. However, in the present analysis which combines the MBER and microwave spectra the emphasis is on the determination of the structure of the KCN molecule. In this analysis

the hyperfine splittings were neglected while the errors in the frequencies are taken such that the uncertainties due to the hyperfine effects are well covered. MBER experiments to determine the electric dipole moment and the hyperfine structure are in progress.

Sixty-eight lines from the $J=4 \rightarrow 3$ transition have been observed in the microwave absorption experiment. Since only five of them belong to the ground vibrational state (one line is missing due to an accidental overlap) lines from at least 11, but most probably from many more excited states contribute to the observed spectrum. These states cover a considerable part of the expected

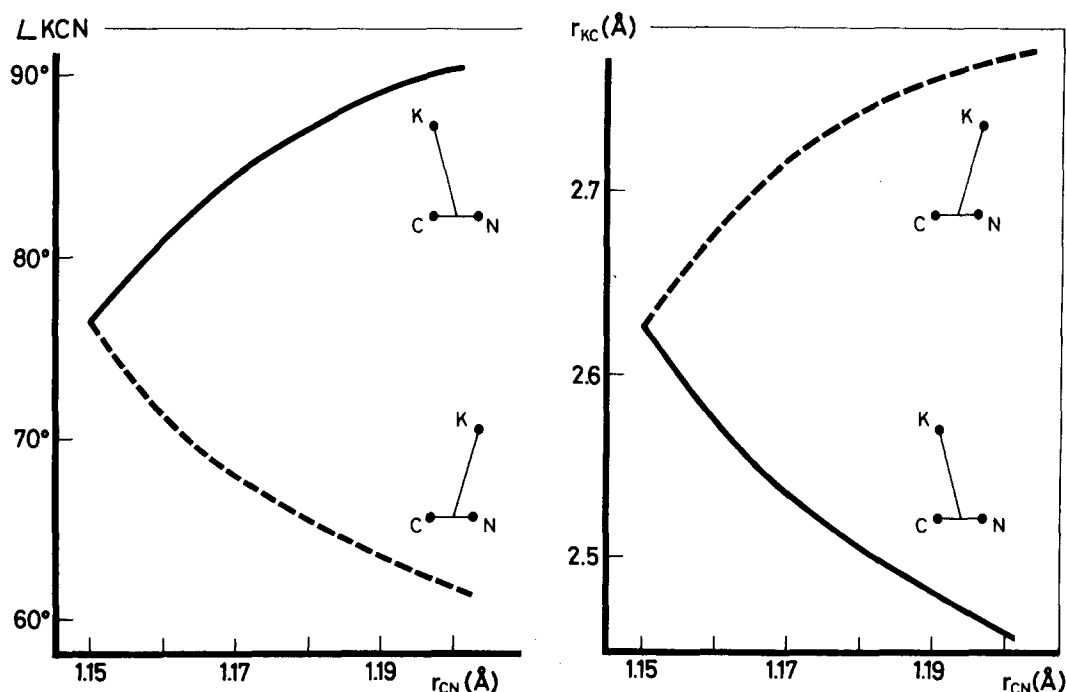


FIG. 2. The \angle KCN and the KC distance vs the CN distance as calculated from the rotational constants. The solid and broken lines correspond to structure A and B, respectively.

TABLE III. Rotational constants for the ground vibrational state of KCN.

Constant	Value (MHz) ^a
A''	58265.81(4)
B''	4940.055(2)
C''	4536.214(2)
τ'_{aaaa}	-5.33(1)
τ'_{bbbb}	-0.02703(3)
τ'_{cccc}	-0.01871(3)
τ_1	-1.5557(4)
τ_2	-0.12083(3)
$H_{JK} \times 10^6$	-5.4(2)
$H_{KJ} \times 10^6$	95(1)
$\Delta\tau \times 10^3$ ^b	-0.86(2)

^aThe uncertainties represent one standard deviation as determined by the least squares fit.¹⁴ The quality of the fit can be judged from $\sigma=0.25$ where $\sigma = [\chi^2/(n-m)]^{1/2}$ with χ^2 the as usual defined chi square value, n the number of lines and m the number of parameters in the fit.

^bReference 14.

potential barrier height for the transition to polytopic bonding and therefore provide a test of the theoretical models describing the large amplitude motions.^{9,11} The results of Bunker and Howe⁹ show that their rigid bender model qualitatively describes the effective asymmetric top structure and the low bending vibrational frequency for a reasonable potential height. An analysis of the spectrum for excited states in KCN will therefore provide valuable information about the height and the shape of the potential. Lines from three excited states have been tentatively assigned, which show that the effect of vibrations on the rotational constants cannot be described by the usual linear v dependence. However, the information from the spectrum is much less complete as compared to the ground vibrational state and more experimental and theoretical work has to be done. The interpretation of spectroscopic data will be complicated by the fact that $2\omega_2$ is nearly equal to ω_1 .

The presently determined structure can be of help to remove discrepancies in the thermodynamic data of KCN as obtained from mass spectroscopic experiments and calculations based on the second and third law. This is not only of theoretical interest but also of some practical importance for the understanding of chemical problems arising in blast furnaces.²³

Preliminary estimates can be made of the structure of the other alkali cyanides as a guideline for future work. The most satisfactory explanation for the trend in the vibrational frequencies ω_2 (Table I) is to assume that LiCN is linear as predicted by the *ab initio* cal-

TABLE IV. Derived molecular constants for KCN assuming planarity.¹⁴ All entries are in MHz except ΔI which is in $\text{amu}\text{\AA}^2$.

	Parameters used for calculation	
	τ_1, τ_2	τ_1, τ'_{cccc}
A^a	58 265.35	58 265.39
B	4 939.658	4 939.661
C	4 536.07	4 536.04
τ_{aaaa}	-5.33	-5.33
τ_{bbbb}	-0.027 03	-0.027 03
τ_{aabb}	0.153	0.069
τ_{abab}	-0.891	-0.814
ΔI^b	0.429 2	0.429 8

^a $A, B,$ and C are the τ -free rotational constants.

^b $\Delta I = (\hbar/8\pi^2) (1/C - 1/A - 1/B)$.

culations and that a change to a T -shaped structure takes place for NaCN. Assuming approximately the same barrier height the slope of the potential function is much steeper for the T -shaped configuration which explains the increase of ω_2 .

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