

## ROTATIONAL SPECTRUM, HYPERFINE SPECTRUM AND STRUCTURE OF LITHIUM ISOCYANIDE

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The rotational spectrum of LiNC has been measured for the first time. We succeeded in producing a supersonic molecular beam ( $\approx 1\%$  LiNC in Ar). The molecular-beam electric-resonance technique has been employed to obtain high-resolution microwave spectra. Two rotational transitions ( $J=1 \rightarrow 0$  and  $J=2 \rightarrow 1$ ) of  $^7\text{LiNC}$  in the ground vibrational state were observed. The hyperfine structure was resolved and identified with the help of microwave-microwave double resonance. The rotational constants  $B_0$  and  $D_0$  and the hyperfine coupling constants  $eQq(\text{Li})$ ,  $eQq(\text{N})$ , and  $c(\text{Li})$  could be deduced. The  $J=1 \rightarrow 0$  rotational transition of  $^6\text{LiNC}$  was observed in natural abundance. From this we conclude that LiNC has a *linear* isocyanide structure. The results for the effective structural parameters are:  $r_{\text{LiN}} = 1.760 \text{ \AA}$ , and  $r_{\text{NC}} = 1.168 \text{ \AA}$ . We did not observe transitions in excited vibrational states or from LiCN. The agreement between the experimental results and recent *ab initio* calculations is good.

### 1. Introduction

The molecular structures of the alkali metal cyanides\* are very sensitive to a subtle balance between a short-range and a long-range component of the interaction energy, as is pointed out by Essers et al. [1]. This leads to different effective structures, which we determined experimentally to be T shaped for KCN [2,3] and NaCN [4], and linear isocyanide for LiNC (current work). Therefore, an experimental determination of the most stable geometries of the alkali metal cyanides is a good test of the predictive power of a variety of increasingly sophisticated *ab initio* methods for calculation of molecular structure.

The structure of gaseous lithium cyanide has been the subject of numerous *ab initio* studies [1,5–9]. These studies indicate that a state of minimum energy exists for both linear LiCN and LiNC with a marginal energy difference of less than 0.3 eV, and with the lithium isocyanide con-

figuration the more stable one. However, there exists a rather large spread among the calculated structures and isomerization energies (i.e. the difference in energy between the two linear configurations), as can be seen in table 1. This is mainly due to the effects of different basis sets in the SCF *ab initio* calculations and whether or not correlation energy was included. Not only for LiCN, but also for HCN [7,10], NaCN [11,12] and KCN [11–13], inclusion of correlation stabilizes the cyanide structure more than the isocyanide structure. In the case of NaCN, the relative stability of the cyanide and isocyanide isomer even reverses [12]. Since no full potential energy surface calculation including correlation is available for LiNC, the possibility of a T-shaped structure cannot be ruled out.

The cyanides are very floppy molecules with bending vibrational frequencies  $\omega_2 = 139, 170$ , and  $120 \text{ cm}^{-1}$  for KCN, NaCN and LiNC, respectively, according to matrix-isolation studies [14], and with large zero-point bending motion amplitudes of up to  $15^\circ$ , predicted by *ab initio* calculations [1,12,13]. Yet, we established [2–4] that the rotational spectra of both KCN and NaCN in the ground vibrational state can be described properly

\* In this paper the alkali metal cyanides are denoted by MCN (where M represents the alkali metal), whatever the structure may be, and the atomic symbol designates the most abundant isotope, unless specified otherwise.

Table 1  
Summary of theoretical predictions for LiCN and LiNC

	Cyanide structure		$\Delta E(\text{cm}^{-1})^{a1}$	Isocyanide structure	
	$r_{\text{LiC}}(\text{\AA})$	$r_{\text{CN}}(\text{\AA})$		$r_{\text{CN}}(\text{\AA})$	$r_{\text{LiN}}(\text{\AA})$
Bak et al. [5]	1.922	1.160	3100	1.157	1.765
Clementi et al. [6]	1.931	1.132	2420	1.154	1.773
Redmon et al. [7]	–	–	1360	–	–
Schmiedekamp et al. [8]	1.930	1.154	2130–3120	1.169–8	1.780–1
Essers et al. [1]	2.003	1.157	2270	1.157	1.768
Marsden [9]	–	–	< 2270	1.174	1.817

<sup>a1</sup> The isomerization energy  $\Delta E$  is the energy difference  $E(\text{LiCN}) - E(\text{LiNC})$ .

by a rigid-rotor model. The bending vibrational frequencies are in the region 110–180  $\text{cm}^{-1}$  which is an intermediate case [13] between typical values of  $\omega_2 = 519 \text{ cm}^{-1}$  for a covalent bonded molecule like  $\text{SO}_2$  [15] and  $\omega_2 = 20 \text{ cm}^{-1}$  for a van der Waals molecule like  $\text{Ar-N}_2$  [16]. In case of the alkali metal cyanides, the M–CN bonding is predominantly ionic and moderate vibrational excitation will be sufficient to overcome the marginal potential-energy barrier in the bending direction so that the  $\text{M}^+$  cation can orbit around the  $\text{CN}^-$  anion. Clementi et al. [6] called this a “polytopic” bonding, since no unique structure can be assigned.

In the current work we present the results of the first successful observation of the microwave spectrum of LiNC. The LiNC molecule has been prepared by two totally different chemical reactions. We succeeded in producing a supersonic molecular beam (1% LiNC in Ar) using a tantalum oven. We measured two rotational transitions ( $J = 1 \rightarrow 0$  and  $J = 2 \rightarrow 1$ ) of  $^7\text{LiNC}$  and one rotational transition ( $J = 1 \rightarrow 0$ ) of  $^6\text{LiNC}$  in the ground vibrational state. The hyperfine structure was resolved and identified. The rotational constants  $B_0$  and  $D_0$ , and the hyperfine coupling constants  $eQq(\text{Li})$ ,  $eQq(\text{N})$ , and  $c(\text{Li})$  have been determined for  $^7\text{LiNC}$ . The rotational constant  $B_0$  of  $^6\text{LiNC}$  could be deduced. We established that LiNC has a linear isocyanide structure.

## 2. Experimental

The spectra were obtained using the molecular-beam electric-resonance (MBER) technique. The

spectrometer has been described in detail elsewhere [2,17]. For this experiment we introduced a few modifications on the apparatus. Only some features relevant to the current work are discussed here.

The LiNC beam intensity was monitored by a surface ionization detector, with an effective aperture of  $3 \times 3 \text{ mm}$ . The iridium ribbon of the surface ionization detector was oxygenated before each run to achieve 100% efficiency for Li compounds. The C-field of the spectrometer, where molecular transitions are induced, consists of two parallel plates. Microwave power is irradiated from a transmitting horn [18] between these two plates, perpendicular to the molecular-beam axis. The transmission line is terminated by an absorber in order to avoid standing waves. The resulting spectral linewidth is determined by the beam velocity and the length of the transition region and is 20–30 kHz. To enable searching over a wide frequency range (9.5–40 GHz) within a reasonable sweep time we artificially broadened the instrumental linewidth to  $\approx 3 \text{ MHz}$  by white noise frequency modulation [19] of the radiation sources [backward wave oscillators (BWO) or klystrons]. In this way the peak intensity of the spectral lines is not affected and a frequency region of 1 GHz could be covered in one scan of 30 min. After preliminary location of a transition, an accurate frequency determination was performed at normal resolution. To make such a detailed scan, the radiation sources were frequency stabilized by phase-locking techniques to a Hewlett-Packard 8660B or 5105A synthesizer. For frequencies higher than 40 GHz, an intermediate X-band oscillator

was used to facilitate locking. The microwave power was modulated at 20 Hz and phase-sensitive detection was applied. In all measurements, the integration time of the lock-in was set at 1 s. The signal-to-noise ratio of the strongest lines was 30. Because of the low signal-to-noise ratio for many of the spectral lines, it was necessary to use signal-averaging techniques. For this purpose a Hewlett-Packard 5480B signal analyser was interfaced with the scan-control unit. Double-resonance measurements were performed by irradiating simultaneously between the parallel plates microwave power at two discrete frequencies, obtained from two separate sources, independently phase locked by two synthesizers.

Very little information is available on the prop-

erties of (gaseous) lithium isocyanide [20]. The chemical stability of LiNC, however, is known to be very poor, especially in the presence of sample impurities or under moisten atmosphere. In the latter case LiOH and HCN are formed by hydrolysis. From the experience we obtained with the production of KCN and NaCN molecular beams we learned that wall reactions in a stainless-steel oven are responsible for part of the problems to maintain a stable beam of alkali metal cyanides. It is also known that LiNC, heated in the presence of Fe, will form  $\text{Li}_2\text{CN}_2$  and C. Facing these problems, we decided to develop a new double chamber oven, made of tantalum. A schematic view is shown in fig. 1. Because leak tight welding of tantalum is very difficult, wedged clamp fittings

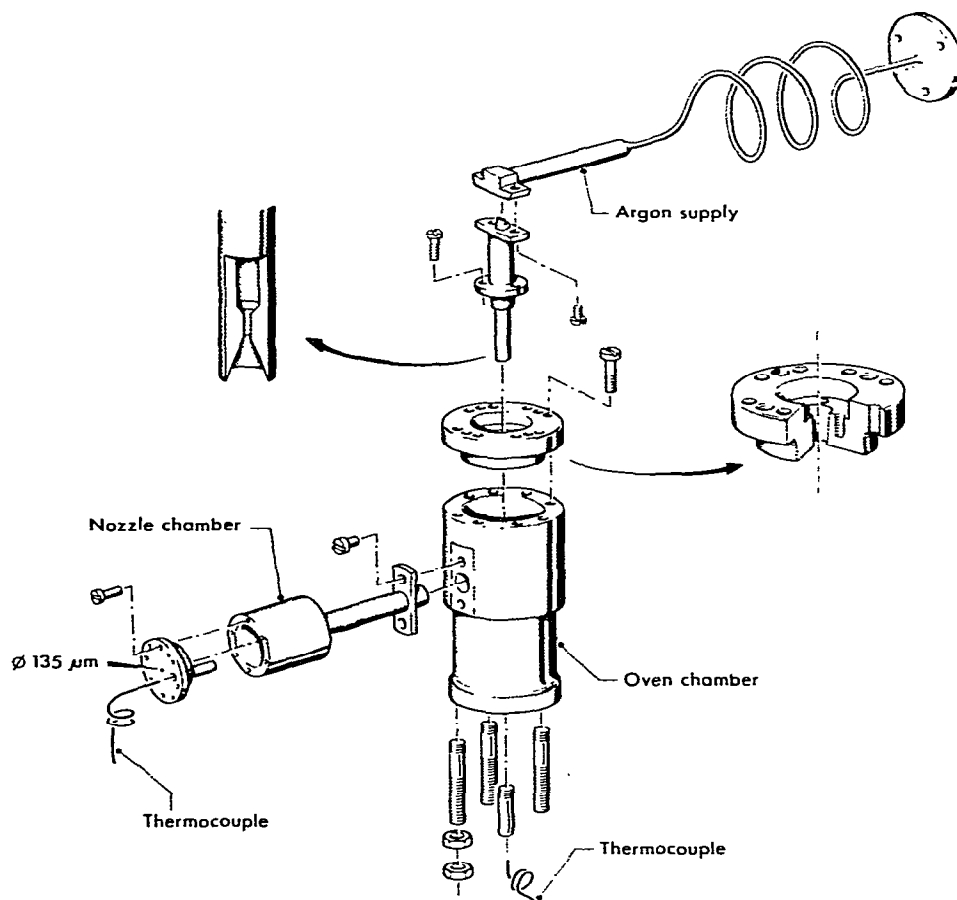


Fig. 1. Exploded view of the tantalum double-chamber oven.

without gaskets were applied for all assembled parts. Sealing is accomplished by tightening the screws which results in plastic deformation of the contact surface of the two parts. The lid could be removed easily by means of screws in the auxiliary screw-holes. It could be re-used many times without any remachining and leakage never occurred. The nozzle with a diameter of 130  $\mu\text{m}$  has been made by scintillating through the tantalum with a tungsten wire. The heating and the temperature monitoring is handled by a method similar to the one described by Töring et al. [2]. In a test run, rotational spectral lines of NaCN were obtained already after 15 min of operation on the required oven and nozzle temperatures. With a stainless-steel oven as used before, it took us several weeks of running until the beam conditions were adequate to observe any transition [4]. Furthermore, the signal-to-noise ratio for the tantalum oven was a factor of four higher than for the stainless-steel oven.

At the start of the experiment, the required oven temperature to obtain sufficient LiNC vapour pressure to produce a molecular beam was unknown. We found out that the oven chamber temperature should be kept at 1040 K to acquire LiNC vapour pressure of a few mbar. To avoid clogging, the nozzle chamber temperature was kept at 1240 K. These are approximately the same temperatures as needed for NaCN (1100 and 1300 K, respectively [4]) and KCN (1150 and 1350 K, respectively [3]). During each start-up, clogging impeded and pressure bursts occurred. However, once stable beam conditions at an elevated temperature were attained, runs of more than 24 h were possible. If the oven temperature was raised above 1040 K, the signal-to-noise ratio of the spectral lines deteriorated and the molecular beam became instable.

The seeded-beam technique was used to concentrate the population in the lower rotational and vibrational levels. The stagnation pressure of the carrier gas argon was 1 bar. The velocity distribution of a pure argon beam has been measured by Meerts et al. [21] under identical conditions. These measurements yielded a translational temperature  $T_i = 30(5)$  K. From the relative intensities of the observed transitions and the dependence of the

LiNC beam intensity on the state selector voltage we estimated the rotational temperature of the LiNC molecules in the beam to be  $T_r = 30(5)$  K. Since no excited vibrational states were observed, the vibrational relaxation of the LiNC molecules is expected to be strong.

Because of the high pyrophoricity of reactants such as powdered lithium metal, and the extreme toxicity of hydrogen cyanide gas, which is formed easily since LiNC is highly hydrolysis sensitive, the preparation of lithium isocyanide is hazardous and precautionary measures have to be taken. In all cases we started with chemical compounds which were dried and heated at an appropriate temperature in vacuum for a few hours. The solvents we utilized were first dried by refluxing over calcium hydride in the case of dimethylformamide (DMF) and lithium tetrahydridoaluminate in the case of tetrahydrofuran (THF), and by subsequent distillation. In order to produce and preserve anhydrous LiNC and for safety reasons, it was necessary to maintain a dry nitrogen atmosphere over the surface of the reaction mixtures and products. This was persevered during filtering off the reaction precipitate and filling the oven. The reaction product was stored under vacuum conditions.

Lithium isocyanide has been obtained by two totally different chemical reactions. The first method, adapted from Hoffman et al. [22], consisted of heating up to 950 K for 30 min an evacuated quartz cell filled with equimolar amounts of LiCl (6.4 g) and NaCN (7.4 g). After cooling and grinding, the solids were leached with 150 ml of dried DMF at reflux for 20 h. Next, the hot solution was filtered, and upon standing and cooling a crystalline precipitate was filtered off. The filtrate,  $\approx 3.8$  g of the adduct LiNC · DMF, was then vacuum dried at 420 K for 5 h, and 2.6 g of DMF was removed. With the resulting solid we managed to produce a molecular beam of lithium isocyanide and measured for the first time microwave transitions of the molecule. However, the molecular beam was not very stable, probably due to residual impurities in the sample. The second method by which we prepared lithium isocyanide is basically the one described by Rossmanith [23]. We distilled 400 ml dried THF over into a flask containing 17.5 g of AgCN, 1 g of powdered Li

metal and 10 g of naphthalene. The resulting solution was refluxed for 6 h and filtered when still hot. After cooling the solvent was filtered off, leaving the product as a greyish solid. This solid was washed with dried petroleum ether until the washings were clear, yielding 3.6 g of the adduct LiNC·THF. The product was dried by heating in vacuum, providing 1.4 g of solid lithium isocyanide. With this sample we checked our previous measurements and performed all the succeeding experiments. Material consumption was very low as a consequence of the seeded-beam technique. A sample of  $\approx 0.25$  g was sufficient to maintain a molecular beam during 20 h.

Other methods were also tried to produce lithium isocyanide. The tantalum oven was loaded with equimolar amounts of two chemical compounds: Li and NaCN, LiCl and NaCN, or Li and AgCN, respectively. Neither of these efforts resulted in the synthesis of LiNC at elevated temperatures under proper molecular-beam conditions.

### 3. Results

The frequencies of the observed microwave transitions of lithium isocyanide in the ground vibrational state are listed in table 2. We measured three hyperfine transitions of the  $J = 1 \rightarrow 0$  rotational transition of  $^7\text{LiNC}$ . The  $J = 2 \rightarrow 1$  transition was observed as a many MHz wide feature

with hardly any structure. By applying microwave-microwave double resonance we were able to resolve and identify unambiguously seven hyperfine components of this rotational transition. The double resonance signals were observed by monitoring the intensity of a specific hyperfine component of the  $J = 1 \rightarrow 0$  rotational transition, while simultaneously another microwave radiation source was scanned around the frequency of the  $J = 2 \rightarrow 1$  rotational transition. The two hyperfine components of the  $J = 1 \rightarrow 0$  transition of the isotopic species  $^6\text{LiNC}$  have been observed in natural abundance. An example of the observed spectra is shown in figs. 2 and 3.

The observed transition frequencies from table 2 were fitted by a least-squares method using a computer program for the hyperfine interaction in molecules with two nuclei possessing couplings of comparable strength. This program [3] employs the general expressions derived by Thaddeus et al. [24] for the matrix elements of the hyperfine hamiltonian including quadrupole, spin-rotation and spin-spin interaction. In the representation used, the nucleus with spin indicated by  $I_1$  couples first to the molecular rotational angular momentum  $J$  to form a resultant  $F_1$ ; then the nucleus with spin  $I_2$  couples with  $F_1$  to form the total angular momentum  $F$ . After diagonalization, the energy states are labeled by the quantum numbers  $J$  and  $F$ , and by a pseudo spin quantum number  $\epsilon$ . For a given  $J$  and  $F$ , the state lowest in energy is de-

Table 2  
Frequencies (in MHz) of the observed and calculated transitions of LiNC in the ground vibrational state

Isotope	$J' \rightarrow J''$	$F'_\epsilon \rightarrow F''_\epsilon$	Obs. frequency	Obs. - calc.	Calc. $\nu_0$ <sup>a)</sup>
$^7\text{LiNC}$	1 $\rightarrow$ 0	$3/2_2 \rightarrow 1/2_1$	26586.5982(50)	-0.0010	26586.4532(40)
		$5/2_2 \rightarrow 3/2_1$	26586.6480(30)	0.0008	
		$3/2_3 \rightarrow 1/2_1$	26587.9252(40)	-0.0008	
	2 $\rightarrow$ 1	$1/2_2 \rightarrow 3/2_3$	53171.3428(30)	-0.0002	53172.1271(25)
		$5/2_3 \rightarrow 3/2_3$	53171.3832(40)	0.0003	
		$3/2_3 \rightarrow 3/2_3$	53171.4258(30)	-0.0004	
		$5/2_3 \rightarrow 5/2_2$	53172.6615(40)	-0.0002	
		$1/2_2 \rightarrow 3/2_2$	53172.6749(70)	0.0051	
		$3/2_3 \rightarrow 5/2_2$	53172.7039(50)	-0.0011	
		$5/2_3 \rightarrow 3/2_2$	53172.7099(70)	0.0002	
$^6\text{LiNC}$	1 $\rightarrow$ 0	$2_2 \rightarrow 1_1$	29183.0291(60)	0.0020	29182.8796(60)
		$1_3 \rightarrow 0_1$	29184.3479(60)	-0.0020	

<sup>a)</sup>  $\nu_0$  is the frequency of the pure rotational transition corrected for nuclear hyperfine displacements.

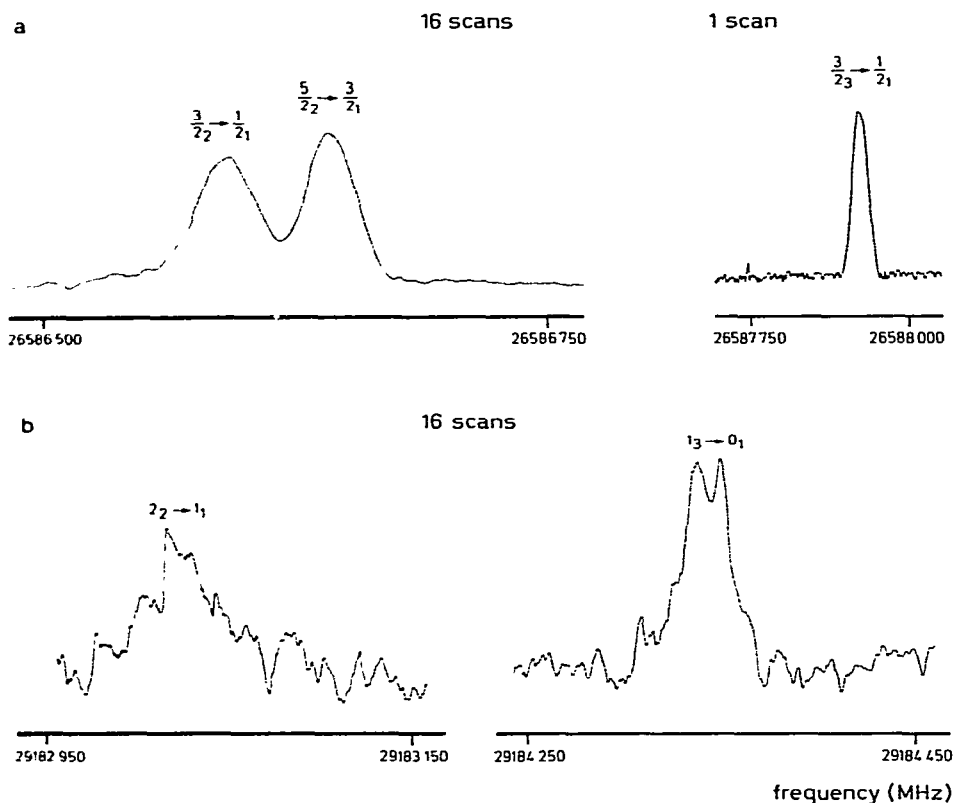


Fig. 2. Spectral recording of the  $J=1 \rightarrow 0$  rotational transitions of  $^7\text{LiNC}$  (a) and  $^6\text{LiNC}$  (b) in the ground vibrational state. The full linewidth at half height is 30 kHz. The hyperfine structure transitions are indicated as  $F'_i \rightarrow F''_i$ .

noted with  $\epsilon = 1$ ; the states higher in energy are labeled  $\epsilon = 2, 3, \dots$  consecutively. In the case of  $^6\text{LiNC}$ , where the energy of the quadrupole interaction of the lithium nucleus is only  $\approx 2$  kHz, we used the same labelling for reasons of consistency.

The best fit values<sup>a</sup> for the frequencies  $\nu_0$  of the hyperfine-free origins of the rotational transitions, the quadrupole coupling constants  $eQq(\text{Li})$  and  $eQq(\text{N})$ , and the spin-rotation coupling constant  $c(\text{Li})$  of  $^7\text{LiNC}$  in the ground vibrational state are given in tables 2 and 3. The spin-rotation coupling of the nitrogen nucleus could not be determined and has been fixed at zero. In the least-squares fit the spin-spin coupling constant  $d(\text{Li-N})$  has been constrained at the value calcu-

lated from the geometry using the relation:

$$d_{12} = g_1 g_2 \mu_N^2 r_{12}^{-3}, \quad (1)$$

where  $g_1$  and  $g_2$  are the nuclear  $g$  factors,  $\mu_N$  is the nuclear magneton, and  $r_{12} = r_{\text{LiN}} = 1.760$  Å (this work). For  $^6\text{LiNC}$ , the hyperfine coupling constants were constrained in the fit at the values obtained for  $^7\text{LiNC}$ , corrected [25] for the change of the nuclear electric quadrupole moment  $Q$  and the nuclear  $g$  factor of Li.

Using the relation [25] for the frequencies of rotational transitions  $J+1 \rightarrow J$  for linear molecules:

$$\nu = 2B_0(J+1) - 4D_0(J+1)^3, \quad (2)$$

we can determine the rotational constants  $B_0$  and  $D_0$  for the ground vibrational state of lithium

<sup>a</sup> All uncertainties stated in this paper represent three times the standard deviation as determined by the least-squares fit.

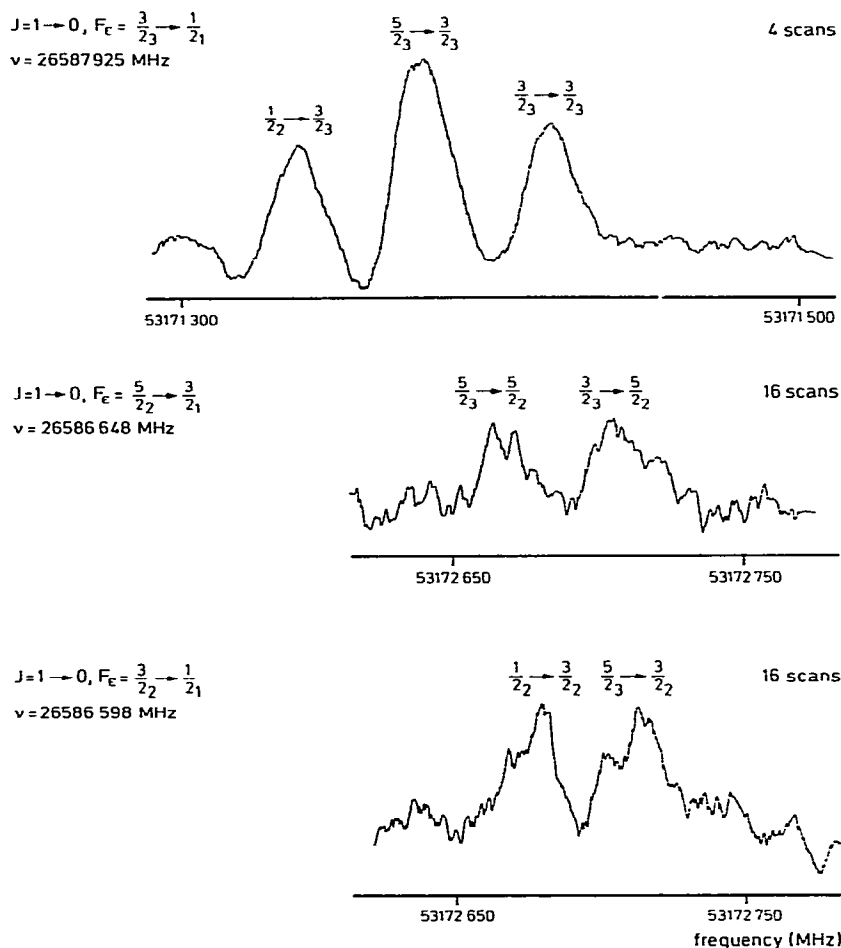


Fig. 3. Spectral recording of the  $J = 2 \rightarrow 1$  rotational transition of  ${}^7\text{LiNC}$  in the ground vibrational state by means of microwave double resonance spectroscopy. The full linewidth at half height is 20 kHz. The hyperfine structure transitions are indicated as  $F'_c \rightarrow F''_c$ . The quantum numbers and frequencies of the hyperfine transitions of the rotational transition  $J = 1 \rightarrow 0$  used for double resonance are stated.

isocyanide. The results are presented in table 3.

A T-shaped structure for LiNC can be excluded, since this would give rise to a spectrum of an asymmetric top molecule with many transitions below 40 GHz. Searches in the region of 9.5–40 GHz for such a spectrum were negative. It is not possible to determine unambiguously the structure of a non-symmetric, triatomic linear molecule from the rotational constants of only two isotopic species. However, the vibrational isotope effects of lithium isocyanide as observed in inert gas matrices clearly indicate [14,26] that under the assumption

of a linear structure the isocyanide configuration is lower in energy than the cyanide configuration. So, in the case of lithium isocyanide there is experimental evidence to remove the ambiguity in the structure and to justify the conclusion that LiNC is more stable than LiCN. The effective structural parameters for the ground vibrational state of lithium isocyanide were calculated using the rotational constants  $B_0$  of  ${}^7\text{LiNC}$  and  ${}^6\text{LiNC}$  from table 3. The results are given in table 4.

Two additional arguments against the cyanide configuration as the most stable structure can be

Table 3  
Hyperfine coupling constants<sup>a)</sup> and rotational constants for the ground vibrational state of LiNC

Isotope	Constant	Value	Unit
<sup>7</sup> LiNC	$eQq(\text{Li})$	0.364(20)	MHz
	$eQq(\text{N})$	-2.941(9)	MHz
	$c(\text{Li})$	1.0(8)	kHz
	$d(\text{Li}-\text{N})$ <sup>b)</sup>	0.61864	kHz
	$B_0$	13293.292(3)	MHz
	$D_0$	32.5(4)	kHz
<sup>6</sup> LiNC	$B_0$ <sup>c)</sup>	14591.505(20)	MHz
	$D_0$ <sup>d)</sup>	32.5	kHz

<sup>a)</sup> The following convention has been used:  $eQq \equiv eQq_{aa} = -2eQq_{bb} = -2eQq_{cc}$ ,  $c \equiv M_{cc} = M_{bb}$ ,  $d \equiv D_{cc} = D_{bb} = \frac{1}{2}D_{aa}$ . The  $a$  axis is the molecular symmetry axis.

<sup>b)</sup> The spin-spin coupling constant  $d(\text{Li}-\text{N})$  has been constrained at the value determined from the structure with  $r_{\text{LiN}} = 1.760 \text{ \AA}$ .

<sup>c)</sup> The uncertainty in  $B_0$  is based on an assumed uncertainty of 30% in the fixed value of  $D_0$ .

<sup>d)</sup> The  $D_0$  constant of <sup>6</sup>LiNC has been constrained at the value of the  $D_0$  constant of <sup>7</sup>LiNC.

inferred from ab initio calculations [1.5–9]. Under the assumption of a linear cyanide configuration, the rotational constants  $B_0$  from table 3 yield the following structural parameters:  $r_{\text{LiC}} = 1.670 \text{ \AA}$ ,  $r_{\text{CN}} = 1.168 \text{ \AA}$ . The ab initio cyanide structures, listed in table 1, predict  $r_{\text{LiC}} \geq 1.92 \text{ \AA}$ . Inclusion of correlation, essential for more accurate predictions [7.9,10,27], even consistently increases the bond length predictions [27], which makes the disagreement between the ab initio bond length  $r_{\text{LiC}}$  and the value obtained from the experiment when assuming a cyanide configuration even larger. The hyperfine quadrupole coupling constants (in MHz) evaluated [28]<sup>\*</sup> from the ab initio calculation by Essers et al. [1] are:  $eQq(\text{Li}) = 0.405$ ,  $eQq(\text{N}) = -2.891$  for LiNC, and  $eQq(\text{Li}) = 0.403$ ,  $eQq(\text{N}) = -4.983$  for LiCN, respectively. Table 3 shows, that the calculated  $eQq(\text{N})$  for LiNC is in close agreement with the experimental value, while the calculated  $eQq(\text{N})$  for LiCN is off by almost a factor of two. The calculated  $eQq(\text{Li})$  is about the same for LiNC and LiCN and is in gratifying agreement with the experimental value.

<sup>\*</sup> We used  $Q(^7\text{Li}) = -0.0366$  barn, and  $Q(^{14}\text{N}) = 0.0166$  barn.

Table 4  
The effective structural parameters for the ground vibrational state of LiNC

Constant	Value (Å)
$r_{\text{LiN}}$	1.760(6)
$r_{\text{CN}}$ <sup>a)</sup>	1.168(6)

<sup>a)</sup> The uncertainty in the CN bond length has been assumed to be twice the uncertainty in the case of KCN [3] and NaCN [17].

#### 4. Discussion

The current study presents the first experimental investigation of the structure of gaseous lithium isocyanide by means of high-resolution molecular-beam electric-resonance spectroscopy. The agreement between our experimental results and the ab initio calculations is good, confirming that the most stable structure is the linear isocyanide configuration. An unambiguous structure determination from the rotational constants is possible by measuring more isotopic species of LiNC. Since the nitrogen nucleus is located very close to the centre of mass, no structural information can be obtained from the isotopic species Li<sup>15</sup>NC. More can be learned from the rotational spectrum of LiN<sup>13</sup>C. An effort to measure this isotopic species in natural abundance was unsuccessful due to lack of sensitivity. An attempt to increase the abundance of LiN<sup>13</sup>C in the molecular beam by loading the tantalum oven with equimolar amounts of LiNC and K<sup>13</sup>CN also failed.

A search for transitions of the LiNC molecule in an excited vibrational state was performed. However, due to the strong relaxation in the seeded supersonic beam, these states are not sufficiently populated to observe their spectrum. Since no transitions of the molecule LiCN were observed, less than 3% of the cyanide molecules in the beam was LiCN, the rest being LiNC. From this result a lower limit for the isomerization energy can be calculated:  $\Delta E \geq 120 \text{ cm}^{-1}$ .

Information on the excited vibrational states will reveal more about the electronic structure of lithium isocyanide. A MBER study might be possible if the vibrational relaxation of the cyanide molecules in the seeded molecular beam is re-



duced, e.g. by using a different carrier gas. Microwave absorption in a high-temperature cell, as used for KCN by Kuijpers et al. [29], is another method to observe the rotational transitions of LiNC in excited vibrational states. Such experiments, currently underway, will provide a further check for ab initio calculations of the shape and depth of the potential-energy surface [1,5–9], the force constants [8], and the ro-vibrational spectrum [1,30] of LiNC.

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