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Structure of sodium cyanide by molecular beam electric resonance spectroscopy

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Until recently all gaseous alkali metal cyanides[1] were assumed to be linear. Quantum mechanical calculations[2] indicated that this is the case for lithium cyanide. The linear isocyanide configuration LiNC is expected to be the most stable. This structure was indeed deduced from vibrational isotope effects of lithium cyanide in inert gas matrices.[3] Using the same method Ismail *et al.*[4] expected sodium and potassium cyanide to have a linear cyanide configuration. Pietro *et al.*[5] calculated the equilibrium geometry of gaseous KCN using a STO-3G basis set and also found a linear cyanide configuration. Recently gas phase spectroscopy determined accurately and unambiguously the structure of KCN,[6,7] which surprisingly was found to be *T* shaped. In this paper we report the experimentally determined structure of NaCN, which is found to be *T* shaped as well.

A report of the experimentally determined gas phase structure of potassium cyanide[6,7] stimulated *ab initio* potential energy surface calculations on both potassium cyanide[8-10] and sodium cyanide.[9,10] As for LiCN, the M–CN bonding is found to be predominantly ionic: there is an almost complete charge transfer between the CN group and the alkali atom. The potential energy surface in the bending direction has very low barriers for internal rotation (0.3 eV or smaller). This implies that moderate thermal excitation of these molecules is sufficient to allow the M^+ cation to move more or less freely around the CN^- anion. Clementi *et al.*[2] referred to this as a "polytopic bond," since in this case no structural formula is preferred. However, it is established that both KCN,[6,7] and NaCN (current work) can be considered rigid in the ground vibrational state. Yet the amplitudes of the zero-point bending motion in both molecules can range up to 10°, while for LiCN this amplitude is expected to be even larger.[2]

In this communication we present the results of the first successful observation of the microwave spectrum of sodium cyanide. Earlier attempts by Kuijpers and Törring in our laboratory to observe microwave absorption of NaCN in the high temperature cell which was used for KCN[11] failed; probably due to polymerization of NaCN in combination with lack of sensitivity. Presently we employed the molecular beam electric resonance technique with essentially the same setup as described before.[6] An argon seeded sodium cyanide beam was used. The temperatures of the supply chamber and the nozzle chamber of the stainless steel oven were typically held at 1100 and 1300 K, respectively. The vapor pressure of NaCN in the supply chamber at this temperature was of the order of 1 mbar, the stagnation pressure of the carrier gas argon was 1 bar. Maintaining a stable beam turned out to be more difficult than for KCN. Clogging occurred after a few hours and before each run the oven had to be cleaned thoroughly. The seeded beam technique was used in order to obtain strong translational, rotational, and vibrational relaxation. Due to the vibrational cooling only transitions of molecules in the ground vibrational state were detected. This simplifies the microwave spectrum and makes identification of the observed transitions feasible. We observed 20 rotational transitions between 9.5 and 40 GHz. The quadrupole hyperfine structure was resolved for most transitions. The linewidth of a single component was about 30 kHz. The signal-to-noise ratio of the strongest lines was 10 using an integration time of 3 s. All the observed rotational transitions were identified as *a*-type (10) and *b*-type (10) transitions of a near-prolate asymmetric top rotor. The observed spectrum

TABLE I. The τ-free rotational constants for the ground vibrational state of NaCN.

Constant	Value (MHz)
A	57 920.9(11)
B	8 368.48(17)
C	7 272.37(17)

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TABLE II. The effective structural parameters for the ground vibrational state of NaCN.

Constant	Value (Å)
r_{CN}[a]	1.169(6)
r_{NaC}	2.366(29)
r_{NaN}	2.243(27)

[a]The CN bond length has been fixed (see text).

was fitted using Watson's reduced Hamiltonian.[12] We determined the three rotational and the five quartic distortion constants. The τ-free rotational constants for sodium cyanide in the ground vibrational state are listed in Table I.

Assuming the CN bond lengths (r_{CN}) in NaCN and KCN to be equal within 0.006 Å and using the rotational constants from Table I, the structure of NaCN can be calculated. The result is presented in Table II. The effective CN bond length of KCN was determined by Vaals *et al.*[7] using the results from three isotopic species. The assumption that within the quoted uncertainty r_{CN} is not affected by the change from potassium to sodium is justified by the following arguments. Both KCN and NaCN have similar T-shaped structures, the M–CN bonding in both molecules is almost completely ionic, and their bending vibrational frequencies ω_2 are about equal. The latter frequencies were estimated from the inertial defects: 0.4295 amu Å^2 for KCN and 0.3769 amu Å^2 for NaCN, yielding[13] $\omega_2 = 157(30)$ cm^{-1} and $\omega_2 = 179(35)$ cm^{-1}, respectively. These values are in good agreement with those found in matrix-isolation studies: $\omega_2 = 139$ cm^{-1} for KCN and $\omega_2 = 169$ cm^{-1} for NaCN.[4]

From the trend in ω_2 found in matrix-isolation studies of LiCN, NaCN and KCN, Törring *et al.*[6] predicted a T-shaped structure for NaCN. Our present measurements have unambiguously confirmed this expectation. Recent *ab initio* computations of the potential energy surface of sodium cyanide[9,10] also favor a T-shaped structure. The equilibrium structures derived from these calculations, however, have still relatively large uncertainties. This is illustrated by the disagreement among the calculated structures (5%) and isomerization energies (50%) that are obtained from various calculations using different basis sets or when electron correlation is included.[2,9,10] The suggestion of Klein *et al.*,[9] that the difference between the computed equilibrium geometry and the experimentally determined effective structure r_0[7] can be explained by the effect of vibrational averaging is not likely. Even for "floppy" molecules like KCN and NaCN these effects are much smaller than the discrepancies between the *ab initio* and experimental structures (e.g., 10% for ∢NaNC). We have made an estimate for KCN[7] of the differences between effective and substitution structural parameters to be less than 0.5% of r_0. This implies that the expected differences between effective and equilibrium structural parameters are about 1% of r_0.

A more accurate structure determination for NaCN, without assuming the CN bond length, will be possible after the evaluation of the rotational spectrum of the ^{13}C isotopically substituted species of sodium cyanide in the ground vibrational state. These experiments are currently underway. A full report of the present work will be published elsewhere.

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