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Laboratory microwave spectroscopy of aluminium cyanide

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Abstract

The pure rotational spectrum of aluminium cyanide (AlCN) between 10 and 21 GHz has been investigated by Fourier transform microwave spectroscopy. Molecular samples were produced by reacting ablated Al metal with cyanogen present in an Ar supersonic jet. Rotational and centrifugal distortion constants and ²⁷Al and ¹⁴N nuclear quadrupole coupling constants and nuclear spin–rotation constants have been determined for the main isotopomer, ²⁷Al¹²Cl⁴N. The spectrum of AlCN was found to be much weaker than that of AlNC thus confirming that AlCN is the less stable of the two isomers. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Over the past decade, transitions of several metal-containing species, including aluminium, sodium, and potassium monohalides [1,2] and sodium and magnesium monocyanides [3–6], have been identified in the circumstellar envelope of IRC + 10216. The metal monocyanides are particularly interesting because they have three possible structural isomers: they can take the linear cyanide, the linear isocyanide or the non-linear T-shaped configurations. Experimentally the most stable isomer of sodium monocyanide is T-shaped [7] but that of magnesium monocyanide is the linear isocyanide species [5]. The T-shaped NaCN isomer [3] has been detected in

IRC + 10216, as have both MgNC [4,5] and its metastable linear cyanide isomer MgCN [6]. The two linear isomers of aluminium monocyanide have also been suggested as possible candidates for detection in this object [8]. As was found for magnesium monocyanide, the linear isocyanide species is again the lowest energy isomer [9]: calculations on the formation of metal monocyanide species in this molecular cloud suggest that most of the aluminium monocyanide should be in the form AlNC not AlCN [10]. Therefore sensitive searches need to be made for both linear isomers to verify this prediction.

Until recently, only theoretical calculations of ground-state structural parameters were available for AlCN and AlNC [8,11,12]. In the past year, several experimental studies of gas-phase AlNC have been published. Millimeter wave transitions, in both the ground vibrational state and excited states of the bending mode (ν_2), have been measured by Robinson et al. [9]. The hyperfine structure in the pure rotational spectrum was investigated by Walker and

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Gerry [13] using Fourier transform microwave (FTMW) spectroscopy. Fukushima observed the vibronic structure of an electronic band system at 28754 cm^{-1} using laser-induced fluorescence (LIF) [14]. He assigned this system as the ${}^{1}A' - {}^{1}\Sigma^{+}$ transition of AINC based on the vibrational analysis of the ground electronic state and the results of his own ab initio calculations. There has also been a matrix isolation infrared study of the monocyanides of all the group 13 metals, including AINC and AICN [15]. Very recently, Gerasimov et al. obtained rotationally resolved fluorescence excitation spectra of an electronic band system at 36389 cm^{-1} which they assigned as the $\tilde{A}^{1}\Pi - \tilde{X}^{1}\Sigma^{+}$ transition of AlNC [16]. They also reassigned the band reported by Fukushima to the ${}^{1}\Pi - {}^{1}\Sigma^{+}$ transition of AlCN. This spectrum is the only reported observation of gas phase AlCN so far.

This Letter is the first report of the microwave spectrum of AlCN. The two lowest frequency rotational transitions, J = 1-0 and J = 2-1, have been measured using a cavity Fourier transform microwave (FTMW) spectrometer. The nuclear hyperfine structure due to ²⁷Al and ¹⁴N nuclei has been observed and nuclear quadrupole and nuclear spin–rotation constants have been calculated. The molecular constants determined from the FTMW spectrum of AlCN will aid in the search for this molecule in circumstellar regions.

2. Experimental

The transitions of AlCN were measured using a pulsed jet cavity FTMW spectrometer [17] which has been described in detail elsewhere [18]. The spectrometer cavity is formed by two spherical aluminium mirrors 28 cm in diameter and placed ~ 30 cm apart. A pulsed nozzle laser ablation source is mounted near the centre of one of the mirrors so that the molecular jet travels parallel to the axis of microwave propagation. This configuration enhances the sensitivity of the spectrometer [19]. It also gives rise to Doppler splitting in the observed spectra so each line appears as a doublet. Transition frequencies were determined by averaging the frequencies of the measured Doppler components. Measurement accu-

racy is estimated to be better than ± 1 kHz. The microwave synthesizer is referenced to a Loran frequency standard, which is accurate to one part in 10^{12} .

The pulsed nozzle laser ablation source has been described elsewhere [20]. An Al rod (Goodfellow, 99.999%) was ablated, using a frequency-doubled Nd:YAG laser (532 nm, ~ 5–10 mJ/pulse), in the presence of a less than 0.03% cyanogen/Ar mixture (stagnation pressure, 5–7 bar). Both AlCN and AlNC were produced in the ablation source. The AlCN signals were particularly sensitive to the amount of $(CN)_2$ in the gas mixtures: lower concentrations of cyanogen produced stronger signals.

3. Observed spectra and analyses

The initial search parameters were determined using the ab initio calculations by Ma et al. [8], since the experimental results of Gerasimov et al [16]. were not available when our study was undertaken. For AlNC, it was found that the calculations made at the TZ2P + fCISD level of theory produced rotational constants closest to the experimental values [13]. Accordingly, the predicted value at the same level of theory was used for AlCN. Nuclear quadrupole coupling constants $eQq_0(^{27}Al)$ from AlNC [13] and $eQq_0(^{14}N)$ from HCN [21] were used to



Fig. 1. Composite spectrum showing the ¹⁴N hyperfine splitting in the J = 1-0 $F_1 = 7/2-5/2$ transition of AlCN. The results of two different microwave experiments were used to produce this composite. Each spectrum was obtained with 2000 averaging cycles and 4K data points.

Transition					Frequency	Obscalc.	
$\overline{J'}$	F_1'	F'	$J^{\prime\prime}$	F_1''	$F^{\prime\prime}$	(MHz)	(kHz)
1	5/2	3/2	0	5/2	5/2,3/2	10043.9734	0.1
1	5/2	7/2	0	5/2	5/2,7/2	10044.4797	-0.5
1	5/2	5/2	0	5/2	5/2,7/2,3/2	10045.6314	0.5
1	7/2	7/2	0	5/2	5/2,7/2	10052.0147	0.1
1	7/2	5/2	0	5/2	5/2,7/2,3/2	10052.7302	-0.1
1	7/2	9/2	0	5/2	7/2	10052.9498	-0.0
1	3/2	3/2	0	5/2	5/2, 3/2	10055.8463	0.3
1	3/2	1/2	0	5/2	3/2	10056.2743	-0.1
1	3/2	5/2	0	5/2	5/2,7/2,3/2	10056.7580	-0.2
2	9/2	9/2	1	7/2	7/2	20102.1140	0.2
2	9/2	11/2	1	7/2	9/2	20102.4836	-0.3
2	9/2, 1/2	7/2, 3/2	1	7/2, 3/2	5/2	20103.1588	0.0
2	7/2	9/2	1	5/2	7/2	20103.3738	0.1

Measured frequencies of J = 1-0 and J = 2-1 transitions of AlCN

estimate the magnitude of the hyperfine splitting. Transitions for J = 1-0 were found within ~ 5 MHz of the prediction.

Thirteen hyperfine components belonging to the two lowest rotational transitions, J = 1-0 and J = 2-1, have been observed for ${}^{27}\text{Al}{}^{12}\text{C}{}^{14}\text{N}$ (98.53% natural abundance). The spectra obtained were significantly weaker than those of AlNC [13]. Several hundred averaging cycles were required to observe the strongest J = 1-0 transitions of AlCN whereas only a few cycles were necessary to observe similar transitions of AlNC. These strongest lines, components of the J = 1-0 $F_1 = 7/2-5/2$ transition, are shown in Fig. 1. Although the relative intensities

confirm that AICN is less stable than AINC, the energy difference between these isomers could not be quantified because the intensities of FTMW spectra are also functions of excitation and cavity parameters as well as molecular populations. Since the signals were so weak for the main isotopomer, species containing the minor isotopes of N and C were not sought.

Nuclear hyperfine structure due to both ²⁷Al (I = 5/2) and ¹⁴N (I = 1) was observed. Because the nuclear quadrupole moment of ²⁷Al is an order of magnitude larger than that of ¹⁴N, the observed lines could be easily assigned in terms of the coupling scheme $\mathbf{J} + \mathbf{I}_{Al} = \mathbf{F}_1$; $\mathbf{F}_1 + \mathbf{I}_N = \mathbf{F}$. The measured

Table 2 Molecular constants calculated for AlCN^a

Parameter	FTMW (MHz)	Theoretical ^b (MHz)	LIF ^c (MHz)				
$ \begin{array}{r} \overline{B_0} \\ D_0 \\ eQq_0(^{27}\text{Al}) \\ eQq_0(^{14}\text{N}) \end{array} $	5025.41235(25) 0.002751(42) - 37.2225(29) - 5.2321(29)	5025 ^d , 4982 ^e	5019(138)				
$C_{I}^{(27}\text{Al})$ $C_{I}^{(14}\text{N})$	0.00438(16) 0.00147(36)						

^aOne standard deviation in parentheses, in units of least significant digit.

 $^{b}B_{e}$ values taken from Ma et al. [8]. B_{e} was calculated since it was determined that B_{e} and B_{0} differ by less than 5 MHz.

^cGround-state rotational constant, B", taken from Gerasimov et al. [16].

^dResult calculated at the TZ2P + fCISD level.

^eResult calculated at the TZ2P + f CCSD(T) level.

Table 1

frequencies and their assignments are given in Table 1. The spectral data were analysed using Pickett's global least-squares fitting program SPFIT [22]. A fit was made to the rotational and centrifugal distortion constants, B_0 and D_0 , and the nuclear quadrupole and nuclear spin-rotation constants, eQq_0 and C_1 , for both the Al and N nuclei. The lines observed for the overlapped hyperfine components of J = 1-0 transition were fit as blended lines using predicted intensities as weighting factors. The constants obtained from the fit are listed in Table 2.

Also listed in Table 2 are the rotational constants obtained in earlier theoretical and experimental studies. As was also found for AlNC, the rotational constant calculated at the TZ2P + fCISD level of theory was the closest to that obtained from experiment. The theoretical value deemed to be the most reliable, that calculated at the TZ2P + fCCSD(T) level, was more than 40 MHz lower in frequency than the experimentally determined constant. The rotational constant from the LIF study, which has a very large uncertainty, is within 6 MHz of that determined by FTMW. This confirms that AlCN is the molecular carrier of the electronic band system at 28754 cm⁻¹.

4. Discussion

The ²⁷Al and ¹⁴N nuclear quadrupole coupling constants can be used to examine the bonding in AlCN. These constants can be interpreted in terms of valence p-electron densities using the Townes–Dailey model [23]. This relates the measured nuclear quadrupole coupling constant, eQq(mol), to the nuclear quadrupole coupling constant of one atomic *n*p electron

$$eQq(\text{mol}) = \left(n_z - \frac{n_x + n_y}{2}\right) eQq_{n10}(\text{atom}), \quad (1)$$

where n_x , n_y , and n_z are the number of electrons in the np_x , np_y and np_z orbitals, respectively, and zaxis is along the molecular axis. Values of eQq_{n10} are tabulated in Ref. [24].

It has been suggested that, for aluminium monocyanide and other group-13 metal monocyanide species, the M–C bonds in the MCN species are 'single bonds' while the M–N bonds in the corresponding MNC molecules have a 'trace of double bond character' [15]. This bonding picture can be examined qualitatively using the Al nuclear quadrupole coupling constants of AlCN and AlNC and Eq. (1). For these species, the most significant contribution to n_{τ} , and thus to $eQq(^{27}Al)$, is sp-hybridisation of the bonding orbitals on Al. Without this, there would be little electron density in the 3p orbital and the Al nuclear quadrupole coupling constant would be negligible [13]. Because the ionic characters of the Al-CN and Al-NC bonds are similar, the sp-hybridisation should not change significantly between the linear cvanide and the linear isocyanide configurations and, therefore, n_{z} should be the same for both isomers. The values of n_x and n_{y} depend on the degree of double bond character in the Al-C or Al-N bond. If these are taken to be single bonds for both species then $n_x = n_y = 0$ and the $eOq(^{27}Al)$ values would be the same. However, if the Al-(CN) bond in one of the species had some double-bond character then $(n_x + n_y)/2$ would be non-zero and this would lower $eQq(^{27}Al)$. Experimentally, the Al nuclear quadrupole coupling constant of AINC (-35.627 MHz [13]) was found to be ~ 1.6 MHz lower than that of AlCN (-37.223)MHz). These results are consistent with the Al-N bond in AINC having more 'double-bond character' than the Al-C bond in AlCN. Although the Al-C bond order in AICN cannot be determined unambiguously, it can be assumed to be ~ 1 because the Al quadrupole coupling constant of AlCN is very close to that of AlF (-37.49 MHz [25]).

Since AlCN is the first linear metal cvanide molecule for which the nuclear hyperfine parameters have been determined, comparisons with similar molecules cannot be made. However, the bonding in the C=N group in AlCN should be similar to that found in HCN. To verify this, Eq. (1) can be used to estimate the N nuclear quadrupole coupling constants of these two linear cyanide compounds. The N atom has an sp-hybrid orbital involved in the C–N σ bond and the counterhybridised orbital has a lone pair of electrons. Assuming that the bonds in the $C \equiv N$ group are completely covalent then each sp hybrid orbital has 50% p character. One of the sp hybrid orbitals has one-half of a bond pair and the other has the lone pair, so $n_z = 3/2$. The p_x and p_y orbitals have one-half of a bond pair each so $n_x = n_y = 1$. Since $eQq_{210}(^{14}N)$ is -10 MHz [24],

 $eQq(^{14}N)$ for these terminal nitrogen containing species should be on the order of ~ -5 MHz. The experimental values are both of this order of magnitude, -5.232 MHz for AlCN and -4.709 MHz for HCN [21]. The difference between these values may come from polarisation effects of M which are not accounted for in this simple picture. The electronegativities of the M atom (Al or H) should give an estimate of such polarisation effects. The value of $eQq(^{14}N)$ should decrease as the electronegativity of M increases because more electron density is drawn away from the N end of the molecule. The electronegativities of Al and H [24] are consistent with this picture.

5. Conclusion

The pure rotational spectrum of AlCN has been studied by FTMW spectroscopy. The nuclear quadrupole coupling constants have been used to investigate the electronic structure of this molecule. The $eQq(^{27}Al)$ value is consistent with the Al–N bond in AlNC having more 'double-bond character' than the Al–C bond in AlCN. The bonding in the C=N groups in AlNC and HCN are found to be similar. The molecular constants determined in this study can be used to predict rest frequencies for astronomical searches.

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