The spectroscopic parameters of sodium cyanide, NaCN ($\tilde{X}^1A'$), revisited

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Abstract

The study of the rotational spectrum of NaCN ($\tilde{X}^1A'$) has recently been extended in frequency and in quantum numbers. Difficulties have been encountered in fitting the transition frequencies within experimental uncertainties. Various trial fits traced the difficulties to the incomplete diagonalization of the Hamiltonian. Employing fewer spectroscopic parameters than before, the transition frequencies could be reproduced within experimental uncertainties on average. Predictions of *a*-type *R*-branch transitions with $K_a \leq 7$ up to 570 GHz should be reliable to better than 1 MHz. In addition, modified spectroscopic parameters have been derived for the ^{13}C isotopic species of NaCN.

Keywords:
rotational spectroscopy, circumstellar molecule, centrifugal distortion, Hamiltonian diagonalization

1. Introduction

There are several ways to form a molecule from a metal M and the CN group. Several metals, such as the transition metals copper and zinc, prefer a linear cyanide arrangement with an MC bond. Linear isocyanides with an MN bond are preferred by others such as the main group metals magnesium and aluminum. Sodium and potassium, however, display a different structural motif, a nearly T-shaped structure with almost equally long MC and MN bonds. As a consequence, both molecules are asymmetric top rotors.

The rotational spectrum of NaCN has been studied by van Vaals et al. [1] between 9 and 40 GHz employing molecular-beam electric-resonance spectroscopy. 20 rotational transitions were recorded, half of them being much weaker *b*-type transitions. NaCN was detected in the circumstellar envelope of the carbon-rich star CW Leo, also known as IRC +10216 [2], soon after three pairs of related unidentified lines, also detected in that source, had been attributed to MgNC [3]. Recently, He et al. [4] described a molecular line survey of CW Leo at 2 and 1.3 mm. In order to analyze the NaCN emission, the spectroscopic parameters of NaCN were reevaluated because initially, the quartic centrifugal distortion parameters were expressed as τ values, which are rarely implemented in current spectroscopy programs. The predictions derived from the resulting parameters were good enough for the NaCN emission features obtained in the course of that line survey as well as for previously published transitions. Observations at slightly higher frequencies and with a better signal-to-noise ratio, however, revealed increasing deviations largely with increasing J, prompting Halfen and Ziurys [5] to study the rotational spectrum of NaCN between approximately 180 and 530 GHz. They encounterted difficulties in reproducing their experimental transition frequencies on average within experimental uncertainties and attributed this to the floppy nature of the molecule.

In the course of creating an updated catalog entry for the Cologne Database for Molecular Spectroscopy (CDMS) [6, 7], the previously reported experimental data for NaCN [1, 5] were critically evaluated. Using fewer spectroscopic parameters than before, it was possible to reproduce both data sets well if the Hamiltonian was diagonalized sufficiently.

2. Considerations for the spectral analysis

One finds rather frequently that the set of spectroscopic parameters, which reproduces a given list of transition frequencies within experimental uncertainties, is not unique. One way of reducing the ambiguity of a parameter set is to reduce the rms error, also knows as the weighted rms, of the fit with as few parameters as possible and reasonable. A reasonable parameter set requires certain lower order term to be used before one of higher order is allowed to be included; e.g., the inclusion of L_{JJK} in the fit requires that at least one of the two parameters H_J or H_{JK} has already been used in the fit. In the absence of strong correlation among the parameters, it suffices to search for the one which reduces the rms error the most. However, such correlation is rather common, such that searches for small parameter sets may be more complex. It is frequently assumed that the smallest parameter set, which reproduces the parameter set best, will provide the most reasonable predictions. It is useful in this context to address the issue of uncertainties attributed to the transition frequencies. Besides appropriate estimates and, less frequently in recent years, no estimates at all,

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one also finds uncertainties which seem to be too optimistic or too pessimistic, leading to weights in enlarged data sets which are too high or too low, respectively, if these estimates stay uncorrected. If the list of transition frequencies is sufficiently large with respect to the number of spectroscopic parameters varied in the fit, an rms error of 1.0 overall as well as for well defined sub-sets of the frequency list can be viewed as an indication of reasonable uncertainty estimates, though caution is advised if a very small set of the lines depends particularly strongly on one or few parameters. An additional criterion for reasonable uncertainty estimates is the distribution of the residuals. Most of the lines, about two third, should fit within the uncertainties, but there may be some lines with residuals exceeding three times the uncertainties, however, their number should decrease very rapidly with the magnitude of the ratio between residual and uncertainty. It is possible that the overall uncertainty estimates in a line list are too pessimistic, but one or few lines have residuals which are too large. A rejection threshold is applied in final fits in particular in larger data sets as a small set of transition frequencies with large residuals may complicate the determination of higher order parameters. A threshold of 3σ is rather common, see e.g. Ref. [8, 9], but other thresholds, usually less strict, may also be found.

3. Spectral analysis

As mentioned in the introduction, NaCN as well as KCN are asymmetric tops, in contrast to most other molecules formed from a metal atom and the CN group. Since for both the N atom is closer to the metal atom [1, 10], they should be viewed as isocyanides rather than cyanides. However, following the convention, we will continue calling these molecules cyanides. Ray's asymmetry parameter κ is -0.9567 for NaCN, the molecule is thus fairly close to the prolate symmetric limit. It has a large a-dipole moment component of $\mu_a = 8.85$ D and a much smaller b-component of $\sim$0.2 D [1] [4]. In spite of the small b-component, van Vaals et al. reported 10 b-type transitions with $\Delta J = \pm 1$, $\Delta K_a = \mp 1$, and $\Delta K_c = \pm 1$ along with 10 a-type transitions with $\Delta J = 0, \pm 1$, $\Delta K_a = 0$, and $\Delta K_c = \pm 1$; the quantum numbers extended to J and K_a of 16 and 3, respectively. The b-type transitions contained essentially all of the $\Delta K_a \neq 0$ information in that data set as well as by far the most $\Delta J \neq 0$ information because most of the a-type transitions followed $\Delta J = 0$ selection rules. Inspection of their residuals suggested that the reported uncertainties are rather conservative; they were assumed to be 3σ uncertainties in Ref. [4]. Employing thirteen parameters and the adjusted uncertainties, the latter authors were able to reproduce these lines with an rms error of 0.840. The fairly large number of parameters compared to the number of lines make it less clear whether the adjusted uncertainties of the transition frequencies were estimated appropriately. Nevertheless, the data permitted good to reasonable predictions well into the millimeter wave region.

[1] https://cdms.astro.uni-koeln.de/cgi-bin/cdmsinfo?file=e049510.cat

Very recently, Halfen and Ziurys published an extensive set of NaCN transition frequencies all pertaining to the strong a-type R-branch transitions with $11 \leq J'' \leq 32$ and $0 \leq K_a \leq 6$ between 179 and 531 GHz [5]. In order to provide an updated entry for the CDMS [6, 7], these data were subjected to combined fits together with the previous data [1]. Since Halfen and Ziurys encountered difficulties in reproducing transitions mainly with higher K_a values, it was decided to add the new transition frequencies with each K_a series separately in the present analysis. Moreover, a tight rejection threshold of 3σ was applied since it seemed plausible that large residuals of one or few lines may have caused the difficulties. Pickett's SPCAT and SPFIT programs [11] were used for prediction and fitting of the spectra, respectively, as has been done in the two previous investigations [4, 5].

Starting with the parameter set of Ref. [4], the previous transition frequencies plus 12 new ones with $K_a = 0$ could be reproduced overall within uncertainties by adding h_2 and omitting H_K and h_3. At this stage, only one of the previous lines deviated from the calculated frequency by slightly more than three times the uncertainty. In later fits, the amount and identity of the lines displaying larger residual changed sometimes.

The sequential addition of transition frequencies having $K_a = 1 - 5$ afforded one new parameter each to be included. These were h_1, h_3, L_{JJK}, l_4, and L_{KKJ}. The addition of $K_a = 6$ lines did not require any new parameter. Trial fits with H_K included in the fit yielded a value of 41 ± 55 Hz with changes in the remaining parameters within the uncertainties. The uncertainties of the predominantly K-dependent terms increased markedly, but in no case by more than a factor of 2. Since H_K was not determined with significance, it was omitted from the final fit. It is noteworthy that the uncertainty is a factor of 4 smaller than the uncertainty derived in Ref. [4] from the microwave data only.

This parameter set is smaller than the one in Ref. [5], but reproduces almost all of the data within the rejection threshold. Two of the new lines had residuals around 200 kHz, and one line deviated from its calculated position by more than 300 kHz. Most of the other lines seemed to have been judged conservatively with an uncertainty of 50 kHz because transition frequencies with $K_a \leq 3$ gave partial rms errors of less than 0.5; the values for $K_a = 4$ and 6 were around 0.6, and only lines with $K_a = 5$ yielded a partial rms error of 1.19. The previous data [1] now yielded a partial rms error of 1.17, indicating that the previously reported uncertainty estimates have been corrected slightly too far. But since none of these lines showed particularly large residuals with respect to the uncertainties, none of these lines were omitted and the uncertainties were left unchanged.

The final set of spectroscopic parameters is given in Table 1 together with NaCN and KCN values from Ref. [4] and results from a fit of the NaCN microwave data to the KCN parameter set. The latter fit has 2 fewer parameters than the one published, but has a larger rms error of 1.055 compared with 0.840; this was the reason to discard this fit and to choose the one which required more parameters.

The list of transition frequencies with assignments, uncertainties, and residuals between experimental frequencies and

Table 1: Spectroscopic parameters[a] (MHz) of NaCN ($\tilde{X}^1A'$) from the present combined fit in comparison to fits employing microwave data only and in comparison to KCN along with dimensionless rms errors of each fit.

Parameter	NaCN, combined fit	$Na^{13}CN$	NaCN, microwave data only		KCN
	Present	Present	Ref. [4]	Present	Ref. [4]
$A-(B+C)/2$	50101.74547 (110)	48021.93283 (314)	50101.74757 (166)	50101.74606 (131)	53528.08107 (268)
$(B+C)/2$	7820.189927 (145)	7652.415049 (391)	7820.190252 (259)	7820.190351 (206)	4737.751389 (93)
$(B-C)/4$	274.1524216 (124)	272.7985489 (396)	274.1525055 (177)	274.1525120 (172)	100.959727 (64)
$D_K \times 10^3$	194.11 (25)	268.89 (142)	196.52 (169)	193.56 (69)	956.79 (247)
$D_{JK} \times 10^3$	800.06 (2)	738.90 (39)	800.23 (34)	800.24 (19)	374.609 (50)
$D_J \times 10^3$	13.3123 (5)	13.2279 (180)	13.3361 (160)	13.3313 (96)	5.24462 (209)
$d_1 \times 10^3$	−2.34537 (23)	−2.42239 (112)	−2.34908 (34)	−2.34914 (33)	−0.51452 (78)
$d_2 \times 10^3$	−1.407340 (56)	−1.379543 (295)	−1.408951 (182)	−1.405461 (226)	−0.237559 (199)
$H_K \times 10^3$	–	–	1.428 (220)	–	–
$H_{KJ} \times 10^6$	327.4 (18)	303.5 (55)	155.9 (184)	314.5 (28)	101.2 (11)
$H_{JK} \times 10^6$	−26.31 (8)	−23.43 (30)	−3.54 (120)	−26.72 (19)	−7.28 (11)
$H_J \times 10^9$	−3.77 (34)	−3.5[b]	0.54 (5)	–	–
$h_1 \times 10^9$	−35.68 (17)	−34.0[b]	–	–	–
$h_2 \times 10^9$	−25.40 (9)	−24.6[b]	–	−47.65 (199)	−5.46 (74)
$h_3 \times 10^9$	19.34 (9)	19.1[b]	39.92 (688)	–	–
$L_{KKJ} \times 10^9$	−0.384 (40)	−0.331[b]	–	–	–
$L_{JJK} \times 10^9$	−0.845 (43)	−0.759[b]	–	–	–
$l_4 \times 10^{12}$	−0.587 (80)	−0.575[b]	–	–	–
rms error	0.746	0.807	0.840	1.055	0.827

[a] Numbers in parentheses are one standard deviation in units of the least significant figures.
[b] Kept fixed to values from the combined NaCN fit multiplied with ratios of the appropriate powers of $A-(B+C)/2$, $B+C$, and $B-C$, see section 3.

those calculated from the final set of spectroscopic parameters is given in the Supplementary material. Predictions of the rotational spectrum along with a documentation will be provided in the catalog section[2] of the CDMS. Line, parameter, and fit files, along with further auxiliary files, will be available in the archive section[3].

Ref. [4] also provided spectroscopic parameters for $Na^{13}CN$. Since predictions for the main isotopic species from that study turned out to be unsatifactory in the upper millimeter and lower submillimeter wave regions, it is rather likely that this applies to the predictions for $Na^{13}CN$ also. 17 rotational transitions had been studied by van Vaals et al. [1]. The quoted uncertainties for the derived hyperfine free transition frequencies were assumed to be $3\,\sigma$ values, as has been done for the main isotopolog. Centrifugal distortion parameters were estimated by multiplying the NaCN values from the combined fit with ratios of the appropriate powers of $A-(B+C)/2$, $B+C$, and $B-C$; e. g., H_{KJ} with the ratio of $(A-(B+C)/2)^2(B+C)$ and h_2 with the ratio of $(B+C)(B-C)^2$. While this scaling can not be expected to hold strictly, it is usually a reasonable asssumption, see e. g. Ref. [4] for isotopic species of SiC_2 and for $Na^{13}CN$ or Ref. [12] for the example of the isotopic species of vinyl cyanide.

An rms error of 1.518 was achieved by just varying the rotational and quartic centrifugal distortion parameters. Significant reduction of the rms error below values of 1.0 were obtained when either H_{KJ}, H_{JK}, H_J, or h_3 were varied in addition, however, the changes for the latter two appeared to be too large in comparison to the respective values and were discarded. A slightly better fit with an rms error of 0.807 was obtained when both H_{KJ} and H_{JK} were released in the fit in addition to the lower order parameters. The resulting fit is also given in Table 1. Updated predictions for $Na^{13}CN$ as well as auxiliary files will be provided in the CDMS.

4. Discussion

It may be surprising that in the present study a better fit was obtained with 17 parameters which is less than 23 employed previously [5]. The reason turned out to be rather mundane. The programs SPFIT and SPCAT require minimum and maximum values for K to be specified. In a prolate type, asymmetric top molecule, the minimum value is obviously 0, and the maximum value has to be at least as large as the highest K_a value in the line list. The numerical diagonalization of the Hamiltonian, however, usually requires the maximum value to be somewhat larger than that value. It appears as if an increase by the highest K_a order of the parameters in the fit is a reasonable estimate for this increase. Transitions in the NaCN line list extend to $K_a = 6$, and the parameter l_4 connects levels differing in K_a by 8, e.g. the $K_a = 4$ asymmetry components. Hence, the maximum K value requested in the fit should be around 14. In fact, no change in parameters and in the rms error occurs for $K_a \geq 15$. The data set for SO_2 in its ground vibrational state extends to $K_a = 28$ [8]; trial fits have shown that a maximum K value of at least 33 should be requested. Even larger maximum K values may have to be requested for predicting a spectrum at room temperature for convergence of the calculated partition function.

As can be seen in Table 1, the lower order spectroscopic parameters, up to the quartic centrifugal distortion terms, agree very well with the previous parameter determined from microwave data only. Since merely selected parameters of higher

[2] https://cdms.astro.uni-koeln.de/classic/entries/
[3] https://cdms.astro.uni-koeln.de/classic/entries/archive/NaNC/

order were employed, in particular for the MW fit, it is probably not surprising, that the agreement for the higher order parameters is not so good. In the alternative MW data fit, which employs exactly the parameters which were used in the KCN fit, the parameters H_{KJ} and H_{JK} agree well with the present values, and only h_2 differs by almost a factor of two. It is interesting to note, that this fit yields much better predictions of the new data [5] than the one published earlier [4]. The $19_{0,19} - 18_{0,18}$ transition, e.g., predicted by the alternative MW fit at 284160.864 (461) MHz was measured at 284161.701 (50) MHz, almost within twice the predicted uncertainty. The previously published fit [4] predicts 284169.538 (634) MHz. Apparently, the parameter set which yields the smallest rms error is not always the best one, and this situation is more likely to occur if the number of parameters is comparatively large with respect to the number of transition frequencies or if a certain parameter is determined by only few transitions.

The present parameter set not only reproduces the experimental transitions well, but it should also permit to a certain degree reliable predictions beyond the experimentally accessed quantum numbers. It should be pointed out that the discussion of the predictive power of the present parameter set is concerned mainly with *a*-type transitions because the *a*-component of 8.85 D is very much larger than the *b*-component of ∼0.2 D. The *b*-type transitions are weaker than the *a*-type transitions by $(\mu_a/\mu_b)^2 \approx 1960$, making them unimportant for radioastronomy. No *b*-type transitions have been provided in the previous CDMS catalog entry, and this will also apply for the new entry.

We consider a prediction to be reliable if the frequency of a transition not yet measured will be found to deviate from the predicted frequency by an amount generally not exceeding three times the predicted uncertainty and never exceeding that value by far. Assuming that the effects of centrifugal distortion parameters not included in the fit do not exceed the predicted uncertainties, predictions may be reliable as long as the uncertainties do not exceed 1 MHz. At low values of K_a this corresponds to J up to around 50. Extrapolation in K_a is very J-dependent. Around $J = 15$, $K_a = 10$ may be predicted reasonably, around $J = 35$, $K_a = 9$ is the limit, and beyond J of 40, even predictions with $K_a = 8$ should be viewed with caution. Since the assumption mentioned above is not necessarily justified, all extrapolations should be viewed with additional caution.

The parameter H_K may be the most important one not yet included in the fit which will have effects on the calculated transition frequencies and energies. Using a value of $H_K = 200$ Hz as fixed, a value almost four times the uncertainty of H_K from trial fits, see section 3, and thus near the upper end of possible values, changes the energies by less than 1 cm^{-1} for $J = K_a \leq 21$. The *a*-type transitions frequencies change by insignificant amounts for the J and K_a range for which the predictions are deemed to be reliable, see above.

The easiest way to improve the K-level structure of NaCN will be recording higher-J *a*-type *R*-branch transitions with $\Delta K_a = 0$ because of their favorable intensities. The $K_c = J$ transition are already approaching oblate pairing as the $J = 33 - 32$ transition frequencies differ by only 60 MHz. Transitions approaching oblate pairing contribute to the determination of purely K-dependent parameters. At still higher J, these transitions will reach oblate pairing and transitions with $K_c = J - 1$ etc. will approach and eventually reach oblate pairing also. In fact, the uncertainty of H_K in present trials fits was reduced to 55 Hz (see section 3), a factor of 4 smaller than the value of 220 Hz obtained from microwave data only [4], see also Table 1, indicating that the newly measred *a*-type *R*-branch transitions [5] have improved the purely K-dependent parameters.

Obviously, $\Delta K_a \neq 0$ transitions probe the K-level structure more directly. In that case, it may be more promising to search for $\Delta K_a = 2$ transitions which are frequently much stronger than *b*-type transitions, in particular in the millimeter wave region. Transitions with $K_a \leq 6$ and not too high J should be predicted sufficiently well with the largest deviations from the predicted frequencies of order of 10 MHz.

The centrifugal distortion parameters which have been varied in the $Na^{13}CN$ fit are close to the initial values obtained by scaling NaCN values. The most pronounced deviation occurs for D_K, which shows a very large isotopic shift. Such large shift, however, can be attributed to the accidentially small value of D_K compared with D_{JK} and is not uncommon. A large isotopic shift was also observed, e. g., for Δ_K of $^{37}Cl^{35}ClO_2$ compared to $^{35}Cl^{35}ClO_2$ which was fully accounted for by the harmonic force field calculation [13]. A relatively much smaller deviation occurs for d_1, whose magnitude for the ^{13}C isotopoic species is actually slightly larger than that of the main species. It is possible that this unexpected relation is caused by the assumptions made for some of the fixed higher order parameters.

Predictions of the rotational transition frequencies of $Na^{13}CN$ should be viewed with much greater caution than those for the main isotopic species because of the much smaller data set. Nevertheless, the predictions should be reliable to reasonable at least up to J of 15, maybe 20, and up to K_a of 4, maybe 5.

Halfen and Ziurys [5] derived a rotational temperature of about 41 K for NaCN in the circumstellar envelope of CW Leo. The Boltzmann peak at this temperature occurs slightly above 200 GHz, and the line intensities appear to be negligible above 500 GHz. Moreover, transitions with $K_a = 10$ are around 3 orders of magnitude weaker than those with $K_a = 0$ or 1. The predictions of the NaCN rotational spectrum derived from the present study should thus be adequate for all observational purposes, at least as far as the ground vibrational state is concerned. The bending mode ($v_2 = 1$) is the excited vibrational state lowest in energy. It is ∼170 cm^{-1} or ∼245 K above ground [1]. Transitions pertaining to this state will be hard to detect in the absence of infrared pumping, which, however, cannot be ruled out.

5. Conclusions

The rotational spectrum of NaCN has been reanalyzed. The previous difficulties in reproducing the experimental transition frequencies [5] have been attributed to the incomplete diagonalization of the Hamiltonian. The predictions generated from

the present data set should be good enough for all observational purposes restricted to the ground vibrational state. The modified parameter set for $Na^{13}CN$ should provide better prediction of the rotational spectrum up to moderate quantum numbers.

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Appendix A. Supplementary material

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/jmsa_hp.htm). Supplementary data associated with this article can be found, in the online version, at doi: 10.1016/j.jms.2011.12.005.

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