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**Fine and Hyperfine Structure of the  $N = 1 \leftarrow 0$  Transition of  $ND(X^3\Sigma^-)$  in Vibrational Excited States**

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## RESEARCH ARTICLE

***Fine and Hyperfine Structure of the  $N = 1 \leftarrow 0$  Transition of ND( $X^3\Sigma^-$ ) in Vibrational Excited States***Luca Dore<sup>a\*</sup>, Luca Bizzocchi<sup>b</sup>, Claudio Degli Esposti<sup>a</sup> and Filippo Tamassia<sup>c</sup><sup>a</sup>*Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, I-40126 Bologna, Italy;* <sup>b</sup>*CAAUL, Observatório Astronómico de Lisboa, Tapada da Ajuda, P-1349-018 Lisboa, Portugal;* <sup>c</sup>*Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, Viale del Risorgimento 4, I-40136 Bologna, Italy*

( )

The deuterated radical ND was produced in a DC discharge cell cooled at liquid nitrogen temperature. The discharge proved to be vibrationally hot, therefore the transient species could be detected in its vibrational excited states up to  $v = 6$ . By scanning in the 431–531 GHz frequency region, several fine-structure components of the  $N = 1 \leftarrow 0$  transition in vibrational excited states were observed, each of them showing a complex hyperfine structure.

A global analysis, including the measured frequencies and previous submillimeter-wave and infrared data, allowed an accurate determination of the equilibrium spectroscopic parameters of the ND radical including fine and hyperfine constants.

A very precise determination of the equilibrium bond length  $r_e$  was obtained. This value is not consistent with the value reported in literature from NH data. This incongruity was discussed in terms of the breakdown of the Born-Oppenheimer approximation.

In view of the recent detection of ND in a solar-mass protostar (A. Bacmann *et al.*, *Astron. Astrophys.* **521**, L42 (2010)), an extended spectroscopic characterization of this deuterated isotopologue of the NH species may prove useful, considering the large deuterium enhancement observed in molecular clouds.

**Keywords:** rotational transitions; fine structure; hyperfine structure; free radical; glow discharge; spectroscopic parameters

**1. Introduction**

Very recently, it has been reported the first astronomical detection of the radical ND towards a young solar-mass protostar [1]; this is one among the wealth of results which are being obtained by the high resolution heterodyne instrument HIFI on board the Herschel Space Observatory. The joint observation of NH hyperfine transitions allowed to estimate deuterium fractionation of imidogen, which results to be very high, with a ratio [ND]/[NH] between 30 and 100%.

The laboratory detection of the pure rotational spectrum of the radical ND in its ground vibronic state  $X^3\Sigma^-$  was achieved by Saito and Goto [2], who observed the three fine-structure components of the  $N = 1 \leftarrow 0$  rotational transition and resolved their hyperfine structure. Five years later, Takano *et al.* [3] reported the observation of the  $N = 2 \leftarrow 1$  transition, with its complex fine and hyperfine

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1 structure: thanks to the determined molecular parameters, they were able to list  
2 accurate frequency predictions for ND rotational transition up to 4 THz.

3  
4 The first seven vibrational levels of ND( $X^3\Sigma^-$ ) were investigated by Ram and  
5 Bernath [4]<sup>1</sup> by observing six vibration-rotation bands at 0.01 cm<sup>-1</sup> resolution  
6 using a Fourier transform spectrometer. For the low  $N$  lines the characteristic  
7 triplet pattern due to the three spin components  $J = N + 1$ ,  $N$ , and  $N - 1$  of each  
8  $N$  level was resolved, while no hyperfine structure was resolved.

9 The present work reports measurements of a number of fine-structure compo-  
10 nents of the  $N = 1 \leftarrow 0$  rotational transition of ND in a number of vibrational  
11 excited states;  $\Delta J = 0, \pm 1$  components for  $v = 1, 2$  and the  $\Delta J = +1$  component  
12 for  $v = 3, 4, 6^2$ . Each fine-structure line was split in several hyperfine components,  
13 so that a total of 69 measured line frequencies are reported.

14 All the line frequencies reported in references [2–4] have been considered in a  
15 global fit with the present measurements in order to obtain an extensive set of  
16 equilibrium spectroscopic parameters.  
17

## 18 2. Experimental details

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20 Measurements were carried out in the frequency range of 431–531 GHz, employ-  
21 ing phase-locked Gunn oscillators (Radiometer Physics GmbH, J. E. Carlstrom  
22 Co) as primary radiation source working in the range of 75–115 GHz; power at  
23 higher frequencies was obtained using harmonic multiplication. Two phase-lock  
24 loops allowed the stabilization of the Gunn oscillator with respect to a frequency  
25 synthesizer, which was driven by a 5-MHz rubidium frequency standard. The fre-  
26 quency modulation of the radiation was obtained by a sine-wave at 16.66 kHz  
27 modulating the reference signal of the wide-band Gunn synchronizer; the signal,  
28 detected by a liquid-helium-cooled InSb hot electron bolometer (QMC Instr. Ltd.  
29 type QFI/2), was demodulated at  $2-f$  by a lock-in amplifier.

30 ND radical was produced in a DC discharge with a current ranging between 20  
31 and 60 mA by flowing N<sub>2</sub> (*ca.* 5 mTorr) and D<sub>2</sub> (1–2 mTorr) in Argon buffer gas  
32 for a total pressure of 15–30 mTorr (2–4 Pa). The Pyrex cell, 3.25 m long and 5 cm  
33 in diameter, was equipped with two cylindrical hollow electrodes 25 cm in length  
34 at either end, and was wound with a plastic pipe for liquid nitrogen circulation to  
35 cool down to *ca.* 90 K.

36 We could detect transitions in excited vibrational states as high as  $v = 6$ , that  
37 is the discharge was vibrationally hot. Figure 1 shows a portion of the hyperfine  
38 spectrum of the  $\Delta J = +1$  fine component for the  $v = 0, 1$ , and 2 vibrational states:  
39 from a series of such spectra, recorded with a controlled power of the radiation  
40 source, we could roughly estimate a vibrational temperature of 2000–3000 K. As  
41 for the mechanism of the excitation, we could observe that discharging ND<sub>3</sub> or a  
42 mixture NH<sub>3</sub>/D<sub>2</sub> led to a better production of ND in the ground vibrational state,  
43 while spectra in the first excited states resulted barely observable. Also, using N<sub>2</sub>  
44 as buffer gas instead of Ar, the vibrational temperature was enhanced. Therefore  
45 we can argue that energy transfer from excited molecular nitrogen is responsible  
46 of the vibrational excitation.  
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57 <sup>1</sup>See references in the article for a full list of the spectroscopic observations concerning ND.

58 <sup>2</sup>Failure of observing lines in  $v = 5$  state is due to poor radiation power in the proper  
59 frequency region.  
60

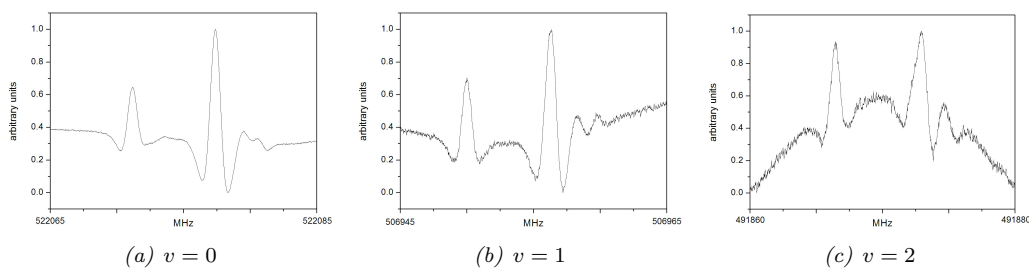


Figure 1. Portion of the hyperfine structure of the  $N = 1 \leftarrow 0$ ,  $J = 2 \leftarrow 1$  fine structure component for different vibrational states.

### 3. Results and Discussion

ND is a diatomic free radical with an  $X^3\Sigma^-$  ground electronic state. From a theoretical point of view, this molecule is well described by a Hund's case (b) basis set. Consequently, the effective Hamiltonian including rotation, fine structure and hyperfine structure terms can be written as follows [5]:

$$H_{eff} = H_{rot} + H_{fs} + H_{hfs}(N) + H_{hfs}(D). \quad (1)$$

where

$$H_{rot} = BN^2 - DN^4 + HN^6 + LN^8, \quad (2a)$$

$$H_{fs} = \frac{2}{3}\lambda(3S_z^2 - S^2) + \gamma N \cdot S + \frac{1}{2}\gamma_D[N \cdot S, N^2]_+ + \frac{1}{2}\gamma_H[N \cdot S, N^4]_+, \quad (2b)$$

$$H_{hfs}(N) = b_F(N)I_N \cdot S + \frac{c(N)}{3}(3I_{Nz}S_z - I_N \cdot S) + \frac{eq_0Q(N)}{4I_N(2I_N - 1)}(3I_{Nz}^2 - I_N^2) + C(N)I_N \cdot N, \quad (2c)$$

$$H_{hfs}(D) = b_F(D)I_D \cdot S + \frac{c(D)}{3}(3I_{Dz}S_z - I_D \cdot S). \quad (2d)$$

According to Hund's case (b) formalism,  $N$  is the rotational angular momentum and  $J = N + S$ , where  $S$  is the electron spin vector. Both nuclei have a non-vanishing spin angular momentum with quantum numbers  $I_N = I_D = 1$ . The hyperfine terms in the Hamiltonian have been split in two terms, relative to the nitrogen and deuterium nuclei, for clarity. While the magnetic hyperfine terms due to the interaction with  $S$  could be determined for both nuclei, the electric quadrupole and nuclear spin-rotation interaction terms were included only for nitrogen. No centrifugal distortion corrections of the hyperfine parameters were considered in the Hamiltonian.

The global fit was performed including our data, the submillimeter-wave data of Ref. [2], the far infrared data of Ref. [3] and the infrared data of Ref. [4]. Because of the great number of transitions involving vibrational excited states, it was necessary to expand the pure vibrational energy to the fourth anharmonicity correction:

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \omega_e z_e(v + \frac{1}{2})^4 + \omega_e w_e(v + \frac{1}{2})^5. \quad (3)$$

Also, the rotational, fine-structure and hyperfine structure terms were expanded in order to include the appropriate vibrational contributions. For each parameter,

the equilibrium value and some vibrational corrections, depending on the case, were determined in the fit. They are reported in the following equations.

$$B = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 + \delta_e(v + \frac{1}{2})^3 + \epsilon_e(v + \frac{1}{2})^4 + \zeta_e(v + \frac{1}{2})^5, \quad (4)$$

$$D = D_e - \beta_e^D(v + \frac{1}{2}) + \eta_e^D(v + \frac{1}{2})^2 + \theta_e^D(v + \frac{1}{2})^3 + \kappa_e^D(v + \frac{1}{2})^4, \quad (5)$$

$$H = H_e - \beta_e^H(v + \frac{1}{2}) + \eta_e^H(v + \frac{1}{2})^2, \quad (6)$$

$$L = L_e - \beta_e^L(v + \frac{1}{2}), \quad (7)$$

$$\lambda = \lambda_e + \lambda_v(v + \frac{1}{2}) + \lambda_{v^2}(v + \frac{1}{2})^2 + \lambda_{v^3}(v + \frac{1}{2})^3, \quad (8)$$

$$\gamma = \gamma_e + \gamma_v(v + \frac{1}{2}) + \gamma_{v^2}(v + \frac{1}{2})^2, \quad (9)$$

$$\gamma_D = \gamma_{D,e} + \gamma_{D,v}(v + \frac{1}{2}) + \gamma_{D,v^2}(v + \frac{1}{2})^2, \quad (10)$$

$$\gamma_H = \gamma_{H,e}, \quad (11)$$

$$b_F = b_{F,e} + b_{F,v}(v + \frac{1}{2}) + b_{F,v^2}(v + \frac{1}{2})^2, \quad (12)$$

$$c = c_e + c_v(v + \frac{1}{2}) + c_{v^2}(v + \frac{1}{2})^2, \quad (13)$$

$$C = C_e + C_v(v + \frac{1}{2}), \quad (14)$$

$$eq_0Q = eq_0Q_e + eq_0Q_v(v + \frac{1}{2}). \quad (15)$$

Table 1 reports the values of the parameters derived from the global analysis, where a total of 677 transition frequencies<sup>1</sup> were fitted to the Hamiltonian of equations (1) and (2) in a weighted-least-squares procedure, as implemented in Pickett's SPCAT/SPFIT program suite [6]. The line frequencies measured in the present work are listed in Table 2 along with the residuals from the fit. The rms error of residuals resulted to be 51 kHz for the pure rotational lines, and 0.0025 cm<sup>-1</sup> for the IR lines; the fit standard deviation is 0.915<sup>2</sup>.

The fit is overall very satisfactory, and the most important parameters have been determined with great accuracy. **The derived parameters are consistent with the previous ones, however a direct comparison is not possible because here are reported equilibrium values obtained with more terms in the vibrational expansions.** The vibrational dependence of the hyperfine terms has been obtained for the first time.

The magnetic hyperfine structure parameters derived for a free radical molecule provide direct information on the electronic distribution and on the composition of the electronic wavefunction [7]. In the spectroscopic approximation, namely where only the unpaired electrons are considered, the Fermi contact term  $b_F$  is directly linked to the spin density at the nucleus  $\sum_i \langle \Psi | 0_i |^2 \rangle$ . Also, the anisotropic dipolar interaction term  $c$  is related to the angular distribution of the electronic wavefunc-

<sup>1</sup>Frequencies and uncertainties of the ground-state rotational transitions included in the fit are listed in Table 1 of reference [3]; the IR lines of the vibration-rotation bands from 1-0 up to 6-5 reported in Table 1 of reference [4] were fitted with an uncertainty of 0.003 cm<sup>-1</sup>.

<sup>2</sup>rms<sub>res</sub> =  $\sqrt{(\sum \text{residual}^2)/(N \text{ observations})}$ ,  $\sigma_{\text{fit}} = \sqrt{(\sum (\text{residual}/\text{uncertainty})^2)/(\text{degrees of freedom})}$ .

tion  $\sum_i \langle (3 \cos^2 \theta_i - 1)/r_i^3 \rangle$ . Namely:

$$b_F/MHz = \frac{10^{-6}}{h} \frac{2}{3} g_e g_N \mu_B \mu_N \mu_0 \sum_i \langle \Psi(0_i)^2 \rangle, \quad (16)$$

$$c/MHz = \frac{10^{-6}}{h} \frac{3}{8\pi} g_e g_N \mu_B \mu_N \mu_0 \sum_i \left\langle \frac{(3 \cos^2 \theta_i - 1)}{r_i^3} \right\rangle, \quad (17)$$

where  $g_e$  is the  $g$ -value for the free electron,  $g_N$  is the nuclear  $g$ -factor,  $\mu_B$  is the Bohr magneton,  $\mu_N$  is the nuclear magneton and  $\mu_0$  the permeability of vacuum. The sums are over the unpaired electrons. The values for the electron densities derived from the fitted equilibrium parameters  $b_{Fe}$  and  $c_e$  are summarized in Table 3. In the same table the value of  $\sum_i \langle 1/r_i^3 \rangle$  relative to the nitrogen nucleus, calculated assuming  $\langle \pi | 3 \cos^2 \theta - 1 | \pi \rangle = -2/5$ , is also reported. This assumption is correct for atomic  $p_\pi$  orbitals and a good approximation for molecular  $\pi$  orbitals [8]. The same approximation is not expected to be valid for the deuterium atom. A comparison with the same values for NH, although not at equilibrium, is shown.

Kristiansen and Veseth [9] calculated the equilibrium values for the hyperfine constants of NH. Since the equilibrium parameters are independent on the isotopic substitution, these values can be compared to our experimental constants, provided the correction for the different nuclear magnetic moments and spins is applied. In fact, the value of  $g_N = \mu_I/(\mu_N I)$  depends on the nucleus and is equal to 0.857438230 for the deuterium nucleus and 5.585694772 for hydrogen. Therefore, we can calculate the equilibrium values of  $b_{Fe}(\text{H})$  and  $c_e(\text{H})$  from our experimental data for deuterium by applying the multiplicative factor (5.585694772/0.857438230). The comparison with Kristiansen's values, reported in Table 4, shows an excellent agreement between computed and experimental parameters.

An equilibrium bond distance of 1.03666599(70) Å was derived from the fitted equilibrium value  $B_e$ . The associated error was calculated with the standard linear error propagation equations and considering the errors on  $B_e$ , the atomic masses, the Planck constant and the amu/kg conversion factor as reported in Ref. [10]. The best determination of  $r_e$  available in literature from ND data is  $r_e = 1.036651(9)$  [4]. Our result is rather consistent with the previous one but an improvement of more than one order of magnitude in the precision of this parameter has been achieved in this work.

It is interesting to point out that the equilibrium distance derived from NH data is different from the one obtained from ND data well beyond the parameter's standard deviation. Such a discrepancy is reproduced by several experimental determinations of  $r_e$  for NH: 1.0371860(19) [11], 1.03756(6) [12], 1.03722(2) [13] Å. We believe that this apparent incongruity arises from the breakdown of the Born-Oppenheimer (BO) approximation. According to Watson [14], the experimentally determined equilibrium bond length in a diatomic molecule AB can be related to the isotopically invariant Born-Oppenheimer bond length through the following equation:

$$r_e = r_e^{\text{BO}} \left\{ 1 + m_e \left( \frac{d_A}{M_A} + \frac{d_B}{M_B} \right) \right\}, \quad (18)$$



where  $m_e$  is the electron mass and  $d_A$  and  $d_B$  are dimensionless parameters. Strictly speaking,  $M_A$  and  $M_B$  are the masses of the nuclei, but a negligible error is introduced if atomic masses are used instead [14]. The Born-Oppenheimer equilibrium bond length  $r_e^{\text{BO}}$ , along with  $d_A$  and  $d_B$ , can be determined from the experimental data, provided that there are at least three different evaluations of  $r_e$ . In this case, where the equilibrium distance has been derived only for two isotopologues, we approximate Eq. (18) to the following pair of equations:

$$r_e^{(\text{NH})} = r_e^{\text{BO}} \left( 1 + m_e \frac{d_A}{M_{\text{H}}} \right) \quad (19)$$

$$r_e^{(\text{ND})} = r_e^{\text{BO}} \left( 1 + m_e \frac{d_A}{M_{\text{D}}} \right), \quad (20)$$

where the contribution due to the nitrogen nucleus has been neglected. Using our result for  $r_e^{(\text{ND})}$ , the value of  $r_e^{(\text{NH})}$  from Ref. [11] and solving for  $r_e^{\text{BO}}$  and  $d_A$ , we obtain  $r_e^{\text{BO}} = 1.036145 \text{ \AA}$  and  $d_A = 1.8454$ .

Alternatively, we can use a more sophisticated approach, which has the advantage to provide an estimate of the error associated to  $r_e^{\text{BO}}$ .

Considering that in the Dunham's expansion  $Y_{01} \simeq B_e$  [15], the Born-Oppenheimer breakdown can be taken into account by using the following relationship [14, 16, 17]:

$$Y_{01}^{\alpha} = U_{01} \mu_{\alpha}^{-1} \left[ 1 + m_e \left( \frac{\Delta_{01}^{\text{H}}}{M_{\text{H}}^{\alpha}} + \frac{\Delta_{01}^{\text{N}}}{M_{\text{N}}^{\alpha}} \right) \right]. \quad (21)$$

Here,  $\alpha$  labels the isotopologue,  $\Delta_{01}^{\text{H}}$  and  $\Delta_{01}^{\text{N}}$  are the electronic BO breakdown parameters for H and N atoms, respectively.  $M_{\text{H}}^{\alpha}$  and  $M_{\text{N}}^{\alpha}$  represent the atomic masses of hydrogen and nitrogen isotopes in the  $\alpha$  isotopologue, and  $\mu_{\alpha}$  the reduced mass of the  $\alpha$  isotopologue. As before, we can derive  $U_{01}$  and  $\Delta_{01}^{\text{H}}$  from  $Y_{01}^{(\text{NH})}$  and  $Y_{01}^{(\text{ND})}$ , whereas  $\Delta_{01}^{\text{N}}$  is experimentally indeterminate. However, since the  $\Delta_{01}$  coefficients are usually comparable in magnitude for the two atoms [17], the value of  $\Delta_{01}^{\text{N}}$  can be assumed equal to that of  $\Delta_{01}^{\text{H}}$ . A more realistic assumption is  $\Delta_{01}^{\text{N}} = \Delta_{01}^{\text{H}} \pm 1$ , as proposed by Cooke and Gerry [18]. In such a case the results are:  $U_{01} = 470801.7(268) \text{ MHz}\cdot\text{amu}$  and  $\Delta_{01}^{\text{H}} = -3.68(13)$ . The errors on  $U_{01}$  and  $\Delta_{01}^{\text{H}}$  have been derived by calculating the difference in their values, as obtained in the two limit cases  $\Delta_{01}^{\text{N}} = \Delta_{01}^{\text{H}} - 1$  and  $\Delta_{01}^{\text{N}} = \Delta_{01}^{\text{H}} + 1$ . The contribution from the errors associated to  $Y_{01}^{(\text{NH})}$  and  $Y_{01}^{(\text{ND})}$  has been taken into account too. The Born-Oppenheimer bond lengths  $r_e^{\text{BO}}$  for NH can be determined using the equation [19]:

$$r_e^{\text{BO}} = \sqrt{\frac{\hbar}{4\pi U_{01} m_u}}. \quad (22)$$

In Eq. (22)  $m_u = 1.6605401(10) \cdot 10^{-27} \text{ kg}$  [10]. Eventually, we obtained  $r_e^{\text{BO}} = 1.036071(29) \text{ \AA}$ , very close to the result obtained with the previous derivation.

Whichever procedure one wishes to follow, the lack of experimental data prevents from a simultaneous determination of the BO bond length and the two correction parameters, either  $\Delta$ 's or  $d$ 's, and some kind of assumption needs to be made.



1 However, the values obtained for  $\Delta_{01}^H$  (-3.68(13)) and  $d_A$  (1.8454), although quite  
2 different, suggest a rather large deviation from the Born-Oppenheimer approxima-  
3 tion. This is consistent with the sizable difference  $r_e^{\text{NH}} - r_e^{\text{ND}} = 0.00052 \text{ \AA}$ . **Further**  
4 **insight into the nature of the BO approximation breakdown, concerning**  
5 **the non-adiabatic contribution due to the interaction with excited elec-**  
6 **tronic states, can be achieved if one knows the value of the  $g_J$  factors for**  
7 **several isotopologues [14]. Since precise  $g_J$  factors for the ground elec-**  
8 **tronic state are known only for  $^{14}\text{NH}$  in excited vibrational states [5] and**  
9 **are very small, we decided not to consider this contribution explicitly in**  
10 **our derivation.** In order to obtain a calculation of  $r_e^{\text{BO}}$  without approximations, it  
11 would be useful to have further experimental determinations of  $r_e$ , from  $^{15}\text{NH}$  and  
12 possibly from  $^{15}\text{ND}$ . This experiment is being currently set up in our laboratory.

13 For a free radical molecule in a  $X^3\Sigma^-$  electronic state, similar arguments hold  
14 also for the spin-spin and electron spin-rotation parameters  $\lambda_e$  and  $\gamma_e$  [20]. However,  
15 the  $d$  and  $\Delta$  coefficients are specific of the spectroscopic constant considered. Since  
16 in the case of NH no equilibrium values are readily available for these parameters,  
17 the determination of  $\lambda_e^{\text{BO}}$  and  $\gamma_e^{\text{BO}}$  can not be performed. It would be possible  
18 anyway to derive  $\lambda_e$  and  $\gamma_e$  for NH from the parameters reported in Ref. [11].  
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#### 26 4. Conclusions

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29 The pure rotational spectrum of the free radical ND in its ground electronic  
30 state  $X^3\Sigma^-$  has been detected in the frequency range 431–531 GHz. Several fine  
31 and hyperfine components of the  $N = 1 \leftarrow 0$  transition have been observed in  
32 the ground and in excited vibrational states with  $v$  up to 6. A global fit including  
33 our data, infrared and far infrared literature data has been performed, leading to  
34 the determination of an extensive set of vibrational, rotational, fine structure and  
35 hyperfine structure parameters. The hyperfine constants  $b_F$  (Fermi contact) and  $c$   
36 (dipolar) have been discussed in terms of the expectation values of the appropriate  
37 operators over the electronic wavefunction. The precise determination of the equi-  
38 librium rotational constant  $B_e$  has allowed the derivation of the equilibrium bond  
39 length  $r_e$ . The comparison with  $r_e$  obtained from NH data has shown a sizable dis-  
40 crepancy, which has been attributed to the breakdown of the Born-Oppenheimer  
41 approximation. The isotopically invariant Born-Oppenheimer bond length  $r_e^{\text{BO}}$  has  
42 been tentatively derived and a value of  $r_e^{\text{BO}} = 1.036071(29) \text{ \AA}$  has been obtained.  
43 Further investigations of the rare isotopologues  $^{15}\text{NH}$  and  $^{15}\text{ND}$  will be carried out  
44 in the near future.  
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Table 1. Spectroscopic parameters derived from a global fit for the vibrational states from  $v = 0$  to  $v = 6$  of  $\text{ND}(X^3\Sigma^-)$ .

Parameter	Value <sup>a</sup>	Parameter <sup>b</sup>	Value <sup>a</sup>
$\omega_e$ / $\text{cm}^{-1}$	2398.9948(25)	$\lambda_e$ /MHz	27541.76(16)
$\omega_e x_e$ / $\text{cm}^{-1}$	41.9800(22)	$\lambda_v$ /MHz	9.80(50)
$\omega_e y_e$ / $\text{cm}^{-1}$	0.07032(79)	$\lambda_{v,2}$ /MHz	-5.70(39)
$\omega_e z_e$ / $\text{cm}^{-1}$	-0.00440(12)	$\lambda_{v,3}$ /MHz	-0.468(86)
$\omega_e w_e$ / $\text{cm}^{-1} \times 10^3$	-0.5260(72)	$\gamma_e$ /MHz	-900.370(25)
$B_e$ / MHz	267067.288(35)	$\gamma_v$ /MHz	33.796(27)
$\alpha_e$ / MHz	7613.20(10)	$\gamma_{v,2}$ /kHz	-33.2(75)
$\gamma_e$ / MHz	20.326(96)	$\gamma_{D,e}$ /kHz	114.4(37)
$\delta_e$ / MHz	-2.253(38)	$\gamma_{D,v}$ /kHz	48.1(34)
$\epsilon_e$ / kHz	-62.1(64)	$\gamma_{D,v^2}$ /kHz	-2.94(30)
$\zeta_e$ / kHz	-9.0(40)	$\gamma_{H,e}$ /kHz	-0.475(19)
$D_e$ / MHz	14.7151(16)	$b_{F,e}(N)$ /MHz	19.096(25)
$\beta_e^D$ / MHz	0.16714(78)	$b_{F,v}(N)$ /MHz	-0.328(28)
$\eta_e^D$ / kHz	8.73(26)	$b_{F,v^2}(N)$ /kHz	-38.6(78)
$\theta_e^D$ / kHz	-0.126(54)	$c_e(N)$ /MHz	-68.067(43)
$\kappa_e^D$ / kHz	0.1087(31)	$c_v(N)$ /MHz	0.294(25)
$H_e$ / Hz	576.(11)	$b_{F,e}(D)$ /MHz	-9.844(16)
$\beta_e^H$ / Hz	-14.9(43)	$b_{F,v}(D)$ /MHz	-0.4622(96)
$\eta_e^H$ / Hz	-5.94(48)	$c_e(D)$ /MHz	14.06(11)
$L_e$ / mHz	-202.(22)	$c_v(D)$ /MHz	-0.192(96)
$\beta_e^L$ / mHz	-15.3(22)	$c_{v,2}(D)$ /kHz	-64.(21)
		$eq_0 Q_e(N)$ /MHz	-3.402(64)
		$eq_0 Q_v(N)$ /MHz	0.290(32)
		$C_e(N)$ /kHz	93.5(83)
		$C_v(N)$ /kHz	-13.0(42)

<sup>a</sup> The quantity in parentheses is one standard deviation in units of the last quoted digit.

<sup>b</sup> The symbol with  $v^n$  as subscript refers to the  $(v + \frac{1}{2})^n$  dependence of the corresponding parameter. See text.

Table 2.: Observed frequencies of the  $N = 1 \leftarrow 0$  transition in vibrational excited states of  $\text{ND}(X^3\Sigma^-)$ .

$J'$	$F'_N$	$F'$	$J$	$F_N$	$F^a$	Frequency <sup>b</sup> MHz	Obs.-calc. <sup>c</sup> kHz	Rel. Int. <sup>d</sup>
						$v = 1$		
2	2	2	1	2	2	506915.118(15)	-26	0.33
2	2	1	1	2	1	506915.118(15)		0.24
2	2	3	1	2	3	506915.118(15)		0.43
2	1	2	1	1	2	506923.534(70)	-29	
2	1	1	1	1	0	506925.012(50)	59	0.71
2	2	1	1	2	2	506925.012(50)		0.29
2	2	2	1	2	3	506932.358(15)	11	
2	1	0	1	1	1	506936.129(10)	-3	
2	1	2	1	0	1	506940.820(25)	49	
2	2	3	1	1	2	506950.011(15)	-40	0.69
2	2	2	1	1	1	506950.011(15)		0.31
2	3	3	1	2	2	506956.276(15)	58	0.40
2	3	4	1	2	3	506956.276(15)		0.60
2	3	2	1	2	1	506958.230(15)	22	
2	2	1	1	1	0	506959.664(20)	0	0.50
2	1	1	1	0	1	506959.664(20)		0.50
2	2	2	1	1	2	506966.855(15)	29	
2	3	2	1	2	2	506968.119(15)	-35	
2	3	3	1	2	3	506973.526(15)	-23	
1	2	2	1	2	1	530918.953(25)	0	0.34
1	2	1	1	2	1	530918.953(25)		0.66
1	2	3	1	2	2	530928.058(30)	-34	0.30
1	2	2	1	2	2	530928.058(30)		0.70
1	2	3	1	2	3	530945.066(30)	78	
1	1	1	1	2	2	530955.318(30)	-56	
1	2	1	1	1	0	530964.056(50)	-73	0.28
1	2	2	1	1	1	530964.056(50)		0.39
1	2	1	1	1	1	530964.056(50)		0.33
1	1	2	1	2	3	530972.307(50)	-23	
1	2	3	1	1	2	530979.373(50)	-94	
1	2	2	1	1	2	530980.599(50)	54	
1	1	1	1	1	0	530990.165(30)	-7	0.21
1	1	2	1	1	1	530990.165(30)		0.79
1	0	1	1	1	1	531002.864(30)	90	
1	1	2	1	1	2	531006.838(30)	28	
1	0	1	1	1	2	531019.333(30)	5	
1	1	2	1	0	1	531024.359(30)	-58	0.42
1	1	1	1	0	1	531024.359(30)		0.58
0	1	1	1	2	2	476706.690(30)	72	0.58
0	1	2	1	2	2	476706.690(30)		0.42
0	1	2	1	2	3	476724.237(30)	-43	
0	1	1	1	1	0	476741.043(30)	-42	
0	1	0	1	1	1	476742.228(30)	34	0.25
0	1	1	1	1	1	476742.228(30)		0.02
0	1	2	1	1	1	476742.228(30)		0.73
0	1	0	1	0	1	476775.965(30)	26	0.31
0	1	1	1	0	1	476775.965(30)		0.50
0	1	2	1	0	1	476775.965(30)		0.19
0	1	0	1	2	1	476696.516(50)	-138	0.44
0	1	1	1	2	1	476696.516(50)		0.48
0	1	2	1	2	1	476696.516(50)		0.08
						$v = 2$		
2	2	3	1	1	2	491866.420(30)	-48	0.69
2	2	2	1	1	1	491866.420(30)		0.31
2	3	3	1	2	2	491872.315(30)	28	
2	3	4	1	2	3	491873.029(30)	-52	
2	3	2	1	2	1	491874.524(50)	-58	
2	2	1	1	1	0	491876.683(50)	-58	0.35
2	1	1	1	0	1	491876.683(50)		0.35
2	2	1	1	1	1	491876.683(50)		0.30
2	2	2	1	2	3	491850.431(50)	-44	
2	1	0	1	1	1	491853.107(30)	-08	
2	1	2	1	0	1	491857.308(30)	04	
2	2	2	1	2	2	491832.128(50)	-22	0.57
2	2	1	1	2	1	491832.128(50)		0.43
2	2	3	1	2	3	491833.063(50)	52	
2	1	2	1	1	2	491840.592(50)	74	
2	2	1	1	2	2	491842.678(50)	44	0.25
2	1	1	1	1	1	491842.678(50)		0.75
2	2	2	1	1	2	491883.960(50)	14	
1	2	3	1	1	2	515821.401(20)	-28	
1	2	2	1	1	2	515823.088(20)	30	
1	1	2	1	2	3	515815.808(100)	42	
1	1	2	1	1	1	515831.769(50)	42	
1	0	1	1	1	1	515844.742(20)	-10	
1	1	2	1	1	2	515849.170(100)	-66	
1	2	2	1	2	2	515771.071(50)	-18	

Continued on next page

Table 2 – continued from previous page

$J'$	$F'_N$	$F'$	$J$	$F_N$	$F^a$	Frequency <sup>b</sup> MHz	Obs.-calc. <sup>c</sup> kHz	Rel. Int. <sup>d</sup>
1	2	3	1	2	3	515788.098(100)	139	
0	1	2	1	2	3	461571.547(50)	31	
0	1	1	1	1	0	461586.418(50)	-40	
0	1	0	1	1	1	461587.497(50)	32	0.25
0	1	2	1	1	1	461587.497(50)		0.75
0	1	1	1	1	2	461604.951(50)	-22	0.43
0	1	2	1	1	2	461604.951(50)		0.57
						$v = 3$		
2	1	0	1	1	1	476770.653(80)	85	
2	1	2	1	0	1	476774.294(20)	-15	
2	2	3	1	1	2	476783.354(15)	24	0.69
2	2	2	1	1	1	476783.354(15)		0.31
2	3	3	1	2	2	476789.130(15)	5	
2	3	4	1	2	3	476790.200(20)	-26	
2	3	2	1	2	1	476791.457(40)	58	
						$v = 4$		
2	2	3	1	1	2	461655.288(20)	-35	
2	3	3	1	2	2	461660.820(20)	5	
2	3	4	1	2	3	461662.276(20)	17	
						$v = 6$		
2	2	3	1	1	2	431026.640(50)	80	
2	3	3	1	2	2	431031.581(100)	-106	
2	3	4	1	2	3	431033.848(50)	-48	0.70
2	3	2	1	2	1	431033.848(50)		0.30

<sup>a</sup>  $F_N = I_N + J$  and  $F = I_D + F_N$ .

<sup>b</sup> Estimated uncertainties are reported in parentheses in units of the last quoted digits.

<sup>c</sup> Residuals from the global fit.

<sup>d</sup> Unresolved transition frequencies are fitted to the sum of the frequencies of the blended components weighted by their relative intensities.

Table 3. Expectation values of distribution functions over the electronic wave function (in units of  $10^{30}\text{m}^{-3}$ ) of N, D and H for ND and NH.

	ND <sup>a</sup>	NH
$\sum_i \langle \Psi(0_i)^2 \rangle_N$	0.39884(52)	0.375(8) <sup>b</sup>
$\sum_i \langle \Psi(0_i)^2 \rangle_{D,H}$	-0.09682(16)	-0.100(2) <sup>b</sup>
$\sum_i \langle (3 \cos^2 \theta_i - 1)/r_i^3 \rangle_N$	-7.9398(50)	-7.09(7) <sup>b</sup>
$\sum_i \langle (3 \cos^2 \theta_i - 1)/r_i^3 \rangle_{D,H}$	0.7723(60)	0.77(2) <sup>b</sup>
$\sum_i \langle 1/r_i^3 \rangle_N$	19.850(13) <sup>c</sup>	20.1(9) <sup>d</sup>

<sup>a</sup> This work. These values are derived from the equilibrium hyperfine constants  $b_{F,e}(N)$ ,  $b_{F,e}(D)$ ,  $c_e(N)$ ,  $c_e(D)$ .

<sup>b</sup> Ref. [21].

<sup>c</sup> For calculation see text.

<sup>d</sup> Ref. [8].

## REFERENCES

Table 4. Experimental and calculated equilibrium hyperfine constants (in MHz) for ND and NH.

	Exp. <sup>a</sup>	Calc. <sup>b</sup>
$b_{F,e}(\text{N})$	19.096	18.94
$c_e(\text{N})$	-68.067	-67.88
$b_{F,e}(\text{D})$	-9.844	
$c_e(\text{D})$	14.06	
$b_{F,e}(\text{H})$	-64.13	-66.35
$c_e(\text{H})$	91.59	91.96

<sup>a</sup> This work. See text.

<sup>b</sup> Ref. [9].

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