Terahertz spectroscopy and global analysis of the rotational spectrum of bis-deuterated amidogen radical ND_2

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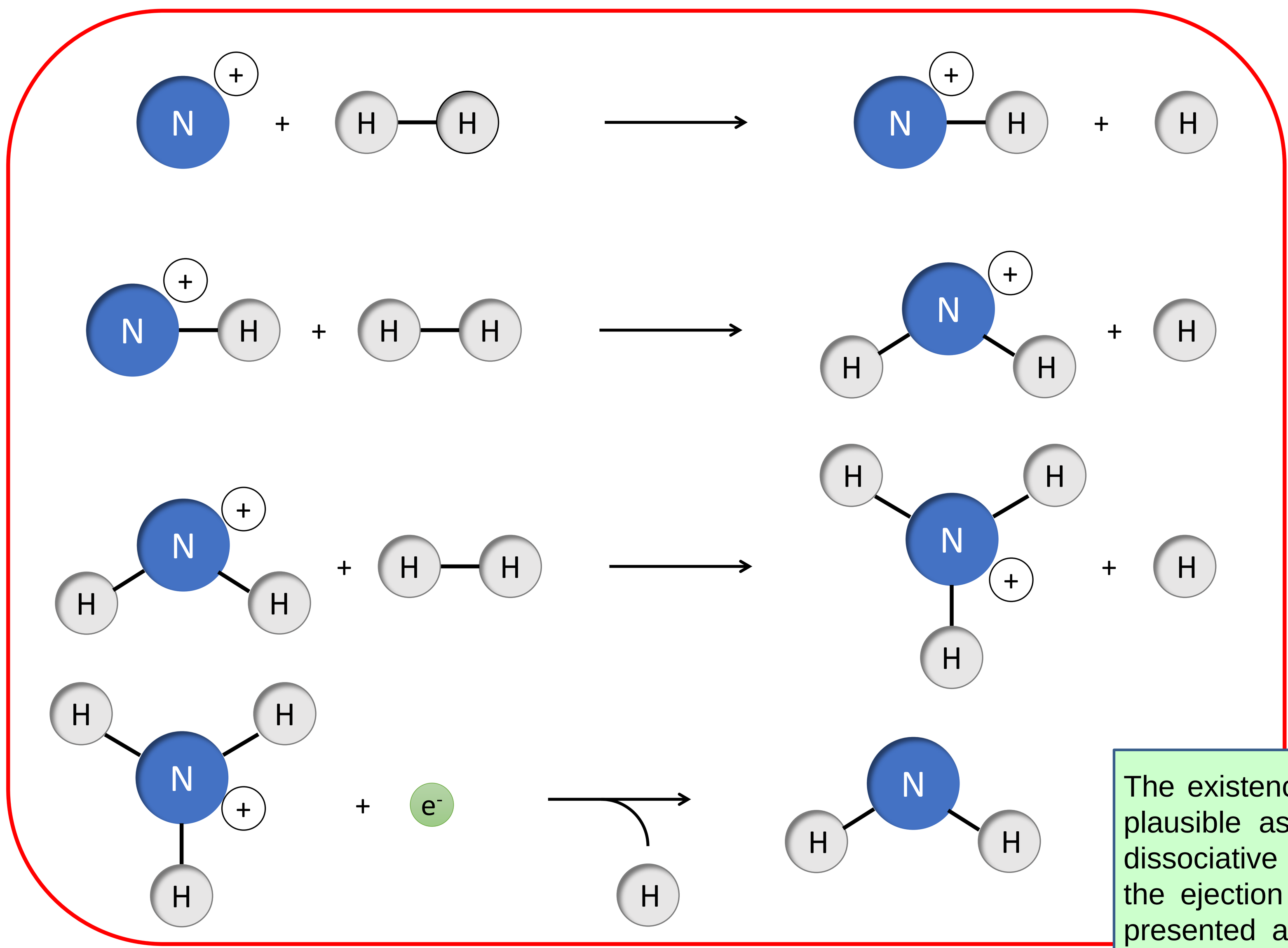
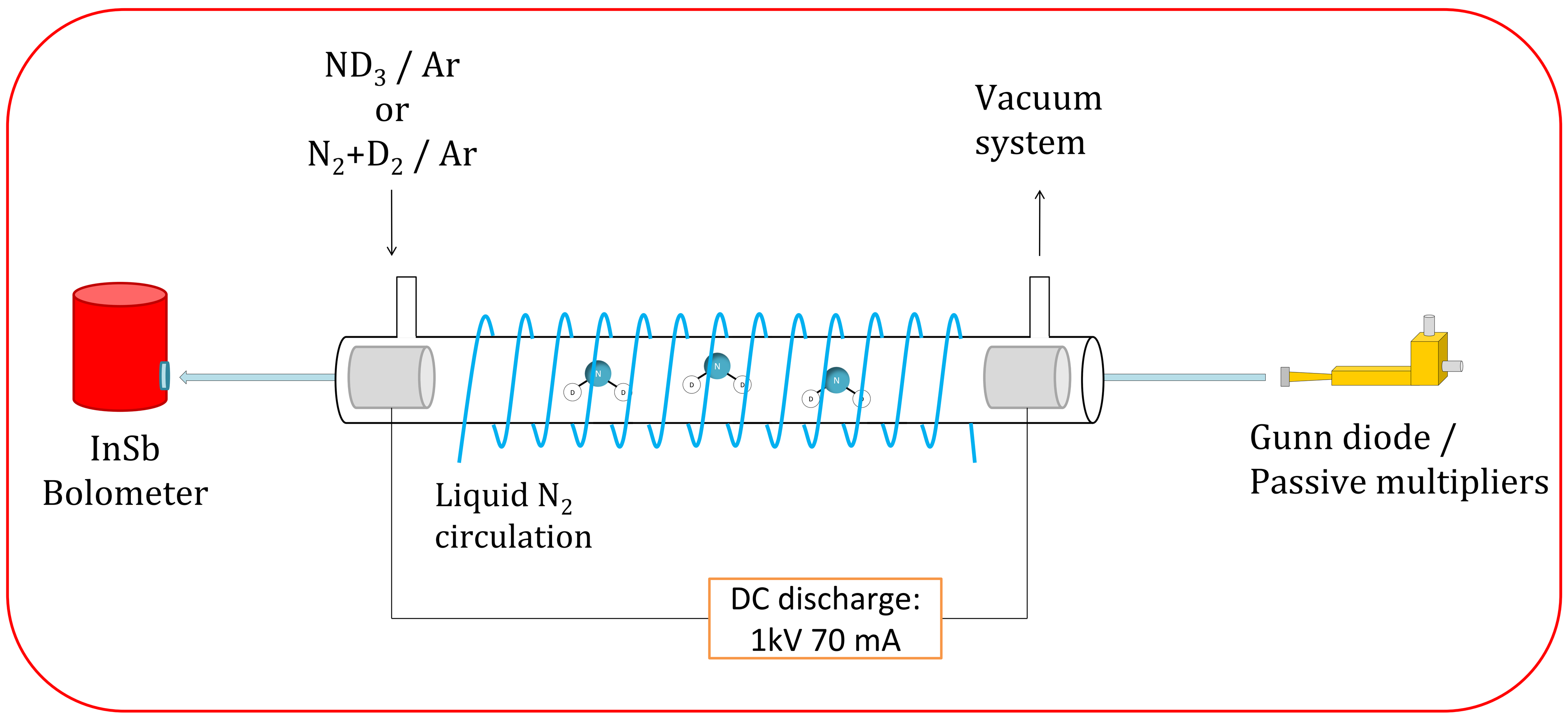
ABSTRACT

The deuteration mechanism of molecules in the interstellar medium (ISM) is still being debated. Observations of deuterium-bearing species in several astronomical sources represent a powerful tool to improve our understanding of the interstellar chemistry. The doubly-deuterated form of the astrophysically interesting amidogen radical could be a target of detection in space. In this work, the rotational spectrum of the ND_2 radical in its ground vibrational and electronic $X\,^2B_1$ states has been investigated between 588 GHz and 1.131 THz using a frequency-modulation millimeter/submillimeter-wave spectrometer. The ND_2 has been produced in a free-space glass absorption cell by discharging a mixture of ND_3 and Ar. Sixty-four new transition frequencies involving J values from 2 to 5 and K_a values from 0 to 4 have been measured. A global analysis including all the previous field-free pure rotational data [1,2,3] has been performed, allowing for a more precise determination of a very large number of spectroscopic parameters. Accurate predictions of rotational transition frequencies of ND_2 are now available from a few GHz up to several THz.

The mechanism of formation in the ISM...

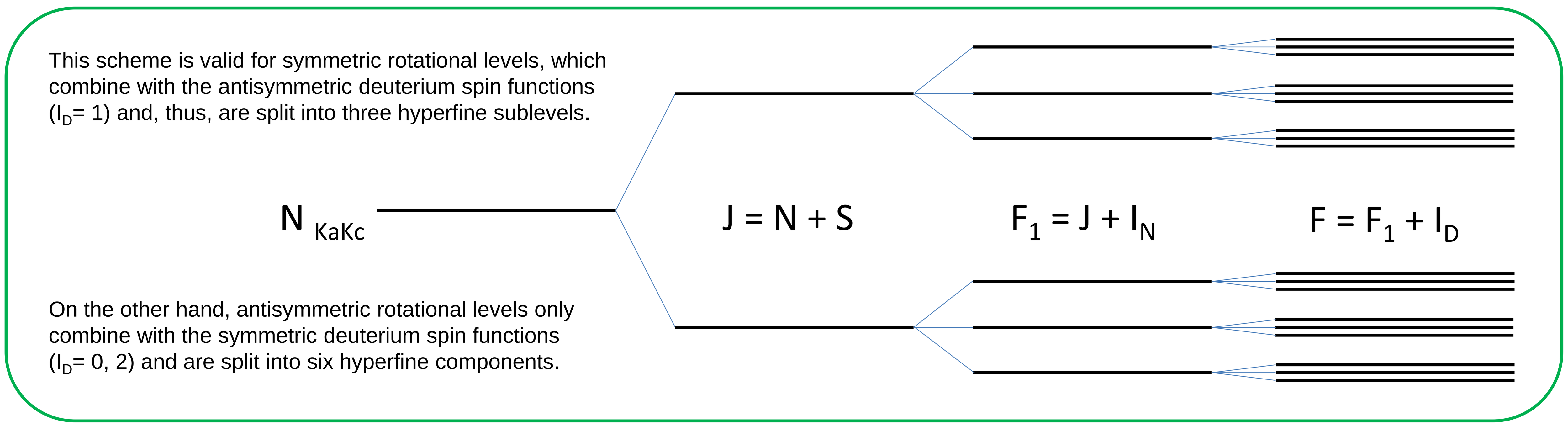


... and in the laboratory

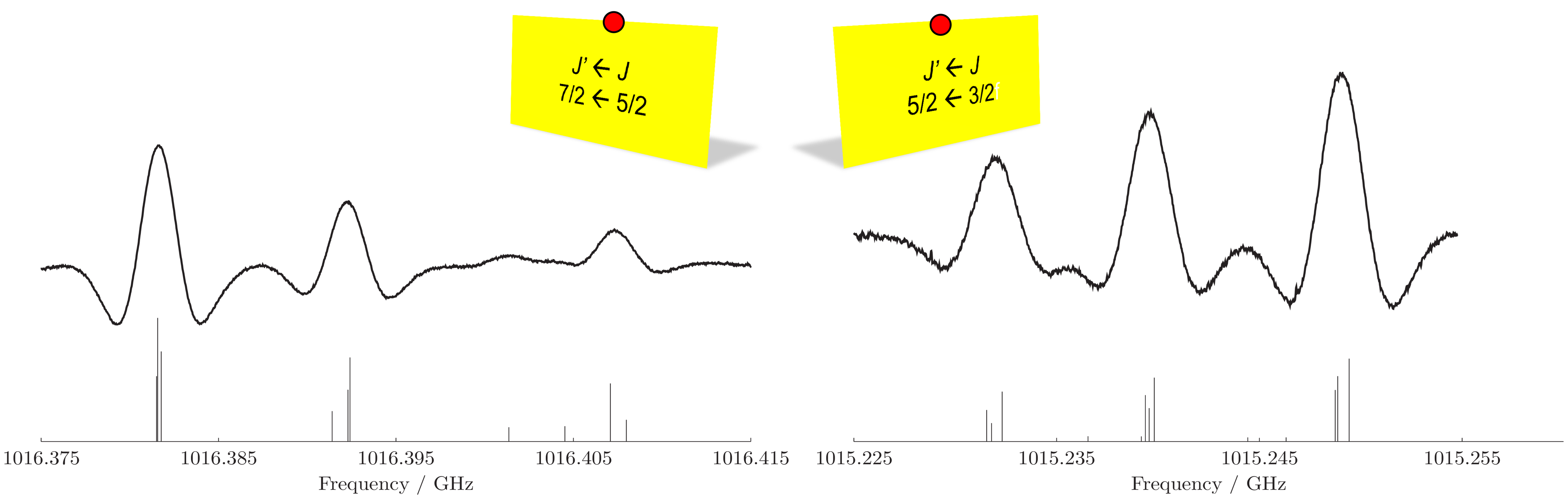


The existence of deuterated forms of amidogen in the ISM seems to be plausible as predicted by the gas-phase chemical models, where the dissociative recombination of partially deuterated intermediates favours the ejection of hydrogen atoms rather than deuterium. Roueff et al. [4] presented a steady state model of the gas phase chemistry aimed at understanding the deuterium fractionation of ammonia. They found that: (i) at high density and high depletion, deuteration of N-containing species results very efficient (ii) the deuterium fractionation is sensitive to the temperature and is large for temperatures between 5 and 20 K. Their model predicts high fractional abundances of ammonia progenitors and their deuterated isotopologues, including ND_2, in dense cores.

Rotational energy levels are split by electric and magnetic interactions



Portion of the Terahertz spectrum – $N'_{K_aK_c} \leftarrow N_{K_aK_c} = 3_{13} \leftarrow 2_{02}$ transition

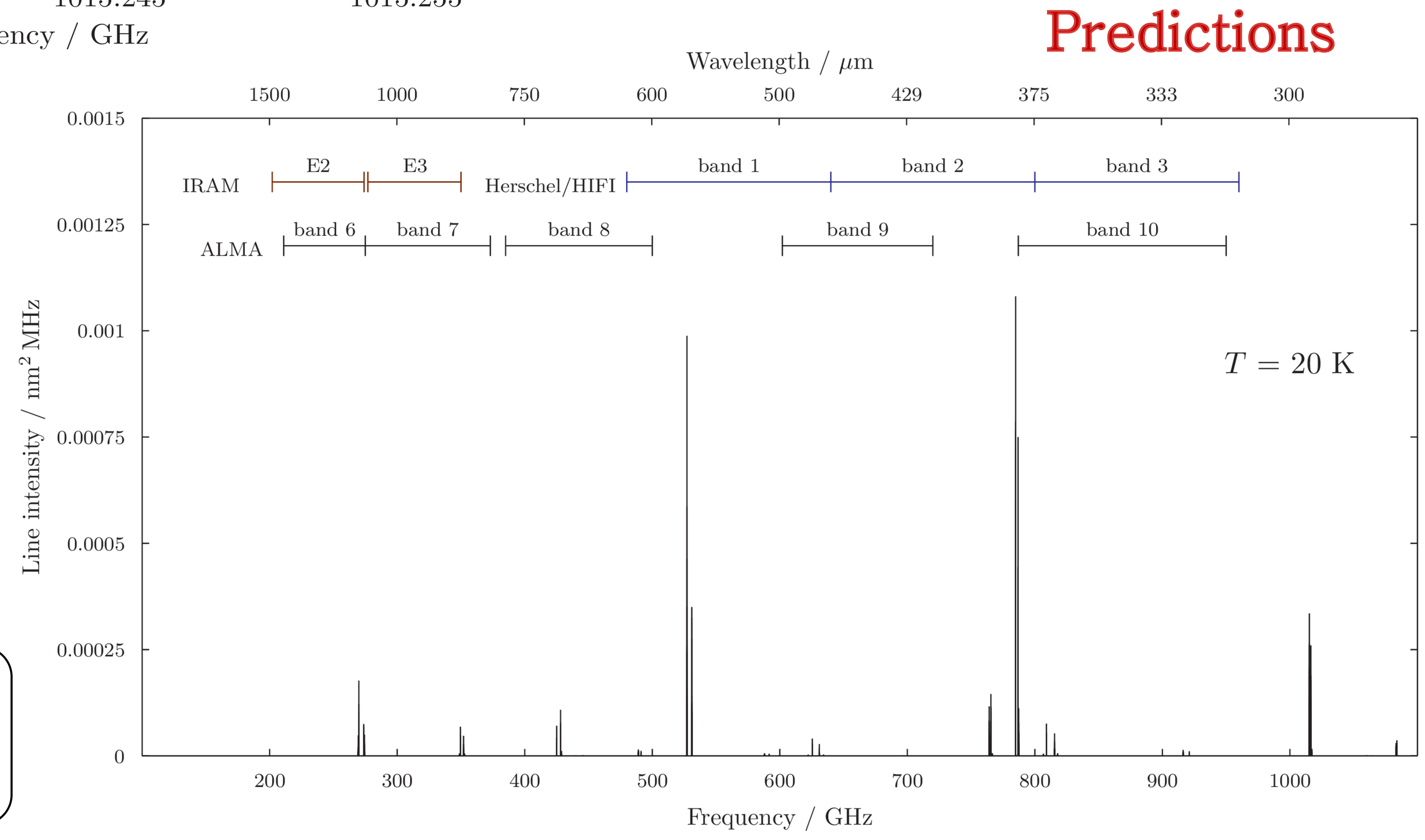


Spectroscopic parameters

Constants		Present work	Previous MW[a]	Previous FIR[b]
A	/MHz	399989.5534(87)[c]	399985.879(81)	399993.92(189)
B	/MHz	194498.1916(150)	194488.65(16)	194498.10(102)
C	/MHz	128610.4447(145)	128613.987(57)	128610.00(126)
Centrifugal distortion				
Δ_N	/MHz	7.86074(33)	7.323(10)	7.8392(108)
Δ_{NK}	/MHz	−33.48376(259)	−33.812(25)	−33.388(42)
Δ_K	/MHz	198.7064(57)	196.771(33)	198.783(84)
δ_N	/MHz	3.080801(201)	3.03[d]	3.0858(36)
δ_K	/MHz	8.5567(82)	6.300(39)	8.2788(294)
Φ_N	/kHz	1.4776(80)		1.376(35)
Φ_{NNK}	/kHz	−6.277(306)		−5.606(35)
Φ_{KKN}	/kHz	−43.70(98)		−43.45(96)
Φ_K	/kHz	320.34(90)		321.0(23)
ϕ_N	/kHz	0.7224(33)		0.7402(140)
ϕ_{NK}	/kHz	−0.834(99)		−1.01(21)
ϕ_K	/kHz	65.90(133)		33.37(65)
L_{KKKN}	/kHz	0.08336(141)		0.0707(38)
L_K	/kHz	−0.7022(85)		−0.694(26)
l_K	/kHz	−0.1230(33)		−0.0311(16)
M_K	/Hz	1.069(38)		1.08(10)
Fine interaction				
ϵ_{aa}	/MHz	−5128.1262(215)	−5127.81(11)	−5127.71(41)
ϵ_{bb}	/MHz	−668.6973(180)	−668.507(78)	−668.759(160)
ϵ_{cc}	/MHz	3.4616(166)	3.413(63)	3.23(12)
Δ^S_N	/MHz	0.07613(57)	0.0469(66)	0.0779(29)
Δ^S_{KN+NK}	/MHz	−0.9498(57)	−0.967(81)	−0.875(29)
Δ^S_{NK}	/MHz	1.045(201)		
Δ^S_K	/MHz	9.8548(76)	9.587(66)	9.476(99)
δ^S_N	/MHz	0.03843(36)		0.0353(16)
δ^S_K	/MHz	0.1005(59)	0.0356(45)	0.150(36)
Φ^S_{NKK}	/kHz	3.76(51)		
Φ^S_K	/kHz	−23.10(81)		−15.36(72)
Hyperfine interaction				
$a_F(N)$	/MHz	28.0577(122)	28.055(33)	
$T_{aa}(N)$	/MHz	−43.1451(183)	−43.136(48)	
$T_{bb}(N)$	/MHz	−44.2715(213)	−44.277(63)	
$C_{aa}(N)$	/MHz	0.2660(75)	0.269(27)	
$C_{bb}(N)$	/MHz	0.0458(55)	0.045(21)	
$C_{cc}(N)$	/MHz	0.0145(64)	0.019(22)	
$a_F(D)$	/MHz	−10.2446(103)	−10.241(28)	
$T_{aa}(D)$	/MHz	2.8536(168)	2.874(45)	
$T_{bb}(D)$	/MHz	−2.0916(247)	−2.108(69)	
$X_{aa}(N)$	/MHz	0.2191(297)	0.213(84)	
$X_{bb}(N)$	/MHz	−3.744(34)	−3.75(11)	
Number of FIR lines				181
Standard deviation of the FIR data /cm-1				6.9×10^{-4}
Number of MODR lines				198
Standard deviation of the MODR data /MHz				0.376
Number of MW lines				182
Standard deviation of the MW data /kHz				51.0
Fit standard deviation				0.87
N'_{max}, $K'_{a\,max}$				13, 10

[a] Kanada et al. (1991)
[b] Morino et al. (1997). The values, originally reported in cm^{-1}, are converted to MHz.
[c] Values in parenthesis denote one standard deviation and apply to the last digits.
[d] Fixed

Predictions



CONCLUSION

The rotational spectrum of the doubly-deuterated amidogen radical ND_2 in its ground electronic state $X\,^2B_1$ has been investigated up to the Terahertz region.
New measurements have been analyzed in a global fit including previous mmW, sub-mmW, MODR and FIR data. Some misassignments or incomplete assignments of previous data sets have been corrected, so that it has been possible to obtain a set of accurate spectroscopic constants which are compatible with the entire body of rotational data available for this radical. Accurate predictions are now available up to 8 THz for transitions with $N < 14$ and $K_a < 11$, providing a set of data very useful for astronomical searches.
Recently, we have also observed and analyzed the pure rotational spectrum of $^{15}ND_2$ (*manuscript in preparation*).

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[1] Cook, J. M. & Hills, G. W. 1983, J. Chem. Phys., 78, 2144. [2] Kanada, M., Yamamoto, S., & Saito, S. 1991, J. Chem. Phys., 94, 3423. [3] Morino, I. & Kawaguchi, K. 1997, J. Mol. Spectrosc., 182, 428. [4] Roueff, E., Lis, D. C., van der Tak, F. F. S., Gerin, M., & Goldsmith, P. F. 2005, A&A, 438, 585.