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Ab initio calculations of ^{14}N and ^{15}N hyperfine structures

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Abstract

Hyperfine structure parameters are calculated for the $2p^2(^3\text{P})3s\ ^4\text{P}_J$, $2p^2(^3\text{P})3p\ ^4\text{P}_J^o$ and $2p^2(^3\text{P})3p\ ^4\text{D}_J^o$ levels, using the *ab initio* multiconfiguration Hartree–Fock method. The theoretical hyperfine coupling constants are in complete disagreement with the experimental values of Jennerich *et al* deduced from the analysis of the near-infrared Doppler-free saturated absorption spectra.

1. Introduction

Doppler-free spectra of the near-infrared N I transitions in the $2p^2(^3\text{P})3s\ ^4\text{P} \rightarrow 2p^2(^3\text{P})3p\ ^4\text{P}^o$ and $2p^2(^3\text{P})3s\ ^4\text{P} \rightarrow 2p^2(^3\text{P})3p\ ^4\text{D}^o$ multiplets have been recorded by Jennerich *et al* [1] using saturated absorption spectroscopy, extending the pioneer work of Cangiano *et al* [2] using a similar set-up. From the analysis of these spectra, Jennerich *et al* [1] determined the hyperfine structure constants for the various J -values of the three multiplets involved, for both isotopes ^{14}N and ^{15}N . The isotope shifts in each multiplet have also been measured, revealing a significant J -dependence of the shifts. These authors recommended a theoretical investigation of the underlying cause of this unexpected phenomenon. Similar measurements, using Doppler-free saturated absorption spectroscopy, have been performed in atomic fluorine [3], chlorine [4] and oxygen [5].

The present work presents a robust *ab initio* theoretical estimation of the relevant hyperfine structure parameters, using the ATSP2K package [6], based on the non-relativistic multiconfiguration Hartree–Fock (MCHF) and configuration interaction (CI) methods. The minimum theoretical background is presented in section 2 for the hyperfine interaction. Section 3 is dedicated to the description of the electron correlation models. A refined calculation for the even-parity term is presented in section 4. A first comparison between theory and observation appears in section 5, revealing unexpected discrepancies. Relativistic effects are investigated in section 6 through the relativistic configuration

interaction (RCI) approach, confirming serious problems in the experimental analysis as discussed in section 7.

2. The hyperfine interaction

The theory underlying MCHF calculations of hyperfine structure parameters can be found in [7, 8]. Neglecting the relativistic effects, the diagonal and off-diagonal A and B hyperfine interaction constants are expressed in terms of the J -independent orbital (a_l), spin-dipole (a_{sd}), contact (a_c) and electric quadrupole (b_q) electronic hyperfine parameters defined by

$$a_l = \langle \gamma L S M_L M_S | \sum_{i=1}^N l_0^{(1)}(i) r_i^{-3} | \gamma L S M_L M_S \rangle, \quad (1)$$

$$a_{\text{sd}} = \langle \gamma L S M_L M_S | \sum_{i=1}^N 2C_0^{(2)}(i) s_0^{(1)}(i) r_i^{-3} | \gamma L S M_L M_S \rangle, \quad (2)$$

$$a_c = \langle \gamma L S M_L M_S | \sum_{i=1}^N 2s_0^{(1)}(i) r_i^{-2} \delta(r_i) | \gamma L S M_L M_S \rangle, \quad (3)$$

$$b_q = \langle \gamma L S M_L M_S | \sum_{i=1}^N 2C_0^{(2)}(i) r_i^{-3} | \gamma L S M_L M_S \rangle, \quad (4)$$

and calculated for the magnetic component $M_L = L$ and $M_S = S$. The first three parameters (1), (2) and (3), contribute to the magnetic dipole hyperfine interaction constant through

$$A_J = A_J^{\text{orb}} + A_J^{\text{sd}} + A_J^c, \quad (5)$$

Table 1. SD-MR-MCHF and CI total energies, specific mass shift and hyperfine interaction parameters (all in atomic units) as a function of the orbital active set, for $2p^23s^4P$. NCSF is the number of CSFs in the wavefunction expansion.

AS	NCSF	E	S_{sms}	a_l	a_{sd}	a_c	b_q
SD-MR-MCHF							
HF	1	-54.032 303	-2.5647	3.7993	0.7599	3.6055	1.5197
3s2p1d	149	-54.116 873	-2.3529	3.5643	0.7310	8.4493	1.2085
4s3p3d1f	652	-54.165 015	-1.3937	3.7020	0.7999	9.2913	1.2704
5s4p3d2f1g	1626	-54.189 786	-1.4252	3.6990	0.7837	7.3833	1.2072
6s5p4d3f2g	3082	-54.196 747	-1.4254	3.6862	0.7713	8.7173	1.2108
7s6p5d4f3g	5020	-54.199 972	-1.4238	3.6869	0.7723	8.1898	1.2281
8s7p6d5f3g	7113	-54.201 188	-1.4238	3.6879	0.7751	8.0753	1.2248
9s8p7d6f3g	9572	-54.201 746	-1.4237	3.6878	0.7752	8.0941	1.2208
10s9p8d6f3g	11728	-54.201 953	-1.4234	3.6884	0.7743	8.1090	1.2231
SDTQ-CI							
∪ 4s3p2d1f	40685	-54.203 791	-1.4282	3.6412	0.7668	9.7166	1.1502
∪ 5s4p3d2f	106472	-54.204 677	-1.4427	3.6170	0.7624	10.511	1.1156
∪ 6s5p4d3f	210533	-54.204 967	-1.4470	3.6090	0.7609	10.780	1.1049

with

$$A_J^{\text{orb}} = G_\mu \frac{\mu_I}{I} a_l \frac{\langle \vec{L} \cdot \vec{J} \rangle}{LJ(J+1)}, \quad (6)$$

$$A_J^{\text{sd}} = \frac{1}{2} G_\mu g_s \frac{\mu_I}{I} a_{\text{sd}} \frac{3 \langle \vec{L} \cdot \vec{S} \rangle \langle \vec{L} \cdot \vec{J} \rangle - L(L+1) \langle \vec{S} \cdot \vec{J} \rangle}{SL(2L-1)J(J+1)}, \quad (7)$$

$$A_J^c = \frac{1}{6} G_\mu g_s \frac{\mu_I}{I} a_c \frac{\langle \vec{S} \cdot \vec{J} \rangle}{SJ(J+1)}, \quad (8)$$

while the last one (b_q) constitutes the electronic contribution to the electric quadrupole hyperfine interaction

$$B_J = -G_q Q b_q \frac{6 \langle \vec{L} \cdot \vec{J} \rangle^2 - 3 \langle \vec{L} \cdot \vec{J} \rangle - 2L(L+1)J(J+1)}{L(2L-1)(J+1)(2J+3)}. \quad (9)$$

Expressing the electronic parameters a_l , a_{sd} and a_c in atomic units (a_0^{-3}) and μ_I in nuclear magnetons (μ_N), the magnetic dipole hyperfine structure constant A is calculated in units of frequency (MHz) by using $G_\mu = 95.41067$. Similarly, the electric quadrupole hyperfine structure constant B is expressed in MHz when adopting atomic units (a_0^{-3}) for b_q , barns for Q and $G_q = 234.96475$.

The electronic parameter governing the mass isotope shift of an atomic energy level is the S_{sms} parameter [9] defined by

$$S_{\text{sms}} = -\langle \gamma LSM_L M_S | \sum_{i < j}^N \vec{\nabla}_i \cdot \vec{\nabla}_j | \gamma LSM_L M_S \rangle. \quad (10)$$

3. Correlation models

The multiconfiguration Hartree–Fock (MCHF) variational approach consists in optimizing the one-electron functions spanning a configuration space and the mixing coefficients of the interacting configuration state functions (CSF) [10] for describing a given term

$$\Psi(\gamma LSM_L M_S) = \sum_i c_i \Phi(\gamma_i LSM_L M_S). \quad (11)$$

Efficient MCHF expansions are often built by allowing single and double excitations from a multireference set (SD-MR-MCHF). As far as hyperfine structures are concerned, successful applications of this method are found for light elements such as Li-like ions [9], Be I, B I, C II and C I [11, 12], N I [13], O I [13, 14] or Na I [15].

For the even parity term $2p^23s^4P$, the configuration expansion is generated from single and double (SD) excitations from the

$$\{2s^22p^23s, 2p^43s, 2s2p^4\} \quad (12)$$

multireference (MR) to increasing active sets (AS) of orbitals that are denoted by specifying the number of orbitals for each l -symmetry. This multireference set captures the dominant correlation effects through a physical good ‘zero-order’ wavefunction. We include only configuration state functions ($\Phi(\gamma_i LSM_L M_S)$) that interact with the multireference, adopting the reversed orbital order, i.e. coupling sequentially the subshells by decreasing n and l . This technique reduces substantially the size of the MCHF expansions while keeping the dominant correlation contributions [12, 16]. With the largest set of orbitals (10s9p8d6f3g) optimized through these calculations, the effect of higher excitations is investigated through configuration interaction (CI) calculations using the configuration state function set obtained by adding to the original SD-MR CSF list, the triple and quadruple excitations from the same multireference to smaller orbital active sets (up to 6s5p4d3f). For generating these lists, some limitations have been introduced by imposing the restriction that there should be at least five orbitals with $n \leq 3$ in the CSFs produced. The merging of the original SD-MR and the TQ-MR CSF lists is noted by the union (\cup) symbol.

For the odd parity states $2p^23p^4P^o$ and $2p^23p^4D^o$, a similar strategy is adopted, using the following multireference set

$$\{2s^22p^23p, 2p^43p, 2s2p^23p3d\}. \quad (13)$$

The total energies (E), the specific mass shift (S_{sms}) and the hyperfine interactions parameter $\{a_l, a_{\text{sd}}, a_c, b_q\}$ defined in section 2, are reported in tables 1–3, respectively. These tables illustrate the smooth convergence of the various parameters

Table 2. SD-MR-MCHF and CI total energies, specific mass shift and hyperfine interaction parameters (all in atomic units) as a function of the orbital active set, for $2p^23p^4P^o$. NCSF is the number of CSFs in the wavefunction expansion.

AS	NCSF	E	S_{sms}	a_l	a_{sd}	a_c	b_q
SD-MR-MCHF							
HF	1	-53.984 055	-2.5786	1.9609	-0.3749	0.0000	-0.7498
3s2p1d	583	-54.062 052	-2.2945	1.9466	-0.3787	5.1320	-0.7123
4s3p2d1f	3879	-54.112 044	-1.2732	1.9752	-0.4086	0.5548	-0.6912
5s4p3d2f1g	10078	-54.134 423	-1.3540	1.9653	-0.3884	0.3990	-0.6708
6s5p4d3f2g	19200	-54.143 169	-1.3318	1.9673	-0.3839	1.1424	-0.6841
7s6p5d4f3g	31245	-54.147 455	-1.3170	1.9709	-0.3835	0.7422	-0.6879
8s7p6d5f3g	44096	-54.148 983	-1.3187	1.9705	-0.3837	0.6826	-0.6887
9s8p7d6f3g	59110	-54.149 672	-1.3185	1.9702	-0.3850	0.7044	-0.6864
10s9p8d6f3g	72070	-54.149 921	-1.3188	1.9704	-0.3843	0.7449	-0.6849
SDTQ-CI							
U 4s3p2d1f	124029	-54.150 179	-1.3136	1.9710	-0.3844	0.8878	-0.6848
U 5s4p3d2f	252690	-54.150 330	-1.3139	1.9714	-0.3844	0.9168	-0.6845
U 6s5p4d3f	459494	-54.150 406	-1.3138	1.9717	-0.3843	0.9429	-0.6845

Table 3. SD-MR-MCHF and CI total energies, specific mass shift and hyperfine interaction parameters (all in atomic units) as a function of the orbital active set, for $2p^23p^4D^o$. NCSF is the number of CSFs in the wavefunction expansion.

AS	NCSF	E	S_{sms}	a_l	a_{sd}	a_c	b_q
SD-MR-MCHF							
HF	1	-53.987 051	-2.5789	3.9263	0.7462	0.0000	1.4926
3s2p1d	720	-54.064 819	-2.2937	3.8979	0.7539	5.1069	1.4194
4s3p2d1f	4747	-54.114 835	-1.2729	3.9574	0.8137	0.5229	1.3775
5s4p3d2f1g	12197	-54.137 237	-1.3541	3.9575	0.7769	0.3613	1.3421
6s5p4d3f2g	23072	-54.146 073	-1.3259	3.9674	0.7698	1.1034	1.3472
7s6p5d4f3g	37372	-54.150 182	-1.3163	3.9688	0.7661	0.6698	1.3768
8s7p6d5f3g	52558	-54.151 947	-1.3186	3.9688	0.7658	0.6258	1.3800
9s8p7d6f3g	70266	-54.152 646	-1.3188	3.9678	0.7692	0.6472	1.3730
10s9p8d6f3g	85436	-54.152 903	-1.3191	3.9682	0.7688	0.6864	1.3686
SDTQ-CI							
U 4s3p2d1f	156938	-54.153 165	-1.3139	3.9695	0.7691	0.8307	1.3684
U 5s4p3d2f	334710	-54.153 318	-1.3142	3.9706	0.7690	0.8600	1.3678
U 6s5p4d3f	620614	-54.153 406	-1.3138	3.9711	0.7689	0.8848	1.3677

while improving the correlation model by increasing the size of the orbital active set. For the even parity term $2p^23s^4P$ (table 1), triple and quadruple excitations from the multireference affect the a_l and a_{sd} parameters at the level of 2% while the contact term a_c is much more sensitive (33%). For the odd parity $2p^23p^4P^o$ and $2p^23p^4D^o$ terms (tables 2 and 3), all hyperfine parameters reach a high degree of convergence, except the contact parameter that is strongly affected (around 30%) by TQ excitations. For the three terms, the last layer added at the SDTQ-CI level of approximation brings a negligible increment, except for the contact contributions (3%). The convergence patterns of the contact contributions, as well as the sensitivity for TQ excitations, are similar to the one found for the $2p^33s^5S^o$ term in O I [13].

4. On a larger multireference set for $2p^2(^3P)3s^4P$

We investigate the reliability of the theoretical parameters by extending the multireference set. Amongst the three terms considered, we focus on the even parity $2p^2(^3P)3s^4P$ one, realizing that it is one for which the hyperfine interaction parameters A_J are the most sensitive to TQ excitations due

to the large contribution of the contact term. The following multireference (MR')

$$\{2s^22p^23s, 2p^43s, 2s2p^4, 2s2p^33p, 2s2p^23s3d\} \quad (14)$$

is selected, after a detailed analysis of the eigenvector weights obtained with the first approach. The results are reported in table 4. The comparison of the last lines of table 1 (MR) and table 4 (MR') illustrates the global stability of the hyperfine parameters, the largest variation (3.6%) being observed for the a_c contact contribution.

5. Comparison with experiments

The hyperfine constants A_J and B_J are estimated for both isotopes ^{14}N and ^{15}N from the hyperfine structure parameters calculated with the most elaborate correlation models (last lines of tables 2–4), using the nuclear data taken from Stone [17] and summarized in table 5.

From equations (6)–(8), one realizes that the ratio between the magnetic hyperfine constants characterizing a given J -level of the two isotopes should be

$$A_J(^{15}\text{N})/A_J(^{14}\text{N}) = \frac{\mu_I(^{15}\text{N})I(^{14}\text{N})}{\mu_I(^{14}\text{N})I(^{15}\text{N})} = -1.4028. \quad (15)$$

Table 4. SD-MR'-MCHF and CI total energies, specific mass shift and hyperfine interaction parameters (all in atomic units) as a function of the orbital active set, for $2p^23s\ ^4P$. NCSF is the number of CSFs in the wavefunction expansion.

AS	NCSF	E	S_{sms}	a_l	a_{sd}	a_c	b_q
SD-MR'-MCHF							
HF	1	-54.032 303	-2.5647	3.7993	0.7599	3.6055	1.5197
3s2p1d	461	-54.117 540	-2.3595	3.5468	0.7276	9.0794	1.1821
4s3p2d1f	2543	-54.168 450	-1.3886	3.6009	0.7798	5.8010	1.1433
5s4p3d2f1g	6447	-54.192 356	-1.4432	3.6402	0.7761	9.6255	1.1132
6s5p4d3f2g	12210	-54.199 795	-1.4511	3.6101	0.7584	11.3959	1.0968
7s6p5d4f3g	19832	-54.203 174	-1.4498	3.6078	0.7589	10.8596	1.1146
8s7p6d5f3g	28014	-54.204 436	-1.4505	3.6080	0.7615	10.7556	1.1106
9s8p7d6f3g	37595	-54.205 011	-1.4509	3.6075	0.7615	10.7965	1.1068
10s9p8d6f3g	45958	-54.205 221	-1.4505	3.6084	0.7607	10.7996	1.1094
SDTQ-CI							
U 4s3p2d1f	93412	-54.205 400	-1.4538	3.5997	0.7592	11.0883	1.0953
U 5s4p3d2f	208694	-54.205 456	-1.4540	3.5977	0.7588	11.1538	1.0922
U 6s5p4d3f	393284	-54.205 469	-1.4543	3.5972	0.7588	11.1705	1.0913

Table 5. Nuclear data for ^{14}N and ^{15}N [17].

Isotope	I	μ_I (nm)	Q (b)
^{14}N	1	+0.40376100(6)	+0.02001(10)
^{15}N	$\frac{1}{2}$	-0.28318884(5)	0.0

These non-relativistic (NR) theoretical A_J and B_J hyperfine constants are reported in table 6 and compared with those derived by Jennerich *et al* [1] using saturated absorption spectroscopy⁴. The comparison reveals huge discrepancies between theory and observation. Inconsistencies appear not only in the magnitude of the parameters, but also in the relative signs of the parameters for the different J -levels arising from the same term.

Rewriting equations (1)–(4) as

$$A_J^{\text{orb}} \equiv G_\mu \frac{\mu_I}{I} a_l K_J^{\text{orb}}, \quad (16)$$

$$A_J^{\text{sd}} \equiv \frac{1}{2} G_\mu g_s \frac{\mu_I}{I} a_{\text{sd}} K_J^{\text{sd}}, \quad (17)$$

$$A_J^c \equiv \frac{1}{6} G_\mu g_s \frac{\mu_I}{I} a_c K_J^c, \quad (18)$$

$$B_J \equiv -G_q Q b_q K_J', \quad (19)$$

the numerical factors K_J^{orb} , K_J^{sd} , K_J^c and K_J' are calculated from the expectation values of the angular momentum scalar products and reported in table 7 for each J -values of the (odd and even) 4P and 4D terms. The consistency of the theoretical values calculated for the different J -values within a given LS term with the relative weights of the different contributions making the total hyperfine constant, is obviously satisfied, by construction. However there is no such constraint in the experimental analysis and one can show that no physical set of underlying $\{a_l, a_{\text{sd}}, a_c\}$ parameters fits the experimental A_J -values with the numerical factors of table 7.

Some ambiguity was pointed out in the line assignment of the spectra of the $^4P_{1/2} \rightarrow ^4D_{1/2}^o$ transition for both

isotopes. Due to this identification problem, Jennerich *et al* [1] determined two possible values for each of the hyperfine constants of the $^4P_{1/2}$ and $^4D_{1/2}^o$ states, both reported in table 6. Based on the crossover intensity arguments, they gave their preference to the first set. Looking at our theoretical values, we claim that their choice was definitely not a good one. Another surprise appears: they deduced a large B value for $^4D_{3/2}^o$ ^{14}N that contrasts with the zero numerical factor $K_{3/2}'$ of table 7.

6. Relativistic corrections

Relativistic effects influence atomic wavefunctions basically in two ways: through contraction of radial orbitals and through LS term mixing. Contraction effects may be large for high Z , but remain relatively unimportant in light elements such as nitrogen [18]. However, term mixing may affect the wavefunction and the computed hyperfine interaction constants in significant ways, especially when fine-structure levels belonging to different terms are closely spaced. To investigate term mixing we first perform reference MCHF calculations for configuration expansions generated by SD-excitations from, respectively, $\{2s^22p^23s, 2p^43s\}$ and $\{2s^22p^23p, 2p^43p\}$ to active sets (4s3p2d1f). The resulting non-relativistic radial orbitals are converted to Dirac spinors using the Pauli approximation [19]

$$P(n\kappa; r) = P^{\text{MCHF}}(nl; r),$$

$$Q(n\kappa; r) = \frac{\alpha}{2} \left(\frac{d}{dr} + \frac{\kappa}{r} \right) P(n\kappa; r). \quad (20)$$

Here α is the fine structure constant and κ is the relativistic quantum number

$$\kappa = (j + 1/2)\eta \quad \text{when} \quad l = j + \eta/2, \quad \eta = \pm 1. \quad (21)$$

This is followed by relativistic configuration interaction (RCI) calculations for configuration expansions generated by SD-excitations from the multireference sets above to the Dirac spinors (see [20, 21] for details about the conversion of radial orbitals and the relativistic computer codes). In relativistic theory only J is a good quantum number and the relativistic configuration expansions account for LS term mixing. The

⁴ As discussed in [1], the hyperfine constants derived by Cangiano *et al* [2] for 4P_J and $^4P_J^o$ agree qualitatively with those of Jennerich *et al* [1].

Table 6. Hyperfine constant comparison between observation [1] and theory (present work): non-relativistic (NR) *ab initio* and relativistically corrected (+RC) results. All values are in MHz.

Levels	¹⁵ N			¹⁴ N					
	Exp. [1]	Theory		Exp. [1]		Theory			
		NR	+RC			NR		+RC	
A	A	A	A	B	A	B	A	B	
⁴ P _{1/2}	{ +103.4(14) -153.1(23) ^a	-139.85	-140.56	{ -69.76(90) +112.3(13) ^a	0.0	99.70	0.0	100.21	0.0
⁴ P _{3/2}	-47.93(48)	-88.29	-87.62	35.52(44)	-0.98(48)	62.94	4.10	62.46	4.10
⁴ P _{5/2}	-90.71(71)	-174.75	-175.12	64.76(42)	-3.9(10)	124.58	-5.13	124.84	-5.12
⁴ P _{1/2} ^o	167.1(13)	75.24	73.29	-133.2(22)	0.0	-53.64	0.0	-52.25	0.0
⁴ P _{3/2} ^o	70.0(12)	-68.15	-71.60	-48.56(74)	8.69(87)	48.58	-2.58	51.04	-2.95
⁴ P _{5/2} ^o	46.20(74)	-41.11	-46.52	-32.83(44)	5.0(11)	29.30	3.22	33.16	2.57
⁴ D _{1/2} ^o	{ +153.1(23) -103.4(14) ^a	-106.89	-104.02	{ -112.3(13) +69.76(90) ^a	0.0	76.20	0.0	74.15	0.0
⁴ D _{3/2} ^o	92.4(17)	-49.14	-44.49	-64.41(79)	10.46(88)	35.03	0.0	31.71	0.30
⁴ D _{5/2} ^o	41.5(14)	-56.74	-51.57	-28.19(62)	-0.2(15)	40.45	-2.30	36.76	-1.69
⁴ D _{7/2} ^o	-9.35(55)	-77.76	-78.04	6.31(72)	-12.6(13)	55.43	-6.43	55.63	-6.44

^a Second proposition of Jennerich *et al* (see text).

Table 7. *J*-dependence of the hyperfine contributions to *A_J* and *B_J* constants for ⁴P and ⁴D terms.

<i>J</i>	⁴ P				⁴ D			
	<i>K_J^{orb}</i>	<i>K_J^{sd}</i>	<i>K_J^c</i>	<i>K'_J</i>	<i>K_J^{orb}</i>	<i>K_J^{sd}</i>	<i>K_J^c</i>	<i>K'_J</i>
1/2	- $\frac{2}{3}$	$\frac{10}{9}$	$\frac{10}{27}$	0	1	$-\frac{7}{3}$	$-\frac{2}{9}$	0
3/2	$\frac{4}{15}$	$-\frac{68}{45}$	$\frac{22}{135}$	$-\frac{4}{5}$	$\frac{2}{5}$	$-\frac{14}{15}$	$\frac{2}{45}$	0
5/2	$\frac{2}{5}$	$\frac{2}{5}$	$\frac{2}{15}$	1	$\frac{11}{35}$	$-\frac{37}{105}$	$-\frac{26}{315}$	$\frac{9}{25}$
7/2					$\frac{2}{7}$	$\frac{2}{7}$	$\frac{2}{21}$	1

hyperfine interaction constants obtained from the MCHF and RCI wavefunctions are displayed in table 8. One observes that the relativistic effects are far from negligible, changing the hyperfine parameters in many cases by more than 10%. Assuming that the differences between the relativistic and non-

relativistic values of the hyperfine constants in the limited calculations with active sets (4s3p2d1f) are representative of the true differences, we add the former to the non-relativistic results in table 6 to obtain the final relativistically corrected values (in column ‘+RC’) of the hyperfine interaction constants. It is clear that relativistic effects cannot explain the huge global theory–observation conflict.

7. Conclusion

The strong disagreement between theory and observation [1] is really disconcerting. Hyperfine parameters have indeed been estimated *ab initio* successfully using similar methods for different atomic systems such as carbon, nitrogen, oxygen or sodium, as described in section 1. The present calculated hyperfine structure constants disagree so strongly with experiments in comparison with the achieved theoretical

Table 8. Hyperfine interaction constants from matching RCI and MCHF calculations. The relativistic orbitals were obtained from the non-relativistic ones in the Pauli approximation. All values are in MHz.

Levels	¹⁵ N			¹⁴ N					
	RCI	MCHF	Difference	RCI		MCHF		Difference	
	A	A	Δ <i>A</i>	A	B	A	B	Δ <i>A</i>	Δ <i>B</i>
⁴ P _{1/2}	-79.79	-79.08	-0.71	56.88	0.0	56.37	0.0	0.51	0.0
⁴ P _{3/2}	-59.96	-60.63	0.67	42.74	5.06	43.22	5.06	-0.48	0.0
⁴ P _{5/2}	-158.07	-157.70	-0.37	112.68	-6.32	112.42	-6.33	0.26	0.01
⁴ P _{1/2} ^o	84.01	85.96	-1.95	-59.89	0.0	-61.28	0.0	1.39	0.0
⁴ P _{3/2} ^o	-69.63	-66.18	-3.45	49.64	-2.97	47.18	-2.60	2.46	-0.37
⁴ P _{5/2} ^o	-42.81	-37.40	-5.41	30.52	2.60	26.66	3.25	3.86	-0.65
⁴ D _{1/2} ^o	-102.87	-105.74	2.87	73.33	0.0	75.38	0.0	-2.05	0.0
⁴ D _{3/2} ^o	-40.95	-45.60	4.65	29.19	0.30	32.51	0.0	-3.32	0.30
⁴ D _{5/2} ^o	-48.61	-53.78	5.17	34.65	-1.70	38.34	-2.31	-3.69	0.61
⁴ D _{7/2} ^o	-76.34	-76.06	-0.28	54.42	-6.48	54.22	-6.47	0.2	-0.01

convergence of the hyperfine parameters that we presently cast doubt on Cangiano *et al*'s [2] and Jennerich *et al*'s [1] analysis. We therefore encourage further experimental spectroscopic studies and/or reinterpretation of the near-infrared spectra. Last but not least, the extracted isotope shifts from the same spectra revealed a significant unexpected J -dependence of the specific mass shifts in both multiplets. However, the authors themselves [1] pointed out that the experimental isotope shift values are critically dependent on the correct interpretation of the hyperfine structures of the ^{14}N and ^{15}N spectra. The present questioning on the experimental determination of the hyperfine parameters could also be relevant in their isotope shift discussion.

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