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Calculation of ESR Spin- Spin Relaxation Times (1/T_2) Transition Metal Ion Complexes: A DFT Application

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ABSTRACT

Only a limited experimental ESR research had been carried out in this field because high values of spin orbit constants of transition metal ions which provide an important energy transfer mechanism would affect the values of ESR parameters (especially A_{ten}) of their complexes. Therefore, theoretical predictions were useful. DFT implemented in ADF: 2012.01 was applied by giving a set of commands like *Single Point, LDA, Default, Spin Orbit, ZORA, Unrestricted, None*, *Collinear, Nosym* using *TZP* or *TZ2P Basis sets* in its ESR/EPR/EFG/ZFS Program after optimization of each one of 141 complexes to obtain their ESR parameters: g_{11}, g_{22}, g_{33}, g_{iso}, a_{11}, a_{22}, a_{33}, A_{ten}. ESR Spin- Spin Relaxation Times (1/T_2) whose values, to the best of our knowledge, were never reported before were, then, calculated from the g_{iso} values of the complexes.

Keywords: Spin-spin and Spin–lattice Relaxation, Saturation Effect, Line Width, DPPH.

INTRODUCTION

Magnetic resonance was associated with a typical a problem not encountered in higher energy forms of spectral techniques as the two spin levels were nearly equally populated[1-3] as at 298K with value: N_{upper}/N_{lower}=0.9986 at 3000G. But even this slight excess population in the lower level would lead to energy absorption. In order to maintain a population excess in the lower level, electrons from upper level gave up energy to return to lower level (Maxwell–Boltzmann law).This energy releasing process was called spin relaxation process. The relaxation processes were two types: spin–lattice relaxation and spin–spin relaxation.

Spin-lattice relaxation[1-3]

Spin–lattice implied the interaction between the species with unpaired electrons, called "spin system" and the surrounding molecules, known as "lattice". The energy was dissipated within the lattice as vibrational, rotational or translational energy. The spin lattice relaxation characterized by a relaxation time $T_{\_1}$, was the time for the spin system to lose $1/e^{th}$ of its excess energy. Spin-lattice rate constant was equal to $1/T_{\_1}$. Rapid dissipation of energy (short $T_{\_1}$) was essential to maintain the population difference of the spin states. Slow spin-lattice relaxation, which frequently occurred in systems containing free radicals, especially at low temperatures, might cause saturation of the spin system which implied that the population difference of the upper and lower spin states approached zero and EPR signal would cease. Systems with a long $T_{\_1}$ were weakly coupled to the surroundings and thus would be easily saturated while those with shorter $T_{\_1}$ were more difficult to saturate. The effect of saturation was interpreted by a set of macroscopic equations proposed by Flex Bloch (1946) to calculate nuclear magnetization (M) as a function of relaxation times $T_{\_1}$ and $T_{\_2}$.

As spin-orbit coupling provided an important energy transfer mechanism, it was found that odd-electron species with light atoms (organic radicals) possessed long $T_{\_1}$ s while those with heavier atoms(transition metal ions) had shorter $T_{\_1}$ s.

Spin-spin relaxation[1-3]

In Spin-spin relaxation (Cross relaxation), energy exchange takes place between electrons in a higher energy spin state and nearby electrons or magnetic nuclei in a lower energy state, without transferring to the lattice. Analogously, the spin–spin relaxation was characterized by spin-spin relaxation time $T_{\_2}$.

Ideally, both spin–spin and spin–lattice relaxations would contribute to the EPR signal. Resonance line width (ΔH) or line width or half line width was the distance measured from the line's center to the point at which absorption value had half of maximal absorption value in the center of resonance line. It was represented as:

$$\Delta H \propto 1/T_{\_1}+1/T_{\_2} \qquad \text{...(a)}$$

When $T_{\_1} >> T_{\_2}$, ΔH depends, primarily, on spin–spin interactions.

The following points were helpful to compare the two relaxation times:

(a) Spin-Lattice ($T_{\_1}$) was known as longitudinal relaxation, or relaxation in the z-direction and Spin-Spin ($T_{\_2}$) was called transverse relaxation or relaxation in the x-y plane. Decreasing the spin-spin distance, which represented the spin concentration, $T_{\_1}$ would become very short i.e. less than 10^{-7} second. *Spin-lattice relaxation has a larger influence on the line width than spin-spin relaxation*

(b)In some cases, EPR lines were broadened beyond detection. When a spin system was weakly coupled to the lattice, i.e. the system possessed a long $T_{\_1}$; electrons had no time to return to the ground state. The population difference of two levels would tend to approach zero to decrease the intensity of EPR signal. This effect, called saturation, could be avoided by exposing the sample to low intensity microwave radiation.

Systems with shorter $T_{\_1}$ are more difficult to saturate.

(c)$T_{\_2}$ would represent the loss of phase coherence among nuclei.$T_{\_2}$ was less than or equal to $T_{\_1}$ .If $R_1 =1/T_{\_1}$, $R_2 = 1/T_{\_2}$, $R_2 \geq R_1$.

Short $T_{\_1}$ means NMR signal can be acquired faster.

Methodology

ESR technique was used to calculate ESR Spin-Spin Relaxation times [$T_{\_2}$] of the 1st, 2nd and 3rd transition metal ion complexes with the help of ADF 2012.01 by installing it on Windows XP.

ESR Parameters[4-6]

After *optimization* of complexes, the ADF software was run by using *Single Point, LDA, Default, Spin Orbit, ZORA, Unrestricted, None*, *Collinear, Nosym* using TZP or TZ2P *Basis sets* in ESR/EPR Program to obtain ESR parameters: g_{11}, g_{22}, g_{33}, g_{iso}. The g_{iso}, values of metal ions (g_{M}^{n+}) were, then, used to calculate (1/T_2) values of complexes.

RESULTS

Calculated values of ESR spin-spin relaxation times ($T_{\_2}$) of 141 complexes of the 1st,

Table: 1: Calculation of ESR Spin-Spin Relaxation Time of 1st, 2nd and 3rd Transition Series Complexes

S. No.	Complex	Point group	g_M^{n+}	g_{DPPH}	v_{DPPH}	v_M^{n+} [MHz] [13]	$T_{—2 * 10^{-12} sec}$ [14]
1	$[TiF_4]^{1-}$	D_{4h}	1.938444	2.0023	8388.255	8120.7424	9.7953
2	$[TiCl_4]^{1-}$	D_{4h}	1.930215	-do-	-do-	8086.2686	9.8371
3	$[TiBr_4]^{1-}$	D_{4h}	1.911538	-do-	-do-	8008.0249	9.93322
4	$[TiI_4]^{1-}$	D_{4h}	1.877360	-do-	-do-	7864.8426	10.1140
5	$[Ti(OH_2)_4]^{3+}$	C_1	1.844705	-do-	-do-	7728.0407	10.2930
6	$[TiF_4]^{2-}$	T_d	1.999110	-do-	-do-	8374.8911	9.4981
7	$[TiCl_4]^{2-}$	T_d	1.933860	-do-	-do-	8101.5386	9.8186
8	$[TiI_4]^{2-}$	D_{4h}	1.658980	-do-	-do-	6949.9812	11.4454
9	$[Ti(OH_2)_4]^{2+}$	S_4	1.956630	-do-	-do-	8196.9292	9.7043
10	$[TiF_6]^{3-}$	D_{6h}	1.980815	-do-	-do-	8298.2477	9.5858
11	$[TiCl_6]^{3-}$	O_h	1.997868	-do-	-do-	8369.6880	9.5040
12	$[TiBr_6]^{3-}$	D_{6h}	1.911538	-do-	-do-	8008.0249	9.9332
13	$[TiI_6]^{3-}$	O_h	2.003800	-do-	-do-	8394.5390	9.4759
14	$[TiF_6]^{4-}$	O_h	1.995846	-do-	-do-	8361.2172	9.5136
15	$[TiCl_6]^{4-}$	O_h	2.022666	-do-	-do-	8473.5745	9.3875
16	$[TiBr_6]^{4-}$	O_h	1.996820	-do-	-do-	8365.2976	9.5090
17	$[TiI_6]^{4-}$	O_h	1.979552	-do-	-do-	8292.9566	9.5919
18	$[VF_4]$	D_{4h}	1.914735	-do-	-do-	8021.4181	9.9166
19	$[VCl_4]$	D_{4h}	1.925441	-do-	-do-	8066.2688	9.8615
20	$[VBr_4]$	D_{4h}	1.931780	-do-	-do-	8092.8249	9.8291
21	$[VI_4]$	D_{4h}	1.882660	-do-	-do-	7887.0460	10.0856
22	$[VF_4]^{1-}$	T_d	1.937673	-do-	-do-	8117.5125	9.7992
23	$[VCl_4]^{1-}$	T_d	1.947051	-do-	-do-	8156.7998	9.7520
24	$[V Br_4]^{1-}$	T_d	1.968615	-do-	-do-	8247.1381	9.6452
25	$[V I_4]^{1-}$	D_{4h}	1.514479	-do-	-do-	6344.6217	12.5375
26	$[VF_6]^{4-}$	D_{12}	1.999780	-do-	-do-	8377.6979	9.4949
27	$[VCl_6]^{4-}$	O_h	1.989060	-do-	-do-	8332.7886	9.5461
28	$[VBr_6]^{4-}$	O_h	2.001700	-do-	-do-	8385.7414	9.4858
29	$[VI_6]^{4-}$	O_h	2.036600	-do-	-do-	8531.9483	9.3232
30	$[V(OH_2)_6]^{2+}$	C_1	1.985757	-do-	-do-	8318.9512	9.5620
31	$[CrF_6]^{3-}$	O_h	1.983129	-do-	-do-	8307.9417	9.5746
32	$[CrCl_6]^{3-}$	O_h	1.992457	-do-	-do-	8347.0196	9.5298
33	$[CrBr_6]^{3-}$	O_h	2.022007	-do-	-do-	8470.8137	9.3905
34	$[CrI_6]^{3-}$	O_h	2.054592	-do-	-do-	8607.3224	9.2416
35	$[Cr(CN)_6]^{3-}$	O_h	1.997817	-do-	-do-	8358.8209	9.5163
36	$[Cr(NH_3)_6]^{3+}$	D_6	1.995274	-do-	-do-	8358.8209	9.5163
37	$[CoF_4]^{2-}$	T_d	2.155870	-do-	-do-	9031.6073	8.8075
38	$[CoCl_4]^{2-}$	T_d	2.156391	-do-	-do-	9033.7900	8.8053
39	$[CoBr_4]^{2-}$	T_d	2. 175937	-do-	-do-	9115.6742	10.9701
40	$[CoI_4]^{2-}$	T_d	2.199261	-do-	-do-	9213.3856	8.6337
41	$[Co(NCS)_4]^{2-}$	D_{2d}	2.125062	-do-	-do-	8902.5430	8.9351
42	$[Co(OH_2)_4]^{2+}$	C_1	2.118590	-do-	-do-	8875.4298	8.9624
43	$[CoF_6]^{4-}$	$D_{\infty h}$	2.203720	-do-	-do-	9231.7851	8.6164
44	$[CoCl_6]^{4-}$	D_{6h}	2.072360	-do-	-do-	8681.7580	9.1624

45	$[NiF_6]^{4-}$	O_h	2.119700	-do-	-do-	8880.0800	8.9577
46	$[NiCl_6]^{4-}$	O_h	2.097238	-do-	-do-	8785.9797	9.0537
47	$[NiBr_6]^{4-}$	O_h	2.091462	-do-	-do-	8761.7822	9.0787
48	$[NiI_6]^{4-}$	O_h	2.078646	-do-	-do-	8708.0920	9.1347
49	$[Ni(OH_2)_6]^{2+}$	C_2	2.083166	-do-	-do-	8727.0277	9.1148
50	$[Ni(NH_3)_6]^{2+}$	D_{6h}	2.053778	-do-	-do-	8603.9123	9.2453
51	$[Ni(CH_3NH_2)_6]^{2+}$	C_1	2.049893	-do-	-do-	8587.6368	9.2628
52	$[Ni(NH_3)_4(NCS)_2]$	C_1	2.058390	-do-	-do-	8623.2334	9.2246
53	$[NiCl_4]^{2-}$	T_d	2.266900	-do-	-do-	9496.7464	8.3761
54	$[NiBr_4]^{2-}$	T_d	2.041699	-do-	-do-	8553.3096	9.2996
55	$[NiI_4]^{2-}$	T_d	2.086793	-do-	-do-	8742.2609	9.099
56	$[Ni(NCO)_4]^{2-}$	D_{2d}	2.171650	-do-	-do-	9097.7146	8.7435
57	$[CuF_4]^{-2}$	D_{4h}	2.090142	-do-	-do-	8756.252	9.0844
58	$[CuCl_4]^{-2}$	D_{4h}	2.052880	-do-	-do-	8600.150	9.2493
59	$[CuBr_4]^{-2}$	D_{4h}	2.063943	-do-	-do-	8646.497	9.1997
60	$[CuI\ _4]^{-2}$	D_{4h}	2.055866	-do-	-do-	8612.660	9.2359
61	$[Cu(gly)_2]$	C_2	2.07501	-do-	-do-	8692.860	9.1507
62	$Cu(edta)]^{4-}$	C_2	2.086651	-do-	-do-	8741.627	9.0996
63	$[Cu(en)_2]^{2+}$	C_1	2.05848	-do-	-do-	8623.610	9.2241
64	$[Cu(teta)]^{2+}$	C_1	2.05301	-do-	-do-	8600.695	9.2487
65	$[Cu(tepa)]^{2+}$	C_1	2.23504	-do-	-do-	9363.275	8.4955
66	$Cu(peha)]^{2+}$	C_1	2.046089	-do-	-do-	8571.701	9.2800
67	$[Cu(deta)F_2]$	C_s	2.08732	-do-	-do-	8744.430	9.0977
68	$[Cu(deta)Cl_2]$	C_s	2.08709	-do-	-do-	8743.467	9.0977
69	$[Cu(deta)Br_2]$	C_s	2.12923	-do-	-do-	8920.004	8.9176
70	$[Cu(deta)I_2]$	C_s	2.10717	-do-	-do-	8827.588	9.0110
71	$Cu(deta)(NCS)_2$	C_s	2.00729	-do-	-do-	8409.160	9.4594
72	$[Cu(tpy)F_2]$	C_{2v}	2.07546	-do-	-do-	8694.745	9.1487
73	$[Cu(tpy)Cl_2]$	C_{2v}	2.06772	-do-	-do-	8662.320	9.1829
74	$[Cu(tpy)Br_2$	C_{2v}	2.11244	-do-	-do-	8849.656	8.8985
75	$[Cu(tpy)I_2]$	C_1	2.06119	-do-	-do-	8634.963	9.2120
76	$[Cu(tpy)(NCS)_2]$	C_s	2.00552	-do-	-do-	8401.745	9.4625
77	$[Bipy_2\ Ti]^{3+}$	D_{2d}	1.992097	-do-	-do-	8345.5115	9.5315
78	$[Bipy_2\ V]^{3+}$	-do-	1.961116	-do-	-do-	8215.7225	9.6821
79	$[Bipy_2\ V]^{4+}$	-do-	1.950899	-do-	-do-	8172.9203	9.7338
80	$[Bipy_2\ Mn]^{2+}$	-do-	2.001587	-do-	-do-	8385.2680	9.4863
81	$[Bipy_2\ Co]^{2+}$	-do-	2.143333	-do-	-do-	8979.0859	8.8590
82	$[Bipy_2\ Ni]^{2+}$	-do-	2.118079	-do-	-do-	8873.2891	8.9646
83	$[Bipy_2\ Cu]^{2+}$	-do-	2.261892	-do-	-do-	9475.7663	8.3946
84	$[Phen_2\ Ti]^{3+}$	-do-	1.985933	-do-	-do-	8319.6886	9.5611
85	$[Phen_2\ V]^{3+}$	-do-	1.961116	-do-	-do-	8215.7225	9.6821
86	$[Phen_2\ Cr]^{3+}$	-do-	1.989331	-do-	-do-	8333.9238	9.5447
87	$[Phen_2\ Mn]^{2+}$	-do-	2.00177	-do-	-do-	8386.0347	9.4855
88	$[Phen_2\ Co]^{2+}$	-do-	2.083097	-do-	-do-	8726.7387	9.1151
89	$[Phen_2\ Ni]^{2+}$	-do-	2.100 81	-do-	-do-	8800.9439	9.0383
90	$[Phen_2\ Cu]^{2+}$	-do-	2.051877	-do-	-do-	8595.9484	9.2538
91	$[Bipy_3\ V]^{2+}$	**D_3**	1.992534	-do-	-do-	8347.3422	9.5294
92	$[Bipy_3\ Cr]^{3+}$	-do-	1.994097	-do-	-do-	8353.8900	9.5220
93	$[Bipy_3\ Ni[^{2+}$	-do-	2.049848	-do-	-do-	8587.4483	9.2630
94	$[Phen_3\ V]^{2+}$	-do-	1.995046	-do-	-do-	8357.8657	9.5174

95	$[Phen_3Cr]^{3+}$	-do-	1.99303	-do-	-do-	8349.4200	9.5271
96	$[ZrF_6]^{3-}$	D_{6h}	1.978506	-do-	-do-	8288.5746	9.597
97	$[ZrCl_6]^{3-}$	D_{3d}	1.78472	-do-	-do-	7476.7450	10.639
98	$[ZrBr_6]^{3-}$	D_{6h}	1.905875	-do-	-do-	7984.3008	9.963
99	$[Hf~F_6]^{3-}$	D_{6h}	1.935841	-do-	-do-	8109.8377	9.809
100	$[Hf~Cl_6]^{3-}$	O_h	1.638886	-do-	-do-	6865.8012	11.586
101	$[HfBr_6]^{3-}$	O_h	1.687085	-do-	-do-	7067.7217	11.255
102	$Hf(NH_3)_6]^{3+}$	D_{12}	1.939677	-do-	-do-	8125.9079	9.789
103	$[NbF_6]^{2-}$	D_{3d}	1.939395	-do-	-do-	8124.7265	9.791
104	$[NbCl_6]^{2-}$	D_{3h}	1.966684	-do-	-do-	8239.0485	9.655
105	$[NbI6]^{2-}$	C_{2v}	2.08641	-do-	-do-	8740.6178	9.1007
106	$[Nb~(NCS)_6]^{2-}$	C_2	1.99901	-do-	-do-	8374.4722	9.499
107	$[Nb(NH_3)_6]^{4+}$	D_{12}	1.891714	-do-	-do-	7924.9760	10.038
108	$[TaCl_6]^{2-}$	D_{3h}	1.682027	-do-	-do-	7046.5322	11.289
109	$[TaBr_6]^{2-}$	O_h	1.69233	-do-	-do-	7089.6995	11.220
110	$[MoF_6]^{3-}$	O_h	1.958172	-do-	-do-	8203.3891	9.697
111	$[MoCl_6]^{3-}$	O_h	1.984449	-do-	-do-	8313.4716	9.569
112	$[MoBr_6]^{3-}$	$(O_h$	2.014495	-do-	-do-	8439.3436	9.426
113	$Mo(NCS)_6]^{3-}$	O_h	1.977407	-do-	-do-	8285.3685	9.601
114	$[Mo(OH_2)_6]^{3+}$	C_1	1.976455	-do-	-do-	8279.9823	9.607
115	$[W~F_6~]^{-3}$	Oh	1.80193	-do-	-do-	7548.8430	10.538
116	$[WCl_6]^{-3}$	Oh	1.868252	-do-	-do-	7826.6864	10.164
117	$[W~Br_6]~^{-3}$	Oh	1.893263	-do-	-do-	7931.4652	10.029
118	$[W(OH_2)_6]^{+3}$	C_1	1.859795	-do-	-do-	7791.2574	10.210
119	$[W(NH_3)_6]~^{+3}$	C_1	1.925022	-do-	-do-	8064.5135	9.864
120	$[TcCl_6]^{4-}$	D_{6h}	2.080509	-do-	-do-	8715.8967	9.127
121	$[TcBr_6]^{4-}$	D_{6h}	1.986792	-do-	-do-	8323.2872	9.557
122	$[Tc(NCS)_6]^{4-}$	C_2	1.933744	-do-	-do-	8101.0527	9.819
123	$[Tc(NH_3)_6]^{2+}$	D_6	2.968741	-do-	-do-	12436.9758	6.396
124	$[ReCl_6]^{4-}$	O_h	2.346133	-do-	-do-	9828.6780	8.093
125	$[ReBr_6]^{4-}$	O_h	2.39061	-do-	-do-	10015.0059	7.927
126	$[Re(NH_3)_6]^{2+}$	D_6	1.76930	-do-	-do-	7412.1458	10.732
127	$[RuF_6]^{3-}$	O_h	2.818343	-do-	-do-	11806.9119	6.737
128	$[RuCl_6]^{2-}$	O_h	2.853948	-do-	-do-	11956.0723	6.653
129	$[RuBr_6]^{2-}$	O_h	2.742377	-do-	-do-	11488.6668	6.924
130	$[OsF_6]^{3-}$	O_h	2.110344	-do-	-do-	8840.8848	8.999
131	$[OsCl_6]^{3-}$	D_{6h}	2.008006	-do-	-do-	8412.1592	9.456
132	$[Os~Br_6]^{3-}$	O_h	2.170049	-do-	-do-	9091.0075	8.750
133	$[Os(NH_3)_6]^{3+}$	D_{12}	2.126494	-do-	-do-	8908.5421	8.929
134	$[RhF_6]^{2-}$	O_h	2.327833	-do-	-do-	9752.0136	8.157
135	$[RhCl_6]^{2-}$	O_h	2.233967	-do-	-do-	9358.7800	8.500
136	$[RhBr_6]^{2-}$	O_h	2.1426	-do-	-do-	8976.0152	8.862
137	$[Rh(NH_3)_6]^{4+}$	D_6	2.30505	-do-	-do-	9656.5685	8.238
138	$[IrF_6]^{2-}$	O_h	1.960903	-do-	-do-	8214.8301	9.683
139	$[IrCl_6]^{2-}$	O_h	1.938232	-do-	-do-	8119.8543	9.797
140	$[IrBr_6]^{2-}$	O_h	1.92585	-do-	-do-	8067.9823	9.860
141	$[Ir(NH_3)_6]^{4+}$	D_{12}	2.259355	-do-	-do-	9465.1380	9.397

2nd and 3rd transition series metal ions with their symmetry point groups were given in Table: 1.

DISCUSSION

The discussion was divided into two parts
ESR Spin-spin relaxation time (T_{-2}) was calculated as follows:

(a) As was known from relation (a) line width of a peak would depend both on Spin–lattice relaxation time: T_{-1} and Spin–spin relaxation time: T_{-2}

$$\Delta H \sim (1/T_{-1}) + (1/T_{-2}) \qquad ...(1)$$

But when spin-spin relaxation time [T_2] was very fast [‹ ‹10^$^{-7}$ s], then electrons would remain in the upper state for an infinitesimally small time to cause broadening. In such a case, T_1 was neglected to represent ΔH as:

$$\Delta H \approx (1/T_{-2}) \qquad ...(2)$$

(b) The life time of a given spin state would influence the spectral line width via Heisenberg's Uncertainty Principle as follows[7]:

$$\Delta E \,_*\Delta t \geq h/\, 4\pi \qquad ...(3)$$

$$h_*\Delta v \,_*\Delta t \geq h/\, 4\pi \qquad ...(4)$$

$$\Delta t \geq 1/\, 4\pi_*\Delta v \qquad ...(5)$$

Putting $\Delta t = T_{-2}$ and applying (2), it would become:

$$\Delta t = T_{-2} = 1/\, [\Delta H] \qquad ...(6)$$

Then from (5):

$$T_{-2} \geq 1/\, 4\pi_*\Delta v \qquad ...(7)$$

(c) ESR spectrum was scanned by using a constant frequency oscillator and changing the field (H_0). Also for 8388.255 MHz (8388.255*10 ^{6} Hz) in a 0.30T, the g value of the standard substance DPPH (2, 2-diphenyl-1-picrylhydrazyl) was reported to be: g_{DPPH} =2.0023.

(d) Using the basic ESR relation as:

$$E = g\,_*\,\beta_*H_o \qquad ...(8)$$

For DPPH, the above relation was represented as:

$$E_{\,DPPH} = h.\, v_{DPPH} = g_{DPPH.*}\, B\,_*\, H_o \qquad ...(9)$$

For a metal ion ($M^{\,n+}$) it, would, analogously, become:

$$E_M = h_*\, v_{\,M}^{\,n+} = g_{\,M}^{\,n+}\,_*\,\beta\,_*\, H_o \qquad ...(10)$$

$$g_{\,M}^{\,n+}\,_/\, g_{\,DPPH} \;_= v_{\,M}^{\,n+}\,_/\, v_{\,DPPH} \qquad ...(11)$$

$$v_M^{\,n+} \;_= g_{\,M}^{\,n+}\,_*\, v_{DPPH}\,_/\, g_{DPPH} \qquad ...(12)$$

Putting $g_{\,DPPH}$ =2.00232 and v_{DPPH} = 8388.255* 10^6 cm^{-1}(Hz)

$$v_{\,M}^{\,n+}\,(Hz) = g_{\,M}^{\,n+}\, {*}8388.255{*}\, 10^6\, /2.0023 \qquad ...(13)$$

(1 cm^{-1}=Hz)

On replacing Δv by $v_M^{\,n+}$ in (7) and putting its value in (13), ESR spin-spin relaxation time would become(sec^{-1}):

$$T_{-2}\, H"\, 1.8987723151_*\, 10^{-11}\,_/\, g_{\,M}^{\,n+} \qquad ...(14)$$

ESR spin-spin relaxation times (T_{-2}) of 141 complexes were calculated in Table: 1.

CONCLUSION

As expected, the spin- spin relaxation times of all the 141 complexes fall in picosecond range.

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