Ligand-field Calculations for Cobalt(II) Compounds

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g Factors are calculated for tetragonal low-spin d^7 complexes using a d^3 hole ligand-field model. It is shown that the unpaired electron lies in the d_{z^2} orbital (*i.e.* that the ground state is Γ_6 or $^2A_1$) in all forms of cobalt phthalocyanine, as well as in vitamin B_{12r} and its model compounds.

In spite of a similarity in structure, cobalt phthalocyanines differ from other low-spin tetragonal $[Co^{II}N_4]$ complexes, such as cobalt corrins and vitamin B_{12} model compounds in several respects. Cobalt phthalocyanines do not form particularly stable σ cobalt–carbon bonds [1] and they appear to react with molecular oxygen only at low temperatures.[1-4] Moreover β-cobalt phthalocyanine has *g* factors,[5,6] $g_{\parallel}$ 1·88—1·92, $g_{\perp}$ 2·87—2·94,† which are quite distinct from the 'normal'

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† Similar abnormal *g* factors are shown by cobalt tetraphenylporphines.[7,8] Moreover, although cobalt tetraphenylporphine has been shown to resemble vitamin B_{12} in several respects [9] it never seems to have been alkylated.

[1] P. Day, H. A. O. Hill, and M. G. Price, *J. Chem. Soc.* (*A*), 1968, 90. However, see also R. Taube, H. Dreus, and T. Duc-Hiep, *Z. Chem*, 1969, **9**, 115.

[2] J. H. Weber and D. H. Busch, *Inorg. Chem.*, 1965, **4**, 472.

[3] A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 61.

[4] E. W. Abel, J. M. Pratt, and R. Whelan, *Chem. Comm.*, 1971, 449.

[5] J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Discuss. Faraday Soc.*, 1958, **26**, 72.

[6] J. M. Assour and W. K. Khan, *J. Amer. Chem. Soc.*, 1965, **87**, 207.

[7] J. M. Assour, *J. Chem. Phys.*, 1965, **43**, 2477.

[8] F. A. Walker, *J. Amer. Chem. Soc.*, 1970, **92**, 4235.

[9] H. W. Whitlock and B. K. Bower, *Tetrahedron Letters*, 1965, 4827.

values of the other compounds [4,6,10–15] where $g_{\|}$ *ca.* 2·01 and $g_{\perp}$ 2·2—2·4 (Table 1). The present calculations were undertaken to see whether these differences could be ascribed to cobalt phthalocyanine having a ground state of unusual symmetry. (Table 2 shows the three most plausible configurations and corresponding ground states a d^7 system could possess.) Conceptually, it is easiest to associate formation of a σ Co–C bond with the $^2A_1$ state and its singly occupied d_{z^2} orbital with its nodes perpendicular to the molecular plane [16] (*z* is the axis perpendicular to the plane of the molecule).

TABLE 1

g Factors of various cobalt(II) compounds

	$g_{\|}$ (or g_{zz})	$g_{\perp}$ (or g_{xx}, g_{yy})
Cobalamin containing benzimidazoles or adenines [a,b]	2·003—2·004	2·32—2·35
Cobalamin + $C_6H_{11}NC$ [c]	1·99	2·22
Cobamide + pyridine [b]	2·004	2·32
Bis(dimethylglyoximato)		
+ pyridine or imidazole [c]	2·02—2·03	2·27—2·29
+ MeCN [c]	2·01	2·24
+ H_2O [c]	1·98	2·20
NN'-Ethylenebis(acetylacetoniminato) + pyridine [d]	2·01	2·39—2·44
NN'-Ethylenebis(salicylideneiminato) + pyridine [e]	2·03	2·26
Pc [f] + *N*-Heterocyclic bases [g]	2·01—2·02	2·26—2·34
Pc in α-ZnPc [h]	2·01	2·42
Tetrasulphonated Pc in DMSO [i]	2·01	2·26
in MeOH [j]	2·005	2·27
Pc in β-ZnPc [h]	1·91 ± 0·01	2·89 ± 0·02, 2·92 ± 0·02
Pc in β-H_2Pc [h]	1·89 ± 0·01	2·94 ± 0·01
Pc in β-NiPc [h]	1·89 ± 0·01	2·94 ± 0·01

[a] At pH 0, where the internal base no longer co-ordinates, the degeneracy of $g_{\perp}$ is removed, a phenomenon which will be discussed separately. [b] Ref. 10. [c] Ref. 11. [d] Ref. 12. [e] Ref. 13. [f] Pc = phthalocyanine. [g] Ref. 14. [h] Ref. 6. Ref. 15. [j] Ref. 4 and personal communication.

TABLE 2

Orbital occupancy in lowest configuration [a]	Ground state (D_{4h})	Ground state (D'_{4h})
$(d_{xz,yz})^4(d_{xy})^2d_{z^2}$	$^2A_1$	Γ_6
$(d_{xz,yz})^4(d_{y^2})^2d_{xy}$	$^2B_2$	Γ_7
$(d_{xy})^2(d_{z^2})^2(d_{xz,yz})^3$	^2E	$\Gamma_6 + \Gamma_7$

[a] The sequence of the filled orbitals can vary (Figure 1).

Unfortunately a full MO calculation including configurational interaction would be prohibitively long. One-electron ligand-field calculations of *g* factors suggest that either a $^2A_1$ or a $^2B_2$ but not a ^2E state is compatible with the values quoted for β-cobalt phthalocyanine.[17] A MO treatment [18] (without configurational interaction) is unrealistic in that the D_4 symmetry is removed so drastically that calculated *g* factors are g_{zz} 2·05, g_{yy} 1·99, and g_{xx} 2·91 (*cf.* Table 1). Here *g* factors and energy levels of excited states are calculated by use of a ligand-field model and all possible configurations of a d^3 hole system (to which d^7 is equivalent). An identical approach has recently been used by Gerloch *et al.* for the d^8 system in C_{4v} symmetry.[19]

CALCULATIONS

The calculations were based on perturbation of the d^7 configuration by the Hamiltonian

$$\mathscr{H} = H_{\text{electrostatic}} + H_{\text{cubic}} + H_{\text{tetragonal}} + H_{\text{spin-orbit}}$$

with empirical parameters F_2, F_4, *Dq*, *Ds*, *Dt*, and ζ, having their usual definitions.[20] The matrix elements of $\mathscr{H}$ were obtained in the $|SLJM_J\rangle$ scheme and the matrix diagonalized with the aid of an Elliott 4130 computer. *g* Factors and magnetic susceptibilities were calculated from the eigenvectors, using the magnetic-moment operator ($kL + 2S$), modified with two orbital reduction factors, $k_{\|}$, and $k_{\perp}$. The equivalence of d^7 to three *d* positions was used throughout, so that *Dq*, *Ds*, *Dt*, and ζ are negative parameters: hence the use of the modulus in the discussion of their behaviour later. (In fact *Ds* and *Dt* change sign if the axial field becomes greater than the in-plane field, a case not applicable here.)

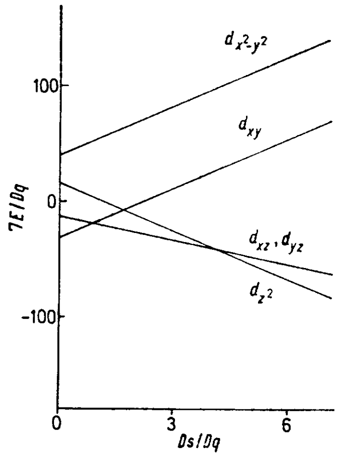

FIGURE 1 Splitting of *d* orbitals in a square planar ligand-field

For square-planar stereochemistry, *i.e.* a tetragonal crystal field with no axial ligands, the parameters *Dq* and *Ds* are sufficient, as $Dt = (4/7)Dq$. Under these circumstances the splitting of the *d* orbital degeneracy has already been given by Bethe [21] (Figure 1). It is clear that with

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[10] S. A. Cockle, H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Biochim. Biophys. Acta*, 1969, **177**, 686; see also J. A. Hamilton, R. L. Blakley, F. D. Looney, and M. E. Winfield, *ibid.*, p. 374, and ref. 11.

[11] G. N. Schrauzer and L.-P. Lee, *J. Amer. Chem. Soc.*, 1968, **90**, 6541.

[12] B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 61.

[13] L. M. Engelhardt, J. D. Duncan, and M. Green, unpublished work.

[14] J. M. Assour, *J. Amer. Chem. Soc.*, 1965, **87**, 4701.

[15] L. D. Rollmann and R. T. Iwamoto, *J. Amer. Chem. Soc.*, 1968, **90**, 1455.

[16] M. Green, J. Smith, and P. A. Tasker, *Discuss. Faraday Soc.*, 1969, **47**, 172.

[17] J. S. Griffith, *Discuss. Faraday Soc.*, 1958, **26**, 81.

[18] G. De Alti, V. Galasso, and A. Bigotto, *Inorg. Chim. Acta*, 1970, **4**, 267.

[19] M. Gerloch, J. Lewis, and W. R. Smail, *J. Chem. Soc.*, 1971 2434.

[20] C. J. Ballhausen, ' Introduction to Ligand Field Theory,' McGraw-Hill, New York, 1962.

[21] H. Bethe, *Ann. Phys.*, 1929, **3**, 133.

this one-electron model the unpaired cobalt d electron must occupy either a d_{x^2} or a d_{xy} orbital (thus an E ground state could only arise by strong configurational interaction). With inclusion of electrostatic repulsion and spin–orbit interaction, the d^7 configuration is split into sixty Kramer's doublets, transforming either as Γ_6 or Γ_7 in the group D'_{4h} (Table 2).[21]

RESULTS AND DISCUSSION

It is impossible to assign precise numbers to parameters for cobalt phthalocyanine. Therefore F_2, F_4, Dq, Ds, and Dt were varied over wide, but not impossible, ranges for low-spin tetragonal cobalt(II) complexes; the resulting g factors are given in the Appendix.* As might be expected the results are more sensitive to changes in the ligand-field parameters, Dq, Ds, and Dt, than to variation in the electron repulsion terms, F_2 and F_4. In a square-planar complex, $Dt = (4/7)Dq$. Introduction of a field due to axial ligands makes $|Dt|$ less than $|(4/7)Dq|$, reduces $|Ds|$, and shifts g factors closer to 2·00. Reduction of ζ below $|-540|$ cm^{-1}, the free-ion value used in most of the results in the Appendix, brings g factors closer to 2·00, the relationship being almost linear (Figure 2). A similar result is observed on reducing $k_{\parallel}$ and $k_{\perp}$ from 1·0 (Figure 2).

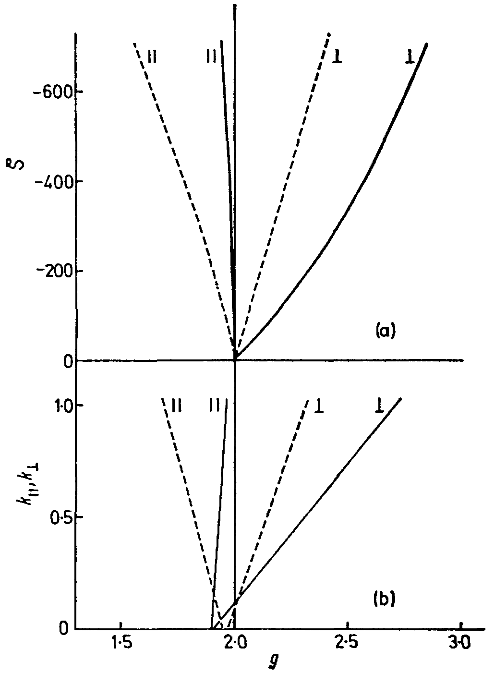

FIGURE 2 (a) Variation of g factors with ζ; $k_{\parallel} = k_{\perp} = 1$. (b) Variation of g factors with k; $\zeta = -540$ cm^{-1}. Dq -1700, F_2 1000, F_4 50 cm^{-1} throughout; dashed line Γ_7 (Ds -6600 cm^{-1}), full line Γ_6 (Ds -6300 cm^{-1})

Spin–orbit coupling removes the distinctive symmetry of the ^2E state. However as the upper Γ_6 and Γ_7 states contain more of the ^2E than the $^1A_1$ and $^2B_2$ states, it is not completely meaningless to say that in terms of the (rather crude) single-configuration ground-state model no evidence for $(d_{xz,yz})^3$ could be found in the compounds considered here.

The parameters F_2 and F_4 do not have a large effect in determining the ground state once the system is low-spin (although they are important in bringing about the change from high-spin). Increase of $|Ds|$ independently of Dq causes a transition from a Γ_6 to a Γ_7 ground state (Figure 3). A reverse effect takes place on increasing $|Dq|$ independently of Ds. Reduction of $|\zeta|$ lowers the value of $|Ds|$ at which the transition occurs (compare Figure 3 and data in the Appendix for F_2 1000, F_4 50, and Dq -1700 cm^{-1}). Naturally $k_{\parallel}$ and $k_{\perp}$ have no effect in determining the ground state.

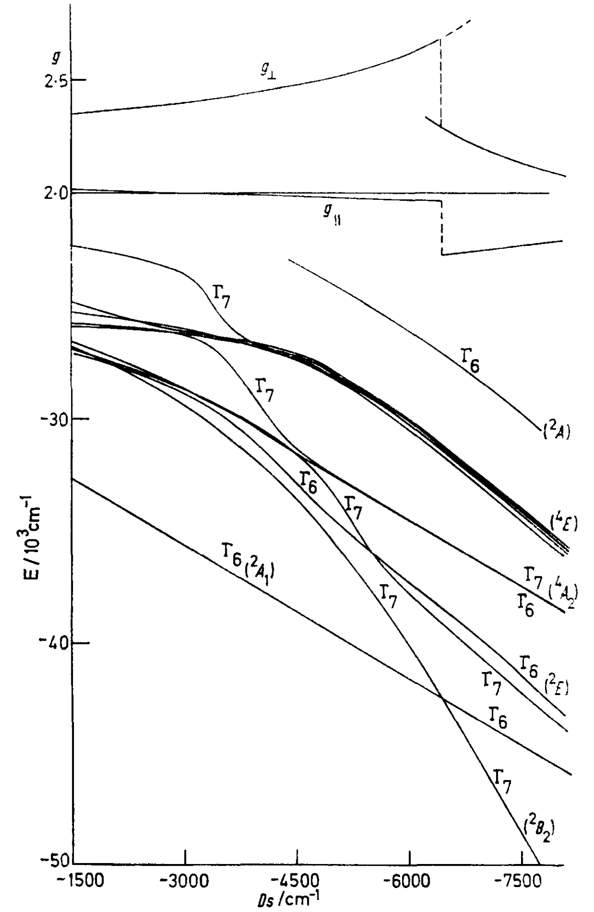

FIGURE 3 Lowest energy-levels and g factors for a d^7 ion in square-planar fields; F_2 1000, F_4 50, Dq -1680, ζ -480 cm^{-1}, $k_{\parallel} = k_{\perp} = 1$

Considering first cobalt corrins and the other [CoN$_4$] complexes with ' normal ' g factors, one can see that these values are compatible only with a Γ_6 ground state, in spite of the large selection of parameters tested. The same follows for the various low-spin [CoN$_2$O$_2$] compounds, which somewhat surprisingly behave as if tetragonal (Table 1) and which resemble vitamin B_{12} in g factors as well as in other properties. In cases where

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* The computer output also includes magnetic moments from 20—400 K and the sixty energy-levels for each set of input parameters. The program has been filed on discs at the Computation Laboratory of the University of York and may be used on request from the Authors.

assignments have been made, these [CoN_4] and [CoN_2O_2] compounds were considered [10,12–14] to have A_1 or Γ_6 ground states, chiefly on the basis of the pronounced tendency of the $g_{\parallel}$ resonance to show superhyperfine splitting due to axial ligands, a property the $g_{\perp}$ absorption did not possess. These calculations confirm this conclusion, for they show that while no unique set of parameters will give observed *g* factors, satisfactory agreement can be reached with several sets all of which result in a Γ_6 ground state. In this context the assignment [22] of a $^2B_2$ or Γ_7 state to derivatives of *NN'*-ethylenebis(salicylideneiminato)cobalt(II) [Co(salen)] on the basis of c.d. studies is surprising, when 'normal' *g* values are shown by the parent compound and its close relatives (Table 2).

In the case of β-cobalt phthalocyanine, the observed *g* values are obtained exactly with one set of parameters and approximately with several others, all of which lead to a Γ_6 state. The data in the Appendix show that increases in $|Ds|$ causes shifts in *g* factors towards the values observed in β-cobalt phthalocyanine as long as the ground state is Γ_6. When the change to Γ_7 occurs, $g_{\perp}$ and $g_{\parallel}$ both fall sharply below the observed values (Figure 3). The data show that the observed *g* factors can only be obtained by use of this model with parameters which inevitably cause a Γ_6 ground state.

In fact, the *g* factors in cobalt phthalocyanine are sensitive to environment; for example, in its α-form and in solution in pyridine, more 'normal' values closer to 2·00 are observed [6,14] (Table 1). Superhyperfine structure [14] in the latter case indicates the presence of pyridine as axial ligands.* However β-cobalt phthalocyanine probably experiences almost no axial co-ordination: the shortest intermolecular length involving the metal atom is Co–N 3·38 Å.[6] The significance of the distance of the axial ligands from the cobalt atom can be seen in the calculations from the relationships, $|Ds| \propto (a^{-3} - b^{-3})$ and $|Dt| \propto (a^{-5} - b^{-5})$, where *a* and *b* (in this context) can be regarded as the equatorial and axial cobalt–ligand distances respectively. Increase in *b* causes rises in $|Ds|$ and $|Dt|$, both of which for a Γ_6 ground state tend to increase $g_{\perp}$ and in general to lower $g_{\parallel}$. For these reasons the abnormal *g* factors in β-cobalt phthalocyanine are attributed to an absence of axial co-ordination (and not to an unusual ground state).

Pictorally the relationship between the axial ligands and *g* factors can be seen as follows. The deviation of *g* factors from 2·00 is primarily due to admixture, *via* spin–orbit coupling, of the Γ_6 or Γ_7 states arising from ^2E, with the ground state. The $\Gamma_6(^2A_1)$ state is equivalent roughly to the $(d_{z^2})^1$ model. Decrease of $|Ds|$ and $|Dt|$ corresponds to approach along the *z* axis of ligands considered as negative point-charges. This raises the energy of the d_{z^2} orbital relative to the $d_{xz,yz}$ orbitals and hence relative to the $\Gamma_6(^2A_1)$ ground state, the $\Gamma_6(^2E)$ becomes less stable. Consequently the ground state has less ^2E character, and the *g* factors tend to 2·00. (Incidentally, in the Γ_6 ground state increase of $g_{\parallel}$ above 2·00 is due solely to contributions from low-lying 'high-spin' states.)

APPENDIX

g Factors calculated from values of F_2, F_4,[a] *Dq*, *Ds*, and *Dt*, with $\zeta = -540$ cm^{-1}, and $k_{\parallel} = k_{\perp} = 1\cdot0$

F_2/ cm^{-1}	F_4/ cm^{-1}	$-Dq$/ cm^{-1}	$-Ds$/ cm^{-1}	Dt/ cm^{-1}	$g_{\parallel}$	$g_{\perp}$	Γ_6 or Γ_7 Ground state
700	35	1000	600	$(2/7)Dq$	2·068	2·209	6
			600	$(4/7)Dq$	2·212	2·421	6
			1800		1·995	2·508	6
			3000		1·963	2·664	6
			4140		1·926	2·905	6
			4200		1·326	2·560	7
			6000		1·569	2·162	7
		1700	1200	$(2/7)Dq$	2·003	2·244	6
			1800	$(4/7)Dq$	2·001	2·399	6
			3000		1·988	2·485	6
			4800		1·974	2·630	6
			5400		1·967	2·701	6
			6600		1·735	2·167	7
			10,200		1·747	2·063	7
		2400	1500		1·997	2·303	6
			1500	−700	2·000	2·185	6
			4500	$(4/7)Dq$	1·990	2·396	6
			6300		1·981	2·500	6
			7500		1·809	2·150	7
			10,500		1·819	2·068	7
700	54	1000	4200	$(4/7)Dq$	1·519	2·365	7
			6000		1·574	2·132	7
			3000		1·946	1·773	6[b]
		1700	1200	$(2/7)Dq$	2·007	2·235	6
			1200	$(4/7)Dq$	2·009	2·395	6
			3000		1·988	2·489	6
			4800		1·970	2·651	6
			6600		1·741	2·136	7
			10,200		1·747	2·057	7
		2400	1500	−700	2·001	2·185	6
			1500	$(4/7)Dq$	1·998	2·305	6
			4500		1·989	2·406	6
			7500		1·814	2·124	7
			10,500		1·820	2·062	7
			14,400		1·821	2·036	7
700	119	1700	3000		1·982	1·522	6[b]
			4800		1·746	2·139	7
			6600		1·749	2·080	7
			10,200		1·748	2·042	7
		2400	1500	−700	2·009	2·167	6
			1500	$(4/7)Dq$	2·019	2·300	6
			4500		1·986	2·438	6
			7500		1·820	2·077	7
			10,200		1·821	2·046	7
1000	50	1700	1200	$(2/7)Dq$	2·012	2·220	6
			1200	$(4/7)Dq$	2·023	2·366	6
			3000		1·995	2·437	6
			6300		1·969	2·713	6
			6600		1·689	2·311	7
		1700	10,200	$(4/7)Dq$	1·746	2·081	7
		2400	1500	−700	2·002	2·180	6
			1500	$(4/7)Dq$	2·001	2·292	6
			4500		1·993	2·370	6
			7500		1·983	2·524	6
			10,500		1·818	2·088	7
	77	1700	1200	$(2/7)Dq$	2·029	2·155	6
			1200	$(4/7)Dq$	2·100	2·304	6
			3000		1·999	2·383	6
			4800		1·981	2·512	6
			6600		1·730	2·207	7
			10,200		1·747	2·069	7

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* Very similar behaviour is shown by cobalt tetra(methoxyphenyl)porphine [8] (see footnote on p. 724).

[22] C. J. Hipp and W. A. Baker, *J. Amer. Chem. Soc.*, 1970, **92**, 792.

F_2/ cm^{-1}	F_4/ cm^{-1}	$-Dq$/ cm^{-1}	$-Ds$/ cm^{-1}	Dt/ cm^{-1}	$g_{\parallel}$	$g_{\perp}$	Γ_6 or Γ_7 Ground state
1000	119		4500		1·967	1·698	6 [b]
			6600		1·747	2·132	7
			10,200		1·748	2·056	7
	77	2400	1500	−700	2·004	2·176	6
			1500	(4/7)Dq	2·007	2·291	6
			4500		1·993	2·378	6
			7500		1·803	2·181	7
			10,500		1·819	2·075	7
	119		1500	−700	2·013	2·157	6
			1500	(4/7)Dq	2·040	2·271	6
			4500		1·993	2·374	6
			7500		1·815	2·119	7
			10,500		1·820	2·060	7
1300	65		1500	−700	2·005	2·173	6
			1500	(4/7)Dq	2·009	2·279	6
			4500		1·996	2·347	6
			7500		1·988	2·476	6
			10,500		1·815	2·120	7
			14,440		1·820	2·054	7
	100		1500	−700	2·013	2·154	6
			1500	(4/7)Dq	2·036	2·263	6
1300			4500		1·997	2·341	6
			7500		1·986	2·488	6
			10,050		1·818	2·094	7
			14,400		1·820	2·047	7
	119		1500	−700	2·021	2·125	6
			1500	(4/7)Dq	2·100	2·233	6
			4500		1·998	2·318	6
			7500		1·981	2·475	6
			10,500		1·819	2·083	7
			14,400		1·821	2·044	7
1590			1500	−700	2·035	2·071	6
			1500	(4/7)Dq	2·448	2·165	6 [b]
			4500		2·002	2·246	6
			7500		1·990	2·371	6
			10,500		1·816	2·123	7
			14,400		1·820	2·055	7

[a] The ' free-ion ' values of F_2 and F_4 are 1550 and 119 cm^{-1} respectively. [b] These states contain a large contribution from one of the quartet configurations.

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