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Theoretical calculations of ^{95}Mo-NMR chemical shifts for compounds $[MoO_{4-n}S_n]^{2-}$

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Summary. Theoretical calculation of ^{95}Mo-NMR chemical shifts for $[MoO_{4-n}S_n]^{2-}$ ($n = 0$–4) compounds is reported here for the first time on the basis of Fenske–Hall method and Sum-Over-State (SOS) perturbation theory. A systematic decrease in shielding of ^{95}Mo nuclei with increase of number of sulfur in $[MoO_{4-n}S_n]^{2-}$, which is observed experimentaly, can be reasonably explained by our calculation. A good linear relationship between chemical shifts of calculation and experiment is obtained. The electronic structure and bonding in these compounds are also discussed.

Key words: ^{95}Mo-NMR chemical shift – Compounds $[MoO_{4-n}S_n]^{2-}$

1. Introduction

^{95}Mo has a relatively high natural abundance (15.7%), good NMR receptivity (better than ^{13}C), and quadrupole moment (-0.019×10^{-28} m^2, similar to that of ^{14}N). Chemical application of ^{95}Mo and ^{97}Mo ($I = 5/2$) NMR was initiated in 1975 by Vold [1] to study the protonation behavior of $[MoO_4]^{2-}$ in the pH range 7–12. Soon after, Lutz, Nolle, and their coworkers investigated the ^{95}Mo-NMR spectroscopies of $Mo(CO)_6$, $[Mo(CN)_8]^{4-}$, and $[MoO_{4-n}S_n]^{2-}$ ($n = 0$–4) [2]. Recently, the study of ^{95}Mo-NMR has further developed [3, 4]. Although a lot of ^{95}Mo-NMR data have been accumulated, theoretical calculations of ^{95}Mo-NMR chemical shifts have not been found in the literature. The results obtained by Fenske–Hall method and SOS perturbation theory are reported in this paper for the first time.

2. Method of calculation

An approximation to the Hartree–Fock–Roothaan technique, the Fenske–Hall method, which is rather rigorous has been described elsewhere [5]. Formulas for

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calculating the NMR shielding constant, σ, on the basis of SOS perturbation theory are first proposed as follows [6]:

$$\sigma = \sigma_d + \sigma_p \tag{1}$$

$$\sigma_d = \frac{2a^2}{3} \sum_i^{\mathrm{OCC}} \langle \Phi_i^{(0)} | \frac{1}{r_m} | \Phi_i^{(0)} \rangle \tag{2}$$

$$\sigma_p = -\frac{a^2}{3} \sum_i^{\mathrm{OCC}} \sum_k^{\mathrm{UNC}} \left[\langle \Phi_i^{(0)} | \frac{L_m}{r_m^3} | \Phi_k^{(0)} \rangle \cdot \langle \Phi_k^{(0)} | L_m | \Phi_i^{(0)} \rangle + \langle \Phi_i^{(0)} | L_m | \Phi_k^{(0)} \rangle \cdot \langle \Phi_k^{(0)} | \frac{L_m}{r_m^3} | \Phi_i^{(0)} \rangle \right] \Big/ (E_k^{(0)} - E_i^{(0)}) \tag{3}$$

in which, σ_d and σ_p are diamagnetic and paramagnetic contributions, respectively. $\Phi_s^{(0)}$ is the eigenfunction of the ground state; r_m is the distance between the mth electron and the magnetic nuclei: L_m is an operator of the angular momentum of the mth electron; a is a constant of 7.297; OCC means occupied orbitals and UNC means unoccupied orbitals; $E_s^{(0)}$ is the eigenvalue of the ground state. Equation (2) can be simplified in the Fenske–Hall approximation:

$$\sigma_d = \frac{2a^2}{3} \sum_i^{\mathrm{OCC}} \langle \Phi_i'^{(0)} | \frac{1}{r_m} | \Phi_i'^{(0)} \rangle + \sigma_{dmc} + \sigma'_{dc} \tag{2'}$$

wherein, σ_{dmc} is a contribution from the core electrons belonging to the magnetic nuclei, which is a constant. σ_{dc} is a contribution of core electrons belonging to other atoms surrounding the magnetic nuclei. $\Phi_j^{(0)}$ is an MO consisting of valence atomic orbitals. σ'_{dc} can be also simply calculated by point-charge approximation, written as:

$$\sigma'_{dc} = \sum_i \frac{2a^2}{3} \frac{N_i}{R_i} \tag{4}$$

in which, N_i is the number of core orbitals for the ith atom, R_i is the distance between the magnetic nuclei and the ith atom. Summation is carried out over all atoms surrounding the magnetic nuclei. By analogy, $\Phi_j^{(0)}$ can be substituted with $\Phi_i'^{(0)}$.

3. Results and discussion

The geometric data of $[\mathrm{MoO}_{4-n}\mathrm{S}_n]^{2-}$ ($n = 0$–4) are taken from [7–9]. Fenske–Hall parameters employed in the calculation are given in Table 1.

The successive substitution of oxygen, O, in $[\mathrm{MoO}_{4-n}\mathrm{S}_n]^{2-}$ by sulfur, S, results in a change of the symmetry from T_d to C_{3v}, C_{2v}, C_{3v}, and T_d, respectively. So, the orbital interaction in these compounds makes a corresponding change, too. For instance, the e irreducible representation in T_d point group represents π interaction, however, σ and π mixed interaction in C_{3v} instead. MO energies and compositions for $[\mathrm{MoO}_{4-n}\mathrm{S}_n]^{2-}$ compounds are summarized in Table 2.

For MoS_4^{2-} compound, as seen in Table 2, the LUMO, $2e$, with main composition of d orbitals of Mo, is π^*-antibonding interaction between d orbitals of MO and p orbitals of S (see Fig. 1a), and $1e$ is π-bonding interaction between d orbitals of MO and p orbitals of S (see Fig. 1b). The HOMO, $3t_2$, is

Table 1. Fenske–Hall parameters

	$\xi(\xi')$													
Atom	1*s*	2*s*	2*p*	2*p*(ξ')	3*s*	3*p*	3*p*(ξ')	3*d*	4*s*	4*p*	4*d*	4*d*(ξ')	5*s*	5*p*
S	15.44271	5.4605	5.68105		2.1045	2.3228	1.32765							
O	7.555	2.25	3.68127	1.65372										
$\mathrm{Mo}^{(0)}$	141.141	16.132	18.545		8.495	8.48		8.524	4.178	3.843	4.31	2.223	2.0	1.80
$\mathrm{Mo}^{(\mathrm{IV})}$[a]	141.138	16.143	18.543		8.49	8.478		8.522	4.248	3.938	6.154	2.812	2.0	1.80

[a] In the compounds $[\mathrm{MoO}_{4-n}\mathrm{S}_n]^{2-}$, although the formal oxidation number of Mo is VI, Fenske–Hall parameter of Mo(IV) is used in our calculation due to consideration of Mo-O or Mo-S covalence

a weak π interaction among p orbitals of S with a little bit of mixing from orbitals of Mo magnetic nuclei. $2a_1$ is responsible for a weak σ interaction between p orbitals of S and s orbitals of Mo, and $2t_2$ for strong σ interaction between p orbitals of S and d orbitals of Mo (see Fig. 1c). $1t_2$ mainly consists of S atoms. The electronic structure and bonding of the other compounds is quite similar to that of MoS_4^{2-}, as shown in Table 2. The MO related diagram among these compounds is pictured in Fig. 2.

The difference in net charge on Mo, which is changed from 2.377 to 2.215, 2.041, 1.864 and 1.714 by successive substitution of O with S, is due to stronger electronegativity of oxygen, compared with sulfur.

It should be mentioned that the MO energies calculated by us are different from those recently computed by the X_α method [10] in an absolute sense. However, a parallel relation in order of MO energies obtained by the two methods is always kept, and the same conclusions on the electronic structure and bonding for these compounds can be drawn out qualitatively.

σ_{dMoc} in Eq. (2′), a contribution from core electrons of Mo magnetic nuclei itself is easily calculated to be $\sigma_{dMoc} = 4004.4$ ppm. σ'_{dc} in (2′), as mentioned above, can be calculated by two ways. The σ_{dc} together with $\langle 1/r \rangle$ listed in Table 3 are calculated by the program employed by us. The σ'_{dc} listed in Table 4 are obtained according to Eq. (4). Both results are almost shown the same values. The first term in Eq. (2′), a contribution from all valence MO designated by σ'_d together with $\langle 1/r \rangle$ and $\sigma'_d + \sigma'_{dc}$ are collected in Table 5. Comparing the $\langle 1/r \rangle$ values from $2t_2$ orbitals of MoS_4^{2-} and MoO_4^{2-}, it will be found that some details of electronic structure in these compounds can be shown clearly. $2t_2$ orbital is of strong σ bonding between d orbital of Mo and p orbital of S or O, as described above. Since $\langle 1/r \rangle = 1.21862$ for $2t_2$ orbitals of MoS_4^{2-} is greater than $\langle 1/r \rangle = 1.0837$ for $2t_2$ orbital of MoO_4^{2-}, it is expected that the electronic density of the σ bonding region for $2t_2$ orbital of MoS_4^{2-} is greater and closed to Mo magnetic nuclei, compared with that of MoO_4^{2-}. A good linear relationship between the net charges on Mo and $\sigma'_d + \sigma'_{dc}$ values for these compounds is given in Fig. 3.

The paramagnetic contributions, σ_p, from significant transitions are summarized in Table 6. As seen from the Table, the $2t_2$-$2e$ transitions in MoO_4^{2-} and MoS_4^{2-} compounds make major contribution to σ_p (over 40% of σ_p). This transition is responsible for transferring σ-bonding interaction to π^*-antibonding interaction. The next major transitions come from $2t_2$-$4t_2$ and $1e$-$4t_2$, associated with σ-σ^* and π-σ^*, respectively. The transitions in MoOS_3^{2-}, $\mathrm{MoO}_2\mathrm{S}_2^{2-}$, and

Table 2. MO energies and compositions of $[MoO_{4-n}S_n]^{2-}$

	MoO_4^{2-} (T_d)						MoS_4^{2-} (T_d)					
MO	Levels (eV)	Compositions					Levels (eV)	Compositions				
		(Mo) *s*	*p*	*d*	(O) *s*	*p*		(Mo) *s*	*p*	*d*	(S)*s*	*p*
$4t_2$	11.56		0.129	0.595	0.002	0.274	4.76		0.094	0.609	0.002	0.285
$2e^a$	7.57			0.736		0.264	2.56			0.750		0.250
$3t_2$	2.23		0.028	0.003		0.970	−1.52		0.052	0.038		0.910
$1t_1$	2.05					1.000	−0.54					1.000
$2a_1$	1.67	0.085				0.914	−2.85	0.134			0.010	0.856
$1e$	0.97			0.264		0.736	−2.11			0.250		0.750
$2t_2$	−1.43			0.297	0.019	0.684	−3.43		0.023	0.288	0.022	0.667
$1a_1$	−16.30	0.052			0.948		−13.71	0.087			0.913	
$1t_2$	−16.53		0.02	0.034	0.945		−13.62		0.042	0.030	0.928	

	$MoO_2S_2^{3-}$ (C_{2v})							
	Levels (eV)	(Mo) *s*	*p*	*d*	(O) *s*	*p*	(S) *s*	*p*
$8a_1$	7.55	0.001	0.106	0.607		0.189		0.096
$5b_2$	6.333		0.091	0.628		0.084	0.003	0.194
$3a_2$	4.42			0.741		0.155		0.104
$7a_1^a$	4.40		0.002	0.741		0.142		0.115
$4b_1$	0.26		0.004	0.005		0.039		0.952
$2a_2$	0.06			0.014		0.213		0.773
$4b_2$	0.06		0.019	0.005		0.049		0.927
$6a_1$	−0.23	0.001	0.033	0.025		0.218		0.723
$3b_1$	−0.53		0.015	0.002		0.969		0.014

$3b_2$	−0.66		0.056	0.006		0.795		0.143
$5a_1$	−1.25	0.111	0.010	0.003		0.208	0.007	0.659
$2b_1$	−1.46		0.005	0.244		0.618		0.133
$1a_2$	−1.48			0.245		0.632		0.122
$4a_1$	−2.35		0.012	0.297		0.076	0.021	0.594
$3a_1$	−3.37		0.003	0.294	0.010	0.535	0.011	0.147
$2b_2$	−4.07			0.302	0.020	0.678		
$1b_1$	−12.36		0.031	0.030			0.939	
$2a_1$	−12.37	0.037	0.016	0.016			0.931	
$1b_2$	−19.17		0.033	0.035	0.932			
$1a_1$	−19.10	0.035	0.016	0.017	0.932			

	MoO_3S^{2-} (C_{3v})								$MoOS_3^{2-}$ (C_{2v})							
MO	Levels (eV)	(Mo) *s*	*p*	*d*	(O) *s*	*p*	(S) *s*	*p*	Levels (eV)	(Mo) *s*	*p*	*d*	(O) *s*	*p*	(S) *s*	*p*
$7e$	10.03		0.128	0.490	0.002	0.262		0.019	5.29		0.089	0.260		0.051	0.002	0.239
$6a_1$	8.23	0.001	0.097	0.627		0.169	0.002	0.102	7.05		0.118	0.593	0.001	0.184	0.001	0.103
$6e^a$	5.84			0.738		0.216		0.046	3.28		0.001	0.743		0.073		0.183
$5e$	0.95		0.011	0.005		0.130		0.854	−0.47		0.005	0.011		0.085		0.899
$4e$	0.62		0.019	0.002		0.977		0.002	−1.13		0.041	0.061		0.166		0.732
$1a_2$	0.59					1.000			−0.22							1.000
$5a_1$	0.58	0.002	0.042	0.008		0.913		0.035	−0.79	0.001	0.036	0.014		0.037		0.912
$4a_1$	−0.06	0.097	0.011			0.463	0.003	0.426	−2.15	0.126	0.006	0.003		0.078	0.013	0.774
$3e$	−0.50			0.259		0.668		0.073	−2.08		0.013	0.204		0.564		0.219
$3a_1$	−1.93		0.005	0.289	0.004	0.365	0.016	0.320	−4.55		0.003	0.295	0.015	0.620	0.006	0.061
$2e$	−2.96			0.301	0.019	0.673		0.007	−2.97		0.015	0.299		0.058	0.021	0.607
$2a_1$	−11.44	0.017	0.019	0.023			0.940		−13.10	0.061	0.009	0.009			0.921	
$1a_1$	−17.90	0.046	0.006	0.009	0.939				−20.02	0.020	0.029	0.025	0.926			
$1e$	−18.04		0.026	0.035	0.939				−13.06		0.037	0.029			0.934	

[a] LUMO

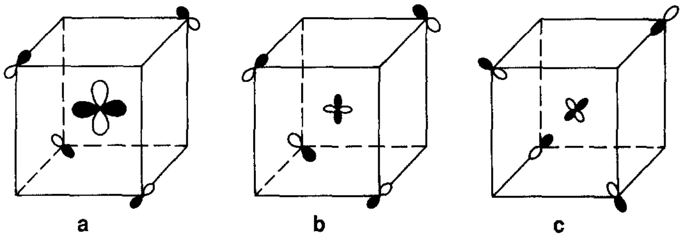

Fig. 1a–c. In MoS_4^{2-} **a** one of the $2e$ orbitals shows π-antibonding interaction between the $Mo(d_{X^2-Y^2})$ and ligand p orbitals; **b** one of the $1e$ orbitals shows π-bonding interaction between the $Mo(d_{X^2-Y^2})$ and ligand p orbitals; **c** one of the $2t_2$ orbitals shows σ-bonding interaction between $Mo(d_{XY})$ and ligand p orbitals

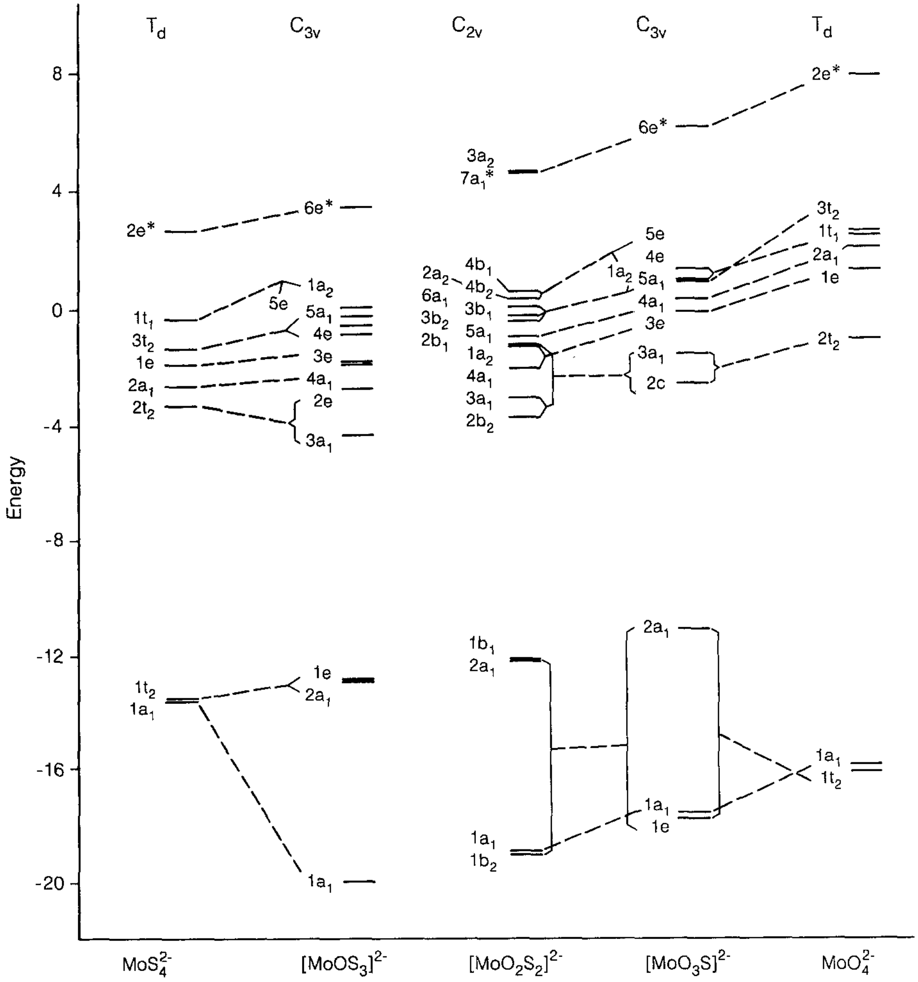

Fig. 2. MO related diagram for $[MoO_{4-n}S_n]^{2-}$ compounds

Table 3. Diamagnetic contributions σ'_{dc} of the electrons of O and S atomic core orbitals

n	0	1	2	3	4
Atom	$\langle 1/r\rangle$	$\langle 1/r\rangle$	$\langle 1/r\rangle$	$\langle 1/r\rangle$	$\langle 1/r\rangle$
O	1.19588	0.89691	0.61574	0.29646	
S		1.21653	2.43846	3.6446	4.88104
σ'_{dc}	42.455 ppm	75.029 ppm	108.427 ppm	139.912 ppm	173.282 ppm

Table 4. σ'_{dc} calculated with Eq. (4)

n	0	1	2	3	4
Atom	N/R	N/R	N/R	N/R	N/R
O	1.19586	0.8969	0.6157	0.29645	
S		1.2165	2.438	3.6445	4.877
σ'_{dc}	42.455 ppm	75.029 ppm	108.409 ppm	139.908 ppm	173.138 ppm

Table 5. Diamagnetic contributions σ'_d of $[\mathrm{MoO}_{4-n}\mathrm{S}_n]^{2-}$

	T_d			C_{3v}			C_{2v}
	$n=0$	4		1	3		2
MO	$\langle 1/r\rangle$	$\langle 1/r\rangle$	MO	$\langle 1/r\rangle$	$\langle 1/r\rangle$	MO	$\langle 1/r\rangle$
$1t_2$	0.93620	0.69880	$1a_1$	0.30782	0.30849	$1a_1$	0.31936
$1a_1$	0.30395	0.21816	$2a_1$	0.25777	0.25819	$1b_2$	0.32365
$2t_2$	1.0837	1.21862	$1e$	0.62648	0.52173	$2a_1$	0.25948
$1e$	0.72725	0.66217	$3a_1$	0.35614	0.29892	$1b_1$	0.26185
$2a_1$	0.24722	0.24743	$2e$	0.76056	0.70419	$2b_2$	0.33713
$1t_1$	0.93052	0.70838	$4a_1$	0.17770	0.20510	$3a_1$	0.33600
$3t_2$	0.84424	0.79396	$3e$	0.71821	0.68594	$1a_2$	0.36922
			$4e$	0.59011	0.52294	$4a_1$	0.37037
			$5a_1$	0.25217	0.20625	$2b_1$	0.35670
			$5e$	0.50639	0.50671	$3b_2$	0.29069
			$1a_2$	0.32661	0.28786	$5a_1$	0.21251
						$3b_1$	0.28090
						$6a_1$	0.21840
						$4b_2$	0.25067
						$2a_2$	0.31790
						$4b_1$	0.27058
σ'_d	180.1 ppm	161.442 ppm	σ'_d	173.239 ppm	159.98 ppm	σ'_d	161.78 ppm
$\sigma'_d+\sigma'_{dc}$	222.555 ppm	334.724 ppm		248.268 ppm	299.892 ppm		270.207 ppm

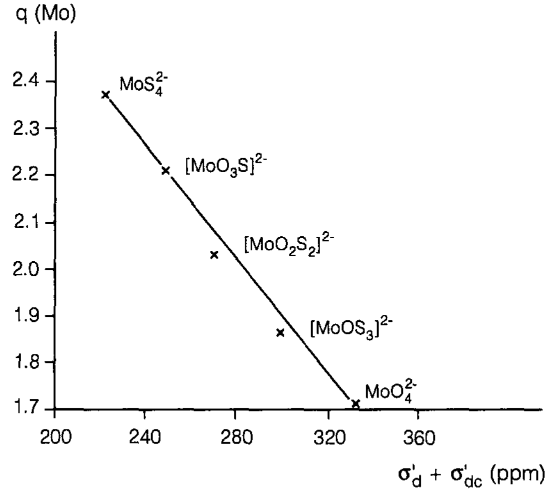

Fig. 3. Relationship between the charges on Mo and $\sigma'_d + \sigma'_{dc}$ for these compounds

MoO_3S^{2-} are similar to that of MoS_4^{2-}, which can be analyzed from related MO's. However, it is noteworthy that the contribution from $3t_2$-$2e$ transition to σ_p in MoS_4^{2-} and MoO_4^{2-} are quite different (−251.691 ppm for MoS_4^{2-} and −0 for MoO_4^{2-}). The $3t_2$ orbital shares to 91% the character of the *p* orbital of sulfur, and the $2e$ orbital to 75% resembles the character of the *d* orbitals of Mo. The transition of $3t_2$-$2e$ is a result of the electron transfer from S to Mo(LMCT), decreasing in shielding of Mo magnetic nuclei. That is one of the reasons why shielding of Mo nuclei decreases with increase of the number of S in $[MoO_{4-n}S_n]^{2-}$ compounds. Another reason for this is that the energy gap among transition orbitals decreases with increase of S, as it is shown that $\sigma_p \propto -1/\Delta E$.

The experimental δ_{exp} and calculated δ_{cal} of chemical shifts for $[MoO_{4-n}S_n]^{2-}$ compounds are given in Table 7. A good linear relationship between δ_{exp} and δ_{cal} can be found in Fig. 4.

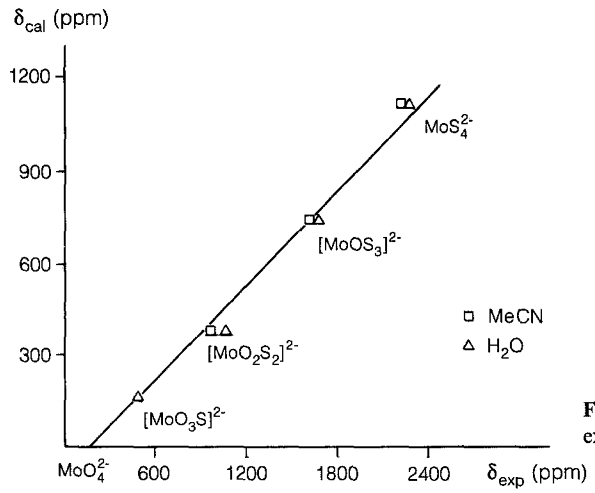

Fig. 4. Calculated chemical shifts vs experimental values

Table 6. Paramagnetic contributions σ_p from some important transitions

n	Transitions	$\left\langle \frac{L}{R^3} \right\rangle \cdot \langle L \rangle$	$-\sigma_p$ (ppm)	% Contributions	Transitions	$\left\langle \frac{L}{R^3} \right\rangle \cdot \langle L \rangle$	$-\sigma_p$ (ppm)	% Contributions
0	$2t_2 \rightarrow 2e$	8.6403	927.553	49.29	$2t_2 \rightarrow 4t_2$	3.62	269.06	14.3
	$1e \rightarrow 4t_2$	6.1670	561.799	29.85	…	…	…	…
					total		1881.99	
1	$2e \rightarrow 6e$	6.1658	677.368	32.74	$3e \rightarrow 6a_1$	2.1003	232.311	11.23
	$2e \rightarrow 6a_1$	1.1618	103.081	4.98	$3e \rightarrow 7e$	3.4867	319.738	15.46
	$2e \rightarrow 7e$	1.5020	111.655	5.40	…	…	…	…
	$3a_1 \rightarrow 6e$	2.8001	347.983	16.82				
	$3a_1 \rightarrow 7e$	1.0283	83.025	4.01	total		2068.8	
2	$2b_2 \rightarrow 7a_1$	2.2286	254.076	11.02	$4a_1 \rightarrow 7a_1$	2.1604	308.981	13.40
	$2b_2 \rightarrow 3a_2$	0.8459	96.196	4.17	$4a_1 \rightarrow 3a_2$	0.7024	100.174	4.34
	$2b_2 \rightarrow 5b_2$	0.8194	76.062	3.30	$1a_2 \rightarrow 8a_1$	0.5520	68.251	2.96
	$2b_2 \rightarrow 8a_1$	1.4924	124.054	5.38	$1a_2 \rightarrow 5b_2$	2.3736	254.018	11.02
	$3a_1 \rightarrow 3a_2$	2.5042	310.314	13.46	$2b_1 \rightarrow 5b_2$	1.6242	201.275	8.73
	$3a_1 \rightarrow 5b_2$	0.7293	72.567	3.15	…	…	…	…
	$2b_1 \rightarrow 5b_1$	1.4193	135.207	5.86	total		2305.6	
3	$3a_1 \rightarrow 6e$	1.9619	242.034	8.96	$2e \rightarrow 7e$	0.7483	87.476	3.24
	$3a_1 \rightarrow 7e$	1.1087	108.778	4.03	$2e \rightarrow 6a_1$	1.8451	177.811	6.58
	$2e \rightarrow 6e$	6.7238	1039.816	38.475	$3e \rightarrow 7e$	4.0024	524.181	19.40
	$3e \rightarrow 6a_1$	1.5164	160.284	5.93				
	…	…	…	…	total		2702.6	
4	$2t_2 \rightarrow 2e$	8.6674	1397.234	45.00	$3t_2 \rightarrow 2e$	1.0635	251.691	8.11
	$2t_2 \rightarrow 4t_2$	3.8514	454.096	14.63	…	…	…	…
	$1e \rightarrow 4t_2$	6.0787	853.788	27.50	total		3104.9	

Table 7. ^{95}Mo-NMR chemical shifts δ_{exp} and δ_{cal} for $[MoO_{4-n}S_n]^{2-}$

Ions	Charge of Mo atom	δ_{exp} (ppm)		δ_{cal} (ppm)
		H_2O	MoCN	
MoO_4^{2-}	2.377	0		0
$[MoO_3S]^{2-}$	2.215	497		161.1
$[MoO_2S_2]^{2-}$	2.041	1066	964	376.0
$[MoOS_3]^{2-}$	1.864	1654	1587	743.3
MoS_4^{2-}	1.714	2258	2207	1110.7

The trend obtained by experimental observations can be satisfactorily explained by our theoretical study and, of course, the difference between δ_{exp} and δ_{cal} in an absolute sense is evident, but quite reasonable, as it is well known that the MO energies, especially vacant MO energies, cannot be calculated correctly. However, the values of σ_p in Eq. (3) obtained by SOS are largely dependent on the difference in energy among transition orbitals. Besides, the Fenske–Hall parameters chosen for the calculation also affect the results. For instance, if 4*d* orbital parameters of $Mo^{(0)}$, instead of $Mo^{(IV)}$, are used for calculation, a linear relationship between δ_{exp} and δ can also be kept, but the values of δ_{cal} are much lower than that of δ_{exp}. If 3*d* orbitals are involved for the sulfur atom, it is found that δ will increase by about 10 ppm for each sulfur atom.

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