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Investigation of Variations of Isotropic g- and A- Values with Orientation of Trapped O_2^-, N_2^- and Cl_2^- Radicals in KCl and NaCl Crystals

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ABSTRACT

We have theoretically studied the electron paramagnetic resonance (EPR) properties of paramagnetic O_2^-, N_2^- and Cl_2^- centers in the KCl and NaCl crystals. The calculations have been performed by the density functional theory (DFT) method with the B3LYP correlation functional at 6-31 G(d) level. The attention has been focused on the calculation of the variations of the EPR parameters such as the isotropic g- and A-values. These parameters were satisfactorily calculated for all three species with the orientation of the trapped radicals along all three axes of the crystals for the first time. Namely the molecular axis of the paramagnetic anions was oriented along the x, y and z directions of the crystallographic axes, which can experimentally never be done, and the variations of the EPR parameters were theoretically determined and analyzed as if the each of them is a tensor. And then their principal values and direction cosines were obtained. It was concluded that the anisotropy of the g- and A-values increases while the bond length of the molecular anion radical increases.

Keywords: Radical; DFT; EPR; Tensor; Crystal

INTRODUCTION

Electron paramagnetic resonance (EPR) is a sophisticated spectroscopic technique that detects free radicals in chemical and biological systems. So, it is the most important technique for the study of defect centers in crystalline and amorphous materials for about 50 years [1-3]. In the last years, a large number of combined theoretical and experimental EPR studies have been reported leading to the unambiguous identification of paramagnetic defect centers or adsorbed radical species [4-7]. The main quantities measured in EPR spectra which allow us a direct comparison of theory with experiment are the g-tensor and the A- hyperfine coupling tensor, respectively. Shifts of the g-tensor from the free electron value provide important information about the spin distribution in a paramagnetic center. The A-tensor is directly related to the spin density at nuclear position and, provides detailed information about the spin distribution in a given defect.

The isotropic hyperfine coupling constant is very sensitive to the spin density at nuclear position, so, it is very difficult to compute in a quantitative agreement with the experimental value [8]. The correlation of a radical structure with spin adducts parameters have been studied by Lawrence and et. al. [9]. The hyperfine

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parameters of some radicals have been calculated by using the density function theory (DFT) and configuration-interaction (CI) methods [10]. Some authors have calculated the g- tensors of some organic radicals by Hartree-Fock (HF) method [11]. The EPR parameters (g- and A- tensors) of sulphur centered radicals have been calculated using multi-configurationally self consistent field (MCSCF) response and DFT/B3LYP methods [12]. DFT provides a solid basis for the theoretical description of defect centers in solids. By DFT the combination of experiment and theory works well particularly for the assignment of the g and hyperfine coupling constants for which significant studies has been accumulated over the years. These comparisons largely depend also on the considered radicals. The calculations of the g-tensors for paramagnetic centers in solids are rare [13-17]. Thus, the literature about the reliability of the g-tensor calculations for defects in solids with the presently available approaches is largely incomplete. The calculations of the g-tensor based on DFT have recently been reported in some studies [18-21].

So, the investigation of the variations of the isotropic g - and A -values at DFT(B3LYP)/6-31 G(d) level is the object of this work. They were calculated by orientating of the center-trapped O_2^-, N_2^- and Cl_2^- radicals in the KCl and NaCl crystals along all three axes of the crystals, for the first time. Taking them as tensors it has also been possible to find the molecular axis of the paramagnetic species relative to the crystallographic axes. Their principal values and direction cosines have also been determined.

COMPUTATIONAL DETAILS

The calculations have been performed by the density functional theory with the hybrid B3LYP functional [22, 23] in combination with the 6-31 G (d) basis set. The crystal structures with the paramagnetic O_2^-, N_2^- and Cl_2^- centers have been optimized with no symmetry constraint using the Gaussian 03 set of program [24] and, displayed at Gauss-View molecular visualization program [25]. So, the real positions of the O_2^-, N_2^- and Cl_2^- radicals in the KCl and NaCl crystals have been found by these optimizations. And then, from 0^o to 360^o the orientations of these paramagnetic ions at every 20^o steps along the directions of the x, y and z axes of the crystals have been done, and the EPR parameters (the isotropic g- and A- values) were obtained by NMR calculations with a (non-dynamic) single point structure as taking the charge of 1.

RESULTS AND DISCUSSIONS

The g value of a free electron is g_e= 2.002319304386 [26] and, describes the interaction of the magnetic moment of the electron with the external magnetic field. When the electron is confined in a molecule, the magnetic field at which resonance occurs at a given frequency becomes dependent on the orientation of the molecule with respect to the field. When the orientation of the radical in the magnetic field is changed, the resonance line shifts. In other words the g-factor is generally different from g_e, and so, it is anisotropic. Shortly, the g tensor summarizes the orientation dependence of the g-value. Similarly the hyperfine interaction characterizes interactions between the electron and nuclear spins in the paramagnetic center. If the rotational motion in the magnetic field does not average the orientation of the paramagnetic specie. The interactions have anisotropic components. Hence, the 3 × 3 dimensional g- and **A-** tensors can be separated into its isotropic and anisotropic components. The g- and **A-** tensor components, g_{kl} and A_{kl}, in the Cartesian coordinate axes of a crystal in the first-order approximation are given by the following equations [27, 28],

$$A^2_k(\theta)= A^2_{ii} \cos^2\theta + A^2_{jj} \sin^2\theta + 2\, A^2_{ij} \sin\theta \cos\theta \quad (1)$$

$$g^2_k(\theta)= g^2_{ii} \cos^2\theta + g^2_{jj} \sin^2\theta + 2\, g^2_{ij} \sin\theta \cos\theta.$$

Where i, j, k= x, y, z, respectively, and θ is the angle of rotation in each crystalline plane with respect to the x, y and z directions. The g^2_{ii}, g^2_{jj} and g^2_{ij}, and A^2_{ii}, A^2_{jj} and A^2_{ij} are the g- and A- tensor elements, respectively, which will be found by fitting [29]. The principal values of the g- and A-tensors and their direction cosines are obtained by the diagonalization of these tensors. If the three diagonal components are equal the g- and A-tensors are referred as isotropic, if the only two components are equal, as axial symmetric, and if the three diagonal components are different, as anisotropic.

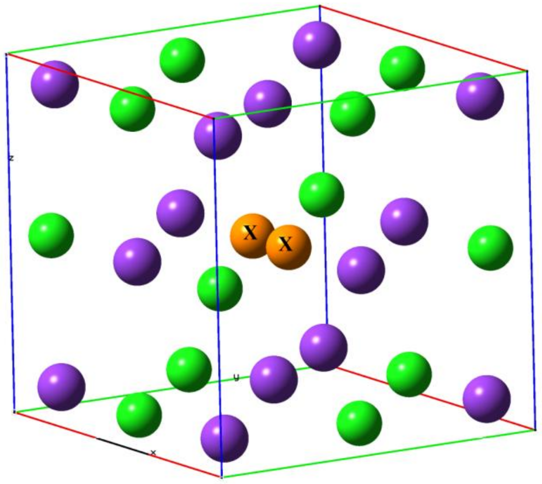
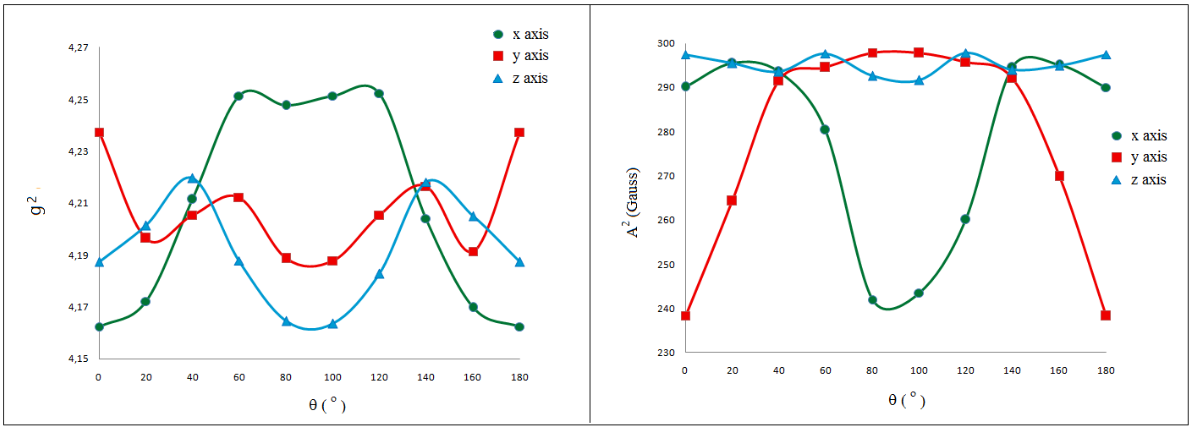


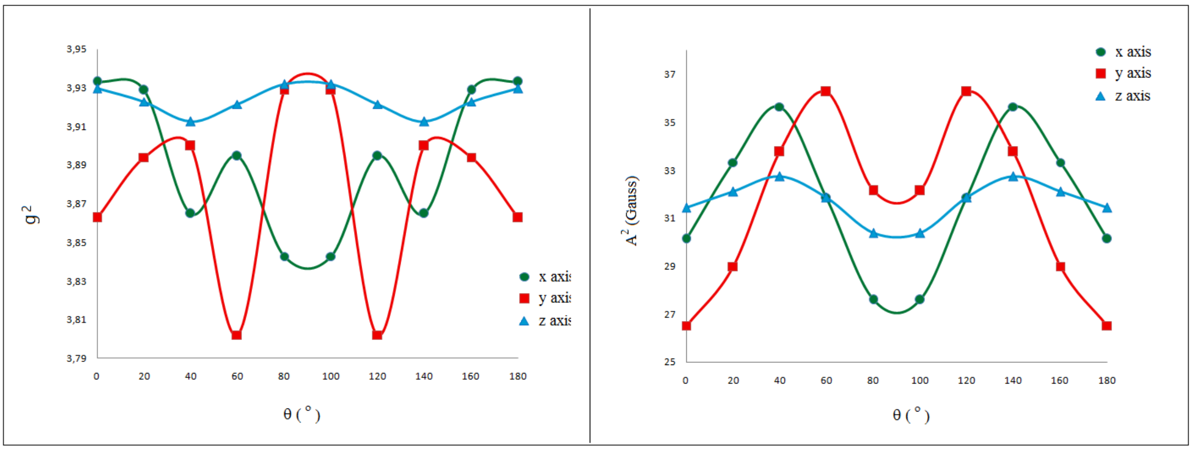
Fig. 1. Optimize structures of KCl crystal with X_2^- = O_2^-, N_2^- and Cl_2^- center.

The paramagnetic centers in the KCl and NaCl crystal are formed by replacing a center Cl^- ion in the lattice with the O_2^-, $N_2^-$and Cl_2^- anions. The formed defects by the addition of the anions to the interstitial cavity can be seen in Fig. 1 and, give an indirect bonds with K or Na and Cl-lattice ions in their optimized state. In this study the anion radicals are oriented along the x, y, z directions of the crystals (see Fig. 1) and, scanned with the changing angles rotated by 20°. This method is different from experimental studies where crystal is oriented around arbitrary axes in magnetic field. The calculated isotropic g^2 and A^2 values of all the radicals are plotted against the rotation angle in three perpendicular planes, and given in Figs. 2 and 3. By taking them as tensors the elements of the g- and A-tensors are found by fitting with Eq. (1). The formed tensors in this way are diagonalized, and their principal values and direction cosines are obtained. The results for all three species are given in Tables 1 and 2. Note that the isotropic values of the g- and A-tensors are very close with those calculated for the optimized structures of the KCl and NaCl crystals with paramagnetic center, which are written in parenthesis in the tables. The experimental isotropic values for the KCl crystal are also given in Table 1 [30]. In addition from the table we can also say that when we take into account the variations of the isotropic g- and A values in the KCl and NaCl crystals as if the each of them is a tensor we see that the N_2^- radicals have nearly isotropic g- and A-tensors, the O_2^- radicals have nearly axial symmetric-, and the Cl_2^- radicals anisotropic-ones, As well known the bond length of the N_2^- is lowest between the used radicals while that of the Cl_2^- is highest. Then we can say that the anisotropy of the g- and A-tensors increases while the bond length of the molecular anion radical increases whatever the host crystal is.

O_2^-



N_2^-



Cl_2^-

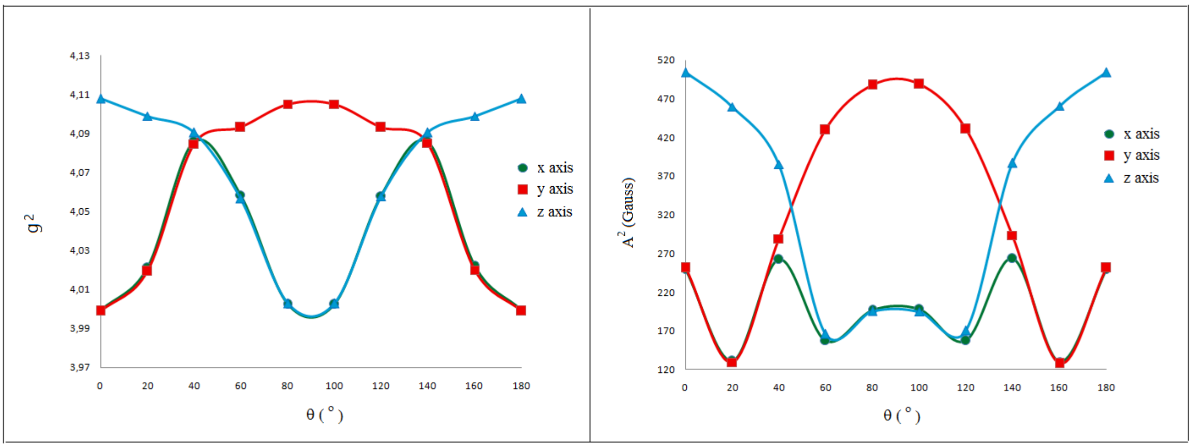
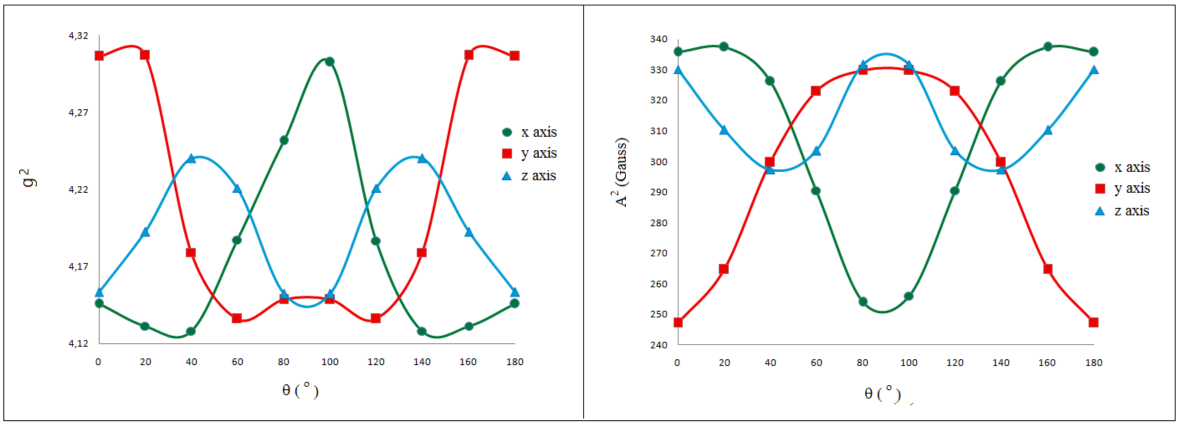
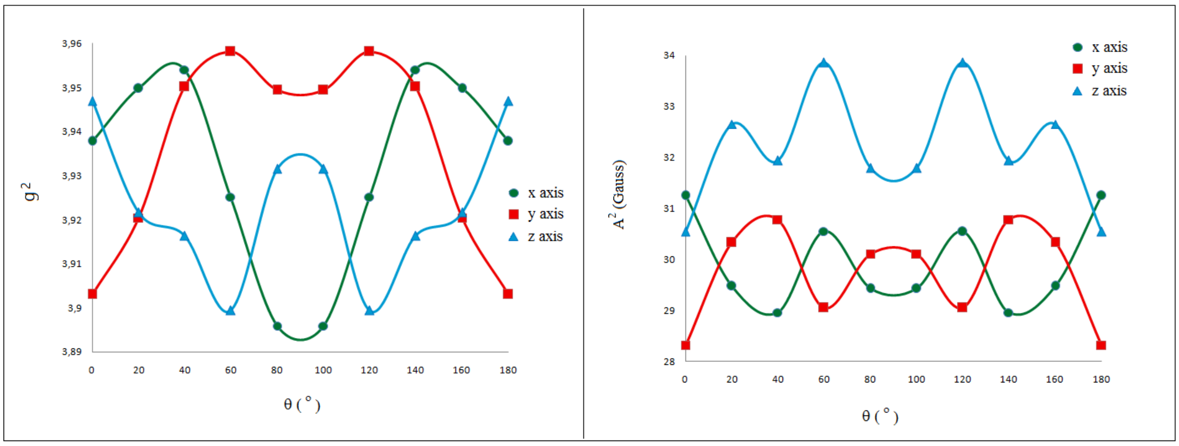


Fig. 2. The angular variations of the g^2- and A^2-values in three crystalline planes of the KCl crystal with O^{-2}, N_2^- and Cl_2^- center, respectively.

O_2^-



N_2^-



Cl_2^-

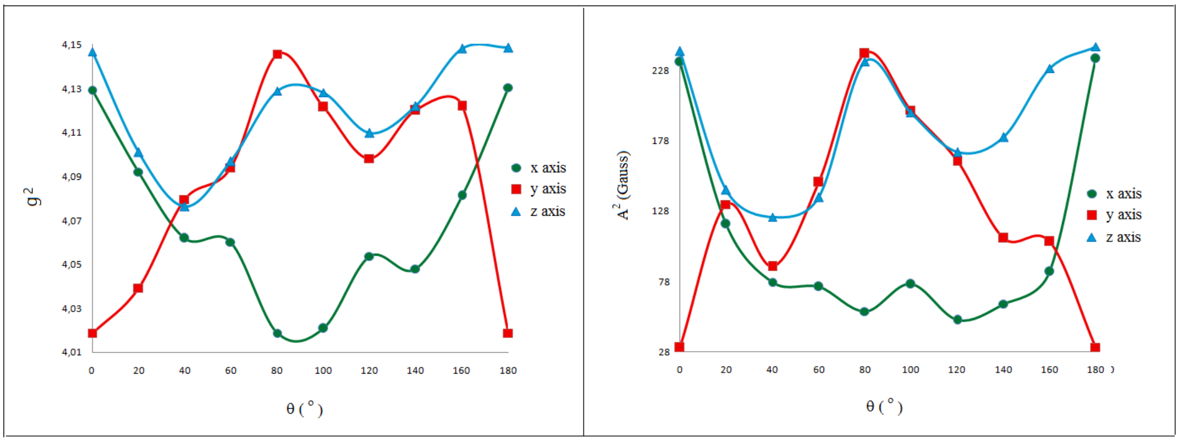


Fig. 3. The angular variations of the g^2- and A^2-values in three crystalline planes of the NaCl crystal with O^{-2}, N_2^- and Cl_2^- center, respectively.

Table 1. The g^2 and A^2 tensors, their principal values and direction cosines for the trapped O_2^-, N_2^- and Cl_2^- radicals in the KCl crystal

		Tensor			Isotropic	Principal Values	Direction Cosines		
O_2^-	g^2	4.1975	0.0017	-0.0007	2.0500	g_{XX}= 2.0688	0.8502	-0.5097	0.1316
		0.0017	4.1688	0.0030	(2.0463)	g_{YY}= 1.9905	0.3075	0.6837	0.6618
		-0.0007	0.0030	4.2409	2.1141[a]	g_{ZZ}= 2.0908	-0.4273	-0.5222	0.7381
	A^2	302.0254	0.0624	-2.2733	16.8363	A_{XX}= 17.4931	0.8772	0.3007	-0.3742
		0.0624	296.8844	7.2121	(17.2496)	A_{YY}= 14.2469	0.4798	-0.5247	0.7032
		-2.2733	7.2121	252.8342	15.9333[a] Gauss	A_{ZZ}= 18.7690	-0.1514	0.7964	0.6046
N_2^-	g^2	3.9008	0	0	1.9738	g_{XX}= 1.9750	1	0	0
		0	3.9261	0	(1.9823)	g_{YY}= 1.9815	0	1	0
		0	0	3.8606	1.9681[a]	g_{ZZ}= 1.9649	0	0	1
	A^2	33.7892	0	0.0010	5.6266	A_{XX}= 5.8124	0.9985	-0.0071	-0.0544
		0	32.1129	0.0003	(5.6067)	A_{YY}= 5.6668	0.0046	0.9989	-0.0458
		0.0010	0.0003	29.1924	3.4000[a] Gauss	A_{ZZ}= 5.4007	0.0547	0.0455	0.9975
Cl_2^-	g^2	4.1170	-0.0005	-0.0004	2.0136	g_{XX}= 2.0416	0.8610	0.5083	0.0187
		-0.0005	4.0217	0	(2.0268)	g_{YY}= 1.9932	-0.3757	0.6603	-0.6503
		-0.0004	0	4.0250	2.0157[a]	g_{ZZ}= 2.0059	-0.3428	0.5529	0.7595
	A^2	499.2276	-2.6756	-2.0002	16.3467	A_{XX}= 22.5886	0.9873	0.1584	0.0075
		-2.6756	177.6390	-0.1488	(22.4453)	A_{YY}= 12.8206	-0.1195	0.7744	-0.6213
		-2.0002	-0.1488	180.2630	36.3333[a] Gauss	A_{ZZ}= 13.6308	-0.1042	0.6126	0.7835

The values in parenthesis are obtained for the optimized structures.

[a] Experimental values [30].

Table 2. The g^2 and A^2 tensors, their principal values and direction cosines for the trapped O_2^-, N_2^- and Cl_2^- radicals in the NaCl crystal

		Tensor			Isotropic	Principal Values	Direction Cosines		
O_2^-	g^2	4.1491	0	0	2.0474	g_{XX}= 1.9894	0	0	1
		0	4.1546	-0.0076	(2.1305)	g_{YY}= 2.1158	0.7830	-0.6220	0
		0	-0.0076	4.2718		g_{ZZ}= 2.0369	0.6220	0.7830	0
	A^2	326.9984	-0.0687	0.0029	17.4478	A_{XX}= 18.3738	-0.5408	0.8412	-0.0016
		-0.0687	330.5367	-0.3312	(18.1696)	A_{YY}= 17.9580	0.8265	0.5317	0.1846
		0.0029	-0.3312	258.8429	Gauss	A_{ZZ}= 16.0115	-0.1561	-0.0986	0.9828
N_2^-	g^2	3.9465	0	0	1.9823	g_{XX}= 1.9866	1	0	0
		0	3.9318	0	(1.9867)	g_{YY}= 1.9829	0	1	0
		0	0	3.9101		g_{ZZ}= 1.9774	0	0	1
	A^2	30.7921	-0.0004	-0.0003	5.5320	A_{XX}= 5.5470	0.9749	0.1030	-0.1976
		-0.0004	31.5587	0	(5.5265)	A_{YY}= 5.4297	0.1978	0.0078	0.9802
		-0.0003	0	29.4955	Gauss	A_{ZZ}= 5.6193	-0.1025	0.9946	0.0128
Cl_2^-	g^2	4.1310	-0.0383	-0.0393	2.0225	g_{XX}= 2.2620	0.6511	0.7546	0.0817
		-0.0383	4.1092	0.0113	(2.0170)	g_{YY}= 1.8627	-0.5508	0.3957	0.7349
		-0.0393	0.0113	4.0317		g_{ZZ}= 1.9428	-0.5222	0.5235	-0.6732
	A^2	206.0502	-56.1281	-0.6926	11.3687	A_{XX}= 19.6165	0.7054	0.6733	-0.2216
		-56.1281	170.8327	22.5877	(13.2779)	A_{YY}= 9.6038	-0.6776	0.5487	-0.4897
		-0.6926	22.5877	45.2999	Gauss	A_{ZZ}= 4.8857	-0.2082	0.4956	0.8432

The values in parenthesis are obtained for the optimized structures.

CONCLUSIONS

In this paper we have theoretically studied the EPR properties of the paramagnetic O_2^-, N_2^- and Cl_2^-centers in the KCl and NaCl crystals. The calculations have been performed by the density functional theory method with the B3LYP correlation functional at 6-31 G(d) level. The variations of the isotropic g- and A-values have been investigated with the orientation of the trapped O_2^-, N_2^- and Cl_2^- radicals along all three axes of both the KCl and NaCl crystals for the first time as if the each of them is a tensor. Namely, the molecular axis of the paramagnetic anions was oriented along the x, y and z directions of the crystallographic axes. So, the principal values and direction cosines of the g- and A-tensors for all three species were obtained. After all these were done it was concluded that the anisotropy of the g- and A-tensors increases while the bond length of the molecular anion radical increases.

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