Investigation of EFG Parameters at the Halogen Site in XO_3 and $XO_3^{2\ominus}$ Radicals ($X = Cl, Br$) in Certain Inorganic Solids*

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Electric field gradients at the halogen site in XO_3 and $XO_3^{2\ominus}$ radicals ($X = Cl, Br$), formed by the γ-irradiation of single crystals of $NaClO_3$, $KClO_3$, $KBrO_3$ and $Sr(BrO_3)_2 \cdot H_2O$ have been evaluated by MO calculations using the CNDO/2 method. The symmetry of the XO_3 radicals is assumed to be that of $XO_3^{\ominus}$ ions which have C_{3v} symmetry, whereas $XO_3^{2\ominus}$ radicals are assumed to have C_s symmetry with one X–O bond distance being stretched due to the excess electron. The results are in good agreement with the experimental values deduced from published ESR studies on these single crystals.

1. Introduction

Investigations of single crystals of $NaClO_3$, $KClO_3$, $KBrO_3$, and $Sr(BrO_3)_2 \cdot H_2O$ after γ-irradiation at 77 K by the ESR technique revealed the formation of XO_3 and/or $XO_3^{2\ominus}$ ($X = Cl, Br$) radicals, and from these studies the electric field gradient (EFG) parameters at the halogen site have been obtained [1–4]. Recently it was demonstrated that the EFG parameters, viz., the nuclear quadrupole coupling constant $e^2 \Phi_{zz} Q h^{-1}$, the asymmetry parameter η, and the orientation of Φ_{zz} with respect to the crystal axes, at the halogen site in $XO_3^{\ominus}$ ($X = Cl, Br, I$) ions, and in $IO_6^{5\ominus}$ may be well predicted from MO calculations [5–7]. Therefore, in the present work, the EFG at $^{35}Cl/^{79}Br$ due to ClO_3, $ClO_3^{2\ominus}$, BrO_3, and $BrO_3^{2\ominus}$ radicals in $NaClO_3$, $KClO_3$, $KBrO_3$, and $Sr(BrO_3)_2 \cdot H_2O$ respectively, has been estimated using the CNDO/2 method and the results have been compared with the ESR experimental data available in the literature.

2. Field Gradient Estimation

The details of the CNDO/2 calculations can be found elsewhere [8]. The configurations of the XO_3 and $XO_3^{2\ominus}$ ($X = Cl, Br$) radicals have been obtained from X-ray crystal structure data of $NaClO_3$, $KClO_3$, $KBrO_3$, and $Sr(BrO_3)_2 \cdot H_2O$ and with the assumptions that the symmetry of the XO_3 radicals is that of the $XO_3^{\ominus}$ ions, and the symmetry of the $XO_3^{2\ominus}$ radical is C_S with one X–O bond being stretched by 10% of the original bond length [3, 9, 10].

3. Results and Discussion

The values of $e^2 \Phi_{zz} Q h^{-1}$, η, and the orientation of Φ_{zz} at the halogen site in the XO_3 and $XO_3^{2\ominus}$ ($X = Cl, Br$) radicals obtained from the CNDO/2 calculations are given in Table 1 along with the experimental values.

From the temperature variation of the $^{35}Cl/^{79}Br$ NQR frequency in the chlorates and bromates from 77 K to 305 K it can be seen that the change in $e^2 \Phi_{zz} Q h^{-1}$ in the temperature range is about 3 to 5 MHz [11, 12]. Therefore, a comparison of the theoretical $e^2 \Phi_{zz} Q h^{-1}$ values with the experimental ESR results at 77 K can be done without loss of generality. In these salts, the $e^2 \Phi_{zz} Q h^{-1}$ value obtained theoretically at the ^{79}Br site in the $BrO_3^{2\ominus}$ radical is slightly smaller than the corresponding experimental value whereas η (^{79}Br) is slightly larger than the experimental value. This may be due to the limitations of the employed calculations and the assumed structure of the $BrO_3^{2\ominus}$ radical. By the shortcomings of the calculations it seems impossible to significantly improve the agreement of $e^2 \Phi_{zz} Q h^{-1}$ and η with the experiment values by adjusting the

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Table 1. Nuclear quadrupole coupling constant $e^2 \Phi_{zz} Q h^{-1}$, asymmetry parameter η, and the direction of Φ_{zz} at the $^{35}\mathrm{Cl}/^{79}\mathrm{Br}$ site in $\mathrm{XO_3}$ and $\mathrm{XO_3^{2\ominus}}$ radicals

Substance	Radical/ion	Method	$\lvert e^2 \Phi_{zz} Q h^{-1} \rvert$ MHz	η	Direction cosines of Φ_{zz} with respect to			Reference
					a	b	c	
$\mathrm{NaClO_3}$	$\mathrm{ClO_3}$	Experimental	42.00	0.00	–	–	–	[1]
		CNDO/2	33.78	0.00	−0.577	0.577	0.577	This paper
	$\mathrm{ClO_3^{\ominus}}$	Experimental	59.96	0.00	−0.577	0.577	0.577	[13]
		CNDO/2	44.22	0.00	−0.577	0.577	0.577	This paper
$\mathrm{KClO_3}$	$\mathrm{ClO_3^{2\ominus}}$	Experimental	–	–	–	–	–	[2]
		CNDO/2	44.90	0.10	0.739	0.000	−0.881	This paper
$\mathrm{KBrO_3}$	$\mathrm{BrO_3^{\ominus}}$	Experimental	346.22	–	–	–	–	[14]
		CNDO/2	366.98	0.00	0.000	0.000	1.000	This paper
	$\mathrm{BrO_3^{2\ominus}}$	Experimental	682.29	0.260	–	–	–	[3]
		CNDO/2	419.15	0.340	−0.504	1.000	0.000	This paper
$\mathrm{Sr(BrO_3)_2 \cdot H_2O}$	$\mathrm{BrO_3^{2\ominus}}$	Experimental	502.74	0.400	–	–	–	[4]
		CNDO/2	410.62	0.460	0.138	−0.448	0.518	This paper

stretching and thus predicting the exact geometrical deformation in the $\mathrm{BrO_3^{2\ominus}}$ radical.

The η (^{35}Cl) value of the $\mathrm{ClO_3}$ radical in $\mathrm{NaClO_3}$ is zero, and the orientation of Φ_{zz} is the same as that obtained for the $\mathrm{ClO_3^{\ominus}}$ ion. This shows that η and the orientations of the EFG axes depend only on the geometry of the radical and not on the charge distribution.

The MO calculations on $\mathrm{XO_3^{\ominus}}$ (X = Cl, Br) in $\mathrm{KClO_3}$ and $\mathrm{Sr(BrO_3)_2 \cdot H_2O}$ have given EFG parameters at the halogen site close to the NQR experimental results [5]. The present calculations of $e^2 \Phi_{zz} Q h^{-1}$ and η at the $^{35}\mathrm{Cl}/^{79}\mathrm{Br}$ site in $\mathrm{NaClO_3}$ and $\mathrm{KBrO_3}$ due to $\mathrm{XO_3^{\ominus}}$ (X = Cl, Br) have given a fair agreement with the corresponding NQR experimental values [13, 14].

The CNDO/2 calculations on the divalent hydrated bromates $\mathrm{Zn(BrO_3)_2 \cdot 6\,H_2O}$, $\mathrm{Cd(BrO_3)_2 \cdot 2\,H_2O}$ and $\mathrm{Sr(BrO_3)_2 \cdot H_2O}$ for the evaluation of the EFG at the ^{79}Br site due to $\mathrm{BrO_2}$ radicals have reproduced the ESR experimental values reasonably well [15]. Evidently the CNDO/2 calculations are well suited for the predictions of $e^2 \Phi_{zz} Q h^{-1}$ and η at the halogen site in any polyatomic group comprising the halogen atom.

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