Investigation of EFG Parameters at the Halogen Site in XO$_3$ and XO$_3^\ominus$ Radicals (X = Cl, Br) in Certain Inorganic Solids*

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Z. Naturforsch. 41 a, 169–170 (1986); revised version received October 22, 1985

Electric field gradients at the halogen site in XO$_3$ and XO$_3^\ominus$ radicals (X = Cl, Br), formed by the γ-irradiation of single crystals of NaClO$_3$, KClO$_3$, KBrO$_3$, and Sr(BO$_3$)$_2$· H$_2$O after γ-irradiation at 77 K by the ESR technique revealed the formation of XO$_3$ and/or XO$_3^\ominus$ (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 $\eta$, and the orientation of $\Phi_{zz}$ with respect to the crystal axes, at the halogen site in XO$_3^\ominus$ (X = Cl, Br, I) ions, and in IO$_3^-$ 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$_3^\ominus$, BrO$_3^-$, and BrO$_3^\ominus$ radicals in NaClO$_3$, KClO$_3$, KBrO$_3$, and Sr(BO$_3$)$_2$· H$_2$O respectively, has been estimated using the CNDO/2 method and the results have been compared with the ESR experimental data available in the literature.

1. Introduction

Investigations of single crystals of NaClO$_3$, KClO$_3$, KBrO$_3$, and Sr(BO$_3$)$_2$· H$_2$O after γ-irradiation at 77 K by the ESR technique revealed the formation of XO$_3$ and/or XO$_3^\ominus$ (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 $\eta$, and the orientation of $\Phi_{zz}$ with respect to the crystal axes, at the halogen site in XO$_3^\ominus$ (X = Cl, Br, I) ions, and in IO$_3^-$ 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$_3^\ominus$, BrO$_3^-$, and BrO$_3^\ominus$ radicals in NaClO$_3$, KClO$_3$, KBrO$_3$, and Sr(BO$_3$)$_2$· H$_2$O 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$_3^\ominus$ (X = Cl, Br) radicals have been obtained from X-ray crystal structure data of NaClO$_3$, KClO$_3$, KBrO$_3$, and Sr(BO$_3$)$_2$· H$_2$O 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$_3^\ominus$ radical is Cs with one X–O bond being stretched by 10% of the original bond length [3, 9, 10].

3. Results and Discussion

The values of $e^2 \Phi_{zz} Q h^{-1}$, $\eta$, and the orientation of $\Phi_{zz}$ at the halogen site in the XO$_3$ and XO$_3^\ominus$ (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$_3^\ominus$ radical is slightly smaller than the corresponding experimental value whereas $\eta$ ($^{79}$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$_3^\ominus$ radical. By the shortcomings of the calculations it seems impossible to significantly improve the agreement of $e^2 \Phi_{zz} Q h^{-1}$ and $\eta$ with the experimental values by adjusting the
stretching and thus predicting the exact geometrical deformation in the BrO$_3^-$ radical.

The $\eta$ ($^{35}$Cl) value of the ClO$_3^-$ radical in NaClO$_3$ is zero, and the orientation of $\Phi_{zz}$ is the same as that obtained for the ClO$_3^-$ ion. This shows that $\eta$ 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 XO$_3^-$ (X = Cl, Br) in KClO$_3$ and Sr(BrO$_3$)$_2$·H$_2$O 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 $\eta$ at the $^{35}$Cl/$^{79}$Br site in NaClO$_3$ and KBrO$_3$ due to XO$_3^-$ (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 Zn(BrO$_3$)$_2$·6H$_2$O, Cd(BrO$_3$)$_2$·2H$_2$O and Sr(BrO$_3$)$_2$·H$_2$O for the evaluation of the EFG at the $^{79}$Br site due to BrO$_3^-$ 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 $\eta$ at the halogen site in any polyatomic group comprising the halogen atom.

Acknowledgement

One of the authors (YUS) thanks the Department of Atomic Energy, Government of India, for the award of a fellowship.