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Basis-Set Dependence of Theoretical Deformation Density in NO_2^-

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Abstract

Electron-density distribution of a nitrite ion was calculated by the *ab initio* molecular-orbital method using STO-3G, STO-6G, MIDI4 and MIDI4* basis sets. The N–O bonding peak, which was observed in the experimental deformation density of $LiNO_2.H_2O$, could be reproduced only by using the MIDI4* basis set. This indicates the importance of polarization functions in the study of charge distribution.

Introduction

The N–O bonding electrons of the NO_2^- ion have been observed in the experimental deformation density of $K_2Na[Co(NO_2)_6]$ (Ohba, Toriumi, Sato & Saito, 1978), $[Ni(NH_3)_4(NO_2)_2]$ (Figgis, Reynolds & Wright, 1983) and $LiNO_2.H_2O$ (Ohba, Kikkawa & Saito, 1985), whereas molecular-orbital calculations using a minimal basis set did not reproduce the N–O bonding peaks (Ohba, Kitaura, Morokuma & Saito, 1979). The discrepancy seemed to be due to the inaccuracy of the theoretical calculations. The flexibility of the basis set affects the deformation density significantly (Feil, 1985). Thus, the basis-set dependence of the deformation density in NO_2^- has been examined to resolve this problem.

Theoretical calculations

The N–O bond length and the O–N–O bond angle were set to 1·252 Å and 114·7°, which are the mean values of neutron studies on $NaNO_2$ (Kay & Frazer, 1961), $Ba(NO_2)_2.H_2O$ (Kvick, Liminga & Abrahams, 1982) and $Sr(NO_2)_2.H_2O$ (Lundgren, Kvick, Liminga & Abrahams, 1985) at room temperature. Single-determinant closed-shell *ab initio* SCF calculations were performed with the program system *MOLYX* (Kamata & Iwata, 1987) on the VAX 11/750 computer of this department, using STO-3G, STO-6G, MIDI4 and MIDI4* basis sets. The MIDI4 basis set consists of three *s*- and two *p*-type contracted Gaussian functions for first-row atoms and two *s*-type functions for hydrogen. For the MIDI4* basis set, one group of *d*-type polarization function was added for first-row atoms and one group of *p*-type function for hydrogen (Tatewaki & Huzinaga, 1980). The basis-set dependence was also examined for related ions and molecules for comparison: NO_3^- with the N–O bond length 1·25 Å from the neutron study of $LiNO_3.3H_2O$ (Hermansson, Thomas & Olovsson, 1980); $HCOO^-$ with the C–O and C–H bond lengths 1·25 and 1·09 Å respectively and the O–C–O bond angle 125·5° from the neutron studies of $LiHCOO.H_2O$ (Tellgren, Ramanujam & Liminga, 1974) and NaHCOO (Fuess, Bats, Dannöhl, Meyer & Schweig, 1982); C_2H_6 in the staggered conformation with the C–C and C–H bond lengths 1·541 and 1·091 Å respectively; and HNO_2 assuming that the geometry of the NO_2 group is the same as that of NO_2^- with the N–H bond length 1·06 Å.

Discussion

The deformation density on the NO_2 plane is shown in Fig. 1. The minimal basis sets, STO-3G and STO-6G, give almost the same features and do not present the N–O bonding peak observed experimentally. The double-ζ basis set, MIDI4, also does not produce the N–O bonding peak. The same situation holds for the 4-31G basis set (Ritchie, 1985). The MIDI4* basis

Table 1. *Basis-set dependence of the bonding peak heights* (e Å^{-3})

	STO-3G	STO-6G	MIDI4	MIDI4*
N–O in NO_2^-	×†	×	×	0·5
N–O in NO_3^-	×	×	×	0·5
N–O in HNO_2	×	—‡	×	0·5
C–O in $HCOO^-$	×	×	0·8	0·4
C–C in C_2H_6	0·2	—	0·9	0·4

† Positive peak not found.
‡ Calculation not made.

Table 2. *Basis-set dependence of the effective charge of the O atoms*

	STO-3G	STO-6G	MIDI4	MIDI4*
NO_2^-	−0·452	−0·454	−0·622	−0·569
NO_3^-	−0·406	−0·407	−0·497	−0·504
HNO_2	−0·168	—	−0·315	−0·303
$HCOO^-$	−0·523	−0·531	−0·727	−0·625

set reproduces the N–O bonding peak of 0·5 e Å^{-3} at the midpoint of the N–O bond axis. The basis-set dependence of the bonding peak heights is summarized in Table 1. The N–O bonding electrons of the NO_3^- and HNO_2 molecules are also reproduced only by using the MIDI4* basis set (see Figs. 2*a* and 2*b*). Whether it is of a neutral molecule or an anion does not affect the deformation density on the N–O axis. Although a small N–O bonding density experimentally observed in a nitro group of nitropyridine *N*-oxide (Coppens & Lehmann, 1976) was attributed to the more than half-filled *L* shells of the N and O atoms (Coppens, 1982), the N–O bonding density has been clearly observed in 1,3-dinitrocubane at 100 K (Pant & Stevens, 1986). A negative trough of −1·4 e Å^{-3} appears above and below the N atom perpendicular to the NO_2 plane at 0·23 Å from the N nucleus (see Fig. 1*e*), which is in qualitative agreement with the observed deformation density of $LiNO_2.H_2O$ (Ohba *et al.*, 1985). However, a trough of −1·4 e Å^{-3} on the N–O bond axis at 0·23 Å from the O nucleus, which did not appear in the experimental density, may be absorbed into the spherical O atom by the refinement procedure. The C–O bonding peak of the formate ion and the C–C bonding

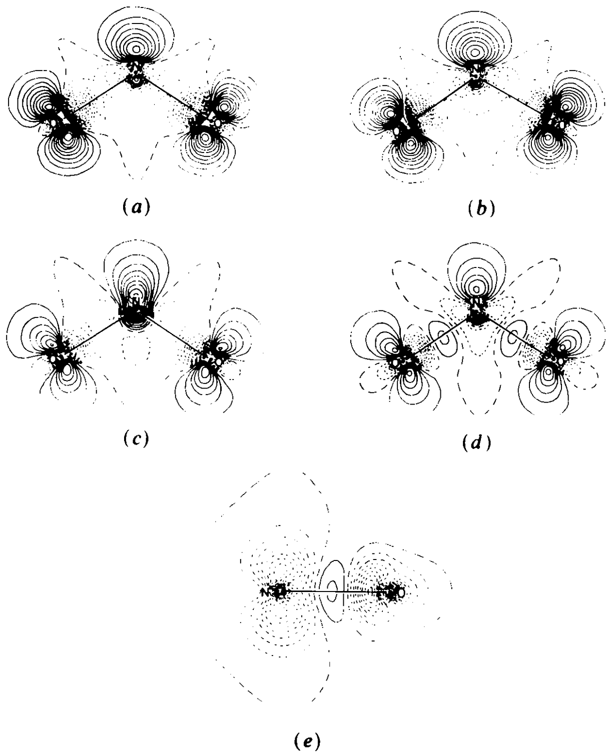

Fig. 1. Static deformation density on the NO_2 plane of the nitrite ion using (*a*) STO-3G, (*b*) STO-6G, (*c*) MIDI4 or (*d*) MIDI4* basis sets. (*e*) MIDI4* deformation density on the plane perpendicular to the NO_2 plane and containing an N–O bond axis. Contour intervals at 0·2 e Å^{-3}. Negative contours broken, zero contours chain-dotted.

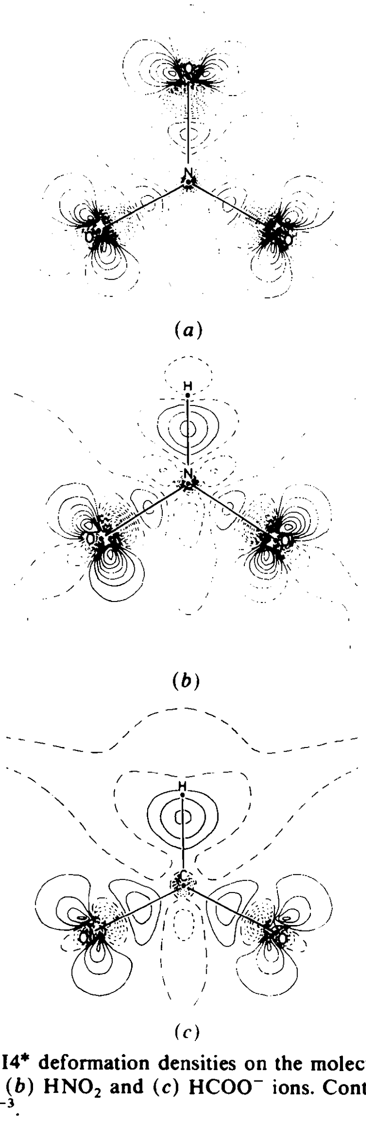

Fig. 2. MIDI4* deformation densities on the molecular plane of (*a*) NO_3^-, (*b*) HNO_2 and (*c*) $HCOO^-$ ions. Contour intervals at 0·2 e Å^{-3}.

peak of the ethylene molecule appear at the double-ζ level. However, their heights are much decreased when polarization functions are introduced. The deformation density of the formate, Fig. 2(*c*), agreed with that using the 4-31G and bond functions (Fuess *et al.*, 1982). A pair of the lone-pair peaks appear at the terminal O atoms in NO_2^-, NO_3^- and $HCOO^-$ ions with angles of 100–110° to the bond axis, suggesting sp^2 hybridization of the O atoms as expected from the experimental deformation densities (Ohba *et al.*, 1985; and references cited therein). Although it is well known that unrealistic gross electron populations on atoms are often obtained by Mulliken population analysis when larger basis sets are used (Iwata, 1980), no drastic basis-set dependence in population analysis is seen from Table 2. The negative charge of NO_2^-, NO_3^- and $HCOO^-$ is almost totally allocated to the O atoms.

The geometric distortion of NO_2^- is induced by an asymmetric $Ag^+\cdots O$ short contact in the crystals of $Ag_2Li(NO_2)_3$. The N–O bond lengths and O–N–O bond angle are 1·24 (1), 1·29 (1) Å and 111·9 (8)° (Ohba, Matsumoto, Ishihara & Saito, 1986). In accord with the higher bond order of the shorter N–O bond axis, a bonding peak higher by 0·05 e Å^{-3} than that on the longer N–O bond axis was obtained on the MIDI4* deformation density. Another calculation was made to estimate the influence of the crystal field in $LiNO_2.H_2O$ on the charge density. The deformation density of the nitrite ion remained almost unchanged when the neighboring two Li^+ and two hydrate H atoms in hydrogen bonding were replaced by four point charges.

Note added in proof: An independent study of the role of polarization functions in the theoretical deformation density of NO_2^- has recently been reported by Cruickshank & Eisenstein (1987). The results are similar to those given here.

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A Deformation Electron Density Study of Potassium Oxalate Monohydrate at 100 K*

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Abstract

The deformation electron density in $K_2C_2O_4.H_2O$ at 100 K has been studied using Hirshfeld-type deformation density functions [Hirshfeld (1971). *Acta Cryst.* **B27**, 769–781]. $K_2C_2O_4.H_2O$, $M_r = 184{\cdot}24$, monoclinic, $C2/c$, $a = 9{\cdot}0687\,(5)$, $b = 6{\cdot}2128\,(3)$, $c = 10{\cdot}5941\,(5)$ Å, $\beta = 110{\cdot}820\,(1)°$, $V = 557{\cdot}92$ Å^3, $Z = 4$, $D_x = 2{\cdot}193$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}610$ mm^{-1}, $F(000) = 368$, $T = 100$ K. $wR\,(F^2)$ values for 3543 $F_o^2 > 0$ reflections: 0·0568 (deformation refinement); 0·0623 (conventional refinement). The static deformation density for the H_2O molecule shows an O–H bond maximum of 0·25 e Å^{-3} and an oxygen lone-pair maximum of 0·35 e Å^{-3}. The static

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