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Electronic Structure of Unstable Intermediates

IV. The Electronic Structure of NCO

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The geometry of the ground state of the linear molecule, NCO, has been investigated within the restricted Hartree-Fock LCAO-MO-SCF approximation. Several one-electron properties have been calculated at the computed geometry for the BA + P basis set, for which the bond lengths are $R(\text{N–C}) = 2.3167$ bohr, $R(\text{C–O}) = 2.1426$ bohr.

Key words: NCO molecule – Unstable triatomic intermediates

1. Introduction

We report in this paper the results of further *ab-initio* calculations of the electronic structure and molecular properties of unstable intermediates [1–3]. In the present case, we have studied the ground state of linear NCO.

Dixon [4, 5] has observed a transient species in emission spectra during flash photolysis of HNCO vapour. He assigned the bands to linear NCO. Without isotopic data, he was unable to assign the bond lengths, but he obtained an upper limit on their sum as 4.5505 bohr. Apart from the study of the electronic spectrum, Milligan and Jacox [6] have studied the UV and IR spectra in argon matrix isolation experiments. More recently, the elegant gas place E.S.R. technique has been developed by Carrington *et al.* [7] and several molecular parameters of NCO have been obtained.

Although McLean and Yoshimine [8] have investigated the anion, NCO^-, the radical has not been previously studied theoretically. The electronic configuration of the ground state was assumed by Dixon to be:

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^3\,{}^2\Pi$$

and we have only investigated this configuration.

2. Method of Calculation

Calculations were performed on an IBM 370/195, using the computer programme ALCHEMY [9]. This programme computes wave functions for linear molecules using a basis set of Slater-Type Orbitals (STO's), with the restricted Hartree-Fock approximation for open-shell species as formulated by Roothaan [10]. Included in the programme package are routines for the usual Mulliken population analysis [11], and for the computation of the expectation values of various one-electron operators. In performing the calculations, the total energy was minimised with respect to each bond length, as described in a previous paper [2].

3. Basis Sets

Two basis sets were used in the calculations. The initial calculations were carried out with a double-zeta (DZ) basis set, with added polarisation functions. The DZ basis was taken from the tabulation by Clementi [12]. The exponents for the polarisation functions, $3d\sigma$, $3d\pi$, $4f\sigma$, $4f\pi$, on each atom, were taken from the calculations on NCO^- by McLean and Yoshimine [8]. This basis we refer to as DZ + P.

The second basis set used was the Bagus-Gilbert "best-atom" set, listed by McLean and Yoshimine in their compilation [8], with the same set of polarisation functions as used for the DZ + P basis. This larger basis we refer to as BA + P.

4. Results

The calculated bond lengths, energy and virial ratio for the two basis sets are given in Table 1 [1].

For the set of calculations using the BA + P basis set, the optimum geometry of R(N–C) = 2.3167 bohr, R(C–O) = 2.1426 bohr was obtained from least-square analysis of energy against bond length, as described in a previous paper [3], and the total energy was then calculated at this geometry, together with expectation values of various one-electron operators.

Table 1. Computed values of bond lengths, energy and virial ratio for the DZ + P and BA + P basis sets for $^2\Pi$ NCO

Basis	R(NC)	R(CO)	Energy	Virial ratio
DZ + P	2.38	2.25	−167.00401	−2.0061
BA + P	2.3167	2.1426	−167.18798	−2.0001

The results of the population analysis for the BA + P basis set are given in Table 2, and computed molecular properties obtained from the best wave function in Table 3.

5. Discussion

The electronic spectra of the species has been investigated by Dixon [4, 5]. The ground state configuration quoted above is in agreement with the configuration used by McLean and Yoshimine [6] in their *ab initio* investigation of the anion, NCO^-. The computed bond lengths are similar to those postulated by Eyster *et al.* [14] [R(N–C) and R(C–O) equal to 2.27 bohr] from electron dif-

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[1] Details of the individual calculations at the different bond lengths are available on request from the authors.

Table 2. Population analysis of the valence orbitals in NCO for the BA + P wave function

Orbital	Total population for centres		
	N	C	O
4σ	0.0228	0.5369	1.4403
5σ	1.2054	0.7653	0.0294
6σ	0.0537	0.2106	1.7357
7σ	1.7375	0.2118	0.0507
1π	0.1064	1.2493	2.6434
2π	1.9431	0.7588	0.2982
Total	7.0679	5.7339	8.1983

Table 3. Values of one-electron properties of NCO, calculated at optimum geometry for the BA + P basis set

Property		Value	
		Atomic units	C.G.S. units
Dipole moment		0.198467	0.50441 Debye
Quadrupole moment		−7.048881	−9.480 barn
Force on nucleii	N	0.12012	
	C	0.006756	
	O	−0.13213	
Total		−0.005254	
g values	g_s	0.5043507	
	g_r	0.1073899	
Field gradient	N	0.345653	
	C	1.017193	
	O	0.828905	
Force constants:			
N–C bond:		0.7094	1.1043×10^6 dyn cm^{-1}
C–O bond:		1.0208	1.5890×10^6 dyn cm^{-1}
Electric fied gradient			
q_N		0.3436	
^{14}N Quadrupole Coupling constant		1.92×10^{10}	1.26 MHz

fraction work on isocyanic acid, HNCO, and their sum is in reasonable agreement with Dixon's upper limit [5].

As a generalisation, the deviation of the calculated molecular energy from the Hartree-Fock limit is at least as large as the deviation of the sum of the atomic energies from Hartree-Fock for the same basis. For BA + P quality calculations, the atom energies are within 0.002 hartree of the Hartree-Fock values [13], and the molecular Hartree-Fock energy is probably ~0.005 hartree lower than our best value. The contribution to the dissociation energy for a given basis set is the difference between the molecular energy with that basis and the sum of the atom energies with the same basis. For the DZ basis, the sum of Clementi's atom energies [10] is -166.8887 hartree. The computed molecular energy at our optimum geometry is -167.0125 hartree; so, the contribution to the dissociation energy with this basis is 0.1348 hartree. For the BA basis, the corresponding sum of the atom energies is [6] -166.8989 hartree. As the optimum molecular energy is -167.1880 hartree, the contribution to the dissociation energy is 0.2891 hartree in this case.

The full population analysis, which we have reported summarily for the best calculation in Table 2, indicates that there are significant populations of the polarisation functions in the valence shell orbitals. As only the other sigma and the pi orbitals have appreciable populations on more than one centre, only these can be interpreted in the normal bonding terms: 4σ is a carbon to oxygen sigma bond, of *sp* character on carbon, *s* on oxygen; 5σ is a nitrogen to carbon sigma bond, *s* character on nitrogen, *sp* on carbon; 6σ and 7σ are lone pairs, of *sp* character, on oxygen and nitrogen respectively; the two pi symmetry molecular orbitals, although extending over all three centres, are predominantly carbon-oxygen and nitrogen-oxygen respectively. The total atomic population shows only small transfer of charge along the molecule to the oxygen centre. This is supported by the calculated value of the dipole moment which is only 0.5 D with sign indicating electronic charge accumulation on oxygen.

The calculated values of several one electron properties are given in Table 3. The formulae for these have been published by McLean and Yoshimine [15, 16]. The pi-radical NCO, is isoelectronic with N_3. An *ab initio* treatment of the latter and its two monoions has been performed by Sabin and Archibald [17]. They used a basis of Gaussian functions, of quality approximating to double zeta Slater-type, obtaining as their optimum geometry an asymmetric, $C_{\infty v}$ geometry with bond lengths of 2.345 and 2.160 bohr. These values are similar to those which we have found for NCO, the values being nearer for the BA + P than the DZ + P basis. The calculated force constants are also similar to those obtained for N_3 [17]. Dixon [4], gives a value for the sum of the force constants as approximately 3×10^6 dyn cm^{-1}. Our calculated force constants give a sum of 2.69×10^6 dyn cm^{-1}, which is in reasonable agreement with Dixon. The values of $f_{NC} = 1.082 \times 10^6$ dyn cm^{-1} and $f_{CO} = 1.293 \times 10^6$ dyn cm^{-1} of Milligan and Jacox [6] are fairly close to our values, but these were obtained assuming bond lengths of $R(\text{N–C}) = 2.324$ Å and $R(\text{C–O}) = 2.230$ Å, and one would expect the experimental f_{NC} to be less and the f_{CO} to be greater in this case.

In the paper by Carrington *et al.* [7], a value for the nitrogen atom quadrupole coupling constant is given as -2.2 MHz. Using the value for the nitrogen nuclear electric quadrupole moment used by Green in a paper on an *ab initio* treatment of the NO molecule [19], of $+0.0156$ bohr, we obtain a quadrupole coupling constant of 1.26 MHz, which is similar in magnitude but of opposite sign. Carrington *et al.* state that they chose the sign of the coupling constant to be the same as that for the NO molecule. The field gradient at the nitrogen atom that we calculate is of positive sign, in contrast to that of NO, as calculated by Green. We therefore suggest that the sign of the coupling constant is in fact positive. Several of the properties we have computed (Table 3) stand as predictions and it is hoped that this work will stimulate further experimental work on this molecule.

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