A Study of the Electronic Density Distribution in Nitric Oxide

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Abstract: The electronic density distributions in NO and NO^+, and the electrostatic forces exerted by the electrons upon the nuclei in NO, have been computed and analyzed. It is found that the process $NO \rightarrow NO^+$ involves a very marked rearrangement of electronic charge within the molecule; this is presumed to account for the observed strengthening of the bond in this process. The question is raised as to whether it is valid to correlate the N–O stretching frequency in nitrosyl compounds with supposed transfer of charge into an NO antibonding π molecular orbital.

Nitric oxide is one of the simplest examples of a molecule which has an odd number of electrons, and it is also the most stable molecule of this type, having a relatively high dissociation energy of 151 kcal/mol.[2] In terms of elementary molecular orbital theory, its ground state electronic structure is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi^1$. The highest energy electron is considered to be in an antibonding π molecular orbital; consequently it is anticipated that loss of this electron, in forming NO^+, will lead to a stronger N–O bond. This is indeed found to be the case; NO^+ has a shorter bond length[3] and a higher vibration frequency and dissociation energy (251 kcal/mol) than does NO.[2,4a]

Nitric oxide can act as a ligand; it forms complexes with transition metals which are somewhat analogous to carbonyls. There appears to be one important difference between the ligand behaviors of NO and CO, however. Whereas carbon monoxide coordinates as the neutral molecule, experimental evidence indicates that many nitric oxide complexes are best viewed as involving first a transfer of an electron from the NO to the metal atom, followed by coordination by NO^+.[4] In the coordination step, the NO^+ is considered to act as a σ donor, sharing its nitrogen lone pair with the metal, and a π acceptor, its empty antibonding π molecular orbital receiving electronic charge from the $d\pi$ orbitals of the metal atom. This back-donation into an antibonding molecular orbital is presumed to weaken the N–O bond, and accounts for the fact that the N–O stretching frequency in these complexes is generally lower than in NO^+.[4,5] NO also combines with the halogens to form an interesting series of compounds, the nitrosyl halides, XNO (X = F, Cl, Br). The N–O stretching frequencies in these molecules are again less than in free NO, and again this has been attributed to charge transfer into its antibonding π molecular orbital, this time from the halogen atom.[6]

Thus, it is possible to rationalize some of the observed behavior of nitric oxide in terms of elementary molecular orbital theory. With the present availability of good molecular wave functions, however, it is both interesting and important to determine the extent to which these wave functions corroborate the earlier qualitative theories. Accordingly, a study has been made of the electronic density distributions in the nitric oxide molecule, in the molecular ion NO^+, and in the molecular ion O_2^+, which was included because it is isoelectronic with NO. The electrostatic forces of attraction between the electrons and the nuclei in NO were also computed. Such calculations of electronic density distributions and electronic forces have been carried out for a number of other molecules in recent years.[7-10]

Procedure

The total electronic density at a point $\vec{r}$ is given by

$$\rho(\vec{r}) = \sum_i N_i \phi_i^*(\vec{r}) \phi_i(\vec{r})$$

where N_i is the number of electrons in molecular orbital ϕ_i. For NO, the density difference function was also computed; this is defined by[11,12]

$$\Delta\rho(\vec{r}) = \rho(\vec{r}) - \sum_j \rho_j(\vec{r})$$

The second term is a summation over the electronic densities of the atoms which constitute the molecule, these being placed at the same positions as in the molecule but assumed to have undergone no interactions with each other and to be undistorted, as in the free state. The density difference function is taken to indicate the overall rearrangement of charge density which occurs when the atoms interact to form the molecule.

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[2] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

[3] "Tables of Interatomic Distances and Configuration in Molecules and Ions," Main Volume and Supplement, Special Publications Nos. 11 and 18, The Chemical Society, London, 1958 and 1965.

[4] (a) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963; (b) H. B. Gray, I. Bernal, and E. Billig, *J. Amer. Chem. Soc.*, **84**, 3404 (1962); W. P. Griffith, *J. Chem. Soc.*, 3286 (1963); H. B. Gray, P. T. Manoharan, J. Pearlman, and R. F. Riley, *Chem. Commun.*, 62 (1965); P. Gans, A. Sabatini, and L. Sacconi, *Inorg. Chem.*, **5**, 1877 (1966).

[5] P. Gans, *Chem. Commun.*, 144 (1965).

[6] R. D. Spratley and G. C. Pimentel, *J. Amer. Chem. Soc.*, **88**, 2394 (1966).

[7] P. Politzer, *J. Phys. Chem.*, 70, 1174 (1966).

[8] R. F. W. Bader, W. H. Henneker, and P. E. Cade, *J. Chem. Phys.*, **46**, 3341 (1967).

[9] B. J. Ransil and J. J. Sinai, *ibid.*, **46**, 4050 (1967).

[10] R. F. W. Bader, I. Keaveny, and P. E. Cade, *ibid.*, **47**, 3381 (1967).

[11] M. Roux, S. Besnainou, and R. Daudel, *J. Chim. Phys.*, **53**, 218, 939 (1956).

[12] M. Roux, *ibid.*, **55**, 754 (1958).

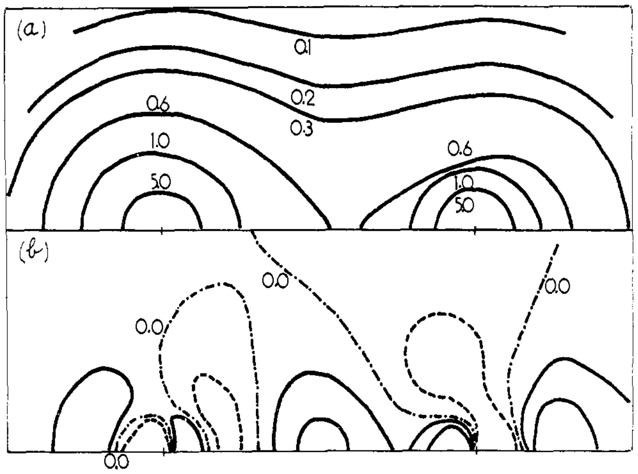

Figure 1. (a) Total electronic density distribution in nitric oxide, (b) density difference function for nitric oxide. The contours come at intervals of 0.04, starting from the 0.0 curves. The dashed curves correspond to negative values.

The total electrostatic attractive force along the molecular axis which the electrons in a diatomic molecule AB exert upon nucleus A, of nuclear charge Z_A, is (in atomic units)[8,13]

$$F_A = \sum_i F_{A-i} = \sum_i Z_A N_i \int \phi_i^*(\vec{r}) \frac{\cos \theta_A}{r_A^2} \phi_i(\vec{r})\, d\vec{r}$$

where F_{A-i} is the force exerted upon nucleus A by the N_i electrons in molecular orbital ϕ_i and θ_A, r_A are polar coordinates measured from nucleus A.

The molecular wave functions used in this work were self-consistent-field LCAO-MO functions written in terms of an extended basis set of Slater-type atomic orbitals.[14] For the atoms, the self-consistent-field functions of Clementi were used;[15] the p-electron distributions were averaged over all spatial directions.[16]

Results and Discussion

The total electronic density distribution in NO, shown in Figure 1a, may be compared with that in O_2^+ (Figure 2). The two molecules are isoelectronic, and also have similar bond properties, with the bond in O_2^+ being somewhat stronger.[17] These facts are reflected in their electronic structures. There is a remarkable similarity between the charge distribution in the oxygen half of NO and that in either half of O_2^+; they are nearly identical. In the nitrogen half of NO, however, one observes a lesser buildup of charge, both in the neighborhood of the nucleus and in the internuclear region. This is clearly consistent with the greater strength of the bond in O_2^+.

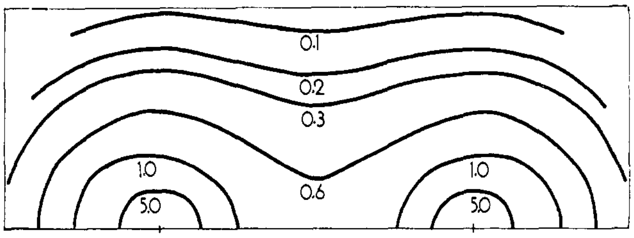

Figure 2. Total electronic density distribution in O_2^+.

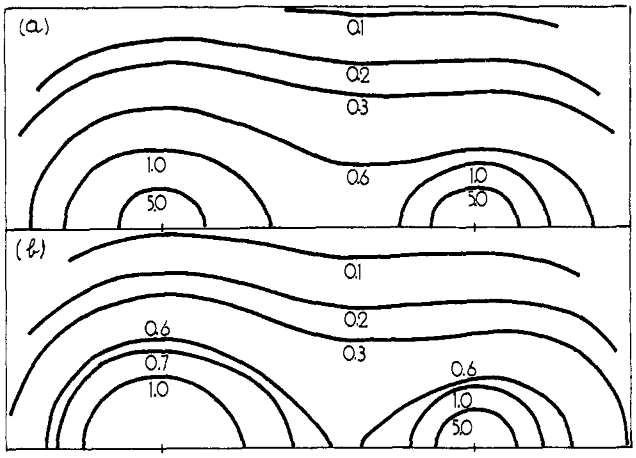

Figure 3. (a) Total electronic density distribution in NO^+, (b) electronic density distribution for NO minus highest energy (2π) electron.

The density difference function for NO is plotted in Figure 1b. It has the same general features as have previously been observed in the density difference functions of other diatomic molecules. Charge buildup has occurred in the internuclear region and to the outside of each nucleus, accompanied by a decrease in charge density in regions near each nucleus, perpendicular to the molecular axis.[8,18]

It is interesting to compare the density difference function for nitric oxide with that for carbon monoxide, which has been discussed recently.[18] The general features are the same in both cases, but both the charge buildup in the internuclear region and the localizations of charge to the outsides of the nuclei (the "lone pairs") are considerably greater in the case of CO. The former helps to explain the much higher dissociation energy of CO (256.9 kcal/mol *vs.* 151 for NO[1]), while the more prominent lone pairs suggest that CO will be a more effective σ donor ligand.

Figure 3a shows the electronic structure of the nitric oxide ion, NO^+. It is evident that the process $NO \rightarrow NO^+$ involves a considerable electronic rearrangement. NO^+ has much greater concentrations of charge in the internuclear region and to the outsides of the nuclei than does NO. (Compare, for example, the 0.6 contours in Figures 1a and 3a.) It is to be expected, therefore, that NO^+ will have a stronger bond than NO, as

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(13) A. C. Hurley in "Molecular Orbitals in Chemistry, Physics, and Biology," P.-O. Lowdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 161.

(14) The molecular wave functions used in this work were obtained from the Laboratory of Molecular Structure and Spectra at the University of Chicago. The authors greatly appreciate the very kind cooperation of Dr. Paul E. Cade.

(15) E. Clementi, "Tables of Atomic Wave Functions," International Business Machines Corp., San Jose, Calif., 1965.

(16) Instead of spherically averaged p-electron distributions, "valence-state" configurations can also be used for the atoms, the p electrons being assigned to σ or π atomic orbitals (ref 8, 10). In this case, however, the density difference function no longer shows the changes from the *free* atoms, but rather from atoms which have already interacted with each other to some extent. This point is discussed more fully in ref 9.

(17) The bond lengths are 1.1502 Å for NO, 1.1227 for O_2^+ (ref 2); the dissociation energies are 151 kcal/mol for NO, 168 for O_2^+ (ref 1); the force constants are 16.0 mdyn/Å for NO, 16.6 for O_2^+: G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1950, Table 39.

(18) M. J. Hazelrigg, Jr., and P. Politzer, *J. Phys. Chem.*, 73, 1008 (1969).

Table I. Molecular Orbital Energies of NO and NO^+ Wave Functions[a]

Molecular orbital	Energy, au	
	NO	NO^+
1σ	−20.69109	−21.21631
2σ	−15.71787	−16.24343
3σ	−1.59394	−2.16665
4σ	−0.92575	−1.35958
5σ	−0.68023	−1.15101
1π	−0.67101	−1.15799
1π	−0.67101	−1.15799
2π	−0.41170	

[a] Reference 14.

is the case.[2-4a] It would also be predicted, on the basis of the greater localizations of charge in the lone-pair regions, that NO^+ will be a better σ donor ligand than NO. Again this is consistent with experimental evidence, which indicates that nitric oxide complexes are best viewed as involving coordination by NO^+ rather than NO.[4]

The fact that NO^+ differs so markedly from NO in its electronic structure is significant. The assumption is sometimes made that the same set of molecular orbitals may be used to describe both a neutral molecule and its ion; it is assumed that the forms of the orbitals do not change. This has been called the "rigid orbital approximation."[13] It was pointed out by Bader, *et al.*, on the basis of analyses of the electronic forces in N_2, O_2, and their ions, that this approximation is not generally valid, because of "significant reorganization of the charge density in orbitals other than the one involved in the ionization process."[8] This conclusion is strongly supported by the present results, which show graphically the considerable rearrangement of electronic charge which occurs in going from NO to NO^+. In order to bring this point out even more clearly, Figure 3b shows the electronic density distribution obtained using the molecular orbitals calculated for NO but omitting the highest energy (2π) electron. In terms of the rigid orbital approximation, this should be the charge distribution in NO^+. The difference between this and the more accurate charge distribution (Figure 3a) obtained from a wave function computed specifically for NO^+ is striking.[19]

The attractive forces exerted by the electrons in each molecular orbital in NO upon the nitrogen and oxygen nuclei are listed in Table II. A positive value for F_{A-i} means that the force on nucleus A due to the electronic charge in molecular orbital ϕ_i is toward nucleus B; a negative value means that the charge in ϕ_i is pulling nucleus A away from B.

Table II. Electrostatic Forces Exerted by the Electrons in Nitric Oxide upon the Nitrogen and Oxygen Nuclei[a]

Molecular orbital, ϕ_i	F_{N-i}, au	F_{O-i}, au
1σ	2.961	0.651
2σ	0.609	3.385
3σ	4.196	4.730
4σ	0.524	−1.715
5σ	−0.742	1.050
1π	2.207	1.730
1π	2.207	1.730
2π	0.041	0.487
Total	12.003	12.048

[a] The force of repulsion between the nuclei is $(Z_AZ_B/R_e^2) = (7)(8)/(2.1747)^2 = 11.841$ au, where R_e is the equilibrium internuclear distance in atomic units.

It is seen from Table II that the highest energy electron in NO, the single 2π electron, exerts a positive force upon each nucleus, meaning that it pulls each nucleus toward the other. It thus has a constructive effect upon the bond, as contrasted to the electrons in the 4σ orbital, which pull the oxygen nucleus away from the nitrogen and thereby weaken the bond. The forces exerted by the 2π electron are very small, however, and in view of the approximate nature of the wave function, it may not be justifiable to attribute a great deal of significance to their exact magnitudes. What does seem safe to conclude is that the 2π electron does not have a pronounced weakening effect upon the bond. The fact that the bond becomes stronger when this electron is removed in the ionization process NO → NO^+ must therefore be attributed, as was proposed earlier, to the redistribution of electronic charge which occurs in this process.

It appears, on the basis of the discussion presented in this paper, that the correlating of the lowered vibration frequency of coordinated NO^+ to back-donation of electronic charge into the 2π orbital is open to question. First, this interpretation is, in effect, invoking the rigid orbital hypothesis, and it has been shown that this is not always valid. Second, even if it should still be meaningful to speak of the 2π molecular orbital of free NO in connection with coordinated NO or NO^+, the evidence of the calculated forces indicates that electronic charge in this orbital does *not* exert a significant bond-weakening force. Thus it is not obvious that transfer of charge into this orbital would bring about a lowering of the vibration frequency.

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(19) Further illustrating the fact that the rigid orbital approximation leads to a rather poor description of NO^+ are the differences between the energies of corresponding molecular orbitals of NO and NO^+, shown in Table I.[14]