Distortions in the Trigonally Symmetric Radicals NO_3 and CO_3^-

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Abstract: The extended Hückel and the INDO molecular orbital methods have been applied to NO_3 and CO_3^- with a view to shedding some light on their ground-state geometry and electronic structure. Both computational models predict a Y-shaped geometry (C_{2v} symmetry) for the two species. Their ground electronic state is found to be of $^2B_2$ symmetry. The distortion from the trigonal arrangement is explained in terms of a Jahn–Teller instability. The electronic transitions involved in the observed spectrum are also discussed. A number of measurements on the species trapped in single crystals indicate a D_{3h} symmetry for the compounds. In those cases the potential barrier must be lowered under the influence of the host lattice, to such an extent that it becomes smaller than the zero-point energy. Under those circumstances the species have a D_{3h} symmetry on the average.

NO_3 and CO_3^- are isoelectronic inorganic free radicals possessing 23 valence electrons.[1] The first of these compounds has been generated over the last decades by a variety of methods: decomposition of ozone in the presence of nitric anhydride,[2] shock photolysis of N_2O_5,[3] flash photolysis of nitrogen dioxide and of nitric acid;[4] it has also been observed as a product of the photolysis of ceric ammonium nitrate in aqueous solution;[5,6] it has been shown to be an intermediate in the thermal decomposition of NO_2.[7] The γ-ray irradiation of various crystals containing the nitrate ion is a convenient way of obtaining the radical, trapped in the crystal lattice.[8] Wood and Pietrzak[9] have recently prepared it by the reaction in a molecular sieve between NO_2 and oxygen atoms. As far as CO_3^- is concerned, its only mode of preparation is, to our knowledge, the γ-ray irradiation of crystals containing the bicarbonate or the carbonate ion.[8a,10]

An unambiguous determination of the geometry of these inorganic radicals has not yet been achieved. Experimentalists are in agreement as to a planar structure for both species; however, some workers[8b–f,10] have proposed a trigonally symmetric geometry (D_{3h} point group), while others[8a] are more in favor of a Y-shaped C_{2v} structure. Walsh,[11] in his famous series of papers on the geometry of molecules, predicts that both systems should be planar, having D_{3h} symmetry, and possessing a $^2A_2'$ ground electronic state. It is to be noted, however, that Walsh considered only out-of-plane distortions leading to pyramidal C_{3v} structures; he did not consider distortions in which the trigonal symmetry is destroyed.

We have undertaken a quantum chemical study of these radicals with the hope of shedding some light on their geometries and their electronic structure. Two relatively simple quantum-chemical methods have been employed in this work. On the one hand, we have used the extended Hückel molecular orbital (XHMO) method,[12] the details of which are well known. The off-diagonal elements of the Hamiltonian matrix are approximated by Cusachs' formula,[13] while the on-diagonal elements are taken as the negative of the valence state ionization potentials.[14] On the other hand, we have carried out spin-unrestricted LCAO–SCF–MO calculations in the spirit of the semiempirical INDO approximation.[15] The INDO method has been developed and tested extensively on small polyatomic molecules by Pople, *et al.*[15] The computational details of the method can be found in ref 15.

It might be argued that the most adequate approach to the problem we are investigating here would be an *ab initio* calculation. However, a detailed investigation by a nonempirical method would present a number of difficulties and would most probably appear prohibitive, owing to the large number of electrons in the two radicals and to the negative charge on one species (it is notoriously difficult to obtain a reasonable wave function for a negative ion). Furthermore, as will be seen later, we find evidence for states of the same symmetry lying in the vicinity of each other, which would necessitate the inclusion of configuration interaction. It is clear, then, that for the time being an *ab initio* treatment would not be practical, and that the approach followed in this work represents the best possible compromise between rigor and actual feasibility.

Since the bond lengths in the inorganic radicals studied here are unknown, as far as we are aware, we have chosen all NO and CO bond lengths equal to 1.25 Å. This value minimizes the INDO energy in trigonally symmetric NO_3 and it is also very similar to

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(1) P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier Publishing Co., New York, N. Y., 1967, pp 162–186.

(2) E. J. Jones and O. R. Wulf, *J. Chem. Phys.*, **5**, 873 (1937).

(3) G. Schott and N. Davidson, *J. Amer. Chem. Soc.*, 80, 1841 (1958).

(4) D. Husain and R. G. Norrish, *Proc. Roy. Soc., Ser. A*, 273, 165 (1963).

(5) T. W. Martin, A. Henshall, and R. C. Gross, *J. Amer. Chem. Soc.*, **85**, 113 (1963); T. W. Martin, R. E. Rummel, and R. C. Gross, *ibid.*, **86**, 2595 (1964).

(6) T. W. Martin, J. M. Burk, and A. Henshall, *ibid.*, **88**, 1097 (1966).

(7) H. S. Johnston, *ibid.*, 73, 4542 (1951); E. W. Graham, Ph.D. Dissertation, University of California, 1966.

(8) (a) G. W. Chantry, A. Horsfield, J. R. Norton, and D. H. Whiffen, *Mol. Phys.*, **5**, 589 (1962); (b) J. Cunningham, *Prepr. Pap. Int. Symp. Free Radicals, 5th, 1961;* (c) P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 4794 (1962); (d) R. Livingston and H. Zeldes, *J. Chem. Phys.*, **41**, 4011 (1964); (e) R. M. Golding and M. Henchman, *6th Int. Symp. Free Radicals*, Cambridge, 1963; *J. Chem. Phys.*, **40**, 1554 (1964); (f) R. Adde, *C. R. Acad. Sci., Paris*, **261**, 685 (1965).

(9) D. E. Wood and T. M. Pietrzak, *J. Chem. Phys.*, **46**, 2973 (1967).

(10) R. A. Serway and S. A. Marshall, *ibid.*, **46**, 1949 (1967).

(11) A. D. Walsh, *J. Chem. Soc.*, 2301 (1953).

(12) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(13) L. C. Cusachs and B. B. Cusachs, *J. Phys. Chem.*, **71**, 1060 (1967).

(14) J. Hinze and H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

(15) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

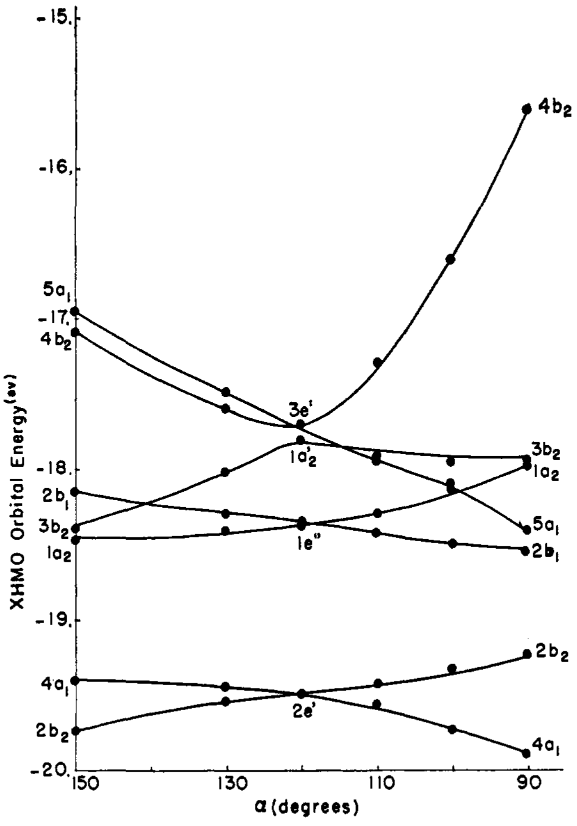

Figure 1. XHMO orbital energy diagram of CO_3^-, as a function of the unique OCO angle α.

the experimental bond length in NO_3^- (1.24 Å in dinitrogen pentoxide, see ref 16).

Ground-State Geometry and Symmetry of the Wave Function

Both computational models agree that trigonally symmetric (D_{3h}) NO_3 and CO_3^- should be stable with respect to out-of-plane bending since this distortion results in a sharp increase in the total energy. Thus, for example, in the case of CO_3^-, distorting away from D_{3h} symmetry to C_{3v} symmetry (90°) results in an energy increase of about 7 eV according to INDO calculations and of 10 eV by the XHMO method; similar results are obtained for NO_3. The calculations thus confirm Walsh's conclusion that the planar D_{3h} configuration should be more stable than the pyramidal C_{3v} configurations for 23 valence electron systems.[11] On the other hand, our calculations also suggest that the D_{3h} species are unstable with respect to an in-plane bending distortion and that the radicals belong to the C_{2v} point group. This is in agreement with the experimental results and the qualitative reasoning of Chantry, *et al.*[8a]

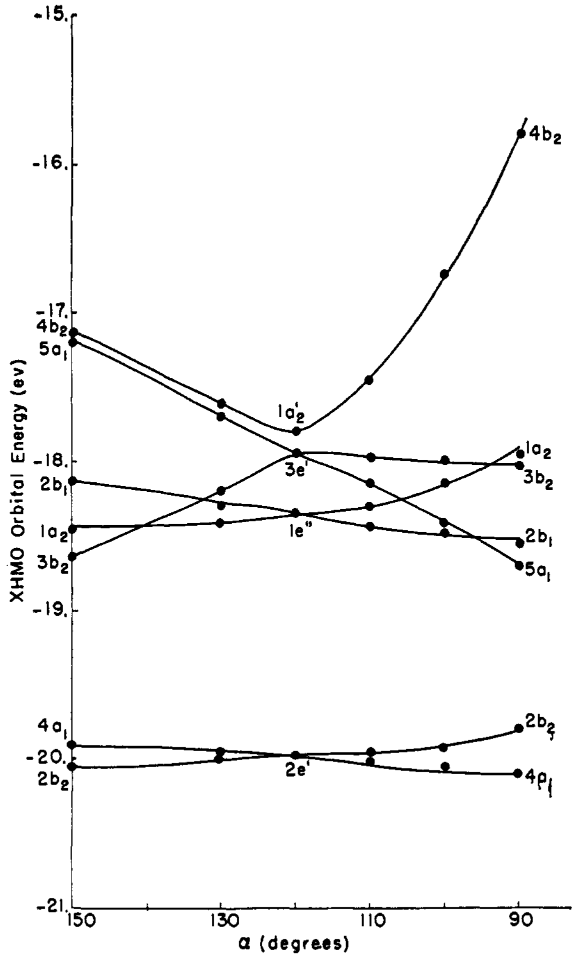

Figure 2. The XHMO orbital energy diagram of NO_3, as a function of the unique ONO angle α.

The XHMO calculations give rise to the orbital energy diagrams represented in Figures 1 and 2, where the abscissa is the unique bond angle α. For the sake of simplicity the five lowest and the four highest energy molecular orbitals are not shown. In the simple extended Hückel model, where interelectronic interaction is ignored, the orbital energy diagram is independent of the number of electrons of the system. It is the same for a neutral species and its ions. In a previous publication,[17] an extended Hückel treatment was carried out for CO_3 assuming all CO bond lengths equal to 1.20 Å. The slight change of 0.05 Å in bond length introduced in the present work does not bring in any significant modification to the orbital energy diagram.

Figures 3 and 4 give the molecular energies for the first few electronic states of the species as a function of the unique angle α. In each of the two figures, the set of curves associated with the $^2E'$ state arises from the electronic configuration $(1a_2')^2(3e')^3$; the $^2A_2'$ state stems from the $(1a_2')^1(3e')^4$ configuration and $^2E''$ from the $(1e'')^3(1a_2')^2(3e')^4$ electronic configuration.

The XHMO method predicts for both radicals a $^2B_2$ ground state; the deviation from trigonal symmetry is sizable: the computed unique angle is 108° in CO_3^- and 110° in NO_3.

Because the $1a_2'$ and $3e'$ levels are inverted as one goes from CO_3^- to NO_3 (see Figures 1 and 2), the symmetry of the lowest electronic state is not the same for both species in the trigonal arrangement; the lowest state symmetries are also different when α is

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(16) "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 15, The Chemical Society, London, 1965.

(17) J. F. Olsen and L. Burnelle, *J. Amer. Chem. Soc.*, **91**, 7286 (1969).

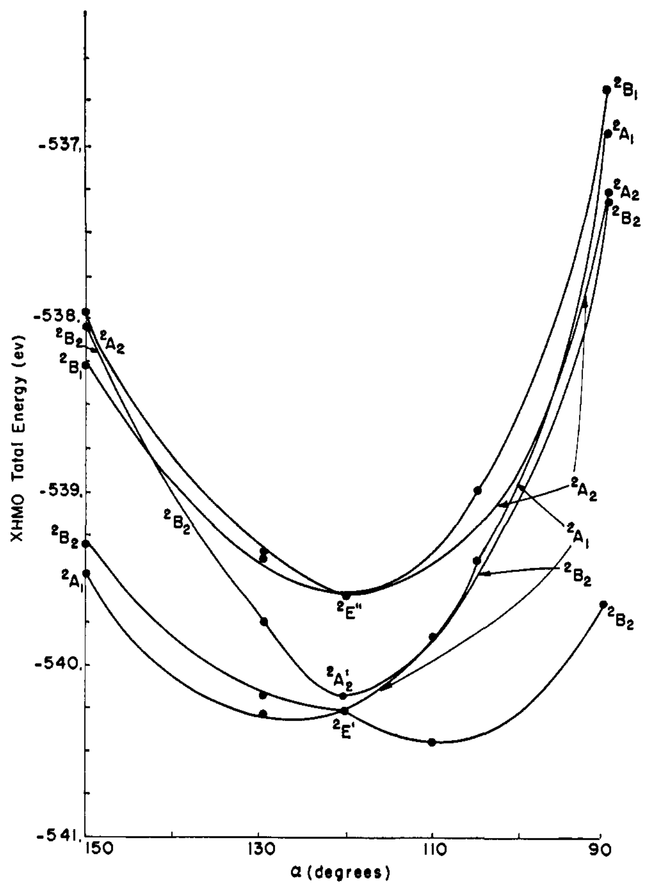

Figure 3. Lower XHMO state energies of CO_3^- as a function of α.

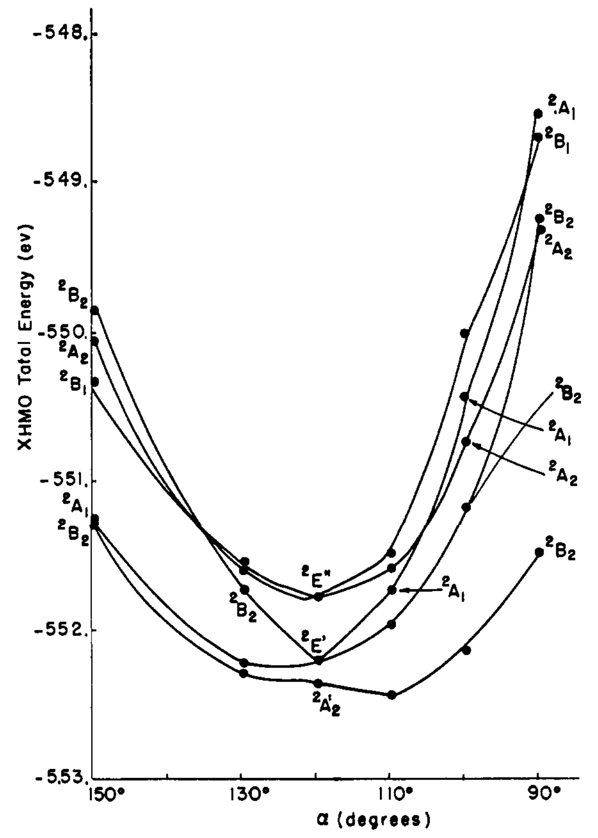

Figure 4. Lower XHMO state energies of NO_3 as a function of α.

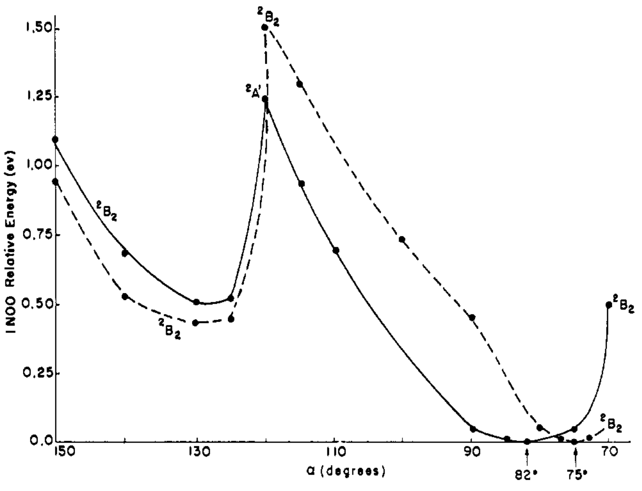

Figure 5. Relative INDO energy for the $^2B_2$ state of CO_3^- (—) and NO_3 (- - -) *vs.* α.

larger than 120°. The orbital degeneracy of the ground-state wave function of CO_3^- for α equal to 120° makes the distortion to the C_{2v} symmetry appear as a manifestation of the Jahn–Teller effect,[18] while this is not the case for NO_3, according to this treatment. Note, however, the closeness of the two levels $1a_2'$ and $3e'$.

The INDO method also predicts a Y-shaped ground state for the two radicals, of symmetry $^2B_2$. The computed equilibrium angles (82° for CO_3^-, 75° for NO_3) are smaller than those resulting from the XHMO calculations. A similar situation has been encountered in CO_3, where α_{eq} computed by the INDO theory was 17° smaller than the XHMO value.[17] It was shown that the INDO result was probably more realistic for this molecule and we are inclined to believe that this is probably the case for the two radicals studied here. Support in favor of this contention is provided by the treatment of F_2CN (isoelectronic with CO_3^- and NO_3). The INDO theory predicts an FCF bond angle of 110°, in good agreement with the experimental value of 113.5°.[19] The calculations were made with the bond lengths $r_{CN} = 1.27$, $r_{CF} = 1.31$ Å. The ground state of F_2CN, like that of NO_3 and CO_3^-, is predicted by INDO theory to be $^2B_2$.

Figure 5 shows the ground-state energy variation with α for the two radicals, as results from the INDO calculations. Two points are worthy of notice: first, the lowest state for values of α larger than 120° is predicted to be a $^2B_2$ state; second, the wave function for the trigonal arrangement of the bonds does not transform according to an irreducible representation of the D_{3h} point group, but of a subgroup of D_{3h} (C_{2v} for NO_3 and C_s for CO_3^-).

This latter point is an indication that we deal with a state which in actuality is $^2E'$. The INDO procedure imposes the single occupancy of one component of the degenerate $3e'$ orbital, thereby producing an uneven molecular charge distribution.

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(18) H. A. Jahn and E. Teller, *Proc. Roy. Soc., Ser. A*, **161**, 220 (1937).
(19) R. N. Dixon, G. Duxbury, R. C. Mitchell, and J. P. Simons, *ibid., Ser. A*, **300**, 405 (1967).

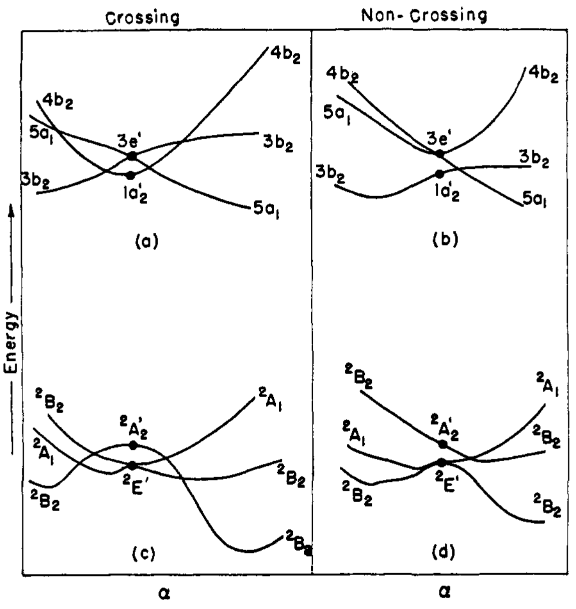

Figure 6. Schematic orbital and lower state energy diagrams for NO_3 and CO_3^- before and after the application of the noncrossing rule.

The fact that a $^2B_2$ state (correlating with $^2E'$) is obtained on each side of $\alpha = 120°$ appears offhand hard to reconcile with a model based on the one-electron approximation. Indeed, as Figures 3 and 4 indicate, one would expect the two lower states correlating with $^2E'$ to be $^2B_2$ for small values of α but $^2A_1$ for large values of the angle. A plausible explanation can be provided for the observed diagram if one supposes that it results from the interaction between states of the same symmetry and from an application of the noncrossing rule.[20]

The interpretation we suggest is represented in a schematic way in Figure 6, where for simplicity we have only indicated the levels correlating with $1a_2'$ and $3e'$. We start from the XHMO orbital energy diagram for NO_3 (see Figure 2) but suppose that for $\alpha = 120°$, the $1a_2'$ level lies *lower* than $3e'$. This is not unrealistic since, as pointed out earlier, the two levels lie quite close to each other. The diagram represented in a is thus obtained. Applying the noncrossing rule to the levels of b_2 symmetry gives the scheme b. The possible ways of distributing five electrons among the various one-electron levels then gives rise to the diagram d, which, as far as the ground state is concerned is in general agreement with the INDO curves of Figure 5. An alternate route to diagram d consists in applying the noncrossing rule to the electronic states rather than to the one-electron levels. This is illustrated in c.

It thus appears that the electronic structure of NO_3 and CO_3^- is not as simple as the XHMO picture might lead us to think. There is apparently a strong interaction between states of B_2 symmetry. INDO calculations on CO_3^- locate the low-lying $^2A_2'$ state at a position 2.7 eV higher than the $^2B_2$ ground-state minimum and 1.6 eV above the $^2E'$ state.

In spite of the complications characterizing the energy diagrams of the two compounds, there is strong evidence that the Y-shaped arrangement adopted by the two radicals is a consequence of the Jahn–Teller effect. The XHMO and the INDO procedures agree on that point for CO_3^-. For NO_3, a slight modification in the XHMO diagram leads to an agreement with the INDO result. (Curiously enough, the INDO method predicts, for a considerable squeeze of the angle α, the emergence of a low-lying $^2B_1$ state in NO_3, which actually becomes the ground state for $\alpha < 70°$. We have disregarded it as spurious.)

The approximate nature of the diagrams of Figure 6 has to be stressed. It should also be mentioned that it is possible to conceive other schemes, slightly different from the one presented here, which account for the curves generated by the INDO treatment. Nevertheless, the important point is that they all involve an interaction between two $^2B_2$ states.

Approximate as they may be, the ground-state electronic configurations resulting from our treatment are instructive. At the equilibrium unique bond angle, the XHMO method gives the same configuration for CO_3^- and NO_3, namely $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$-$(4a_1)^2(2b_2)^2(2b_1)^2(1a_2)^2(5a_1)^2(3b_2)^2(4b_2)^1$: $^2B_2$. From the INDO treatment one obtains the following ground-state wave functions for NO_3: $|\{1a_12a_11b_23a_11b_14a_12b_2$-$5a_13b_22b_11a_24b_2\}^\alpha\{1a_12a_11b_21b_13a_12b_24a_15a_12b_13b_21a_2\}^\beta|$: $^2B_2$, and for CO_3^-: $|\{1a_12a_11b_21b_13a_14a_12b_25a_11a_22b_13b_2$-$4b_2\}^\alpha\{1a_12a_11b_21b_13a_12b_24a_12b_15a_11a_23b_2\}^\beta|$: $^2B_2$.

According to the two computational models, the orbital housing the odd electron, namely $4b_2$, is largely antibonding for the two symmetry-equivalent oxygens, labeled O′ and O″, respectively. Consequently, the progressive occupancy of this orbital causes a gradual opening of the unique bond angle. Table I illustrates this effect for carbon trioxide and its ions. The angle computed for CO_3^{2-} agrees with experiment.[16] In CO_3 the low apex angle is primarily due to the large stabilization of the $5a_1$ orbital occurring as α is lowered below 120°. The $4b_2$ level acts in the exactly opposite direction.

Table I. Variation of α_{eq} with the Occupancy of the $4b_2$ Level in the Carbon Trioxides

Species	Number of electrons in $4b_2$	Equilibrium angle XHMO	INDO	Ref
CO_3	0	82°	65°	17
CO_3^-	1	108°	82°	This work
CO_3^{2-}	2	120°	120°	This work

Wave Function Population Analysis

The effect presented in Table I also manifests itself in the electron population analysis. In CO_3, calculations by the authors[17] indicate the presence of a formal bond between O′ and O″ (a moderately strong σ bond plus a weak π antibond). In CO_3^- the bond has practically disappeared, as can be seen from Table II which records the O′–O″ electron density for the carbon trioxides

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(20) L. D. Landau and E. Lifshitz, "Quantum Mechanics, Nonrelativistic Theory," Addison-Wesley, Reading, Mass., 1958, p 265.

at their equilibrium angles. The XHMO quantities given in the table are the σ and π total overlap populations.[21] In CO_3^{2-} both quantities are negative, as would be expected for nonbonded atoms. The table also contains the INDO quantity Wiberg[22] refers to as the bond index and which is defined as

Table II. Electron Density between the Symmetry-Equivalent Oxygen Atoms in the Carbon Trioxides

	$CO_3{}^a$	CO_3^-	CO_3^{2-}
XHMO $\sigma_{O'O''}$	0.310	0.002	−0.050
XHMO $\pi_{O'O''}$	−0.020	−0.005	−0.003
INDO $W_{O'O''}$	0.87	0.22	0.11

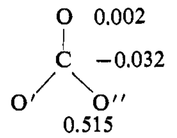
[a] r_{CO} = 1.20 Å.

$$W_{AB} = \sum_{\mu}^{A}\sum_{\nu}^{B} P_{\mu\nu}{}^2$$

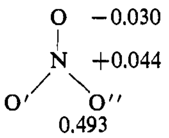
where $P_{\mu\nu}$ is the orbital bond order between atomic orbitals ϕ_μ and ϕ_ν, and where the summations are carried out over all the atomic orbitals on each atom. The trend observed for $W_{O'O''}$ along the series parallels that of the angle α. It should be mentioned that the INDO π bond orders are also negative, in agreement with the XHMO π overlaps.

The INDO spin density in the valence s orbital can be used to evaluate the isotropic hyperfine coupling constants[15] of ^{13}C in CO_3^- and of ^{14}N in NO_3. For the former species the calculated ^{13}C hyperfine constant of −12.9 G compares very favorably with the experimental values of −11.0[8a] and −11.9[10] G. This occurs in spite of the fact that we have neglected vibronic effects[23] and have used a spin-unrestricted spin-unprojected wave function.[24] For NO_3 the calculated ^{14}N isotropic hyperfine coupling constant is 1.5 G. The signs of the experimental coupling constants have actually not been determined, but Chantry, *et al.*,[8a] offer convincing arguments in favor of negative signs. This idea is also supported by the INDO calculations for CO_3^- and for F_2CN where for the latter a ^{13}C constant of −18.7 G is computed (for α = 110°). Assuming a negative sign, the experimental values for the ^{14}N constant in NO_3 are −4.5,[8b,8c] −3.7,[8d] and −1.7[8e] G. It is to be pointed out that the computed quantity is rather sensitive to the value of the bond angle. When the angle opens, it decreases, and at α = 90° it reaches the value of −3.7 G. In view of the approximate nature of our treatment, it is difficult to draw definitive conclusions from these observations. They might be considered as indicating that the value computed for α in NO_3 by the INDO method is somewhat too small, but this is not at all certain.

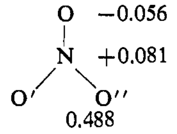
The INDO *atomic* spin densities for CO_3^-, NO_3, and F_2CN are as follows.



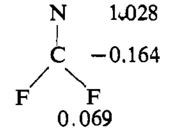
$^2B_2$ (α = 82°)



$^2B_2$ (α = 90°)



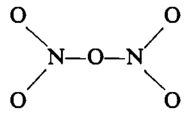
$^2B_2$ (α = 75°)



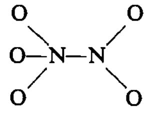
$^2B_2$ (α = 110°)

The odd electron in CO_3^- and NO_3 is seen to be primarily distributed over the two symmetry-equivalent oxygens. This is in agreement with the expression for the unpaired electron orbital $4b_2$. This orbital has its major contribution from the head-on oriented 2p orbitals of O′ and O″.

The predominant spin density on O′ and O″ is supported by the chemical reactivity of NO_3. Indeed, there is evidence[7] that NO_3 reacts with NO_2 in the gas phase to form N_2O_5, whose structure is most probably (see ref 25)



and not



The latter structure would be expected if the odd electron in NO_3 would be concentrated predominantly on nitrogen (as it is in NO_2).

In F_2CN, the odd-electron orbital is largely localized on the nitrogen atom, accounting for the large atomic spin density on that center. This agrees with the qualitative deductions of Dixon, *et al.*[19]

Absorption Spectrum

Experimentally, NO_3 exhibits two absorption systems:[2,4,8a,26,27] one in the visible region, in the vicinity of 6600 Å, the other in the near-ultraviolet, with a maximum around 3300 Å. In CO_3^- the ultraviolet spectrum is obscured by other species, and only one band in the visible region has been assigned to the compound. Chantry, *et al.*,[8a] through the irradiation of single crystals of potassium bicarbonate, observe it at 5350 Å. On the other hand, Serway and Marshall,[10] in their study of α-irradiated single calcite crystals, place it at 6500 Å.

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(21) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343, (1955).

(22) K. Wiberg, *Tetrahedron*, 24, 1083 (1968).

(23) D. L. Beveridge and K. Miller, *Mol. Phys.*, 14, 401 (1968).

(24) P. O. Löwdin, *Phys. Rev.*, 97, 1509 (1955).

(25) (a) W. L. Jolly, "The Inorganic Chemistry of Nitrogen," W. A. Benjamin Co., New York, N. Y., 1964, p 83; (b) "Mellor's Modern Inorganic Chemistry," revised and edited by G. D. Parks, John Wiley and Sons, New York, N. Y., 1967, p 470.

(26) L. Dogliotti and E. Hayon, *J. Phys. Chem.*, 71, 3802 (1967).

(27) D. A. Ramsay, *Proc. Colloq. Spectrosc. Int., 10th*, 583 (1962).

According to Figure 6, the longest-wavelength transition in both compounds should be the allowed, z-polarized transition $^2B_2 \leftarrow {}^2B_2$. This is in agreement with the observation by Chantry, *et al.*,[8a] that the transition in both compounds is polarized in the molecular plane, and with their measured values for the oscillator strength ($f \sim 0.01$ in CO_3^- and $f \sim 0.013$ in NO_3). Note that both the excited state and the ground state are of C_{2v} symmetry. In his vibrational analysis of the band system in gaseous NO_3, Ramsay[27] does not observe long progressions, which indicates that upon excitation there is little change in the geometry of the system. The transition can be roughly described by the electron jump $3b_2 \rightarrow 4b_2$; judging from the difference in the slope of the two orbital energies, one would expect a sizable opening of the angle α in the excited state. The simple one-electron description is not adequate, however, since there must be an important interaction between the states of B_2 symmetry. It is quite possible that proper inclusion of configuration interaction would lead to a value of α in the excited state close to that of the ground state.

The second transition, according to our results, is $^2A_1(^2E') \leftarrow {}^2B_2$ and is also allowed. Chantry, *et al.*,[8a] have estimated its oscillator strength in NO_3 at 0.009, which agrees with our interpretation. Contrary to the first transition, this one involves a drastic change in the geometry of the system.

Concluding Remarks

The calculations reported here point to a Y-shaped structure for the two species CO_3^- and NO_3, in the gaseous state at least. As was the case for carbon trioxide, both methods used in this work agree as to the geometry of the ground state and as to the symmetry of the wave function, namely $^2B_2$. It is therefore tempting to speculate that a more elaborate treatment, of the nonempirical type, would not alter these conclusions.

The present treatment provides evidence that the deviations from the trigonal arrangement are related to the Jahn–Teller theorem. The approach followed in this work is different from those usually utilized in theoretical investigations on the Jahn–Teller effect, which generally make use of the perturbation method, and in which the Hamiltonian is expanded in terms of normal vibration coordinates. However, the main point is that we verify, without resorting to perturbation theory, that orbital degeneracy and stability are not compatible in a nonlinear molecule, as implied by the Jahn–Teller theorem.[18] An interesting result is the hugeness of the deviations reported here, as well as in the case of carbon trioxide.[17] Such large deviations have not yet been observed, to our knowledge, in other degenerate systems.

Whereas both the extended Hückel and the INDO methods agree on the presence of a minimum for α smaller than 120°, they lead to different values for the depth of the potential well. By the XHMO method this quantity is found equal to 1530 and 830 cm^{-1} for CO_3^- and NO_3, respectively, while in the INDO method the corresponding values are 10,096 and 12,400 cm^{-1}. This is not surprising when it is realized how delicate is the calculation of such a potential barrier. In CO_3, the barrier was found an order of magnitude higher, so in that case there is practically no doubt that the molecule is bound to remain in one of the potential wells. In CO_3^- and NO_3 one does not deal with such a clear-cut case. Quantitatively, our results suggest that the radicals cannot oscillate from one minimum to another, but in view of the approximate nature of the calculations, such a possibility cannot be precluded.

Experimentally, the majority of the esr measurements on both species lead to a g tensor of axial symmetry, thus indicating a trigonal structure. It is only for NO_3 trapped in urea nitrate and for CO_3^- in potassium bicarbonate that a g tensor lacking cylindrical symmetry has been observed.[8a] It is important to note that the measured magnetic properties of both radicals vary sizably with the nature of the host crystal.[10]

Adde[8f] has suggested that the species observed by Chantry, *et al.*,[8a] through the γ irradiation of urea nitrate is not NO_3. However, the two band systems they observe coincide with those measured for the species when generated by the flash photolysis of ceric ammonium nitrate, which makes Adde's proposal very doubtful. We feel that the difference between the various observations are not due to misinterpretation, but rather that they are an indication of the high sensitivity of the radicals to the nature of the matrix. The interpretation which comes then readily to mind is that in urea nitrate for NO_3 and in potassium bicarbonate for CO_3^- the environment causes the barrier to be quite high, thus preventing a rapid reorientation of the radicals, whereas in the other crystals investigated the barrier is lowered to such an extent that the radicals appear to have the D_{3h} symmetry.

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