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CNDO Calculations: Electronic Spectra and Nitrogen-14 N.M.R. Shielding Constants for Some Small Nitrogen Ions

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The ^{14}N chemical shifts of the series NO_2^-, NO_3^-, NO_2^+, CN^-, N_3^-, and NH_4^+ have been calculated using CNDO molecular orbitals. The required average energies ΔE were obtained by a simple virtual orbital method. The electronic spectra of the nitrite, nitrate and cyanide ions are discussed.

Die chemischen Verschiebungen des ^{14}N werden für die Reihe NO_2^-, NO_3^-, NO_2^+, CN^-, N_3^- und NH_4^+ mit CNDO-Molekülorbitalen berechnet. Die benötigten mittleren Energien ΔE werden mit einer einfachen Virtual-Orbital-Methode erhalten. Die Elektronenspektren der Nitrit-, Nitrat- und Cyanidionen werden diskutiert.

Les déplacements chimiques ^{14}N dans la série: NO_2^-, NO_3^-, NO_2^+, CN^-, N_3^- et NH_4^+ ont été calculés en utilisant des orbitales moléculaires CNDO. Les énergies moyennes ΔE nécessaires ont été obtenues par une simple méthode à orbitale virtuelle. Les spectres électroniques des ions nitrite, nitrate et cyanure sont discutés.

Introduction

The independent electron molecular orbital theory of diamagnetism applied to ^{13}C and ^{19}F NMR chemical shifts has given satisfactory agreement with experimental data [1, 4, 7, 13]. The same method has been reported to reproduce the ^{14}N chemical shifts in linear [8, 19] and sp^2-hybridized [7] nitrogen-containing molecules and ions, employing π-only LCAO molecular orbitals. Also, the large nitrogen and proton chemical shifts between pyridine and the pyridinium ion have been explained assuming a distribution of the σ-electrons [6]. However, Emsley [4] has shown recently that within the CNDO molecular orbital framework [14] (i. e. no assumption concerning the σ-electron distribution) the calculated nitrogen chemical shift between pyridine and the pyridinium ion is practically zero.

Applications of Pople's theory of chemical shifts requires a knowledge of the electronic charge distribution in the ground state of the molecule as well as an average excitation energy, ΔE, for the magnetically allowed transitions. A common factor of all the above mentioned applications of Pople's theory is an assumption concerning the required ΔE value. The present CNDO calculations were undertaken to obtain the electronic excitation energies by a simple virtual orbital method for a series of small nitrogen ions: NO_2^-, NO_3^-, NO_2^+, CN^-, N_3^-, and NH_4^+. This approximate description of the excited states coupled with the ground state atomic charges from CNDO molecular orbitals provides a basis for testing the ability of the chemical shift theory to reproduce the observed ^{14}N chemical shift range (approximately 600 ppm) [3] for the above series of ions.

Calculations

Modified CNDO/1 calculations were performed on a CDC 6400 computer using a Fortran IV program [10]. Details and approximations for the calculations of molecular orbital eigenvectors, eigenvalues, electronic state wave functions, and excitation energies are given in Ref. [10]. In all cases except the nitrate ion the configuration interaction included all possible one electron determinants resultant from the filled and virtual molecular orbitals. The three lowest filled orbitals of the nitrate ion were not used in the configuration interaction calculation for the nitrate ion.

Calculations of the ^{14}N shielding constants were performed considering only the "paramagnetic" contribution. Neglecting the two-center integrals and using the average energy approximation, the mean value of the local paramagnetic chemical shielding tensor for atom A has the form [7]

$$\sigma_p^{AA} = -\frac{e^2 h^2}{2m^2 c^2 (\Delta E)_{av.}} \langle r^{-3} \rangle_{2p} \sum_{B} Q_{AB} \tag{1}$$

where

$$\begin{aligned} Q_{AB} = {} & \tfrac{4}{3} \delta_{AB} P_{x_A x_B} + P_{y_A y_B} + P_{z_A z_B}) \\ & - \tfrac{2}{3} (P_{y_A y_B} P_{z_A z_B} + P_{z_A z_B} P_{x_A x_B} + P_{x_A x_B} P_{y_A y_B}) \\ & - \tfrac{2}{3} (P_{y_A z_B} P_{z_A y_B} + P_{z_A x_B} P_{x_A z_B} + P_{x_A y_B} P_{y_A x_B}) . \end{aligned} \tag{2}$$

Here, the $P_{\mu\nu}$ are charge-density bond-order matrix elements for the $2p$ orbitals on atoms A or B. The average excitation energies $(\Delta E)_{av.}$ for the magnetically allowed transitions were taken as the eigenvalue of the lowest electronic state of proper symmetry. Any possible localization of the excitation on particular atoms was ignored. The average inverse cubic radius for a nitrogen $2p$ electron was calculated as

$$\langle r^{-3} \rangle_{2p} = \tfrac{1}{3} (Z_A / 2a_0)^3 \tag{3}$$

where Z_A is the nuclear charge obtained by Slater's rules considering the net electron density ϱ_A on the nitrogen atom A

$$Z_A = 3.90 - 0.35(\varrho_A - 1) .$$

Results and Discussion

Electronic Spectra

Nitrite ion. Experimentally determined bond lengths and angles, $r_{NO} = 1.23$ Å and $\sphericalangle$ ONO $= 116°$ [18], were used in the calculation of the electronic spectrum. The calculated and experimental transition energies and oscillator strengths for the nitrite ion are listed in Table 1. Only the lowest calculated transition energies of each symmetry are included in the table.

In an earlier calculation, McEwen [11][1] assigned the observed nitrite transition energies at 3.50, 4.20, and 5.95 eV to symmetries of $^1B_1$, $^1A_2$, and $^1B_2$, respectively. The spacing of the three corresponding transitions in Table 1 is the same as that obtained by McEwen within 4%. In addition, two more states of low energy are predicted, one allowed at 6.03 eV ($^1A_1$) and one forbidden at 5.92 eV ($^1A_2$). Considering the calculated and observed oscillator strengths for the various transitions, the assignment proposed by McEwen seems most reasonable. Thus, assignment of the calculated 4.91 eV ($^1B_2$) transition to the observed band at 4.20 eV

Table 1. *Electronic transitions for the nitrite, nitrate, and cyanide ions*

Ion	Symmetry	Energy (eV) and Oscillator Strength[a]	
NO_2^-	$^1B_1$	2.16 (3.50); 7.22; 8.31	0.0024 (0.0005)[b]
	$^1A_2$	3.59 (4.20); 5.92; 13.1	0 (0.0004)[b]
	$^1B_2$	4.91 (5.95); 10.2; 14.4	0.038 (0.20)[b]
	$^1A_1$	6.03; 7.96; 11.1	0.0046
NO_3^-	$^1E'$	4.39 (4.10); 6.34 (6.26); 10.8	0.0054 (0.0001); 0.25 (0.15)[b]
	$^1A_2'$	4.56; 10.6; 16.2	
	$^1A_1'$	12.2	
	$^1E''$	4.06; 4.84; 9.89	
	$^1A_1''$	5.45	
CN^-	$^1\Pi$	5.69 (3.92); 11.5; 12.4	0.013 (---)[c]
	$^1\Delta$	7.46	
	$^1\Sigma^-$	7.46	
	$^1\Sigma^+$	9.27; 16.2; 19.1	

[a] Only the lowest calculated transition energies are given; experimental values follow in parentheses. In some cases the oscillator strengths, both calculated and observed, are listed in the fourth column for the lowest-value transition energies.

[b] See Ref. [11].

[c] This work.

is precluded due to the large calculated oscillator strength. The experimental work of Strickler and Kasha [16] has also shown that the same assignment is reasonable on the basis of solvent effects on the absorption spectrum of nitrite. Possibly the calculated 6.03 eV ($^1A_1$) band is the high energy shoulder on the 5.95 eV band observed by Strickler and Kasha in the nitrite spectrum in acetonitrile.

Nitrate ion. Calculations were carried out assuming D_{3h} symmetry and with $r_{NO} = 1.21$ Å [18]. Two allowed transitions, both of E' symmetry, are predicted as shown in Table 1. The lower energy E' transition arises from a low energy a_1^* antibonding orbital originally suggested by McEwen [11] to account for the lower energy band in the electronic spectrum. The calculated oscillator strengths for both E' transitions exceed the corresponding experimental values, but qualitative agreement is all that is expected [12]. Both nitrate bands have been observed [15]

[1] In addition to McEwen's semiempirical method (Ref. [11]) involving self-consistent π-orbitals combined with a Hückel type σ-system, Kato *et al.* (Kato, H., L. Yonezawa, K. Morokum, and K. Fukui: Bull. chem. Soc. Japan, **37**, 1710 (1964)) and Burnelle *et al.* (Burnelle, L., P. Beaudouin, and L. Schaad: J. physic. Chem. **72**, 2240 (1967)) have applied extended Hückel calculations to the nitrite ion. Our CNDO molecular orbitals compare best with McEwen's orbitals. Also, the extended Hückel method gives a different ordering for the highest filled molecular orbitals; this is a common phenomenon of extended Hückel calculations (Ref. [10] and references therein).

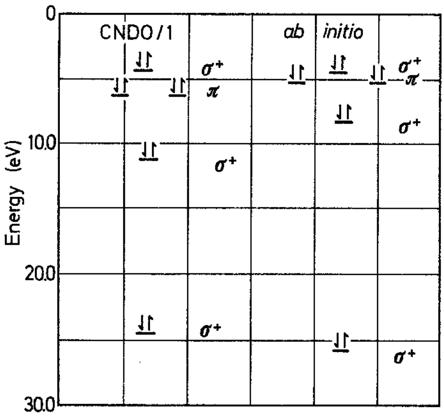

Fig. 1. Comparison of the filled molecular orbital energies obtained by CNDO/1 vs. those by an *ab initio* method for the cyanide ion

to have E' polarization in agreement with the above assignments. Strickler and Kasha [17] have made an alternate assignment for the lower energy band on the basis of the effects of solvent and temperature. They assign the 4.10 eV band as the highly forbidden $n \rightarrow \pi^*$ transition of A_1'' symmetry. According to our calculations this assignment is unsatisfactory.

Cyanide ion. The carbon-nitrogen bond distance was taken as 1.13 Å, the value obtained in the crystal structure of KCN [18]. CNDO molecular orbitals and energies were calculated and the ordering of the molecular orbitals is compared in Fig. 1 with that obtained by an *ab initio* calculation[2]. In the latter case a "double zeta plus polarization basis" was used [2], where the polarization consisted of one $3d\sigma$ and one $3d\pi$ function for the carbon and nitrogen with orbital exponents of 1.70, 1.80, 1.90 and 2.00, respectively. No optimization of orbital exponents was attempted, for it is reasonable to expect the molecular orbital energies would be close to convergence. As seen in Fig. 1, the CNDO ordering is quite similar to the *ab initio* ordering for the cyanide ion.

For the cyanide ion the ultraviolet region shows one peak at 3.92 eV shouldering on the end absorption[3]. Calculated transition energies and the calculated oscillator strength for the allowed $^1\Pi$ transition at 5.59 eV are listed in Table 2. It seems reasonable to assign the observed band at 3.92 eV to the lowest calculated $^1\Pi$ transition energy. It was not possible to determine an oscillator strength for this band, but the molar extinction coefficient was found to be approximately 2.0 *l*/mole-cm.

Azide, Ammonium, and Nitryl Ions. Molecular dimensions obtained in standard structure determinations [18] were used for the calculations on the azide, ammonium, and nitryl ions. The calculated transition energies for these ions are listed in Table 2. No experimental data are available as a check on the calculations.

[2] The *ab initio* calculations were completed using QCPE 104, "McLyosh Linear Molecule Program I", A. D. McLean and M. Yoshimine. Dr. McLean's assistance is gratefully acknowledged.

[3] Measurements on aqueous solutions of KCN were completed using a Cary 14 spectrophotometer. For previous mention of the CN^- absorption spectrum see: Buck, R. P., S. Singhadeja, and L. B. Rogers: Anal. Chem. **26**, 1240 (1954).

Table 2. *Electronic transitions for the ammonium, azide, and nitryl ions*

Ion	Symmetry	Energy (eV)
NH_4^+	$^1T_2$	9.40; 23.1; 30.5
	$^1T_1$	22.5
	$^1E_1$	22.5
	$^1A_1$	25.4; 34.4
N_3^-	$^1\Pi_g$	3.69; 7.08; 17.5
	$^1\Sigma_g^-$	9.77
	$^1\Sigma_g^+$	12.0; 17.1; 22.4
	$^1\Delta_g$	9.78
	$^1\Pi_u$	8.61; 12.3; 13.3
	$^1\Sigma_u^-$	2.62
	$^1\Sigma_u^+$	6.94; 15.8; 19.8
	$^1\Delta_u$	26.2
NO_2^+	$^1\Pi_g$	3.78; 7.23; 16.6
	$^1\Sigma_g^+$	8.60
	$^1\Sigma_g^+$	11.3; 17.2; 24.2
	$^1\Delta_g$	8.60
	$^1\Pi_u$	7.92; 13.4; 14.4
	$^1\Sigma_u^-$	4.37
	$^1\Sigma_u^+$	6.81; 17.5; 22.4
	$^1\Delta_u$	4.37

^{14}N-*Shielding Constants*

The usual applications of Eq. (1) for the calculation of chemical shifts for a series of structurally similar molecules involves the assumption of one ΔE value for all molecules. Often, a "reasonable" adjustment in ΔE is made. However, for the diversified series of ions under study here, the ΔE's were chosen as the eigenvalue for the lowest electronic state of proper symmetry; only very qualitative agreement between calculated and observed ^{14}N-chemical shifts were obtained (Column 6, Table 3).

The disparities in the qualitative trend between our calculated and the observed chemical shifts may be attributed, at least in part, to differences in the effectiveness of the amount of configuration interaction considered for each ion. Thus, for the electronic spectrum of cyanide ion, the calculation for the lowest electric dipole

Table 3. *Calculated and observed* ^{14}N *chemical shifts*

Ion	$\sum_B Q_{AB}$	$\langle r^{-3}\rangle_{2p}$	ΔE (eV)	$-\sigma_{p\,(calc.)}$ ($\times 10^6$)	$\delta_{calc.}$ (ppm)	δ_{obs}[a] (ppm)
NO_2^-	2.878	2.539	2.16	2453	$\equiv 0$	$\equiv 0$
NO_3^-	2.934	2.768	4.06	1450	1003	254
NO_2^+	2.564	3.039	3.78	1494	958	260
CN^-	2.186	2.143	5.69	597	1856	380
N_3^- inner	2.493	2.537	3.69	1243	1210	383
N_3^- outer	2.247	2.124	3.69	938	1515	532
NH_4^+	1.901	2.498	22.5	153	2300	600

[a] See Refs. [3] and [20].

transition gives an energy 1.77 eV in excess of the value determined for the only peak observed. On the other hand, for the nitrite ion the experimental transition energies exceed their corresponding calculated values; as a result the calculated nitrogen chemical shift between nitrite and cyanide ions is too large. Accordingly, adjustment of the ΔE value for the nitrite ion to 3.0 eV will improve the quantitative agreement in many cases. A better ΔE could be obtained if a weighted average of the eigenvalues for the lowest electronic states of proper symmetry was used. This would require more refined excited state eigenfunctions and transition energies, secured possibly by using an improved virtual orbital approach [9].

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