AnAB initio study of the geometrical structures and vibrational spectra of the free ion NO 2 ? and the LiNO2 molecule

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AN *AB INITIO* STUDY OF THE GEOMETRICAL STRUCTURES AND VIBRATIONAL SPECTRA OF THE FREE ION NO_2^- AND THE $LiNO_2$ MOLECULE

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The Hartree—Fock—Roothaan method has been used in a two-exponential basis with and without the inclusion of polarization defunctions on the nitrogen and oxygen atoms to calculate the geometry and the vibrational characteristics of the free NO_2^- ion and the $LiNO_2$ molecule. The results are compared with published data as regards the nitrite ion and the alkali-metal nitrites. The parameters of the LiO_2N rings in $LiNO_3$ and $LiNO_2$ are compared. A study has been made of the effects of the polarization defunctions on the calculated parameters of NO_2^- and $LiNO_2$. The rigid rotor-harmonic oscillator approximation has been used to calculate the thermodynamic parameters of $LiNO_2$ in the ideal-gas state.

So far there have been no experimental studies on the geometry and vibrational spectrum of the $LiNO_2$ molecule. The spectroscopic data [1, 2] and electron diffraction [3, 4] indicate cyclic structures for the molecules MNO_2 (M = Na, K, Rb, Cs). Nevertheless, no final conclusion has been drawn [1-4] on the symmetry of the equilibrium configurations in these molecules.

In accordance with the data of [1-4], nonempirical calculations on MXO_2 (M = Li, Na; X = N, P) [5] have shown that the least energy occurs in a cyclic structure of the form
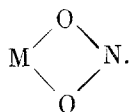
Also, according to [5], the potential surface for a molecule of this type has three further local minima corresponding to the structures Li—O—N,

, and
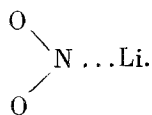
There have been no theoretical studies on the force fields and vibrational spectra of the alkali metal nitrites.

In previous *ab initio* studies on the free NO_2^- ion (see for example [6] and references in [7]), only the electronic and geometrical structures were considered.

Here we examine the geometrical structure and vibrational spectra of the $LiNO_2$ molecule and the free NO_2^- ion by the SCF MO LCAO method by the use of fairly broad and flexible bases.

CALCULATION DETAILS

All the calculations were performed with the MOLECULE program [8] at the computing center at Ivanovo Chemical Technology Institute. We used the following sets of grouped gaussian functions: $DZ - (9s5p/4s2p)_{N,O}$, $(9s4p/4s2p)_{Li}$ [9, 10] and $DZ + P$ being the smae basis supplemented with polarization functions of d type on the nitrogen and oxygen atoms with the exponents 0.80 (N) and 0.85 (O) [11].
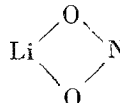
The geometrical parameters of the cyclic structure (C_{2v}) and of the NO_2^- ion

TABLE 1. Characteristics of the Free NO_2^- Ion*

Parameter	Ab initio calc.		Published data
	DZ	DZ+P	
$-E$	204,02512	204,12419	
R_e(N—O)	1,273	1,235	(1,23±0,05) [7]
α_e(O—N—O)	116,7	116,6	(118±5) [7]
Q(N)	+0,420	+0,116	
Q(O)	−0,710	−0,580	
q(N—O)	0,338	0,589	
f_d	8,547	11,587	7,50 [17]
f_{dd}	2,033	3,013	1,66 [17]
f_α	1,614	1,952	1,67 [17]
$f_{d\alpha}$	0,359	0,467	0,394 [17]
$\nu_1(A_1)$	1394	1623	(1330±20) [7]
$\nu_2(A_1)$	800	888	(810±20) [7]
$\nu_3(B_2)$	1354	1554	(1245±40) [7]
$(\partial\mu/\partial Q_1)^2$	1,00	0,90	
$(\partial\mu/\partial Q_2)^2$	0,45	0,29	
$(\partial\mu/\partial Q_3)^2$	17,13	20,65	
μ†	0,803	0,626	
IP	4,10	3,58	2,36±0,10 ‡ [7]

*Here and in Tables 2 and 5, we use the following symbols and dimensions: E total energy (au), R, internuclear distance (Å), α bond angle (deg), Q charge on an atom (au), q populations in the bonds (au), f force constant (mdyn/Å), ν frequency (cm^{-1}),

$(\partial\mu/\partial Q_i)^2$ square of the derivative of the dipole moment coordinate Q_i ($D^2\,\text{Å}^{-2}\,\text{a.m.u.}^{-1}$), μ dipole moment (D); IP ionization potential (eV), and l mean amplitude (Å).

† The center of mass coincides with the center of the coordinates.

‡ Electron affinity of the NO_2 Molecule.

TABLE 2. Characteristics of the $LiNO_2$ Molecule Calculated *Ab initio*

Parameter	DZ	DZ+P	Parameter	DZ	DZ+P
$-E$	211,52362	211,63045	Q(N)	+0,350	+0,347
R_e(N—O)	1,277	1,238	Q(O)	−0,569	−0,552
R_e(Li—O)	1,934	1,886	q(N—O)	0,315	0,544
R_e(Li ... N)	2,341	2,255	q(Li—O)	0,184	0,168
α_e(O—N—O)	111,4	113,6	μ	6,42	6,13
Q(Li)	+0,788	+0,757	IP	11,5	11,0

were optimized not only in the DZ basis but also D_Z+P. Also, in DZ we optimized the

$$\text{Li—}O_b\text{—N}^{\diagup O_t} \quad (C_s)$$

structure with the linear Li—O_b—N, fragment, which according to [5] is the isomer having the energy closest to that of the cyclic structure. We obtained the following internuclear distances for the C_s configuration: R(N—O_t) 1,232, R(N—O_b) 1,306, R(Li—O_b) 1,636 Å and the bond angle α(O_t—N—O_b) 115,4°. Table 1 and 2 give the calculated characteristics for NO_2^- and $LiNO_2$.

TABLE 3. Force Constants of the LiNO$_2$ Molecule (mdyn/Å)
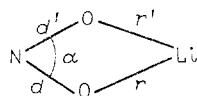
Force constant	DZ	DZ+P	Force constant	DZ	DZ+P
f_r	0,701	0,833	f_{dr}	0,260	0,339
f_{rr}	0,194	0,072	f_α	2,113	2,350
f_d	8,411	11,027	$f_{r\alpha}$	−0,214	−0,165
f_{dd}	2,539	3,033	$f_{d\alpha}$	0,691	0,783
f_{dr}'	−0,234	−0,309	f_ω	0,214	0,186

TABLE 4. Vibration Frequencies ν_i (cm^{-1}), Values of $(\partial\mu/\partial Q_i)^2$ $(D^2 Å^{-2}$ a.m.u.$^{-1})$, Potential-Energy Distribution PED Over the Natural Coordinates, and Isotopic Shifts $\Delta\nu_i$ (^{6}Li—^{7}Li) (cm^{-1}) for the LiNO$_2$ Molecule

Type	DZ		DZ+P		PED *(DZ)	$\Delta\nu_i$(^{6}Li—^{7}Li)	
	ν_i	$(\partial\mu/\partial Q_i)^2$	ν_i	$(\partial\mu/\partial Q_i)^2$		DZ	DZ+P
A_1	ν_1 1423	0,86	1590	0,74	$0,80d + 0,20\alpha$	0,2	0,1
	ν_2 882	0,51	959	0,36	$0,85\alpha$	0,2	0,5
	ν_3 589	2,79	589	2,90	$0,98r$	40,9	40,8
B_2	ν_4 1266	17,49	1490	21,20	$1,00d$	0,5	0,5
	ν_5 340	0,32	422	0,38	$0,91r$	15,8	19,8
B_1	ν_6 301	1,77	279	1,44	$1,00\omega$	4,3	3,7

*Contributions to PED less than 0.15 have been omitted

[14]* for LiNO$_2$. Then a similarity transform was applied to matrix F to find the force constants in the natural coordinates (Table 3).

DISCUSSION

NO$_2^-$Ion. We found changes in the theoretical values of the geometrical parameters and characteristics for the nitrite ion on including the polarization d functions in the DZ basis analogous to those obtained previously for the BO$_2^-$, NO$_3^-$ and CO$_3^{2-}$ [16]. The shortening of the R_e(N—O) internuclear distance is accompanied by reductions in the magnitudes of the charges on the atoms and by increases in the bond populations. The force constants f_d, f_{dd}, f_α, and $f_{d\alpha}$, increase by 36, 48, 20, and 30%, while the frequencies ν_1, ν_2, and ν_3 increase by 16, 11, and 15% correspondingly. The calculations with the DZ basis on the whole reproduce the experimental data better than do those with DZ + P. While the force constants obtained with the DZ basis differ from the experimental values [17] by on average 12%, the differences for DZ + P is 42%. The deviations in the frequencies of the normal vibrations are 4.5% (DZ) and 19% (DZ + P).

The isotopic shifts calculated with the DZ basis for the vibrational frequencies of NO$_2^-$ under the substitutions ^{14}N → ^{15}N, ^{16}O → ^{18}O also agree well with the experimental values [17] (mean deviation 7%, maximum 11.7%).

LiNO$_2$ Molecule. The calculations showed that the C$_{2v}$ configuration for the lithium nitrite molecule lies lower in energy than does C$_s$. The difference $E(C_s) - E(C_{2v})$ is 27.6 kJ in the DZ basis or 62.3kJ † in the DZ + P basis. Therefore, a difference from LiBO$_2$ [18] is that adding the polarization functions to the basic sets of atoms in the acid residue increases the molecular rigidity as regards the motion of the lithium around the NO$_2$ fragment in the plane.

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*In the case of LiNO$_2$, instead of the S(B$_1$) coordinate adopted in[4] we used $S(B_1) = \sqrt{RD/2}(\omega_1 - \omega_2)$ [15].
†Difference in energy between structures whose geometrical parameters were found in the DZ basis.

A check with the DZ basis showed that the C_S structure is not an isomer and does not correspond to any singular point on the potential surface. Movement of the lithium atom that causes the $Li-O_b-N\overset{/O_t}{}$ to form a ring reduces the energy, while motion in the opposite direction increases it. This result casts doubt on the conclusions of [5] on the existence of two other isomers for the MXO_2 molecule.

We now consider the changes in the $LiNO_2$ molecule on extending the basis by including polarization d functions. In the case of the NO_2 section, the changes in the geometrical parameters and electron-density distribution are the same as in the NO_2^- ion. The $Li-O$ bond resembles $N-O$ in shortening when there is the corresponding increase in the force constant f_r. The changes in the nondiagonal force constants means that there is a decrease in the difference between the frequencies of the symmetrical and antisymmetric stretching vibrations of the NO_2 and LiO_2 fragments. The diagonal force constants and vibrational frequencies increase when d functions are included in the basis: ν_1 by 12%, ν_2 by 8%, and ν_5 by 24%. An exception is represented by f_ω and the corresponding frequency ν_6 (B_1), which corresponds to nonplanar ring bending (ν_6 decreases by 8%), while ν_3 hardly alters.

The calculations indicate that the $R_e(N-O)$ internuclear distances in $LiNO_2$ and NO_2^- are similar, although there is an altered electron-density distribution in $LiNO_2$ and a reduction in f_d. The other force constants f_α, f_{dd}, $f_{d\alpha}$ increase. There are certain differences in the changes in ν_{sym} (N-O) on going from NO_2^- to $LiNO_2$ in the DZ and DZ + P bases: While the value increases in DZ (mainly due to increase in f_{dd}), it decreases in DZ + P.

Table 4 gives the frequencies of the normal vibrations ν_j and the values of $(\partial\mu/\partial Q_i)^2$, which are proportional to the intensities of the IR bands. No experimental value have been published. For other MNO_2 (M = Na, K, Rb, Cs), measurements have been made only of the wave numbers of the strongest band ν_4 [1, 2], which is close to $\nu_3 = 1245 \pm 40$ cm^{-1} [7] for the nitrite ion, and also $\nu_2 = 802$ and 808 cm^{-1} for KNO_2 [1] (doubling due to band splitting in the matrix), which are close to $\nu_2 = 810 \pm 20$ cm^{-1} [7] in NO_2^-. The constancy of ν_4 in the sequence MNO_2 (M = Na, K, Rb, Cs) and the similarity of ν_4 and ν_2 to the corresponding frequencies for NO_2^- would indicate that the vibrations of the NO_2 section in the MNO_2 molecules are highly characteristic, including vibrations of totally symmetric type $\nu_{.sym}(N-O)$. Therefore, a comparison with the measured frequencies for the free NO_2^- ion [7] enables one to estimate the errors in calculating ν_1, ν_2, and ν_4 for $LiNO_2$; the errors evidently do not exceed 10% in the DZ basis or 20% in DZ + P. The error in calculating $\nu_3(Li-O)$ in the DZ basis is probably of the same order as for $\nu(Li-O)$ in $LiNO_3$ ($\delta = 7.4\%$) [19]. On the whole, as for NO_2^-, the addition of the d functions to the DZ basis leads to an increase in the relative error in determining the frequencies for $LiNO_2$. A similar conclusion can probably be drawn for the frequencies of the fragment $Li\diagdown{}^O_O\diagup N$ in $LiNO_3$.

The calculated isotopic shifts for NO_2 due to the substitutions $^{14}N \to {}^{15}N$ and $^{16}O \to {}^{18}O$ are similar to those for the nitrite ion [17].

We now compare the structure and parameters of MNO_2 with those of the fragment MO_2N in the MNO_3 molecule. Vapor electron diffraction [3, 20, 21] has shown that the effective internuclear distances and the mean vibration amplitudes of the $RbNO_2$ and $CsNO_2$ molecules and of the $M\diagdown{}^O_O\diagup N$ ring in $RbNO_3$ or $CsNO_3$ are the same within the limits of the experimental error. In the interpretation of the internuclear distances for MNO_3, it was assumed [20, 21] that the NO_3 fragment has D_{3h} symmetry. The internuclear distances $R(N-O)$ and $R(O...O)$ derived in [20, 21] correspond therefore to certain effective values $\bar{R}(N-O) = [R(N-O_t) + 2R(N-O_b)]/3$ and $\bar{R}(O...O) = [R(O_b...O_b) + 2R(O_b...O_t)]/3$. The quantities $\bar{l}(N-O)$ and $\bar{l}(O...O)$ were determined analogously.

It is evident from Table 5 that $R_e(N-O)$, $l(N-O)$ in $LiNO_2$ and $\bar{R}(N-O)$, $\bar{l}(N-O)$ in $LiNO_3$ are virtually the same. The characteristicity of the $R(M-O)$ bond lengths for the heavy atoms and the mean amplitudes $l(M-O)$ in the ring [3, 20, 21] apply also for $Li-O$. The force

TABLE 5. Comparison of the Parameters of the Li$\langle$O$\rangle$N Ring in $LiNO_2$ and $LiNO_3$ Calculated in the DZ Basis

Parameter	$LiNO_2$	$LiNO_3$ [19]	Parameter	$LiNO_2$	$LiNO_3$ [19]
$R(N-O)$	1,277	1,313	$l(Li \cdots N)$	0,102	0,102
$\bar{R}(N-O)$		1,278	$l(O \cdots O)$	0,056	0,065
$R(Li-O)$	1,934	1,926	$\bar{l}(O \cdots O)$		0,063
$R(Li \cdots N)$	2,341	2,305	f_r	0,701	0,744
$\alpha(O-N-O)$	111,4	113,3	f_{rr}	0,194	0,205
ν_{sym} (Li—O)	589	567	f_d	8,411	6,084
ν_{sym} (N—O)	1423	1013	f_{dd}	2,539	1,230
ν_{asym} (Li—O)	340	351	$f_{dr'}$	−0,234	−0,074
ν_{asym} (N—O)	1266	1240	f_{dr}	0,260	0,099
ν_{op}	301	185	f_α	2,113	1,801
$l(Li-O)$*	0,139	0,133	$f_{r\alpha}$	−0,214	−0,212
$l(N-O)$	0,047	0,051	$f_{d\alpha}$	0,691	0,298
$\bar{l}(N-O)$		0,047	f_ω	0,214	0,245

*Values given for T = 800°K

TABLE 6. Thermodynamic Functions for $LiNO_2$ Ideal Gas in J/mole·°K

T, K	100	298,15	500	1000	1500	2000	2500	3000
c_p	37,01	54,64	65,77	76,99	80,19	81,43	82,03	82,37
Φ^*	177,00	217,80	241,53	280,00	306,04	325,86	341,85	355,28
S^0	211,05	260,17	291,29	341,20	373,13	396,40	414,64	429,63

constants show that NO_2 in $LiNO_2$ is more rigid than in the Li$\langle$O$\rangle$N ring in $LiNO_3$: the values of $f_d, f_{dd}, f_\alpha, f_{d\alpha}$ in the nitrite are larger than those in the nitrate. On the other hand, f_r and f_{rr} are larger in $LiNO_3$. Nevertheless, in spite of certain differences, there are analogous force fields and similarity between certain frequencies for lithium nitrite and nitrate. For example, ν_{sym}(Li—O) and ν_{sym}(Li—O) for $LiNO_3$ and $LiNO_2$, which are related to motion of the lithium relative to the acid residue in the plane of the molecule.

We used the molecular parameters of $LiNO_2$ obtained in the DZ basis (Tables 2 and 4) for the rigid rotor-harmonic oscillator approximation to calculate the thermodynamic functions of $LiNO_2$ in the ideal-gas state (Table 6), which are required to calculate high-temperature processes involving lithium nitrite vapor.

The *ab initio* calculations give the energy for the dissociation of $LiNO_2$ into Li^+ and NO_2^- as 690 kJ/mole* in the DZ basis or 709 kJ/mole in the DZ + P. The energies for dissociation into Li plus NO_2 were calculated from data on the ionization potential of the lithium atom (IP(Li) = 5.39178 ± 0.00001 eV [22]) and the electron affinity of NO_2 (EA (NO_2) = 2.36 ± 0.10 eV [7]) as 397 and 417 kJ/mole in the DZ and DZ + P bases correspondingly.

Therefore, we have derived the complete force field and vibrational spectrum for the lithium nitrite molecule. The calculations show close analogies in structure and properties between $LiNO_2$ and the Li$\langle$O$\rangle$N ring in $LiNO_3$ as previously observed for compounds of the heavy alkali metals [3, 20, 21]. The data will be useful in future theorethical and experimental studies on $LiNO_2$ and similar molecules.

*E(Li^+) = −7.23599 au.

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