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## He I Photoelectron Spectra of Gaseous Alkali Nitrates

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The He I photoelectron spectra of the high-temperature gas-phase molecules  $\text{KNO}_3$ ,  $\text{RbNO}_3$ , and  $\text{CsNO}_3$  have been obtained by use of a modified cylindrical-mirror electron spectrometer equipped with an internally located, resistance-heated sample oven. Attempts to obtain data for  $\text{LiNO}_3$  and  $\text{NaNO}_3$  were unsuccessful because of decomposition. The identities of the vapor-phase molecules were determined by use of data derived from the techniques of electron diffraction, mass spectrometry, and matrix-isolated infrared spectroscopy. The ionization energies were assigned molecular-orbital origins through the use of MO calculations, comparisons with X-ray and He II photoelectron data from investigations of solids, and analogies with other ionic compounds of similar type.

### 1. Introduction.

In recent years there has been an increasing interest in obtaining UV PES (ultraviolet photoelectron spectroscopy) data on vapors of substances which are solids at room temperature. This interest has stemmed from an attempt to understand better the structure and bonding of high-temperature gas-phase molecules. As yet, very few oxyanion-containing compounds have been investigated, although considerable data have been collected on the gaseous forms of these compounds by mass spectrometry, electron diffraction, and matrix-isolation infrared spectroscopic investigations. In addition, a substantial quantity of X-ray photoelectron data, He II photoelectron data, and X-ray emission data for the solid compounds is available along with numerous theoretical MO calculations for the free anions. The compounds which so far have been studied by UV PES are  $\text{TlBO}_2$ ,  $\text{TlNO}_3$ ,  $\text{Ti}_2\text{SO}_4$ ,  $\text{TiReO}_4$ ,<sup>1</sup>  $\text{LiReO}_4$ ,  $\text{NaReO}_4$ ,  $\text{KReO}_4$ ,  $\text{RbReO}_4$ , and  $\text{CsReO}_4$ .<sup>2</sup>

The results of several studies of the vapors over heated alkali-metal nitrates indicate different degrees of stability for  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ , and  $\text{KNO}_3$ , depending on the pressure, the atmosphere, the composition of the sample container, the rate of heating, and the presence of impurities, especially water. The data from mass spectrometric investigations on  $\text{LiNO}_3$  and  $\text{NaNO}_3$  may be taken to indicate considerable decomposition in the 650–750 K range; however, similar studies of  $\text{RbNO}_3$  and  $\text{CsNO}_3$  indicate little or no decomposition in the vapor state. These studies and others of related interest which attribute stability to at least some of the alkali-metal nitrates prompted this UV PES investigation of the vapors over heated  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{RbNO}_3$ , and  $\text{CsNO}_3$ .

### 2. Experimental Procedure

All compounds were commercially obtained, were quoted as being at least 99.9% pure, and, except for drying, were used as obtained.

All spectral measurements presented in this paper were made with a truncated cylindrical-mirror analyzer (as previously described<sup>3</sup>) equipped with a resistance-heated tantalum-strip-wound quartz cell coated with Astroceram, a high-temperature ceramic cement obtained from Chemo-Thermic Industries. The cell was heated by a 0–12 V pulse supply. The procedures for sample heating and spectral accumulation have been described previously<sup>1</sup> and will not be repeated here.

Table I. Nitrate Data

approach	value, eV
$\text{KNO}_3$ vapor (exptl He I)	8.96, <sup>a</sup> 9.94, <sup>a</sup> 10.52, <sup>a</sup> 16.13, <sup>a</sup> 16.72 <sup>a</sup>
$\text{RbNO}_3$ vapor (exptl He I)	8.89, <sup>a</sup> 9.91, <sup>b</sup> 10.59, <sup>b</sup> 15.86, <sup>b</sup> 16.57 <sup>b</sup>
$\text{CsNO}_3$ vapor (exptl He I)	8.78, <sup>c</sup> 9.84, <sup>b</sup> 10.46, <sup>b</sup> 15.76, <sup>b</sup> 16.63, <sup>d</sup> 17.66, <sup>d</sup> 18.99 <sup>d</sup>
$\text{NO}_3^-$ (ab initio calcn) <sup>e</sup>	1a <sub>2</sub> ', 9.9; 1e'', 10.1; 4e', 11.4; 3e', 17.7; 1a <sub>2</sub> '', 18.9; 4a <sub>1</sub> ', 20.5
$\text{NO}_3^-$ (ab initio calcn) <sup>f</sup>	1a <sub>2</sub> ', 9.9; 1e'', 10.1; 4e', 11.6; 3e', 17.8; 1a <sub>2</sub> '', 18.8; 4a <sub>1</sub> ', 20.5
$\text{NO}_3^-$ (ab initio calcn) <sup>g</sup>	1a <sub>2</sub> ', 9.9; 1e'', 10.0; 4e', 11.4; 3e', 17.5; 1a <sub>2</sub> '', 19.3; 4a <sub>1</sub> ', 19.6
$\text{NO}_3^-$ (ab initio calcn) <sup>h</sup>	1a <sub>2</sub> ', 9.9; 1e'', 10.4; 4e', 11.9; 3e', 17.6; 1a <sub>2</sub> '', 19.1; 4a <sub>1</sub> ', 19.8
$\text{NO}_3^-$ (ab initio calcn) <sup>i</sup>	1a <sub>2</sub> ', 9.9; 1e'', 9.9; 4e', 11.4; 3e', 17.5; 1a <sub>2</sub> '', 18.1; 4a <sub>1</sub> ', 20.7
$\text{MNO}_3$ solid (exptl X-ray) <sup>j</sup>	1a <sub>2</sub> '-1e''-4e', 10.8; 3e'-1a <sub>2</sub> '', 17.2; 4a <sub>1</sub> ', 19.8
$\text{KNO}_3$ solid (exptl He II) <sup>k</sup>	1a <sub>2</sub> ', 9.9; 1e'', 10.8; <sup>o</sup> 4e', 11.6; <sup>o</sup> 3e', 16.8; 1a <sub>2</sub> '', 17.4; 4a <sub>1</sub> ', 19.5
$\text{F}_3\text{-CHg-NO}_3$ vapor (exptl He I) <sup>l</sup>	1a <sub>2</sub> ', 11.1; 1e'', 12.1; 4e', 12.6 <sup>n</sup>
$\text{TlNO}_3$ vapor (exptl He I) <sup>m</sup>	1a <sub>2</sub> ', 9.9; 1e'', 11.1; 4e', 11.4; 3e', 16.7; 1a <sub>2</sub> '', 17.2

<sup>a</sup> ±0.03 eV. <sup>b</sup> ±0.04 eV. <sup>c</sup> ±0.06 eV. <sup>d</sup> ±0.07 eV. <sup>e</sup> Reference 18 adjusted by  $Q = 4.1$  eV. <sup>f</sup> Reference 20 adjusted by  $Q = 4.1$  eV. <sup>g</sup> Reference 19 (without d orbitals) adjusted by  $Q = 5.1$  eV. <sup>h</sup> Reference 19 (with d orbitals) adjusted by  $Q = 5.5$  eV. <sup>i</sup> Reference 21 adjusted by  $Q = 3.6$  eV. <sup>j</sup> Reference 22. <sup>k</sup> Reference 21. <sup>l</sup> Reference 23. <sup>m</sup> Revised interpretation of spectrum in ref 1 with line at 14.2 eV being assigned to a decomposition product. <sup>n</sup> Further lines obscured by  $\text{F}_3\text{C}$  lines. <sup>o</sup> Values obtained by deconvolution.

### 3. Results

Representative spectra of the vapors above heated  $\text{KNO}_3$ ,  $\text{RbNO}_3$ , and  $\text{CsNO}_3$  are presented in Figure 1. Each is typical of 25 or more spectra obtained for each compound. The unlabeled peak in each spectrum is due to methylene

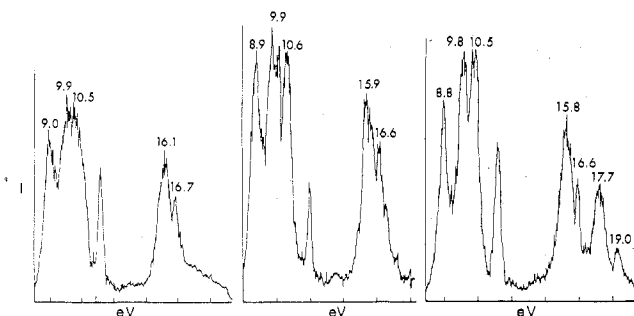


Figure 1. He I photoelectron spectra of vapors of  $\text{KNO}_3$ ,  $\text{RbNO}_3$ , and  $\text{CsNO}_3$ .

dichloride (11.52 eV) which was employed as a calibrant.<sup>28</sup> The values assigned to the peaks for each compound are listed in the first three rows of Table I. The values represent unweighted averages of the values taken from all spectra obtained and are characterized by the indicated 95% confidence limits.

When  $\text{LiNO}_3$  and  $\text{NaNO}_3$  were heated, the spectra obtained included characteristic lines due to  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{N}_2$  of such intensities as to suggest that  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and to a lesser extent  $\text{N}_2$  had been evolved indicating the decomposition of both compounds. This is reasonable on the basis of vapor studies which have shown various decomposition products for metal nitrates with  $\text{NO}$  probably being predominant at high temperatures.<sup>4</sup> (The reaction usually given is  $2\text{MNO}_3 \rightarrow \text{M}_2\text{O} + 2\text{NO} + \frac{3}{2}\text{O}_2$ .) It is possible that total decomposition did not occur, as small peaks perhaps due to metal nitrate were observed in the case of  $\text{NaNO}_3$ , but these were less intense than the  $\text{N}_2\text{O}$  and  $\text{NO}$  peaks and were partially masked by them. It is thus reasonable to assume that, at least in the case of  $\text{NaNO}_3$ , total decomposition does not occur. For  $\text{LiNO}_3$ , indications were that essentially complete decomposition took place, there being little evidence that  $\text{LiNO}_3$  vapor was being produced in any appreciable quantity.

#### 4. Interpretive Tools

The high-temperature stability and volatility of all the alkali-metal nitrates as well as thallium nitrate have been studied by various vapor-phase techniques. There is, however, conflicting reportage on decomposition of almost all of the compounds. No doubt this is because the onset of decomposition is difficult to determine as it seems to be affected by pressure, composition of the atmosphere, the material of the sample container (and perhaps its construction), and the presence of impurities, especially water. They all, however, appear to be stable under certain conditions up to about 800 K without appreciable decomposition.<sup>5,6</sup>

The mass spectral analyses of the vapors over the heated alkali nitrates indicate that for  $\text{LiNO}_3$  and  $\text{NaNO}_3$  the corresponding monomer and dimer species exist in about equal amounts along with significant decomposition products,<sup>7</sup> whereas for  $\text{RbNO}_3$  and  $\text{CsNO}_3$  the vapor consists of almost all monomer with only a few percent dimer and little or no decomposition products.<sup>8,9</sup>  $\text{TlNO}_3$  also shows a predominance of monomer in the vapor along with small amounts of dimer and some thermal decomposition products, primarily  $\text{NO}$  and  $\text{N}_2\text{O}$ .<sup>10</sup>

Vapors of  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , and  $\text{RbNO}_3$  have been isolated in noble gas matrices and subjected to infrared analysis.<sup>13-15</sup> Assignments of lines were made on the basis of a  $C_{2v}$  structure with the alkali-metal cation occupying a bidentate bridging position between two oxygen atoms of a trigonal-planar nitrate group. In addition, the vapors over  $\text{CsNO}_3$  and  $\text{TlNO}_3$  have been investigated by infrared spectroscopy.<sup>16</sup> Bands were also assigned on the basis of a  $C_{2v}$  structure, but because a band associated with M-O bonding

was not observed, definite assignments could not be ensured.

Electron diffraction data for the vapors above  $\text{LiNO}_3$  and  $\text{NaNO}_3$  have been obtained, but adequate structural conclusions could not be drawn. The electron diffraction results for  $\text{TlNO}_3$  vapors<sup>12</sup> have, however, been fit by assuming a superposition of three  $\text{TlNO}_3$  models: a  $C_s$  molecule with a planar-triangular nitrate and the Tl attached to one oxygen, a  $C_{2v}$  molecule with a planar-triangular nitrate and the Tl bridging two oxygens, and a  $C_{3v}$  molecule with a planar-triangular nitrate and the Tl above the nitrate to form a pyramid. The combination which fits the data best is 11%  $C_s$ , 71%  $C_{2v}$ , and 18%  $C_{3v}$ . The authors also considered a dynamic model in which the  $\text{Tl}^+$  and  $\text{NO}_3^-$  were viewed as continually moving with respect to each other or in which the  $\text{Tl}^+$  is viewed as belonging to all the ligand oxygens with equal probability (the so-called polytopic bond).

Rambidi<sup>17</sup> has employed a simple electrostatic model to examine the potential energy surfaces associated with the distribution of the  $\text{Cs}^+$  cation about the  $\text{NO}_3^-$  anion in  $\text{CsNO}_3$  vapor. He has concluded that the nature of the bonding at high temperatures is polytopic in that large displacements of the  $\text{Cs}^+$  in a plane normal to the  $\text{NO}_3^-$  group can be brought about by small variations in the total system energy. This behavior may be characteristic of other nitrates as well as other oxyanion-containing compounds.

Theoretical MO calculations for the free nitrate ion have been carried out by several means including ab initio approaches.<sup>18-21</sup> The results of the ab initio calculations are summarized in the 4th through the 8th rows of Table I. Upon examination of the theoretical MO data, the outer MO's ( $1a_2'$ ,  $1e''$ ,  $4e'$ ) are found to be predominantly composed of O 2p AO's, the next two MO's ( $3e'$ ,  $1a_2''$ ) have strong contributions from both the O 2p and N 2p AO's, and the  $4a_1'$  MO has N 2s, O 2s, and O 2p as its major AO contributors. In addition to these theoretical results, X-ray photoelectron data are available for solid  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ , and  $\text{KNO}_3$ ,<sup>22</sup> He II photoelectron data are available for solid  $\text{KNO}_3$ ,<sup>21</sup> and He I photoelectron data are available for  $\text{TlNO}_3$  vapor<sup>1</sup> and  $\text{F}_3\text{C-Hg-ONO}_2$  vapor.<sup>23</sup> The results of the experimental work are presented in the last four rows of Table I. Upon examination of the He I and He II spectra, the intensities of the  $a_2''$  lines are found to be considerably less than those of the  $a_2'$ ,  $e'$ , and  $e''$  lines.

For the present work UTARC (an extended Hückel method) calculations have been carried out on  $\text{KNO}_3$  and on the  $\text{NO}_3^-$  ion with various structural parameter alterations. Computations have been made on  $\text{KNO}_3$  in  $C_{3v}$  structures,  $C_{2v}$  bidentate configurations,  $C_{2v}$  monodentate configurations, and in  $C_s$  configurations, all subjected to variations in both the O-N-O angles and the K-N distances. Computations have also been made on the  $\text{NO}_3^-$  ion with appropriate alterations in the O-N-O angles. The purpose of these computations was to observe the changes in MO orbital levels and the splittings of MO levels when bond angle and bond length alterations were made. The results of selected calculations are presented in Table II where the shifts and splits have been imposed upon the ab initio MO values. The data may be taken to indicate that small changes in the O-N-O angles or substantial changes in the K<sup>+</sup> position or both do not strongly affect the MO energy values, leaving the ordering unchanged. Changes in the K-N distance have similar small effects. In all of these changes the dissolution of the  $D_{3h}$  symmetry of the  $\text{NO}_3^-$  results in only very small MO splits, usually no more than a few tenths of 1 eV.

#### 5. Conclusions

Comparisons of the energy values of the bands in Figure 1 have been made with the ab initio MO calculations of Table I (altered by subtraction of 0.9-1.0 eV), the X-ray PES results

**Table II.** NO<sub>3</sub><sup>-</sup> and KNO<sub>3</sub> Shift and Split Calculations (-eV)<sup>a</sup>

entity	MO's and energies, <sup>a</sup> -eV
D <sub>3h</sub> NO <sub>3</sub> <sup>-</sup> anion, N-O = 1.22 Å	1a <sub>2</sub> ', 9.0; 1e'', 9.2; 1e'', 9.2; 4e', 10.6; 4e', 10.6; 3e', 16.7; 3e', 16.7; 1a <sub>2</sub> '', 17.9
C <sub>2v</sub> NO <sub>3</sub> <sup>-</sup> anion, N-O = 1.22 Å, O-N-O = 115°	4b <sub>2</sub> ', 9.0; 1a <sub>2</sub> ', 9.2; 2b <sub>1</sub> ', 9.5; 3b <sub>2</sub> ', 10.7; 5a <sub>1</sub> ', 10.8; 2b <sub>2</sub> ', 16.8; 4a <sub>1</sub> ', 16.8; 1b <sub>1</sub> , 17.9
C <sub>2v</sub> NO <sub>3</sub> <sup>-</sup> anion, N-O = 1.22 Å, O-N-O = 105°	4b <sub>2</sub> ', 9.0; 1a <sub>2</sub> ', 9.4; 2b <sub>1</sub> ', 10.1; 3b <sub>2</sub> ', 11.2; 5a <sub>1</sub> ', 11.5; 2b <sub>2</sub> ', 17.0; 4a <sub>1</sub> ', 17.3; 1b <sub>1</sub> , 18.4
C <sub>3v</sub> K <sup>+</sup> NO <sub>3</sub> <sup>-</sup> pyramidal, N-O = 1.22 Å, K-N = 1.82 Å	1a <sub>2</sub> ', 9.0; 5e, 9.6; 5e, 9.6; 4e, 11.3; 4e, 11.3; 3e, 18.1; 3e, 18.1; 4a <sub>1</sub> ', 19.0
C <sub>3v</sub> K <sup>+</sup> NO <sub>3</sub> <sup>-</sup> pyramidal, N-O = 1.22 Å, K-N = 2.22 Å	1a <sub>2</sub> ', 9.0; 5e, 9.6; 5e, 9.6; 4e, 11.2; 4e, 11.2; 3e, 17.8; 3e, 17.8; 4a <sub>1</sub> ', 18.8
C <sub>3v</sub> K <sup>+</sup> NO <sub>3</sub> <sup>-</sup> pyramidal, N-O = 1.22 Å, K-N = 2.62 Å	1a <sub>2</sub> ', 9.0; 5e, 9.5; 5e, 9.5; 4e, 11.1; 4e, 11.1; 3e, 17.6; 3e, 17.6; 4a <sub>1</sub> ', 18.7
C <sub>2v</sub> K <sup>+</sup> NO <sub>3</sub> <sup>-</sup> bidentate, N-O = 1.22 Å, K-N = 2.42 Å	4b <sub>2</sub> ', 9.0; 2b <sub>1</sub> ', 9.3; 1a <sub>2</sub> ', 9.5; 5a <sub>1</sub> ', 11.2; 3b <sub>2</sub> ', 11.2; 4a <sub>1</sub> ', 17.7; 2b <sub>2</sub> ', 17.8; 1b <sub>1</sub> , 18.6
C <sub>2v</sub> K <sup>+</sup> NO <sub>3</sub> <sup>-</sup> bidentate, N-O = 1.22 Å, K-N = 2.82 Å	4b <sub>2</sub> ', 9.0; 2b <sub>1</sub> ', 9.4; 1a <sub>2</sub> ', 9.5; 5a <sub>1</sub> ', 11.2; 3b <sub>2</sub> ', 11.2; 4a <sub>1</sub> ', 17.6; 2b <sub>2</sub> ', 17.7; 1b <sub>1</sub> , 18.6
C <sub>2v</sub> K <sup>+</sup> NO <sub>3</sub> <sup>-</sup> bidentate, N-O = 1.22 Å, K-N = 3.22 Å	4b <sub>2</sub> ', 9.0; 2b <sub>1</sub> ', 9.4; 1a <sub>2</sub> ', 9.4; 5a <sub>1</sub> ', 11.1; 3b <sub>2</sub> ', 11.2; 4a <sub>1</sub> ', 17.4; 2b <sub>2</sub> ', 17.5; 1b <sub>1</sub> , 18.5
C <sub>2v</sub> K <sup>+</sup> NO <sub>3</sub> <sup>-</sup> monodentate, N-O = 1.22 Å, K-N = 3.22 Å	4b <sub>2</sub> ', 9.0; 1a <sub>2</sub> ', 9.4; 2b <sub>1</sub> ', 9.6; 3b <sub>2</sub> ', 11.6; 5a <sub>1</sub> ', 11.7; 2b <sub>2</sub> ', 17.8; 4a <sub>1</sub> ', 18.1; 1b <sub>1</sub> , 19.1
C <sub>s</sub> K <sup>+</sup> NO <sub>3</sub> <sup>-</sup> monodentate, N-O = 1.22 Å, K-N = 3.19 Å, N-O-K = 105°	5a <sub>1</sub> ', 9.0; 4a <sub>1</sub> '', 9.3; 7a <sub>1</sub> ', 9.5; 3a <sub>1</sub> '', 11.4; 6a <sub>1</sub> ', 11.5; 2a <sub>1</sub> '', 17.8; 5a <sub>1</sub> ', 18.1; 4a <sub>1</sub> ', 19.1

<sup>a</sup> All values adjusted to 1st MO = 9.0 eV.

on solid MNO<sub>3</sub> compounds<sup>22</sup> of Table I (altered by subtraction of 0.9 eV), the He II PES results on solid KNO<sub>3</sub><sup>21</sup> (altered by subtraction of 0.9 eV), the He I PES results on F<sub>3</sub>C-Hg-ONO<sub>2</sub> vapor<sup>23</sup> (altered by subtraction of 2.1 eV), and the He I PES results on TiNO<sub>3</sub> vapor<sup>1</sup> (altered by subtraction of 0.9 eV). Comparisons of the bands in Figure 1 have also been made with band areas and shapes of the He II solid KNO<sub>3</sub> spectrum,<sup>21</sup> the He I F<sub>3</sub>C-Hg-ONO<sub>2</sub> spectrum,<sup>23</sup> the He I TiNO<sub>3</sub> spectrum,<sup>1</sup> and the spectra of neutral D<sub>3h</sub> compounds such as those of BF<sub>3</sub>,<sup>24</sup> BCl<sub>3</sub>,<sup>24</sup> BBr<sub>3</sub>,<sup>24</sup> and SO<sub>3</sub>.<sup>25</sup> It has been concluded that the energy order in each of the three vapors (KNO<sub>3</sub>, RbNO<sub>3</sub>, CsNO<sub>3</sub>) is 1a<sub>2</sub>', 1e'', 4e', 3e', 1a<sub>2</sub>''. It needs to be recognized that this ordering has been based on calculations on ground-state entities and that therefore relaxation has not been taken into direct consideration. This is also the situation in the cases of the other D<sub>3h</sub> molecules mentioned above. Relaxations for the delocalized or bonding MO's can often be estimated from the constituent AO contributions, but relaxations from localized MO's are somewhat more difficult to estimate particularly because of the electron flow considerations.<sup>29</sup> The outer three MO's (1a<sub>2</sub>', 1e'', 4e') are localized ones and therefore it is they that might need to be reordered in light of relaxation phenomena. It is to be noted that the ordering of the 1e'' and 4e' MO's is still uncertain in the BX<sub>3</sub> compounds, there being a good possibility that considerable interaction between the two may be occurring.<sup>30</sup>

The first three MO's (1a<sub>2</sub>', 1e'', 4e') are largely O 2p in character, 1a<sub>2</sub>' and 1e'' being entirely nonbonding and 4e' being slightly N-O bonding by virtue of a small percentage of N 2p AO. Unlike the He II data on solid KNO<sub>3</sub><sup>21</sup> and the He I data on gaseous F<sub>3</sub>C-Hg-NO<sub>3</sub>,<sup>23</sup> the 1e'' and 4e' ionizations are resolved (as they are in gaseous SO<sub>3</sub>,<sup>25</sup> BCl<sub>3</sub>,<sup>24</sup> BBr<sub>3</sub>,<sup>24</sup> BI<sub>3</sub>,<sup>24</sup> and TiNO<sub>3</sub><sup>1</sup>). The splittings which sometimes can be seen in the 1e'' and 4e' ionizations (note the 9.9 eV peak in

Figure 1, the 9.8 eV and 10.5 eV peaks in Figure 1, and the 11.1 eV and 11.4 eV peaks in the previously published TiNO<sub>3</sub> spectrum<sup>1</sup>) may be actual, but they cannot be consistently reproduced. This may be due to the variability of the resolution in the high-temperature experiments.

The next two bands originate from the 3e' and the 1a<sub>2</sub>' MO's. These orbitals are principally N-O bonding ones. Again the bands are resolved, unlike the situation in the He II spectrum of solid KNO<sub>3</sub>.<sup>21</sup> In the spectrum of CsNO<sub>3</sub> (Figure 1) the 6th and 7th bands (at 17.7 and 19.0 eV) are assigned to the 5<sup>2</sup>P<sub>3/2</sub> and 5<sup>2</sup>P<sub>1/2</sub> states of Cs<sup>2+</sup>. These assignments are analogous to those of Potts and Williams<sup>26</sup> for the gaseous cesium halides and to those of Vick et al.<sup>2</sup> for gaseous CsReO<sub>4</sub>.

In all of the spectra (solid KNO<sub>3</sub>,<sup>21</sup> gaseous KNO<sub>3</sub>, gaseous RbNO<sub>3</sub>, gaseous CsNO<sub>3</sub>, gaseous TiNO<sub>3</sub>,<sup>1</sup> gaseous BCl<sub>3</sub>,<sup>24</sup> gaseous BBr<sub>3</sub>,<sup>24</sup> gaseous BI<sub>3</sub>,<sup>24</sup> gaseous SO<sub>3</sub>,<sup>25</sup> gaseous F<sub>3</sub>C-Hg-NO<sub>3</sub>,<sup>23</sup>) the bands are generally quite broad. These breadths may be associated with a number of factors (symmetry-dissolution of the D<sub>3h</sub> NO<sub>3</sub><sup>-</sup> group by attached entities in the cases of the nitrates, Jahn-Teller effects in the ionization of degenerate levels in all entities, differences in the potential energy surfaces between the un-ionized original entity and the ionized entity, thermal excitation of vibrational modes, and banding in the solids). In all of the nitrate compounds, whether solid or gaseous, whether covalent or ionic, and whether room temperature or high temperature, the bands show strong similarities in shapes, breadths, and positions. And further, they all resemble the SO<sub>3</sub> spectrum<sup>25</sup> with the energy envelope of the five outer occupied MO's compressed. All of these observations may be taken to indicate that the NO<sub>3</sub><sup>-</sup> entity has considerable symmetry integrity, being perturbed only minimally by variations in external influence. Such an inference is in agreement with the calculational results in Table I. Any hope of distinguishing between C<sub>3v</sub>, C<sub>2v</sub>, and C<sub>s</sub> forms of the gaseous M<sup>+</sup>NO<sub>3</sub><sup>-</sup> molecules is precluded by the small splits produced by perturbations, by the observed band breadths, and by the instrumental resolution which is no better than 0.15 eV at high temperatures (largely due to sample deposition on the walls of the sample chamber and on the slits). Neither can a judgment be made concerning the polytopicity of the vapor-state M<sup>+</sup>NO<sub>3</sub><sup>-</sup> molecules.<sup>17,27</sup>

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**Registry No.** KNO<sub>3</sub>, 7757-79-1; RbNO<sub>3</sub>, 13126-12-0; CsNO<sub>3</sub>, 7789-18-6.

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## Electron Paramagnetic Resonance of Low-Spin Cobalt(II) Complexes: Effect of Axial Ligation upon the Ground State

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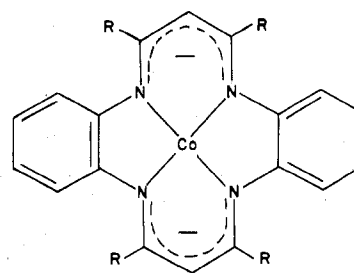
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EPR studies of frozen solutions of cobalt(II) dibenzo[*b*,*l*][1,4,8,11]tetraazacyclotetradecaheptaene reveal that the ground state changes upon coordination of an axial ligand. In the presence of weak ligands such as sulfur and oxygen donors, the cobalt remains four-coordinate and the ground state is  $(d_{xz}d_{x^2-y^2}d_{yz})^6d_{z^2}^1$ . Ligands containing nitrogen and phosphorus donor atoms form 1:1 adducts which have  $(d_{xz}d_{x^2-y^2}d_{yz})^6d_{z^2}^1$  ground state. The results are compared with those reported for a nonplanar analogue and for Co(II) porphyrins. The effects of ring size and deviations from planarity upon the ground state are also discussed.

In recent years extensive use has been made of EPR to study the electronic structure of low-spin Co(II) compounds.<sup>1-22</sup> In particular, studies of Co(II) porphyrins and related four-coordinate complexes have aroused much interest because there was some controversy over the nature of the ground state and also because they readily undergo axial ligation to form five- and six-coordinate structures. For all such five- and six-coordinate complexes studied to date, the ground state is  $(d_{x^2-y^2}d_{yz}d_{yz})^6d_{z^2}^1$ .<sup>1-7</sup> Much greater uncertainty accompanies the assignment of the ground state of the four-coordinate complexes. Examples of  $(d_{x^2-y^2}d_{xz}d_{z^2})^6d_{yz}^1$ ,<sup>8-12</sup>  $(d_{xz}d_{yz}d_{z^2})^6d_{x^2-y^2}^1$ ,<sup>13</sup> and  $(d_{x^2-y^2}d_{xz}d_{yz})^6d_{z^2}^1$ <sup>13-20</sup> ground states have been reported although recently many of the initial assignments have been modified as more advanced theoretical treatments of low-spin  $d^7$  systems have become available.<sup>20-22</sup>

We recently reported the results of an EPR investigation of axial ligation of the macrocyclic Co(II) Schiff base complex, I.<sup>17</sup> Although this complex possesses a number of structural features in common with porphyrins, it differs structurally from the naturally occurring macrocyclic compounds in two important respects. The inner ring of I has only 14 members compared to the 16 interior members of a porphyrin ring. Furthermore, extensive crystallographic investigations<sup>23-28</sup> have shown that the Schiff base is saddle shaped and that the *o*-phenylene and diiminate moieties are displaced on opposite sides of the plane defined by the four nitrogen donor atoms, whereas the porphyrins are planar.<sup>26-31</sup>

The EPR results for 1:1 adducts of I were found to differ in several important respects from the analogous adducts of



I, R = CH<sub>3</sub>

II, R = H

Co(II) porphyrins. Although all adducts have a  $d_{z^2}^1$  ground state, the EPR parameters for the adducts of I do not have axial symmetry, and 2:1 adducts are not formed. Furthermore a significantly higher spin density resides on the Schiff base than on the porphyrin ligand. These differences between the two systems appear to be related to the structural differences in ring size and planarity.

In order to separate the effects that ring size and deviations from planarity have upon the electronic structure and the EPR parameters for this type of macrocyclic complex, we examined the EPR parameters of the Schiff base complex II and its axial adducts. Although II has a 14-membered inner ring, crystallographic studies<sup>32</sup> reveal that the molecule is planar, in contrast to I. This paper reports EPR studies of axial ligation of the planar macrocycle II and compares the results with those