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Contribution from the Chemistry Department,
University of Manchester, Manchester M13 9PL, United Kingdom

Low-Energy Photoelectron Spectroscopy of Solids. Electronic Structure of the Cyanide, Nitrite, and Nitrate Ions

M. CONSIDINE, J. A. CONNOR,* and I. H. HILLIER

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An apparatus for recording the He I and He II photoelectron spectra of materials in the form of evaporated films is described. The photoelectron spectra of cyanide, nitrite, and nitrate ions are presented, and the ionization potentials and photoionization cross sections are interpreted using ab initio molecular orbital calculations. It is shown that low-energy spectra are much more useful than high-energy (ESCA) spectra for obtaining information on the valence electronic structure of solids. A different assignment of the ESCA spectrum of cyanide ion is proposed, and certain ambiguities in the assignment of the ESCA spectra of nitrate and nitrite ions are resolved.

1. Introduction

The use of photoelectron spectroscopy to study molecular electronic structure is now well established. The application of this technique to the study of solid materials has been undertaken predominantly using high-energy photons (ESCA or XPS), which because of their greater energy permit the measurement of core electron binding energies. Moreover, the availability of efficient vacuum locks, resulting from a less stringent vacuum requirement, allows greater ease in the preparation and introduction of samples. However, the use of ESCA to study the valence electron photoionization of solid samples is limited by the inherent line width of the ionizing radiation (ca. 1 eV) and the relatively low ionization cross section of the valence electrons compared with the more tightly bound core electrons.

The use of low-energy photons (ultraviolet photoelectron spectroscopy, UPS) for the study of solids is hampered by a stringent requirement for ultrahigh-vacuum facilities and the problems of producing high intensities of helium(II) in a windowless source under these conditions. If these difficulties can be overcome the potential benefits of UPS in the study of valence electron photoionization are manifold because of the high cross sections and the improvement in resolution arising from the narrow line width of the radiation (less than 10 meV).

Previous studies of the electronic structure of ionic solids using ESCA have shown that the lack of resolution and intensity do not usually allow an identification of all the low-lying ionized states of the molecules. In order to gain a better understanding of the electronic structure of relatively involatile solids, we have developed a photoelectron spectrometer to measure their ionization potentials using He I and He II ionizing radiation. In this paper we describe the application of the technique to the study of the cyanide, nitrite, and nitrate anions.

2. Experimental Section

a. The Spectrometer. The spectrometer chamber is of stainless steel construction with all-metal seals. The chamber is pumped by a 4-in. oil diffusion pump (Edwards E04) which is backed by a rotary pump (Edwards ED50) and is topped by a water-cooled baffle and a liquid nitrogen cold trap. The whole spectrometer chamber can be baked out at temperatures up to 200 °C. Typical pressures attained after baking the chamber for 12 h (overnight) at 160 °C are in the range (1–2) × 10^{-9} Torr, although the ultimate pressure achievable is 2 × 10^{-10} Torr.

The light source is a differentially pumped windowless 5-kV dc helium discharge lamp similar to the type (WG-031) commonly employed on the AEI ES200B spectrometer. He II intensities ($h\nu = 40.8$ eV), obtained by reducing the helium pressure in the lamp, are usually 2–15% of the He I intensities ($h\nu = 21.2$ eV). With the lamp operating in the He II mode the pressure in the main chamber rises to 3 × 10^{-9} Torr; in the He I mode the pressure in the chamber is in the range 5 × 10^{-9}–10^{-8} Torr. The spectrometer chamber is additionally equipped with an argon ion gun (Vacuum Generators AG2) and a quadrupole mass spectrometer (Vacuum Generators Q7). The sample probe is a stainless steel plate isolated from earth and mounted on a rotary motion drive (Vacuum Generators RD3) to which an angle-measuring device has been attached. Included between the rotary drive and the spectrometer chamber is an adjustable bellows which permits alignment of the sample with the light source and the analyzer slit.

The electron energy analyzer is a 5-cm mean radius electrostatic hemispherical analyzer (AEI). Photoelectrons from the sample, after passing through a 1-mm slit, are focused so that the slit is imaged at the analyzer entrance plane. The analyzer is held at a fixed transmission energy and energy analysis is performed by preretardation (or preacceleration) of the electrons before entering the analyzer. This is achieved by floating the hemispheres up on the scanning voltage.

Electrons arriving at the exit slit of the analyzer strike a Channeltron electron multiplier and the pulses, after amplification and shaping, are fed into a ratemeter whose output is displayed on an X-Y recorder. The analyzer resolution for a transmission energy of 10 V has a minimum value of 0.1 V.

b. Sample Preparation. Before evacuation of the spectrometer chamber the sample probe is washed with water, rinsed with acetone, and then dried. The material to be investigated, having been dried in a vacuum oven, is placed in a tantalum boat mounted on a high-current leadthrough flange. Covering the boat is a finely perforated tantalum baffle which assists smooth evaporation and prevents ejection of the material should dehydration be incomplete. The boat and baffle are resistively heated and the sample is evaporated under high vacuum onto the stainless steel probe. Evaporation pressures required for a satisfactory film vary from 10^{-6} to 5×10^{-8} Torr for about 30–60 s for low-boiling and high-boiling solids, respectively. In some instances the steel probe is covered with a gold plate which is first cleaned by ion bombardment and then just covered by the evaporated sample (disappearance of valence band of gold). Studies of the uptake of an applied potential (bias voltage) by the sample indicate that we are dealing with thin films (thickness <300 Å), although we have not been able to measure the thickness directly.

Spectra are calibrated with respect to the vacuum level by observing the secondary electron energy distribution (SEED) from the sample as a function of angle ϕ and bias voltage and maximizing the separation between the threshold voltage (E_T) of the SEED and a selected peak in the spectrum of the sample. ϕ is defined as the angle between the incident photon beam and the plane containing the sample. The E_T is assumed to be the true zero of kinetic energy for electrons emitted from the sample; the validity of this assumption is established by measurements of the work function of gold and silver. The use of a bias voltage is found to be necessary in order to observe the true E_T of the SEED because electrons produced by scattering within the analyzer overlap the energy region of the scattered electrons originating from an unbiased sample. A more detailed discussion of these procedures is reserved for a later paper on alkali metal halides.

c. Materials and Methods. Sodium cyanide was reagent grade (Hopkin and Williams) stated to contain less than 0.02 per cent chlorine. Analysis of this material for potassium showed less than 1 ppm. Potassium nitrite was reagent grade (Hopkin and Williams), stated to contain less than 0.04% chlorine and less than 0.06% sulfate. Potassium nitrate was reagent grade (British Drug Houses), stated to contain less than 0.02% of chlorine and of sulfate. The purity of these materials was checked and they were used without further purification.

Spectra of each compound were recorded at various angles ϕ, in the range 2–45°, and various applied potentials (0–30 V). The samples were deposited on the stage by evaporation at the lowest possible temperature. In the case of each compound, several different samples (films) were prepared in order to ensure consistency and to minimize charging effects. In relation, particularly, to the possible thermal decomposition of KNO_3 and of KNO_2, we are convinced by the detailed reproducibility (relative intensities and shapes of the peaks and the separation between peaks in relation to a constant value for the K 3p binding energy) of the spectra we have obtained that such thermal degradation is not significant under the conditions we have used.[1]

3. Theoretical Interpretation of Photoelectron Spectra

We have performed ab initio molecular orbital (MO) calculations of both the ionization potentials (IP) using Koopmans' theorem and photoionization cross sections (σ) to provide an interpretation of the measured spectra. Calculations were performed using the 5s3p gaussian basis contraction of Dunning[2] at the experimental geometries. We use the plane wave approximation to estimate σ. Thus, the cross section in an element of solid angle dΩ, of MO ψ_i for nonpolarized radiation, is given as

$$d\sigma = (e^2k^3/2\pi mc\omega)|\sum_{\mu} c_{\mu}\langle\phi_{\mu}|\exp(ik\cdot r)\rangle|^2 \, d\Omega \qquad (1)$$

where MO ψ_i is expanded as a linear combination of Gaussian functions (ϕ_μ)

$$\psi_i = \sum_{\mu} c_{\mu}\phi_{\mu} \qquad (2)$$

Table I. Ionization Potentials[a] and Photoionization Cross Sections[b] for Cyanide Ion

			Photoionization cross sections			
	IP, eV		He I		He II	
Orbital	Exptl	Theor[c]	Exptl	Theor	Exptl	Theor
5σ	10.2	10.2	0.6	0.3	0.3	0.5
1π	11.5	10.6	1.0	1.0	1.0	1.0
4σ	13.7	14.1	0.3	0.5	0.3	0.5

[a] In view of the neglect of the effect of the cation on our calculations, a constant, Q, is added to the calculated IP's in Tables I, III, and IV to achieve agreement with the experimentally determined first IP. [b] The cross sections have been normalized to a value of 1.0 for the 1π MO. [c] $Q = 5.5$ eV.

Table II. Photoionization Cross Sections[a] for CO, N_2, and CN^-

	CO[b]		N_2[b]		CN^-	
	Exptl	Theor	Exptl	Theor	Exptl	Theor
			He I Photons			
5σ	0.8	1.7	0.7	1.0	0.6	0.3
1π	1.0	1.0	1.0	1.0	1.0	1.0
4σ	0.2	0.1	0.2	0.2	0.3	0.5
			He II Photons			
5σ	0.3	0.4	0.5	0.4	0.3	0.5
1π	1.0	1.0	1.0	1.0	1.0	1.0
4σ	0.5	0.5	0.2	0.6	0.3	0.5

[a] Values for these molecules derived from ref 4. [b] Normalized to a value of 1.0 for the 1π MO.

Integration over the solid angle Ω in eq 1 yields the total ionization cross sections quoted in the tables. A full discussion of the evaluation of the integrals occurring in eq 1 is to be found in ref 3. Such an approximate model has generally been found to give a good semiquantitative interpretation of photoelectron spectra covering a wide range of photon energies.[4]

a. The Cyanide Ion. The He I and He II spectra (Figure 1) of NaCN show three clearly separated bands which may be attributed to ionization from the 5σ, 1π, and 4σ MO's. A comparison of the relative intensities of these bands and the change in intensity (or photoionization cross section) from He I to He II (Table I) reveals a very close similarity to that of the isoelectronic molecules CO and N_2 (Table II). In CO the order of the ionic states follows the order of the filled MO's and is $^2\Sigma^+ < {}^2\Pi < {}^2\Sigma^+$. In view of this we assign the first peak to ionization from the 5σ MO, the second from the 1π, and the third from the 4σ. The IP's calculated from Koopmans' theorem (Table I) are in agreement with this assignment but underestimate the separation between the 5σ and 1π MO's because of the neglect of relaxation and correlation effects. This problem has recently been treated by the equations of motion method[5] and the difference in the IP between the ($^1\Sigma^+ \rightarrow {}^2\Sigma^+$) and ($^1\Sigma^+ \rightarrow {}^2\Pi$) transitions at the equilibrium geometry of cyanide ion was calculated to be 1.6 eV, which is in much better agreement with the experimental value (1.3 eV).

Comparison of the photoionization cross sections, σ, calculated in the plane wave approximation with the experimental values [determined as A/E, where A is the area under the (deconvoluted) peak and E is the kinetic energy of the electrons at the band maximum] shows (Table I) a satisfactory agreement with the exception of the 5σ MO for He I radiation. A similar discrepancy has been noticed[4] previously (Table II) for CO and N_2; this probably arises because the plane wave description of the final state is rather poor at low photon energies.[6] The diagram (Figure 2) presents a correlation of the experimental orbital energies of cyanide ion with those of the isoelectronic molecules CO, N_2, HCN, and C_2H_2, in which the ionization potential of the least tightly bound MO is taken

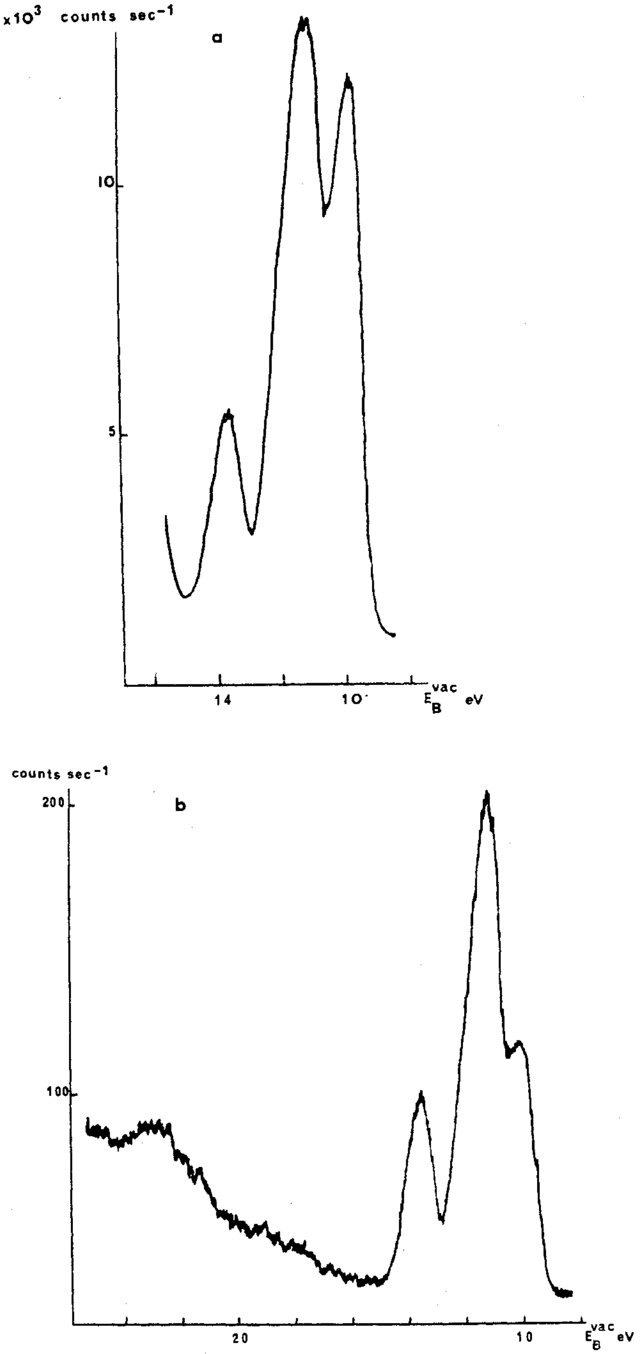

Figure 1. (a) He I photoelectron spectrum of solid NaCN; (b) He II photoelectron spectrum of solid NaCN.

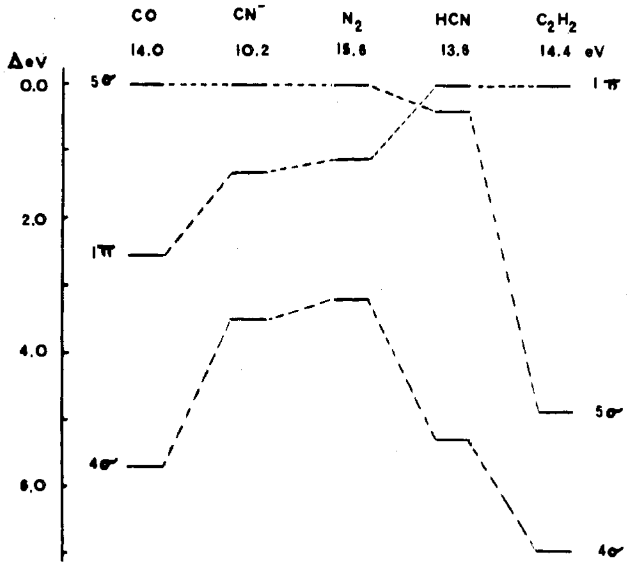

Figure 2. Correlation diagram of valence MO's of CO, CN^-, N_2, HCN, and C_2H_2, referred to the IP of the least tightly bound MO taken as zero. Data taken from (a) CO, M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 4434 (1964); (b) CN^-, this work; (c) N_2, M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 5141 (1963); (d) HCN, D. C. Frost, S. T. Lee, and C. A. McDowell, *Chem. Phys. Lett.*, **23**, 472 (1973); (e) C_2H_2, D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley, London, 1970.

as zero. This illustrates clearly the progressive destabilization of the 1π MO relative to the 5σ MO and the compensating variation of the 4σ MO energy in this series of closely related molecules.

Our assignment of the ionized states of cyanide ion differs from that proposed[7] by Morrison and Hendrickson on the basis of an ESCA spectrum. These workers assigned three rather poorly defined low-energy peaks at 5.3, 9.0, and 12.8 eV (relative to the Fermi level) to ionization from the 5σ, 1π, and 4σ MO's, respectively. Our calculations of the cross section of the peaks in such an XP spectrum give relative values of 1.0 (5σ), 0.6 (1π), and 4.5 (4σ). As is usually found in high-energy photoelectron spectra, ionization from the π MO is predicted to give rise to a very weak peak, whereas Morrison and Hendrickson assigned the most intense of the three low-energy peaks to the 1π MO. In view of our low-energy spectra and the calculated intensities, it is clear that the correct assignment of the XPS data is that the first peak is due to both the 5σ and the 1π MO ionizations which are not resolved, and the second peak to the 4σ MO. The experimental separation of these two peaks (3.7 eV) is in good agreement with the separation of the 5σ and 4σ ionizations in our spectra (3.5 eV).

As the He II spectrum of NaCN (Figure 1b) shows, we observe a broad peak corresponding to an IP of 22.6 eV, in addition to the three principal ionizations. We assign this peak to a configuration interaction (CI) or forbidden transition, in which excitation of a second electron occurs along with the primary ionization.[8] This dual process is made possible by the mixing of ionized states of the same symmetry but different configurations. These bear a formal resemblance to shake-up transitions in XPS. Similar configuration interaction transitions have been observed[8] in the low-energy photoelectron spectra of N_2 and CO. In CO, the CI band is at 11.2 eV to higher binding energy of the 1π MO and has been assigned to the $^1\Pi$–$^2\Pi$ and $^3\Pi$–$^2\Pi$ transitions; a similar assignment seems reasonable for cyanide ion. Returning to the XP spectrum, we would suggest that the peak at 17.0 eV, which was tentatively assigned[7] to a potassisum impurity, may be due to shake-up because its separation from the 5σ (11.7 eV) is similar to that observed (12.4 eV) in our He II spectrum. We know that the sample of NaCN we have used did not contain a significant (not greater than 1 ppm) amount of potassium. We are unable to suggest as assignment for the peak at 12.8 eV in the XP spectrum reported by Morrison and Hendrickson.

b. The Nitrite Ion. The He II spectrum of KNO_2 is shown in Figure 3. We do not show the He I spectrum of either KNO_2 or KNO_3 as in both cases only the first band can be observed because of inelastic electron scattering. The peak at lowest binding energy in Figure 3 clearly arises from ionization of the $6a_1$, $1a_2$, and $4b_2$ MO's which are composed of mainly oxygen 2p AO's. It is probable that the shoulder at low IP corresponds to ionization from the $6a_1$ MO. Approximate deconvolution of the more intense component of the first band gives two peaks with maxima at 9.7 and 10.4 eV,

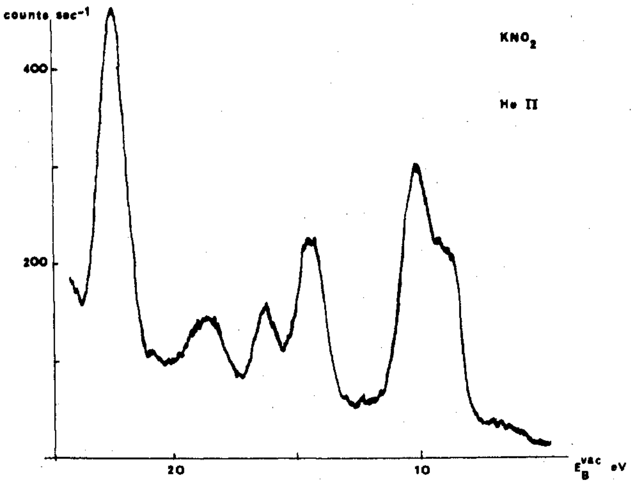

Figure 3. He II photoelectron spectrum of solid KNO_2. The K 3p ionization is at 22.3 eV.

Table III. Ionization Potentials and Photoionization Cross Sections for Nitrite Ion

	IP, eV		Cross section, σ^b					
			He II			Mg Kα		
Orbital	Exptl^d	Theor^c	Exptl	Theor		Exptl^a	Theor	
$6a_1$	8.7	8.7	1.0	1.0	1.0	1.0	1.0	1.0
$1a_2$	(9.7)	9.4		1.1			0.7	
$4b_2$	(10.6)	10.2		1.0			0.9	
$1b_1$	(14.1)	15.4	0.7	0.9	0.9	0.9	0.5	3.8
$3b_2$	(14.8)	15.9		0.8			1.8	
$5a_1$	16.2	16.5		1.0			0.9	
$4a_1$	18.7	20.9	0.3	1.2	0.4		6.7	

^{a} Measured on the spectra shown in ref 9. ^{b} Measured relative to the lowest binding energy peak(s) taken as 1.0. ^{c} $Q = 4.8$ eV (see Table I). ^{d} IP values in parentheses obtained by deconvolution of the band envelope.

in good agreement with calculation (Table III). The second band in the E_B^{vac} range 14–16 eV arises from the three MO's $1b_1$, $3b_2$, and $5a_1$ which contribute to the N–O bonds in the ion. An approximate deconvolution of this band yields three peaks whose separations are in satisfactory agreement with the calculated values. The third, weak band at 18.7 eV is produced by ionization from the $4a_1$ MO of mainly (70%) s character. The calculated ionization cross sections for each of the first seven MO's of nitrite ion are seen to be approximately the same for He II radiation. This is in line with our assignment for three MO's contributing to each of the first two peaks and of one MO contributing to the third. The agreement between the calculated and experimental values of σ for He II is satisfactory.

The increased information on the valence orbitals made available by this technique compared with ESCA is strikingly apparent when a comparison is made between the He II spectrum (Figure 3) and our previously published[9] ESCA spectrum of $LiNO_2$. In the latter, only two low-energy bands (IP < 20 eV) are evident, the first associated with the group of orbitals $6a_1$, $1a_2$, and $4b_2$ and the second with the $4a_1$ MO which has a large σ value for x-ray photons (Table III) because of the large 2s component of this MO. The three important (N–O bonding) MO's $1b_2$, $3b_2$, and $5a_1$ appear as a broad, weak shoulder to a low binding energy of the intense band from the $4a_1$ MO.

c. The Nitrate Ion. The He II spectrum of KNO_3 (Figure 4) shows three bands which may be attributed to the nitrate anion. The first band, centered at 10.8 eV, is produced by ionization from the $1a_2'$, $1e''$, and $4e'$ MO's of mainly oxygen 2p character. The $1a_2'$ and $1e''$ MO's are completely nonbonding while the $4e'$ MO has 8% nitrogen 2p character and a small N–O bonding interaction. The shoulder at 9.9 eV on this band suggests that the lowest IP arises from the nondegenerate MO and indicates that the separation of the $1a_2'$ and $1e''$ MO's which we have calculated is too small. In any event, the $1e''$ and $4e'$ ionizations are not resolved although a rough deconvolution of the band would suggest that their IP's are at approximately 10.8 and 11.6 eV, respectively. The second band in the spectrum arises from the closely spaced $3e'$ and $1a_2''$ MO's which have large N–O bonding interactions. The shoulder at high IP is probably due to the $1a_2''$ MO, the calculated separation (0.6 eV) from the $3e'$ being in very good agreement with the experimental value. The third band at 19.4 eV is assigned to ionization from the $4a_1'$ MO which is also N–O bonding in character. The trends in the intensities which we observe are rather well reproduced by our calculations (Table IV).

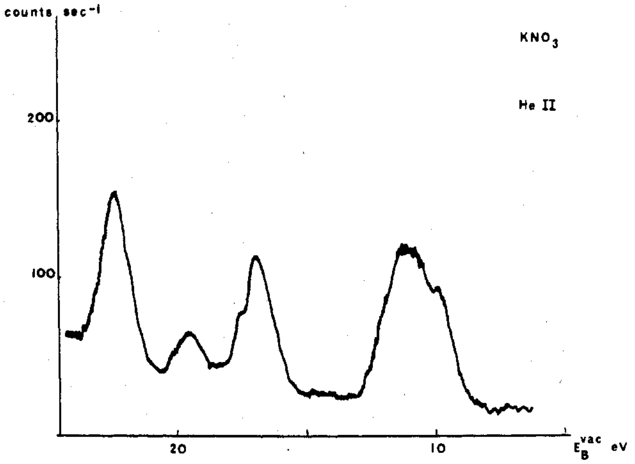

Figure 4. He II photoelectron spectrum of solid KNO_3. The K 3p ionization is at 22.3 eV.

Table IV. Ionization Potentials and Photoionization Cross Sections for Nitrate Ion

	IP, eV		Cross section, σ^b					
			He II			Mg Kα		
Orbital	Exptl^d	Theor^c	Exptl	Theor		Exptl^a	Theor	
$1a_2'$	9.9	9.9	1.0	1.0	1.0	1.0	1.0	1.0
$1e''$	(10.8)	9.9		1.7			1.7	
$4e'$	(11.6)	11.4		1.5			1.8	
$3e'$	16.8	17.5	0.4	1.6	0.6	2.0	5.5	1.3
$1a_2''$	17.4	18.1		0.8			0.5	
$4a_1'$	19.5	20.7	0.2	1.2	0.3	3.2	7.8	1.6

^{a} Measured on the spectra shown in ref 9. ^{b} Measured relative to the lowest binding energy peak(s) taken as 1.0. ^{c} $Q = 3.6$ eV (see Table I). ^{d} IP values in parentheses obtained by deconvolution of the band envelope.

In the XP spectrum[9,10] of $LiNO_3$, three low-energy (<20 eV) peaks are also observed which are due to the ($1a_2'$, $1e''$, $4e'$), ($3e'$, $1a_2''$), and $4a'$ groups of MO's, respectively. Our intensity calculations for the ESCA spectrum are in satisfactory agreement with the experimental values and confirm our previous suggestion that the $^2A_2''$ state arising from the $1a_2''$ MO will be very weak and unresolved, due to the lack of s atomic character in this MO.

The ESCA spectrum of KNO_3 has been reported and interpreted[7] with the aid of semiempirical calculations. Bands with IP's of 11.6, 14.6, and 17.4 eV (relative to the Fermi level) were assigned to ionizations from the $3e'$, $1a_2''$, and $4a_1'$ MO's, respectively. Ionization from K 3p was also assigned to the 17.4-eV band. In the light of our UP spectrum and the ab initio calculations, the ESCA spectrum must be reassigned so that the band at 11.6 eV arises from the $3e'$ and $1a_2''$ MO's, the band at 14.6 eV arises from the $4a_1'$ MO ionization, and the peak at 17.4 eV is attributed to K 3p ionization exclusively.

The difference of approximately 4.9 eV between the binding energies we report and those measured by Morrison and Hendrickson[7] for NaCN and KNO_3 represents the work function of the sample Ψ_s ($E_B{}^{vac} - E_B{}^{Fermi}$).

4. Conclusions

We have demonstrated that it is possible to record the UP spectra of some simple ionic solids and thereby to obtain significant information on their molecular electronic structure. The advantages of UPS over XPS in studies of the valence-electron photoionization of solids have been clearly exemplified. While there are still some technical problems, not dealt with here, which require solution before this technique is generally applicable to solids, it must be apparent that in its present form there is much to be gained from a study of the UP spectra of inorganic (and organic) compounds in the solid phase.

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Registry No. NaCN, 143-33-9; KNO_2, 7758-09-0; KNO_3, 7757-79-1; CN^-, 57-12-5; NO_2^-, 14797-65-0; NO_3^-, 14797-55-8.

References and Notes

(1) Sodium cyanide (mp 564 °C; bp 1469 °C) gives a vapor which contains both monomeric and dimeric molecules at ca. 730 °C (R. F. Porter, *J. Chem. Phys.*, **35**, 318 (1961)). Both potassium nitrate (mp 334 °C) and potassium nitrite (mp 440 °C) melt without decomposition. At temperatures above 560 °C (KNO_3; E. A. Bordyushkova, P. I. Protsenko, and L. N. Venerovskaya, *Zh. Prikl. Khim.* (*Leningrad*), **40**, 1438 (1967)) or 530 °C (KNO_2; P. I. Protsenko and E. A. Bordyushkova, *Zh. Neorg. Khim.*, **10**, 1215 (1965)) the melts begin to release nitrogen, oxygen, and oxides of nitrogen (mainly NO and NO_2). This decomposition is essentially complete at temperatures above 900 °C ("Gmelins Handbuch der anorganischen Chemie", Potassium, System No. 22). For the experiments reported here we developed the following procedure. The sample was degassed by heating at ca. 160 °C for 12–18 h at a pressure of 10^{-8}–10^{-9} Torr. At the end of this time, the gold plate covering the sample stage was cleaned by ion bombardment until the valence-band structure of gold was well defined (resolved), thereby ensuring that contamination was minimized. The temperature of the sample was then raised to just below the melting point of the solid, when the pressure in the chamber began to rise very slowly. The temperature of the boat was then increased to be slightly (10–50 °C) above the melting point of the solid and the pressure in the chamber was allowed to rise to about 10^{-7} Torr for 30 s at this temperature. Heating was then immediately discontinued. The mass spectrum of the vapor produced in this way showed *m*/*e* peaks consistent with the presence of the molecular ion in the vapor (*m*/*e* 101, KNO_3; *m*/*e* 85, KNO_2), as well as peaks due to potassium (*m*/*e* 39, 41), nitrogen (*m*/*e* 28), oxygen (*m*/*e* 32), and oxides of nitrogen (*m*/*e* 30, 46). The vapor produced by heating the solid was allowed to condense on the clean gold plate, which was not cooled to avoid occlusion of gaseous products within the solid. The UV photoelectron spectrum of the solid was measured. At the end of the experiment the condensate could be isolated by washing it from the stage; qualitative analysis showed that it contained sodium and cyanide or both potassium and either nitrate or nitrite, as appropriate. Separate experiments showed that the thermal decomposition of KNO_3 and of KNO_2 could be easily detected: rapid heating of the sample ca. 800 °C resulted in a sudden increase in pressure (to 10^{-6} Torr) in the chamber (release of N_2, NO, O_2, and NO_2) without any detectable deposition of the potassium salt on the gold plate.
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Contribution from the Department of Chemistry,
Jadavpur University, Calcutta-700032, India

Kinetics of Oxidation of Hydrazinium Ion by Platinum(IV)

KALYAN K. SEN GUPTA,* PRATIK KUMAR SEN, and SHIPRA SEN GUPTA

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The kinetics of oxidation of hydrazinium ion by platinum(IV) has been studied spectrophotometrically in sodium acetate–acetic acid buffer. Hydrogen ion has no effect on the rate. Sodium perchlorate accelerates whereas sodium chloride inhibits the rate of oxidation. The empirical rate equation for the reaction is $-d[PtCl_6{}^{2-}]/dt = k_1k_2[PtCl_6{}^{2-}][N_2H_5{}^+]/(k_{-1}[Cl^-] + k_2[N_2H_5{}^+])$. The evidence for intermediate formation of platinum(III) has been demonstrated. The reaction seems to proceed via the formation of intermediate protonated hydrazyl radical followed by the decomposition of the latter to give N_2 and $NH_4{}^+$.

The reactions of hydrazine with several oxidizing agents like manganese(VII),[1] vanadium(V),[2] cobalt(III),[3] manganese(III),[4,5] iron(III),[5,6] copper(II),[7] perdisulfate,[8] thallium(III),[9] and chromium(VI)[10] have been studied. However, the mechanism of the oxidation of hydrazine by platinum(IV) is yet to be understood. The present investigation reports the results of the oxidation of hydrazinium ion by platinum(IV) under various experimental conditions and a possible reaction mechanism has been proposed.

Experimental Section

Reagents. Hydrazine hydrochloride and other inorganic materials were of AnalaR (BDH) grades. Hydrazine solutions were standardized with potassium iodate under the usual Andrews conditions.[11] A stock solution of hexachloroplatinate was prepared by dissolving platinic acid (Johnson-Mathey) in dilute hydrochloric acid and was standardized iodometrically. Sodium perchlorate was prepared by the neutralization of perchloric acid with sodium hydroxide. All solutions were made in doubly distilled water. Dioxane was purified by distilling twice with metallic sodium, each time collecting the middle fraction.

Absorption Spectra of Platinum(IV) Solution. The absorption spectra of platinum(IV) solution in the ultraviolet region and in the concentration range (1.84–5.75) × 10^{-5} M were recorded. No spectral shift was noticed with changes in the concentration of platinum(IV) and the spectrum exhibits a single maximum at 261 nm. Beer's law is found to be valid in this concentration range (1.84–9.2) × 10^{-5} M.

Kinetic Measurements. The rate of decrease of platinum(IV) concentration was followed from the measurements of absorbancies at 261 nm (where platinum(IV) has its maximum absorbance) in a