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## On the Use of the Photoelectron Spectrum of a Molecule in the Interpretation of the Electronic Spectrum of the Corresponding Cation

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The photoelectron spectra obtained from the molecules  $I_2$ ,  $Br_2$ , ferrocene, and chlorine dioxide are used to assign the electron spectra of their respective cations.

Photoelectron spectroscopy (pes) provides an energy profile of some of the unipositive states of a cation. The incidence of a photon upon the molecule causes an electron to be ejected from an occupied orbital in the molecule. The energy of this electron then reflects the energy of the corresponding cation state. Thus the results of a photoelectron spectrum can be cast into an energy level diagram showing the relative energies of different ionic states compared to that of the ground ionic state. This fact enables us to correlate the electronic spectrum of a cation with the photoelectron spectrum of the corresponding neutral molecule.

Consider, for example, a closed-shell molecule; the first and second ionization processes correspond to the removal of an electron from the highest and penultimate doubly occupied orbital, respectively. The energy difference between these two doublet states corresponds to the excitation of an electron from the highest doubly occupied orbital of the doublet state to the singly occupied orbital of the cation. Providing this transition is allowed, therefore, we are able, in principle, to predict the position of the electronic absorption band corresponding to this transition from the photoelectron spectrum. Of course for such a comparison the appropriate level of the ion is the vibrational ground state; that is, the excitation energies of the cation will be referred to the first adiabatic ionization of the parent molecule. If the electronic ground state of the ion is produced by removal of the nonbonding electron then the adiabatic ionization potential is readily determined. However, it is often the case that the orbital from which the electron was removed has bonding or antibonding character resulting in a geometry change on ionization. Such changes in potential surface lead to the excitation of vibrational modes in the molecule which cause a broadening of the pes band with concomitant difficulty in determining the adiabatic ionization potential.

In the presence of well-resolved vibrational structure the adiabatic ionization potential can be readily determined from an analysis of the vibrational fine structure provided the 0-0 band can be identified. When the vibrational frequency is such that the fine structure is ill resolved, then the adiabatic ionization potential corresponds approximately to the onset of the pes band, and unfortunately even this estimate can be in error due to the presence of vibrational "hot bands" (see for example ref 1).

Once the adiabatic ionization potential to the ground state of the cation has been established or estimated, the question of the geometry of the first excited state of the

cation becomes crucial if an estimate of the electronic excitation energy is to be made. The first excited state of the cation may have a different geometry from the ground state of the ion or the parent molecule. As a consequence it is very likely that the vertical electronic transition of the cation will not correspond to the vertical second ionization potential of the molecule, certainly not to the second adiabatic ionization potential of the parent molecule. Figure 1 indicates an example for a homonuclear diatomic molecule in which the ground doublet state and its first excited state have bond lengths shorter and larger than the parent molecule, respectively. This situation obtains for the halogens. It will be seen from the diagram that the best estimate of the electronic transition is the difference between the first adiabatic IP and the second vertical IP of the parent molecule and that such an estimate will often be a lower bond. Obviously we can construct hypothetical potential energy curves such that this estimate will equal the electronic transition energy; this might occur when the bond length change of the first excited state is intermediate between that of the cation and the parent molecule.

The correspondence between pes and the emission spectra of cations in the gas phase is well known.<sup>2</sup> The usefulness of the comparison in modern physical and inorganic chemistry will revolve around the identification of cations stabilized in the liquid or solid state. As a consequence the possible noncorrespondence of the Frank-Condon factors on going from pes to electronic spectroscopy will be compounded by solvent shifts. In addition pes will tell us nothing about electron excitation to virtual orbitals of the cation, but by mutual exclusion this can be very useful.

All of the foregoing conclusions are equally applicable to open-shell systems, except that here the pes is complicated by multiplet splitting from the corresponding singlet and triplet states of the cation. However in this case the electronic spectrum of the cation, if it is available, should shed some light on the interpretation of the pes of the radical.

It is the purpose of this short article to illustrate the usefulness of this technique with the cations  $I_2^+$ ,  $Br_2^+$ , and  $ClO_2^+$  observed in superacid media and the ferrocinium ion by relating their electronic spectra to the pes of the parent molecule.

(a)  $I_2$  and  $I_2^+$ .—The oxidation of iodine in strong acids has been the subject of some debate as to whether the blue color observed is due to  $I^+$  or  $I_2^+$ .<sup>8</sup> Gillespie

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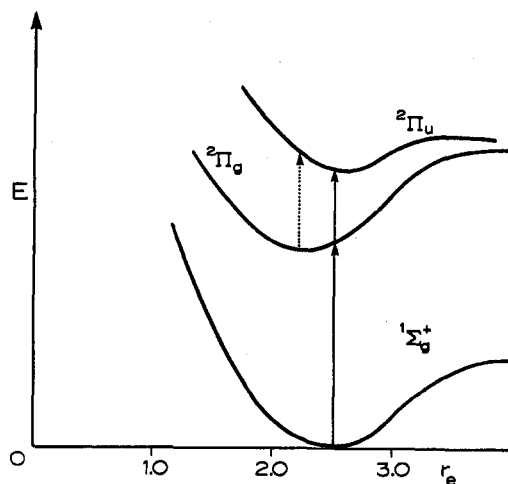


Figure 1.—Hypothetical potential energy curve for a homonuclear diatomic molecule, *e.g.*, one of the halogens. The solid arrows represent the first two vertical ionization potentials of the molecule. The dotted arrow represents a vertical electronic transition from the ground state of the ion.

and Milne interpreted the result of oxidation of iodine in  $S_2O_2F_2$ – $HSO_2F$  media as being due to  $I_2^+$  (together with  $I_3^+$  and  $I_5^+$ ) and suggested that this cation gives rise to the blue color. They observed electronic transitions at 640, 490, and 410 nm together with a weak infrared band at  $5190\text{ cm}^{-1}$ . These transitions are assigned as follows:  $\sigma_g^2\Pi_u^4\Pi_g^3 \rightarrow \sigma_g^2\Pi_u^3\Pi_g^4$  ( ${}^2\Pi_{3/2,g} \rightarrow {}^2\Pi_{3/2,u}$ ), 640 nm;  $\sigma_g^2\Pi_u^4\Pi_g^3 \rightarrow \sigma_g^2\Pi_u^3\Pi_g^4$  ( ${}^2\Pi_{3/2,g} \rightarrow {}^2\Pi_{3/2,u}$ ), 490 nm;  $\sigma_g^2\Pi_u^4\Pi_g^3 \rightarrow \sigma_g^2\Pi_u^4\Pi_g^2\sigma_u$  ( ${}^2\Pi_{3/2,g} \rightarrow {}^2\Delta_u$ ), 410 nm; the spin-forbidden  ${}^2\Pi_{3/2,g} \rightarrow {}^2\Pi_{1/2,u}$  transition is at  $5190\text{ cm}^{-1}$ .

The results of the photoelectron spectrum of  $I_2^+$  observed by Cornford, *et al.*,<sup>4</sup> and Potts and Price<sup>1</sup> provide an ideal test of the ideas presented earlier. First of all, the spin-orbit splitting on the first band of the  $I_2^+$  pes provides an estimate of the  ${}^2\Pi_{3/2,g} \rightarrow {}^2\Pi_{1/2,g}$  transition energy which would be predicted to occur at  $5125\text{ cm}^{-1}$ , in good agreement with the value given by Gillespie and Milne especially when one considers the drastically different media in which the two spectra were observed and the fact that the  ${}^2\Pi_{1/2,g}$  state is slightly more bonding than the  ${}^2\Pi_{3/2,g}$  state; *i.e.*, they may have slightly different bond lengths.

The pes studies<sup>1,4</sup> have shown that there is a considerable difference in bond lengths between the  ${}^2\Pi_g$  and  ${}^2\Pi_u$  states. Previously it was indicated that the best procedure for estimating electronic transition energies in such cases is to use the first adiabatic IP (as this corresponds to the ground state of the ion) and successive vertical IP's. Therefore for the  ${}^2\Pi_{3/2,g} \rightarrow {}^2\Pi_{3/2,u}$  transition we use the values 9.22 and 11.0 eV for the first adiabatic and second vertical IP's of iodine.<sup>1,4</sup> The value of the wavelength at maximum absorption ( $\lambda_{\text{max}}$ ) is then estimated to be 693 nm ( $14,440\text{ cm}^{-1}$ ) which is too long, as we previously indicated it would be. The third vertical IP is separated from the second by the value of the spin-orbit coupling constant in the ion and occurs at 11.80 eV. The use of this value with that of the first adiabatic IP leads to a  $\lambda_{\text{max}}$  value of 480 nm which is in good agreement with

that quoted by Gillespie and Milne. That the predicted value of  $\lambda_{\text{max}}$  is to a slightly shorter wavelength may reflect the fact that the  ${}^2\Pi_{1/2,u}$  component is slightly more bonding than the  ${}^2\Pi_{3/2,u}$  component as in the case of the  ${}^2\Pi_g$  states.<sup>1</sup> We note that the pes can say nothing about the  ${}^2\Pi_{3/2,g} \rightarrow {}^2\Delta_u$  transition as this involves a state formed by excitation to a virtual orbital of the cation.

(b)  **$Br_2$  and  $Br_2^+$ .**—Geometry changes similar to those associated with  $I_2$  occur on ionization of  $Br_2$ , so that we follow the same procedure as before for estimating the  ${}^2\Pi_{3/2,g} \rightarrow {}^2\Pi_{3/2,u}$  (550 nm) and  ${}^2\Pi_{3/2,g} \rightarrow {}^2\Pi_{1/2,u}$  (340 nm) transition wavelengths from the pes. Gillespie and Morton<sup>5</sup> assigned the electronic transition at 510 nm (observed when bromine monofluorosulfate is dissolved in the superacid media  $HSO_3F$ – $SbF_5$ – $3SO_3$ ) as being due to  $Br_2^+$ . They implied that this corresponds to the  ${}^2\Pi_{3/2,g} \rightarrow {}^2\Pi_{3/2,u}$  transition by comparison with  $I_2^+$ , and we see that the pes confirms their assignment. It would appear from the pes results that the shoulder in the spectrum given by Gillespie and Morton at 380 nm is in fact due to the  ${}^2\Pi_{3/2,g} \rightarrow {}^2\Pi_{1/2,u}$  transition (*cf.* 340 nm) of  $Br_2^+$ .

(c) **Ferrocene ( $Cp_2Fe$ ) and the Ferrocinium Ion ( $Cp_2Fe^+$ ).**—An interesting application of the comparison between the pes of a cation and the electronic spectrum of the parent molecule is afforded in the case of ferrocene. The work of Wilkinson, *et al.*,<sup>6</sup> on the structure of ferrocene also contained the electronic spectrum of the ferrocinium cation. There are two allowed transitions observed, with energies of about 2 eV ( $16,000\text{ cm}^{-1}$ ) and 5 eV ( $39,500\text{ cm}^{-1}$ ), the latter being the more intense. The transitions almost certainly arise from the excitation of an electron from a doubly occupied orbital to the singly occupied orbital. The pe spectrum<sup>7</sup> of ferrocene shows two ionic states of the ion at about 7 eV, another two at 9 eV, and a number of states between 12 and 15 eV. The adiabatic ionization potential to the first doublet state is readily obtainable from the pe spectrum as being 6.6 eV (vertical 6.8 eV), the other bands have vertical IP's of 7.2, 8.8, 9.4, and 12.2 eV. The vertical values of the higher IP's are the ones we shall use in this case since these are the most readily determined; however, it is possible that in the case of larger molecules, where geometry changes may be small on ionization and electron excitation, the adiabatic values should be used.

Although numerous calculations have been carried out on ferrocene<sup>8</sup> only that of Shustorovich and Dyatkina<sup>9</sup> gives the correct order for the first two orbitals (mainly metal 3d) assigned from the pe spectrum on the basis of the 2:1 intensity ratio, *i.e.*,  $e_{2g} > a_{1g}$ . The ground state of the ion will be  ${}^2E_{2g}$ ; thus electronic transitions to  ${}^2E_{1u}$  state are the only allowed ones. The state at 12.2 eV in the pes is certainly a  ${}^3E_{1u}$  state by comparison with the electronic spectrum, but which of the states occurring at about 9 eV is the other  ${}^2E_{1u}$

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state is not certain. The adiabatic third IP of the ferrocene agrees best with the electronic spectrum, being almost exactly 2 eV above the ground state of the ion; however the contour of the 9.4-eV band makes the estimation of the ionization potential difficult. On the basis of the pes we would assign the first five levels in ferrocene to be  $e_{2g} > a_{1g} > e_{1u} > e_{1g} > e_{1u}$ .

(d) **Chlorine Dioxide and the Chloryl Cation.**—The  $\text{ClO}_2^+$  cation has been identified by Carter, Johnson, and Aubke.<sup>10</sup> They reported an electronic spectrum consisting of two bands and a shoulder at 270, 220, and 330 nm, respectively, the two low-energy bands being assigned to  ${}^1A_1 \rightarrow {}^1B_1$  and  ${}^1A_1 \rightarrow {}^1B_2$  transitions. The photoelectron spectrum of  $\text{ClO}_2$  has been observed by Cornford, *et al.*,<sup>11</sup> who reported adiabatic (vertical) ionization potentials at 10.36 (10.48), 12.32 (12.94), 15.27 (15.45), 16.25 (17.50), and 17.69 (17.95) eV. The pe spectrum of a free radical is complicated by the occurrence of a multiplet (singlet-triplet) splitting of all bands after the first with the triplet bands being roughly 3 times more intense than the singlet. Thus in a comparison of the electronic spectrum with the pe

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spectrum care must be exercised to distinguish the singlet and triplet states. The intensity of the third band in the pe spectrum of  $\text{ClO}_2$  is such as to identify it as most likely belonging to the  ${}^1B_1$  state and the IP's quoted by Cornford, *et al.*, give a transition energy of  $39,600 \text{ cm}^{-1}$  (250 nm) which is however closer to the  ${}^1A_1 \rightarrow {}^1B_2$  transition assigned by Carter, *et al.* As indicated earlier, estimates of electronic transitions from pes are likely to be too long wavelengths; thus in this case it would appear that solvent interactions have depressed the  ${}^1B_1$  state of  $\text{ClO}_2^+$  some 80 nm relative to the gas phase. It can be noted here that Carter, *et al.*, are careful to point out that the  $\text{ClO}_2^+$  is solvent stabilized. If we assume that the  ${}^1B_2$  state is stabilized roughly by the same amount as the  ${}^1B_1$  state, then this state would correspond to the state at 17.7 eV in the pe spectrum. This would imply that the orbital configuration of  $\text{ClO}_2^+$  is in fact  $\dots b_2^2 - a_2^2 a_1^2$  with the lowest unoccupied orbital being the  $b_1$ .

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## Thermodynamic Properties of Oxygenated Sulfur Complex Ions. Heat Capacity from 5 to 300°K for $\text{K}_2\text{S}_4\text{O}_6(\text{c})$ and from 273 to 373°K for $\text{S}_4\text{O}_6^{2-}(\text{aq})$ . Revised Thermodynamic Functions for $\text{HSO}_3^-(\text{aq})$ , $\text{SO}_3^{2-}(\text{aq})$ , $\text{S}_2\text{O}_3^{2-}(\text{aq})$ , and $\text{S}_4\text{O}_6^{2-}(\text{aq})$ at 298°K. Revised Potential of the Thiosulfate-Tetrathionate Electrode<sup>1</sup>

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The heat capacity and thermodynamic functions for crystalline potassium tetrathionate,  $\text{K}_2\text{S}_4\text{O}_6(\text{c})$ , have been determined by adiabatic calorimetry from 5 to 330°K. The values of the standard thermodynamic functions  $C_p$ ,  $S^\circ$ ,  $-(F^\circ - H^\circ)/T$  at 298.15°K are 55.16, 74.01, and 38.91 cal mol<sup>-1</sup> °K<sup>-1</sup>, respectively. The heats of solution of  $\text{K}_2\text{S}_4\text{O}_6(\text{c})$  in water have been determined at various concentrations between 20 and 95° and extrapolated to infinite dilution to give the standard enthalpies of solution. At 25°,  $\Delta H^\circ_s = 12,403 \text{ cal mol}^{-1}$ . The partial molal heat capacities of  $\text{K}_2\text{S}_4\text{O}_6(\text{aq})$  have been evaluated from the heats of solution. The free energy of solution of  $\text{K}_2\text{S}_4\text{O}_6(\text{c})$  at 25° was determined to be 1510 cal mol<sup>-1</sup>; the resulting entropy of  $\text{K}_2\text{S}_4\text{O}_6(\text{aq})$  was 110.5 cal mol<sup>-1</sup> °K<sup>-1</sup>. Recalculation of previous data in the literature by third-law methods has resulted in revised thermodynamic functions for  $\text{HSO}_3^-(\text{aq})$ ,  $\text{SO}_3^{2-}(\text{aq})$ , and  $\text{S}_2\text{O}_3^{2-}(\text{aq})$ . The standard potential of the  $\text{S}_4\text{O}_6^{2-} - \text{S}_2\text{O}_3^{2-}$  electrode was calculated as 0.169 V at 25°.

### I. Introduction

The thermodynamic functions for large complex oxygenated anions are of continuing interest in inorganic chemistry. The tetrathionate ion,  $\text{S}_4\text{O}_6^{2-}$ , is a representative of these complex species, the salts of which can be obtained in high purity. Moreover, the potential of the thiosulfate-tetrathionate electrode is of analytical importance. Although thiosulfate can

be titrated quantitatively by iodine or triiodide, the great variation in reported potentials for the couple suggests that the electrode itself is not reversible.<sup>5</sup> Consequently, the potential of this electrode will have to be fixed from thermal measurements. Little data exist on the partial molal heat capacities for any complex electrolyte, and this communication provides the first data for such an anion.

### II. Experimental Section

**Apparatus.**—The heat capacity measurements were made at the University of Michigan by the adiabatic intermittent-heating

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