Correspondence

Electronic Structure of Ferrocene

Sir:

The electronic structure of ferrocene has been studied recently with both electronic absorption spectroscopy[1] and helium photoelectron spectroscopy.[2,3] The relative ordering of the one-electron energies of the filled e_{2g} and a_{1g} mainly iron 3d orbitals has been assessed by each method. The measured photoionization potentials (e_{2g}, 6.8 eV; a_{1g}, 7.2 eV) indicate that the lowest lying 3d orbital is the a_{1g} orbital. On the other hand, ligand field theory applied to the d–d absorption spectrum of ferrocene yields[1] the reverse order ($\epsilon_{e_{2g}}{}^{\mathrm{core}} - \epsilon_{e_{1g}}{}^{\mathrm{core}} = -7100\ \mathrm{cm}^{-1}$) for the one-electron core energies (ϵ^{core}) of these two levels. In this communication, it will be shown that such an apparent reversal in level ordering is expected in certain cases.

The Hamiltonian for the i valence metal d electrons in a transition metal complex can be written as

$$\mathcal{H} = \sum_i \mathcal{H}_i{}^{\mathrm{core}} + {}^1\!/_2 \sum_{\substack{\text{valence}\\ \text{electrons}}}^{i \neq j} \frac{1}{r_{ij}}$$

In this expression the first term represents the summation of the kinetic energy and potential energy "core" operators for the i valence electrons and the second term gauges the electron repulsion between these electrons. Thus $\mathcal{H}^{\mathrm{core}}$ incorporates the kinetic energy of a valence electron as well as the attractions to the various nuclei in the complex and the repulsions from the core electrons. Minimization of the total energy of the above system using the variational principle leads to the Roothaan–Hartree–Fock equations.[4,5] These equations provide a procedure whereby the best molecular orbitals can be found; this procedure is iterative and yields orbitals and eigenvalues that are self-consistent. The one-electron orbital energies ($\epsilon_i{}^{\mathrm{SCF}}$) from this self-consistent field treatment can be expressed as

$$\epsilon_i{}^{\mathrm{SCF}} = \epsilon_i{}^{\mathrm{core}} + \sum_{j=1}^{n} (2J_{ji} - K_{ji})$$

Here the summation runs over the n filled valence orbitals, the one-electron orbital energies $\epsilon_i{}^{\mathrm{core}}$ are eigenvalues[6] of $\mathcal{H}_i{}^{\mathrm{core}}$

$$\epsilon_i{}^{\mathrm{core}} = \int \psi_i{}^* \mathcal{H}^{\mathrm{core}} \psi_i \, d\tau$$

and J_{ji} and K_{ji} are the electron repulsion integrals

$$J_{ji} = \int \psi_j{}^*(1)\psi_j(1)\frac{1}{r_{12}}\psi_i{}^*(2)\psi_i(2)\, d\tau_1 d\tau_2$$

$$K_{ji} = \int \psi_j{}^*(1)\psi_i(1)\frac{1}{r_{12}}\psi_j(2)\psi_i{}^*(2)\, d\tau_1 d\tau_2$$

Thus there is a relation between the one-electron orbital energies resultant from a Hartree–Fock SCF–MO calculation and the one-electron orbital energies ($\epsilon_i{}^{\mathrm{core}}$) obtained in a ligand field calculation for the same system.[7] Finally, Koopmans' theorem[8] states that the *vertical* ionization energy for the ionization of an electron from the ith orbital will be equal to $-\epsilon_i{}^{\mathrm{SCF}}$. If Koopmans' theorem is assumed, the connection between a measured ionization potential and the ligand field theory $\epsilon_i{}^{\mathrm{core}}$ is straightforward.

The ground state of ferrocene[1] is ${}^1A_{1g}(e_{2g})^4(a_{1g})^2$. The vertical ionization potentials measured for the photoionization of the e_{2g} (6.8 eV) and a_{1g} (7.2 eV) mainly iron 3d electrons should be equal within the limitations of Koopmans' theorem to $-\epsilon_{e_{2g}}{}^{\mathrm{SCF}}$ and $-\epsilon_{a_{1g}}{}^{\mathrm{SCF}}$, respectively. These two one-electron SCF–MO energies are given in terms of one-electron core energies and repulsion integrals as

$$\epsilon_{a_{1g}}{}^{\mathrm{SCF}} = \epsilon_{a_{1g}}{}^{\mathrm{core}} + 4J_{a_1e_2} - 2K_{a_1e_2} + J_{a_1a_1}$$

$$\epsilon_{e_{2g}}{}^{\mathrm{SCF}} = \epsilon_{e_{2g}}{}^{\mathrm{core}} + 2J_{e_2a_1} - K_{e_2a_1} + 3J_{e_2e_2} - K_{e_2{}^+e_2{}^-}$$

The difference in ϵ^{SCF} for the a_{1g} and e_{2g} levels or difference in vertial ionization potentials if Koopmans' theorem holds is equal to the difference in ϵ^{core} *plus* a difference in electron repulsion integrals. In this case, we have

$$\epsilon_{a_{1g}}{}^{\mathrm{SCF}} - \epsilon_{e_{2g}}{}^{\mathrm{SCF}} = \epsilon_{a_{1g}}{}^{\mathrm{core}} - \epsilon_{e_{2g}}{}^{\mathrm{core}} + 2J_{a_1e_2} - K_{a_1e_2} + J_{a_1a_1} - 3J_{e_2e_2} + K_{e_2{}^+e_2{}^-}$$

These J_{ij} and K_{ij} can be expressed[9] in terms of the Racah parameter B such that

$$\Delta\epsilon^{\mathrm{SCF}}(a_{1g}\text{–}e_{2g}) = \Delta\epsilon^{\mathrm{core}}(a_{1g}\text{–}e_{2g}) - 20B$$

The recent LF treatment of ferrocene found $\Delta\epsilon^{\mathrm{core}}(a_{1g}\text{–}e_{2g}) = 7100\ \mathrm{cm}^{-1}$ and $B = 390\ \mathrm{cm}^{-1}$. Substitution of these LF parameters into the equation gives $\Delta\epsilon^{\mathrm{SCF}}(a_{1g}\text{–}e_{2g}) = -700\ \mathrm{cm}^{-1}$. A reversal in ordering of ϵ^{SCF} and ϵ^{core} is predicted for the e_{2g} and a_{1g} levels of ferrocene.

The photoelectron measurements, however, give $\Delta\epsilon^{\mathrm{SCF}}(a_{1g}\text{–}e_{2g}) = -0.40\ \mathrm{eV} = -3230\ \mathrm{cm}^{-1}$ if we invoke Koopmans' theorem. The reversal is even greater than is predicted. In the ferrocene LF treatment B and $\Delta\epsilon^{\mathrm{core}}(a_{1g}\text{–}e_{2g})$ are evaluated from differences in transition energies without further approximations The disagreement between the predicted $\Delta\epsilon^{\mathrm{SCF}}(a_{1g}\text{–}e_{2g}) = -700\ \mathrm{cm}^{-1}$ and the measured difference between the vertical ionization potentials ($= -3230\ \mathrm{cm}^{-1}$) can probably be attributed to a breakdown in Koopmans' theorem. This theorem only holds if the molecu-

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(1) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 3603 (1971).

(2) D. W. Turner in "Physical Methods in Advanced Inorganic Chemistry," H. Hill and P. Day, Ed., Interscience, New York, N. Y., 1968, Chapter 3.

(3) D. W. Turner, *Advan. Mass Spectrom.*, **4**, 755 (1968).

(4) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(5) R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, New York, N. Y., 1963.

(6) This is an approximation; $\mathcal{H}^{\mathrm{core}}$ is not exactly diagonal in the SCF eigenfunction basis. In crystal field theory, the eigenfunctions are metal orbitals. Extension of the utilization of $\epsilon_i{}^{\mathrm{core}}$ values to ligand field calculations is only an approximation, since the "metal valence" eigenfunctions are assumed to be partially ligand in character.

(7) For a further discussion of the relation between ϵ^{core} and ϵ^{SCF}, see C. J. Ballhausen and H. B. Gray in "Chemistry of the Coordination Compounds," Vol. I., A. E. Martell, Ed., Van Nostrand-Reinhold, Princeton, N. J., in press, Chapter 1.

(8) T. Koopmans, *Physica*, **1**, 104 (1934); C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 61 (1951).

(9) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962.

lar orbitals of the ionized molecule are those of the parent molecule. Electronic relaxation (*i.e.*, change of orbitals) in the ionized molecule or a difference in correlation energies (not included in SCF–MO treatment) will invalidate Koopmans' theorem. Thus a difference in electronic relaxation energies for photoionization of the e_{2g} electron as compared to the a_{1g} electron or a difference in correlation energy differences is the probable cause of this disagreement.

It would be interesting to have photoelectron ionization data for other metallocenes. The ligand field treatment of ruthenocene[1] gave $\Delta\epsilon^{\text{core}}(a_{1g}–e_{2g}) = -6600$ cm^{-1} and $B = 260$ cm^{-1}. In this case we would predict $\Delta\epsilon^{\text{SCF}}(a_{1g}–e_{2g}) \cong +1400$ cm^{-1}, and, if the collapse of Koopmans' theorem is no more extensive in ruthenocene, the ionization potentials of the ruthenocene 4d a_{1g} and e_{2g} electrons should be closer in energy than those for the ferrocene 3d electrons.

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On the Exchange of Oxygen between Sulfate and Water

Sir:

A good deal of conflicting data on the rate and mechanism of oxygen exchange between sulfate and water has been reported;[1] for example, the exchange in 1 *N* NaOH at 100° has been reported to be as great as 85% in 26 hr[1a] and as little as <1% in 456 hr.[1d]

More recently, Hoering and Kennedy[2] reported some experiments on the acid-catalyzed exchange of oxygen between sulfuric acid and water. The results of these experiments, coupled with earlier reports (*e.g.*, ref 1a), suggest that there may be a change in the exchange mechanism from acid-catalyzed dehydration to, for example, nucleophilic displacement by H_2O and/or OH^- at higher pH values. We wish to report a reinvestigation of this question using ^{18}O-labeled sulfate (91.9 atom % excess obtained from Miles-Yeda Ltd.).

In these experiments solutions of 0.1 *M* $Na_2S^{18}O_4$ were incubated at 100° for 63 days in Teflon bombs, either with no additions of in the presence of 1 *N* NaOH. A 0.1-ml aliquot of the incubated solution was then introduced with a syringe into an evacuated 5-ml stoppered serum vial containing sufficient $NaHCO_3$ to produce 5 ml (at STP) of CO_2 upon acidification. An excess of 85% lactic acid (0.05 ml) was then added to release the CO_2. (The small dilution of ^{18}O label due to H_2O–lactic acid oxygen exchange was accounted for in the calculation of exchange rates.) After an equilibration time of 18 hr at room temperature (sufficient for complete isotopic equilibration[3]), the CO_2 was introduced into a modified CEC isotope ratio mass spectrometer through a syringe–needle inlet and the $^{18}O:^{16}O$ ratio of the CO_2 determined (at m/e 46 and 44). Preliminary experiments showed that, under the conditions used for equilibration with CO_2, no exchange of ^{18}O between the sulfate and water occurred. Therefore, it was not necessary to separate the water from the salt solutions before analyses.

Four readings were made on each of three replicates for each experimental condition. Measurements of "standard CO_2" (derived from $NaHCO_3$ in the same manner) were interspersed between experimental measurements to detect and correct for any drift in the mass spectrometer readings. Preliminary experiments using $H_2{}^{18}O$ indicated that we could reliably detect an exchange of 0.1% under the conditions employed.

These experiments showed that under neutral or alkaline conditions (1 *N* NaOH), no exchange (<0.1%) occurred at 100° in 63 days. This suggests that the second-order rate constant (k_2) is $<1 \times 10^{-11}$ M^{-1} sec^{-1} using H_2O as a nucleophile. Similarly, using OH^- as a nucleophile, the second-order rate constant (k_2) is $<8 \times 10^{-10}$ M^{-1} sec^{-1}. By way of comparison, we find $k_2 = 5.3 \times 10^{-5}$ M^{-1} sec^{-1} for the acid-catalyzed exchange reaction at 100°, a value in good agreement with the value calculated from the data in ref 2. It thus appears that sulfate oxygen does not undergo appreciable exchange with the oxygen of H_2O by any mechanism other than acid-catalyzed dehydration under these conditions.

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[1] (a) S. C. Datta, J. N. E. Day, and C. K. Ingold, *J. Chem. Soc.*, 1968 (1937); (b) G. A. Mills, *J. Amer. Chem. Soc.*, **62**, 2833 (1940); (c) N. F. Hall and O. R. Alexander, *ibid.*, **62**, 3455 (1940); (d) E. R. S. Winter, M. Carlton, and H. V. A. Briscoe, *J. Chem. Soc.*, 131 (1940); (e) E. R. S. Winter and H. V. A. Briscoe, *ibid.*, 631 (1942).

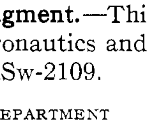
[2] T. C. Hoering and J. W. Kennedy, *J. Amer. Chem. Soc.*, **79**, 56 (1957).

[3] M. Cohn and H. C. Urey, *ibid.*, **60**, 679 (1938).

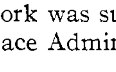
On the Observation of *cis*- and *trans*-Bis(2,2′-bipyridyl)copper(II) by Electron Spin Resonance

Sir:

Several recent investigations of bis(2,2′-bipyridyl)-copper(II), $[Cu(bipy)_2(OH_2)_2]^{2+}$, have been concerned with the existence and relative stability of the two possible geometrical isomers of this complex: one in which the two water molecules are cis to each other and the other in which they are trans.[1–3]



cis



trans

Among these investigations is the comprehensive nmr and esr study of Noack and Gordon[1] of the Cu^{2+}–

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[1] M. Noack and G. Gordon, *J. Chem. Phys.*, **48**, 2689 (1968).

[2] C. K. Jørgenson, *Acta Chem. Scand.*, **9**, 1362 (1955).

[3] Y. I. Skurlatov and A. P. Purmal, *Russ. J. Phys. Chem.*, **43**, 880 (1969).