same time, they are not much lower than the 6.0 ml/mole increase associated with inner-sphere nitrate substitution in $Co(NH_3)_5H_2O^{3+}$. Thus the volume changes provide no clear evidence that the lanthanon nitrate complexes are outer sphere. In fact, their intermediate values suggest that an equilibrium mixture containing comparable fractions of both structural types may be present. The entropy change for $Co(NH_3)_5NO_3^{2+}$ formation has not been determined. If it turned out to be small, the entropy argument for outer-sphere nitrate complexing of the lanthanons would be vitiated. It is relevant to note that Raman spectra provide evidence[31] for distortion of nitrate in cerium(III) solutions. Hester and Plane concluded[32] that in zinc(II) solutions similar distortion of nitrate is due to inner-sphere complexing. It has not been established whether the same conclusion applies to cerium. Very recently Abrahamer and Marcus[33] have demonstrated that most of the nitrate bound to erbium(III) in concentrated lithium nitrate solutions is in the primary coordination sphere.

The present findings on volume changes due to outer-sphere complexing were unexpected. The conclusion seems inescapable that, in dilute solution, the expansion accompanying outer-sphere association of sulfate to $Co(NH_3)_6^{3+}$ or $Co(NH_3)_5H_2O^{3+}$ is nearly as large as that accompanying inner-sphere substitution by sulfate in the latter complex. Both values decrease substantially on raising the ionic medium to 1 *M* $NaClO_4$, but the effect is apparently greater for the outer-sphere volume change. Significantly, the entropy change for sulfate outer-sphere association to $Co(NH_3)_6^{3+}$ or $Co(NH_3)_5H_2O^{3+}$ is also quite large,[9] 16 eu, and decreases markedly, to 3.3 eu, in 1 *M* $NaClO_4$.

We tentatively conclude that volume and entropy changes parallel one another for complex formation in aqueous solution and probably measure essentially the same structural changes. It appears that, contrary to expectations based on simple models, both quantities may have substantial positive values for outer- as well as inner-sphere complex formation, and the former is especially sensitive to the ionic medium used. Furthermore, inner-sphere volume changes, and quite probably entropy changes as well, can vary widely for a given cation, depending on the nature of the anion. Evidently there can be no general criterion for distinguishing between inner- and outer-sphere complexing based either on volume or on entropy changes. Nevertheless, comparison of volume or entropy data with corresponding data for complexes of known structure under closely similar conditions may provide a basis for judgment of structural type. Such comparisons should preferably be carried out at high electrolyte concentrations, where the differences in ΔV and ΔS between inner- and outer-sphere complexes appear to be most pronounced.

Acknowledgments. We are indebted to Professor Walter Kauzmann for much advice and encouragement, to Mrs. Agnes Bodanzky for technical assistance, and to Dr. David Eisenberg for a stimulating discussion from which the idea for this project arose. The work was supported by the Public Health Service under Grant GM-13498 from the National Institute of General Medical Sciences.

---

(31) R. E. Hester and R. A. Plane, *Inorg. Chem.*, 3, 769 (1964).
(32) R. E. Hester and R. A. Plane, *J. Chem. Phys.*, 45, 4588 (1966).
(33) L. A. Abrahamer and Y. Marcus, *Inorg. Chem.*, 6, 2103 (1967).

Ionization Potentials of Tris(β-diketonate)metal(III) Complexes and Koopmans' Theorem(1)

Steven M. Schildcrout,(2) Ralph G. Pearson, and Fred E. Stafford

Contribution from the Department of Chemistry and The Materials Research Center, Northwestern University, Evanston, Illinois 60201. Received November 15, 1967

Abstract: Electron-impact ionization potentials have been determined for 11 complexes of acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone with various trivalent metals, as well as for the two fluorinated uncomplexed diketones. Each of the metal(III) complexes has an ionization potential which is close to that of the corresponding free diketone and which depends only slightly on the metal. This conflicts with predictions based on the application of Koopmans' theorem to the usual molecular orbital theory of these complexes. It is concluded that Koopmans' theorem is not valid for these complexes. There is evidence that the Fe and Co complexes decompose thermally in the mass spectrometer, showing the need for mass analysis in ionization-potential measurements.

According to Koopmans' theorem[3,4] the energy eigenvalue of the highest occupied molecular orbital (MO) has physical significance in that it approximates the negative of the molecular ionization potential (IP). There has been much recent interest in the application of MO, or ligand field, theory to metal complexes.[5] The energy separations among the calculated MO's are often compared with visible–ultraviolet spectroscopic results, but only rarely are attempts made

---

(1) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Paper O80.
(2) Recipient of Public Health Service Fellowship 5-F1-GM-33,565-02 from the National Institute of General Medical Sciences.
(3) T. Koopmans, *Physica*, 1, 104 (1933).
(4) R. S. Mulliken, *Phys. Rev.*, 74, 736 (1948).
(5) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, Inc., New York, N. Y., 1964; B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, New York, N. Y., 1966.

to correlate IP's with the "absolute" energies of the MO's. The scarcity of IP data for metal complexes seems to be the main reason for this.

Complexes for which IP's have been measured include some of the metal carbonyls[6–11] and cyclopentadienyls.[12,13]

Metal β-diketonate complexes are known for a variety of metals and diketones.[14] Theoretical treatment of the tris(acetylacetonate)metal(III) complexes ($M(acac)_3$, where M^{3+} = metal ion and $acac^-$ = $CH_3COCHCOCH_3^-$) has shown that for metals of the first transition series the d orbitals of the metal are split by the nearly octahedral ligand field and that these orbitals lie higher in energy than the highest filled π orbitals of the $acac^-$ ligand.[15] One would then expect that the IP of one of these complexes depends on whether or not the triply charged metal atom has any d electrons. If it has, the IP should reflect the ligand field splitting of the d orbitals.

The present study was undertaken to measure by electron-impact mass spectrometry the IP's of a series of tris(β-diketonate) complexes where the effect of both metal (with varying d electron configurations) and ligand (with varying substituents on the chelate ring) could be tested. These results could then be compared to both the trends and the actual values of the theoretical IP's. The complexes investigated are chiefly those of metals of the first transition series. The ligands are anions of acetylacetone, trifluoroacetylacetone ($tfac^-$ = $CF_3COCHCOCH_3^-$), and hexafluoroacetylacetone ($hfac^-$ = $CF_3COCHCOCF_3^-$). Also considered were the neutral forms of the ligands, Hacac, etc., which in the gas phase should exist predominantly in the hydrogen-bonded enol form[16] and are thus similar to the metal complexes, where the ligand is bidentate *via* its two oxygen atoms.

Experimental Section

The acac complexes of Cr, Mn, and Fe were prepared by standard procedures,[14,17] and those of Al and V were purchased from K & K Laboratories, Inc., Plainview, N. Y. $Co(hfac)_3$ was prepared by the method of Kilner, Hartman, and Wojcicki,[18] and all other fluorinated samples were purchased from Pierce Chemical Co., Rockford, Ill. Sample purities were checked with the mass spectrometer.

The mass spectrometer[19] employed is described elsewhere.[20] One of two methods of sample introduction was used. All of the acac complexes, as well as $Fe(tfac)_3$ and $Rh(hfac)_3$, were studied by placing several milligrams of the powder or fine crystals in a 10-mm i.d. alumina liner, which in turn was placed in a 13-mm i.d. by 30-mm long molybdenum cell mounted in the spectrometer's furnace assembly. The cell had an effusion orifice 1 mm in diameter. It could be heated by radiation from surrounding tungsten filaments until the vapor pressure of the sample was such that it gave a parent ion signal of appropriate intensity. Total pressure in the ion source region was usually about 2×10^{-7} torr. Temperatures between 50 and 110° were used. They were measured by using a Pt-Pt-10%Rh thermocouple spot-welded to the molybdenum cell. Other samples were sufficiently volatile to let the vapor at room temperature leak through a regulating value directly into the ion source chamber, where the total pressure was typically about 2×10^{-6} torr. In these cases the external sample reservoir was immersed in an appropriate constant-temperature bath to maintain a steady vapor pressure.

The emission current of ionizing electrons was regulated at 1.2 mA, corresponding to $\sim 10^{-5}$-A trap current.

Mass-analyzed ion currents were detected by a 20-stage Be–Cu secondary electron multiplier operated at a gain of about 2×10^6.

The parent ion for each sample was identified by mass, isotope ratio, and, in the case of heated samples, shutter effect.[20]

Appearance potentials were obtained by the vanishing current method[21,22] from ionization efficiency curves made directly and automatically with an X–Y recorder.[23] Background $^{202}Hg^+$ arising from mercury from the diffusion pumps was used to calibrate the electron energy scale. Its appearance potential is taken as 10.43 eV.[24] To make the sample curves more comparable to the calibrant curves, the sample pressure was regulated so that at 70 eV the parent ion intensity of the sample was about equal to the intensity of Hg^+. The detectable ion current at onset of ionization was less than 0.01% that at 70 ev. Typically, for each sample, six ionization efficiency curves for the isotopically predominant parent ion and nine calibrant curves were recorded on each of two different days in the sequence three calibrant curves, three sample, etc. The onset potential was determined for each curve, and the results were averaged to give the reported IP's.

Results and Discussion

The IP's determined in this investigation are given in the last three columns of Table I. Values obtained by others for Hacac,[25] $Co(acac)_3$,[26] and the neutral metal atoms[24] are included for comparison.

Although ionization by electron impact is a vertical (Franck–Condon) process, the use of high-sensitivity ion detection with the vanishing current method of interpreting the ionization efficiency curves should extend the effective Franck–Condon region and permit these measured IP's to approach the adiabatic values.[21,27] The value measured here for $Cr(hfac)_3$ is 0.37 eV above the adiabatic photoionization value.[28] It is felt that the agreement is reasonably satisfactory. The most important point is that probably all of the

---

(6) F. I. Vilesov and B. L. Kurbatov, *Dokl. Akad. Nauk SSSR*, **140**, 1364 (1961).

(7) R. E. Winters and R. W. Kiser, *Inorg. Chem.*, **3**, 699 (1964); **4**, 157 (1965); *J. Phys. Chem.*, **69**, 1618, 3198 (1965); *J. Organometal. Chem.* (Amsterdam), **4**, 190 (1965).

(8) A. Foffani, S. Pignataro, B. Cantone, and F. Grasso, *Z. Physik. Chem.* (Frankfurt), **45**, 79 (1965).

(9) S. M. Schildrout, G. A. Pressley, Jr., and F. E. Stafford, *J. Am. Chem. Soc.*, **89**, 1617 (1967).

(10) H. J. Svec and G. A. Junk, *ibid.*, **89**, 2836 (1967).

(11) D. R. Bidinosti and N. S. McIntyre, *Can. J. Chem.*, **45**, 641 (1967).

(12) L. Friedman, A. P. Irsa, and G. Wilkinson, *J. Am. Chem. Soc.*, **77**, 3689 (1955).

(13) R. E. Winters, Ph.D. Thesis, Kansas State University, 1965; *Dissertation Abstr.*, **26**, 4226 (1966).

(14) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 361 (1966), and references therein.

(15) (a) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **22**, 183 (1961); (b) C. K. Jørgensen, *Acta Chem. Scand.*, **16**, 2406 (1962); (c) K. DeArmond and L. S. Forster, *Spectrochim. Acta*, **19**, 1393 (1963); (d) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

(16) (a) J. L. Burdett and M. T. Rogers, *ibid.*, **86**, 2105 (1964); (b) W. Strohmeier and I. Höhne, *Z. Naturforsch.*, **7B**, 184 (1952).

(17) The authors thank Professor Fred Basolo for these samples.

(18) M. Kilner, F. A. Hartman, and A. Wojcicki, *Inorg. Chem.*, **6**, 406 (1967).

(19) Built by Nuclide, Inc., State College, Pa. (type 12 in., 60° sector, HT); W A. Chupka and M. G. Inghram, *J. Phys. Chem.*, **59**, 100 (1955).

(20) (a) A. B. Baylis, G. A. Pressley, Jr., and F. E. Stafford, *J. Am. Chem. Soc.*, **88**, 2428 (1966); (b) A. D. Norman, R. Schaeffer, A. B. Baylis, G. A. Pressley, Jr., and F. E. Stafford, *ibid.*, **88**, 2151 (1966).

(21) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957.

(22) H. J. Svec and G. A. Junk, *J. Am. Chem. Soc.*, **89**, 790 (1967).

(23) R. J. Loyd and F. E. Stafford, Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., 1968, p 127. An example of a directly recorded ionization efficiency curve is given here.

(24) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1949, 1952, 1958.

(25) R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965.

(26) R. W. Kiser, R. M. Teeter, and E. J. Gallegos, private communication.

(27) J. E. Collin in "Mass Spectrometry," R. I. Reed, Ed., Academic Press Inc., New York, N. Y., 1965, p 201.

(28) D. R. Lloyd and E. W. Schlag, private communication.

Table I. Ionization Potentials of Some β-Diketonate Complexes

Complex	IP of neutral atom M[a]	No. of outer d electrons in M^{3+}	Electronic confign of $M(acac)_3$[b]	IP[c] of complex, eV		
				L = acac	L = tfac	L = hfac
HL	13.60	...	...	8.87[d]	9.96 ± 0.10	10.68 ± 0.09
AlL_3	5.98	0	...	8.27 ± 0.13	...	10.30 ± 0.11
VL_3	6.74	2	$t_{2g}{}^2$	7.72 ± 0.10	...	...
CrL_3	6.76	3	$t_{2g}{}^3$	7.87 ± 0.12	...	9.97 ± 0.08[e]
MnL_3	7.43	4	$t_{2g}{}^3e_g$	7.95 ± 0.10	...	...
FeL_3	7.87	5	$t_{2g}{}^3e_g{}^2$	8.64 ± 0.11	9.38 ± 0.11	10.34 ± 0.10
CoL_3	7.86	6	$t_{2g}{}^6$	7.81 ± 0.10[f]	...	10.12 ± 0.15
RhL_3	7.46	6	$t_{2g}{}^6$	...	...	10.15 ± 0.12

[a] Spectroscopic value in eV given by Moore, ref 24. [b] Barnum, ref 15, and references therein. The octahedral group notation is used here as an approximation. [c] In eV, with 90% confidence limits; estimated from the reproducibility of the data; acac = acetylacetone, tfac = trifluoroacetylacetone, hfac = hexafluoroacetylacetone ligands. [d] Photoionization value listed by Kiser, ref 25. [e] Using photoionization, an adiabatic IP of 9.60 eV has been determined for $Cr(hfac)_3$ by Lloyd and Schlag, ref 28. [f] Electron-impact value determined by Kiser, Teeter, and Gallegos, ref 26.

electron-impact values are above adiabatic values by similar amounts (0.2–0.4 eV); hence comparisons among them for different metal ions and different ligands will be valid.

Electron-impact fragmentation patterns have been reported for $M(acac)_3$ (where M = Al, Cr, and Fe,[29,30]) for Hhfac,[30] and for $Al(hfac)_3$.[31] For each of the ML_3 complexes, the intensity of the ML_2^+ ion is reported to be much greater than that of the ML_3^+ ion at 70-eV ionizing energy. This was found to be the case also for all other ML_3 complexes studied in this work. The importance of mass analysis of ions in determining IP's is shown by the observation that, in the cases of $Fe(tfac)_3$ and $Al(hfac)_3$, the roughly measured appearance potentials of the ML_2^+ ions were close to the appearance potentials of the corresponding ML_3^+ ions. In the cases of $Fe(hfac)_3$ and $Co(hfac)_3$, the ML_2^+ ions had *lower* appearance potentials than the corresponding parent ions ML_3^+. This is due possibly to the presence of the molecules $Fe(hfac)_2$ and $Co(hfac)_2$ in the ionization chamber with the corresponding tris complexes. The results of one experiment in which $Fe(hfac)_3$ was pyrolyzed in the mass spectrometer by a method used previously[9] suggest that at temperatures near 200° significant amounts of $Fe(hfac)_2$ are formed by decomposition of $Fe(hfac)_3$. Such pyrolysis could occur in a mass spectrometer ion source as has been shown for B_4H_{10}[20b] and may account for the failure of Sasaki, *et al.*,[30] to detect parent ions for the acac complexes of Cr(III), Fe(III), and Co(III).

The detection in several instances of HL^+ suggests the presence of HL with the ML_3 complex. The presence of such impurities of lower molecular weight should not affect the validity of the given IP's. Since no significant amounts of polymeric ions[29] were found under the present conditions, it seems safe to assume that the appearance potentials measured for the ML_3^+ ions are equal to the IP's of the ML_3 molecules.

Several regularities are observed in the results. (1) For the compounds shown in Table I the ligand, more than the metal, determines the IP. The hfac compounds have much higher IP's than the acac compounds, and the tfac compounds have IP's very nearly the mean of those of their hfac and acac analogs. (2) For a given ligand L, the IP of HL is slightly greater than that of any ML_3. (3) For a given L, AlL_3 and FeL_3 have somewhat higher IP's than the other ML_3's.

There is no obvious correlation between the IP's of the complexes and those of the neutral metal atoms (Table I, column 2). The close agreement between the IP's of $Co(acac)_3$ and Co seems fortuitous.

Since the IP's seem to be determined almost entirely by L, it is reasonable to assume that the ionization involves an MO localized mainly on the ligand. This creates a conflict with the usual MO diagrams for these complexes.[15] While the various calculations differ in detail, they all agree on certain features. There is a triply degenerate π_3 level from the ligands and a triply degenerate t_{2g} level from the metal ion which are of similar energy. In the complex they are mixed by π bonding and produce further splittings.

The important point is that in any case, there will be an $e_g{}^*$ level composed chiefly of the $d_{x^2-y^2}$ and d_{z^2} orbitals of the metals lying above the highest of the previous orbitals. Furthermore, the difference in energy between the $e_g{}^*$ orbitals and the highest of the mixed π_3–t_{2g} orbitals is fixed at about 2.5 eV. This follows from any reasonable interpretation of the visible and uv absorption spectra ($10Dq \approx 2.5$ eV). Figure 1 shows a simplified diagram of the MO's for typical cases of no d electrons ($Al(hfac)_3$), only t_{2g} electrons ($Cr(hfac)_3$) and t_{2g} and $e_g{}^*$ electrons ($Fe(hfac)_3$). It is clearly predicted that the IP of any complex containing $e_g{}^*$ electrons will be some 2.5 eV less than for similar complexes with no $e_g{}^*$ electrons.

It is reasonable for HL and AlL_3 to have similar IP's since neither has any d electrons. From Figure 1, one might have expected complexes containing t_{2g} electrons to have somewhat smaller IP's though the effect of increasing nuclear charge might well be a compensating factor (note the increasing IP's of the neutral atoms in Table I). However, the Mn and Fe complexes with occupied $e_g{}^*$ orbitals should definitely have the lowest IP's; this is not confirmed by experiment.

Barnum[15a] has done simple Hückel-type MO calculations for the $M(acac)_3$ complexes where M = V, Cr, Mn, Fe, Co. His model can easily be extended to Hacac and $Al(acac)_3$ so that by using Koopmans' theorem, IP's can be predicted for all acac complexes whose IP's have been measured. A comparison of the measured and the calculated IP's is given in Figure 2.

---

(29) C. G. MacDonald and J. S. Shannon, *Australian J. Chem.*, 19, 1545 (1966).

(30) S. Sasaki, Y. Itagaki, T. Kurokawa, K. Nakanishi, and A. Kasahara, *Bull. Chem. Soc. Japan*, 40, 76 (1967).

(31) C. Reichert, J. B. Westmore, and H. D. Gesser, *Chem. Commun.*, 782 (1967).

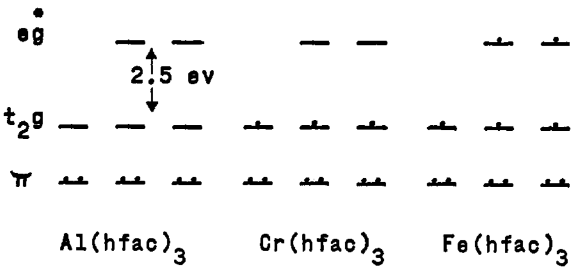

Figure 1. Molecular orbital diagram for ML_3 complexes showing only the highest occupied orbitals. The absolute energies of corresponding orbitals may vary slightly from one metal to another.

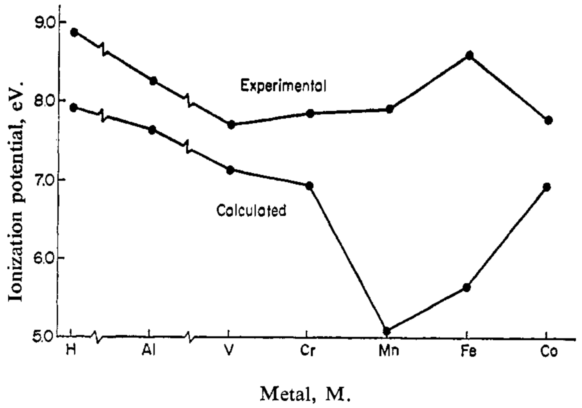

Figure 2. Ionization potentials of Macac (M = H) and M(acac)$_3$ (M = Al, V, Cr, Mn, Fe, Co) as determined experimentally (see Table I) and as predicted using Koopmans' theorem and Barnum's[15a] MO model.

Following Barnum's suggestions, one may extend the calculation to the hfac complexes by considering the inductive effect of the CF_3 groups, as estimated from the group electronegativity.[32] The IP's predicted for the complexes then increase only a fraction of a volt. The observed difference between the M(hfac)$_3$ and the M(acac)$_3$ complexes is about 2 eV. Since the difference in IP between Hhfac and Hacac is also 2 eV, and since the electron surely comes from the ligand in these cases, we can again infer that ionization of the complexes involves an orbital concentrated on the ligand. It is reassuring that the tfac complexes have IP's midway between those of acac and hfac. This indicates that the ionized electron does not come from the methyl group or the trifluoromethyl group but from an orbital spread over the entire ligand.

There are two possible reasons for this apparent failure of the MO theory. Either the metal d orbitals in these complexes do not lie higher in energy than the highest filled π orbitals of the ligand, or Koopmans' theorem is not valid here.

The large body of spectroscopic, magnetic, and chemical evidence[14,15] strongly supports the qualitative correctness of the MO picture of these complexes. Thus it becomes difficult to imagine how these properties could be explained if the diagram of Figure 1 is seriously in error. The ordering and extent of mixing of the π_3 and t_{2g} orbitals is not a factor here, but the e_g^* level must lie some 2.5 eV higher.

The applicability of Koopmans' theorem must then be considered. Part of the difficulty may be that Koopmans' theorem is expected to apply well only to self-consistent-field (SCF) calculations with closed-shell configurations.[4] This would invalidate quantitative comparisons between experimental IP's and simple Hückel calculations for an open-shell system. However, such qualitative features as the dependence of the energy of the highest filled MO on variations in the number of d electrons on the metal area not expected to change in going from the Hückel to the SCF treatment.

Besides neglecting correlation effects, Koopmans' theorem depends on the assumption that the corresponding orbitals of the molecule and its ion are the same; this is sometimes thought to be a good assumption for large systems (many nuclei and electrons).[33] However, it is well known that Koopmans' theorem is not valid for aromatic hydrocarbons.[34] Here also we have a large, polarizable system similar to the ML_3 complexes. It is likely that for such "soft" molecular systems extensive changes in the remaining orbitals occur upon ionization, thus invalidating Koopmans' theorem.

That this assumption has important exceptions for smaller systems is shown by the well-known examples of the transition metal atoms, where an inversion in the ordering of the ns and the $(n - 1)$d $(n = 4, 5, 6)$ orbitals commonly occurs upon ionization.[24] This is accounted for by the rule that as the effective nuclear charge increases, which it does upon ionization, orbital pentration effects become less important, and the atomic terms become more hydrogen-like.[35] The presence of a transition metal atom in a molecule may also be an indication that Koopmans' theorem should be applied with caution. It is interesting to note that what is needed to make Figure 1 consistent with the IP data is to have an inversion of the e_g^* orbitals and the π orbitals upon ionization. Since the e_g^* is largely metal 3d in character, this is similar to the 3d–4s inversion found on ionizing the neutral metals.

Suitable experimental IP data do not seem to be available for many other series of transition metal complexes, so other comparisons with theory are difficult. Two experimental IP studies[12,13] of cyclopentadienyl complexes differ greatly in both the absolute values and trends of their results. Calculations[36] on ferrocene have yielded a wide range of predicted IP's. It is significant, however, that MO calculations predict a substantial difference (about 2 eV) between the IP's of ferrocene and nickelocene.[36d] Both sets of experimental values show very similar IP's for ferrocene and nickelocene (7.05 and 7.06 eV[12] and 7.96 and 8.38 eV[13]).

More experimental data[6-11] are available for the metal carbonyls, and agreement among them is fair,

---

[32] J. Hinze, M. A. Whitehead, and H. H. Jaffé, *J. Am. Chem. Soc.*, **85**, 148 (1963).

[33] F. W. Birss and W. G. Laidlaw, *Theoret. Chim. Acta*, **2**, 186 (1964).

[34] J. R. Hoyland and L. Goodman, *J. Chem. Phys.*, **33**, 946 (1960); **36**, 12 (1962).

[35] G. Herzberg, "Atomic Spectra and Atomic Structure," Dover Publications, New York, N. Y., 1944.

[36] (a) M. Yamazaki, *J. Chem. Phys.*, **24**, 1260 (1956); (b) E. M. Shustorovich and M. E. Dyatkina, *Proc. Acad. Sci. USSR, Phys. Chem. Sect.*, **128**, 885 (1959); (c) J. P. Dahl and C. J. Ballhausen, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.*, **33**, No. 5 (1961); (d) A. T. Armstrong, D. G. Carroll, and S. P. McGlynn, *J. Chem. Phys.*, **47**, 1104 (1967).

usually within 0.5 eV. The measured IP's tend to be near the IP's of the corresponding neutral metal atom rather than that of CO. Recent MO calculations of $M(CO)_6$ give IP's in good agreement with experimental values.[37]

Conclusions

The ionization potentials of tris complexes of acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone with various metals change very little as the central metal atom is varied, but are strongly dependent upon the nature of the ligand. This is contrary to predictions based on Koopmans' theorem and previous LCAO–MO calculations,[15] although the calculations are qualitatively consistent with the generally accepted view of the electronic structure of these complexes.

The applicability of Koopmans' theorem, even as a rough approximation, is doubtful in this case. To constrain theoretical calculations to satisfy Koopmans' theorem[38] may be a dangerous procedure in many cases. Bancroft, *et al.*,[39] report IP's for Hacac and some of the acac complexes reported here. Although different methods of obtaining IP's from the ionization efficiency curves were used, the two sets of IP's agree within 0.1 to 0.3 eV.

Acknowledgments. This work was supported in part by the U. S. Atomic Energy Commission under Grant No. At(11-1)-1087, and in part by the National Science Foundation. The mass spectrometer facility was made possible by grants from Northwestern University, the Northwestern University Materials Research Center, and the Atomic Energy Commission, Document No. C00-1147-23. We thank Professor R. W. Kiser for communicating his results for $Co(acac)_3$ prior to publication, and Mr. G. A. Pressley, Jr., for experimental assistance.

---

(37) H. B. Gray and N. Beach, private communication.

(38) F. L. Pilar, *J. Chem. Phys.*, 47, 884 (1967).

(39) G M. Bancroft, C. Reichert, and J. B. Westmore, *Inorg. Chem.*, 7, 870 (1968).