equilibria of copper ions in acetic acid–water mixtures. The functional form of the behavior of the rate with solvent composition is similar to that of the racemization of trisphenanthrolenenickel(II) in ethanol–water mixtures.[11]

The geometry of the metal ion species does not seem to be very critical in determining the reaction rate. This is true at least in the case of Co(II) in glacial acetic acid. When cobalt acetate is dissolved in acetic acid the Co(II) is octahedrally coördinated.[12] If an excess of sodium acetate is added to the system the Co(II) becomes tetrahedrally coördinated.[12] This change is evident by the color change of the solution from pink to blue. The rates of the reaction of Co(II) with TPyP in the octahedral and tetrahedral forms are 5.18 and 3.81 l. min.$^{-1}$ mole^{-1}, respectively. These rates are very similar and the difference could be due to the change in ionic strength of the solutions. Thus the geometry of the metal ion does not seem to affect the reaction rate greatly.

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(11) N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **50**, 1325 (1954).

(12) P. J. Proll, L. H. Sutcliffe, and J. Walkley, *J. Phys. Chem.*, **65**, 455 (1961).

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Electronic Spectra of β-Diketone Complexes. III. α-Substituted β-Diketone Complexes of Copper(II)

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The electronic spectra of α-substituted β-diketone complexes of copper(II) are presented and the assignments of the various bands discussed. It is concluded that the band at $\sim$250 mμ arises from electron transfer from a ligand orbital to an antibonding orbital associated with the metal. A band observed at $\sim$200 mμ is tentatively assigned to a π–π^* transition primarily localized in the ligand. Hückel molecular orbital calculations for $Cu(acac)_2$ are used in support of these assignments.

Introduction

In an earlier paper in this series,[2] the electronic spectra of an extensive list of acetylacetonate complexes were presented and the general trends in the spectra were discussed. This paper and the following one[3] (part IV) are concerned with the electronic spectra of β-diketone complexes of copper(II).

Belford,[4] *et al.*, attempted to assign the bands observed in the spectrum of copper(II) acetylacetonate, $Cu(acac)_2$, with the help of a simple molecular orbital calculation for the ligand anion. Their assignment (π–π^*) for the 296 mμ band observed in the spectrum of $Cu(acac)_2$ is confirmed[3] by the present study. Belford, *et al.*, also observed but did not discuss the intense band at $\sim$245 mμ but their observations did not extend far enough to detect another strong peak at $\sim$205 mμ. Graddon[5] pointed out the presence of the 245 mμ band but did not discuss its assignment. The band at $\sim$205 mμ has not been reported prior to this study.

Spectra and discussion are presented in this paper establishing the origin of the 245 mμ band in the spectrum of $Cu(acac)_2$ and the changes observed in the ultraviolet and visible spectra, resulting from changes in the α-substituents of the β-diketone, also are discussed. The results obtained from a semi-empirical Hückel molecular orbital calculation are used to support proposed assignments.

Experimental

Preparation of Materials.—The copper(II) complexes of the β-diketones used in this study were prepared by standard methods available in the literature, Table I. Analyses were performed by S. M. Nagy, M.I.T., and Schwarzkopf Microanalytical Laboratory, Woodside, New York. The complexes were found to be stable, when dry, with no decomposition even after two years storage.

Spectra.—Ultraviolet and visible spectra were observed using a Beckman DK-2 spectrophotometer equipped with a microswitch to synchronize the recorder with the wave length scroll. The instrument was calibrated with benzene vapor and a mercury arc.

Spectra were repeated on Cary Model 11 and Model 14 spectrophotometers and were found to be reproducible to better than ±2 mμ from $\sim$450 to $\sim$1200 mμ and ±1 mμ from $\sim$230 to $\sim$450 mμ. Over the region from 180–220 mμ, it was observed that spectra recorded on the DK-2 appeared at $\sim$5 mμ longer wave lengths than on the Cary instrument. Repeated runs with other Cary instruments, flushed with dry nitrogen, were reproducible. These results are given here.

Freshly opened Fisher reagent grade chloroform, Baker "analyzed" cyclohexane, Phillips "Spectrograde" cyclohexane, and Fisher reagent grade methanol were used as solvents. Solutions were prepared to $\sim 10^{-2}$ *M* concentration for visible spectra and $\sim 10^{-4}$–10^{-5} *M* for ultraviolet studies. Calibrated quartz cells were used. The Beer–Lambert law was found to be

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[1] Communications regarding this paper should be directed to J. P. F., Department of Chemistry, Case Institute of Technology, Cleveland, Ohio.

(2) R. H. Holm and F. A. Cotton (part I), *J. Am. Chem. Soc.*, **80**, 5658 (1958).

(3) J. P. Fackler, Jr., and F. A. Cotton, *Inorg. Chem.*, **2**, 102 (1963).

(4) R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

(5) D. P. Graddon, *ibid.*, **14**, 161 (1960).

TABLE I

ANALYSIS OF COPPER(II) COMPLEXES OF α-SUBSTITUTED β-DIKETONES [$R_1C(O)CH_2C(O)R_2$]

α-Substituents		Method of			
R_1	R_2	prepn.	Carbon (%)	Hydrogen (%)	Other (%)
CH_3	H	*b*	41.6 (41.1)[a]	4.3 (4.3)	Cu, 27.3 (27.2)
CH_3	CH_3	*c*	46.0 (45.9)	5.5 (5.4)	Cu, 24.3 (24.3)
CH_2F	CH_3	*d*	40.3 (40.4)	4.0 (4.1)	Cu, 21.4 (21.4); F, 12.7 (12.7)
CF_3	CH_3	(4)	. . .	. . .	Cu, 16.9 (17.2); F, 30.7 (30.8)
CF_3	CF_3	(4)	. . .	. . .	Cu, 13.1 (13.3)
C_2F_5	CH_3	*e*	. . .	. . .	F, 40.7 (40.5)
C_3F_7	CH_3	*e*	. . .	. . .	F, 43.5 (46.6)
$(CH_3)_2CH$	$CH(CH_3)_2$	*f*	57.7 (57.8)	8.1 (8.1)	
$(CH_3)_3C$	$C(CH_3)_3$	*f*	61.0 (61.4)	8.5 (8.9)	

[a] Calculated percentages in parentheses. [b] L. Claisen and N. Stylos, *Ber.*, **21**, 1144 (1888). [c] W. C. Fernelius and B. E. Bryant, *Inorg. Syn.*, **5**, 105 (1957). [d] J. P. Fackler, Jr., and F. A. Cotton, *J. Chem. Soc.*, 1435 (1960). [e] J. D. Park, H. A. Brown, and J. R. Lacher, *J. Am. Chem. Soc.*, **75**, 4733 (1953). [f] F. A. Cotton and J. P. Fackler, Jr., *ibid.*, **83**, 2818 (1961).

TABLE II

SPECTRA OF α-SUBSTITUTED β-DIKETONE COMPLEXES OF COPPER(II)

		λ (mμ); log ε				
β-Diketone	Solvent	Band I	Band II	Band III	Band IV	Band V
$(CH_3CO)_2CH_2$	$CHCl_3$		246; 4.198	296.0; 4.145 [310; 3.7][c]	(560); 1.484	670; 1.560
	CH_3OH		241.2; 4.182	293.7; 4.424 [308; 3.6]	. . .	. . .
	C_6H_{12}	201; 4.19	245.4; 4.255	297; 4.371 (305, 310)	. . .	. . .
$(CF_3CO)_2CH_2$	$CHCl_3$	. . .	243.5; 3.986	310.0; 4.252 [333; 3.6]	. . .	690; 1.562
	CH_3OH	. . .	(230)	307; 4.211 (328)	. . .	. . .
$[(CH_3)_2CHCO]_2CH_2$	$CHCl_3$	. . .	251.2; 4.262	300.0; 4.326 [313; 3.7]	555; 1.623	670; 1.686
	C_6H_{12}	204.0; 4.11[a]	248.1; 4.328	297.8; 4.387 (307)	. . .	. . .
	CH_3OH	. . .	246; 4.198	296; 4.360 (307)	. . .	. . .
$[(CH_3)_3CCO]_2CH_2$	$CHCl_3$	. . .	253; 4.164	300.0; 4.283 [313; 3.6]	540; 1.653	660; 1.819
	C_6H_{12}	201; 4.11[a]	249.9; 4.296	298.5; 4.371 (309)	525; 1.686	640; 1.674
	CH_3OH	. . .	249; . . .	297; . . . (310)	. . .	. . .
CH_3COCH_2COH	$CHCl_3$	. . .	245.6; 4.187	299.5; 4.360 (314)	(545); 1.505	650; 1.550
	C_6H_{12}	196; 4.167[b]	243.4; 4.220	301; 4.318 (307, 313)	. . .	. . .
	CH_3OH	. . .	237; 4.108	295; 4.374 (312)	. . .	. . .
$CF_3COCH_2COCH_3$	$CHCl_3$	. . .	243.9; 4.111	298.9; 4.290 (318)	. . .	. . .
	CH_3OH	. . .	235.5; 3.973	296.3; 4.299 (316)	. . .	. . .
$C_2F_5COCH_2COCH_3$	$CHCl_3$	. . .	244.5; 4.093	301.3; 4.324 (319)	. . .	. . .
	CH_3OH	. . .	237.4; 4.034	298.1; 4.346 (320)	. . .	. . .
$C_3F_7COCH_2COCH_3$	$CHCl_3$	. . .	244.5; 4.149	301.9; 4.396 (319)	. . .	670; 1.591
	CH_3OH	. . .	237.0; 4.041	299.0; 4.349 (320)	. . .	. . .
$CH_2FCOCH_2COCH_3$	$CHCl_3$	. . .	245.6; 4.117	296.5; 4.374 (308)	(560); 1.491	660; 1.568
	CH_3OH	. . .	239.2; 4.090	293.6; 4.389 (308)	. . .	. . .

[a] Observed with two or more concentrations. [b] Calculated from concentration of solution based on intensity of band II. [c] Brackets indicate approximate gaussian values. Parentheses give estimated position of shoulder when gaussian analysis not attempted.

obeyed in all cases checked. Extinction coefficients are believed to be reliable to better than 5% for ultraviolet spectra and 2% for visible spectra.

Results

In Fig. 1, the spectrum of bis-(2,2,6,6-tetramethyl-3,5-heptanediono)-copper(II) in cyclohexane is presented. Five distinct maxima are observed from 180 to 1000 mμ. For purposes of discussion, these bands are labeled I–V. In addition to the easily resolved peaks, shoulders are observed on the long wave length side of band III at $\sim$310 and $\sim$400 mμ. The shoulder at $\sim$310 mμ has been resolved from the main peak in several of the complexes by means of gaussian curves. The band producing the shoulder is found to have an extinction coefficient ($1/lc \log I_0/I = \epsilon$) of $\sim$5000 l. mole^{-1} cm.$^{-1}$. The shoulder at $\sim$400 mμ was not resolved in this work. Bands IV and V appear in the visible region of the spectrum with extinction coefficients close to 50.

The spectrum of Cu(DPM)$_2$ presented is typical of the spectra of all of the copper(II) β-diketone complexes studied. Since the complexes are not all soluble in non-polar solvents transparent over the entire range from 180–100 mμ, it was necessary to use various solvents depending on the particular region of the spectrum to be studied. Chloroform and methanol were found to be satisfactory for comparing bands II through V. Since chloroform begins to absorb strongly near 240 mμ, the position of band II in this solvent is subject to some uncertainty. However, methanol and cyclohexane are transparent in this region. In Table II the spectral data are presented for the α-substituted complexes. The position and intensity of the shoulder on band III at $\sim$310 mμ are enclosed in brackets if resolved by means of gaussian curves. The shoulder at $\sim$400 mμ does not appear in the table due to the difficulty encountered in determining its position with any degree of reliability. Poorly resolved peaks and shoulders, for which a gaussian analysis was not attempted, are enclosed in parentheses.

Hückel Molecular Orbital Treatment of Spectra

Hückel LCAO–MO calculations have been reported previously for the acetylacetonate anion[4] and complexes with trivalent metal ions.[6,7] The results reported here have been obtained by the methods previously discussed.[6,7] D_{2h} symmetry was assumed for the molecule and axes were chosen as indicated in Fig. 2. Semi-empirical estimates were made for the coulomb and exchange integrals, α_i and β_{ij}, in accord with previous practice.[6] These values were obtained: $\alpha_{Cu} = -62{,}000$ cm.$^{-1}$; $\alpha_A = -65{,}700$ cm.$^{-1}$; $\alpha_B = -60{,}900$ cm.$^{-1}$; $\alpha_C = -58{,}700$ cm.$^{-1}$; $\beta_{A-B} = -32{,}900$ cm.$^{-1}$; $\beta_{BC} = -22{,}100$ cm.$^{-1}$. In order to estimate the splitting to be expected in the ligand π system by interaction with the metal d_{xz} and d_{yz} orbitals, calculations were made allowing

$$\beta_{CuA}(2p_\pi - d_{xz}) = \beta_{CuA}(2p_\pi - d_{yz})$$

to vary from 0–20,000 cm.$^{-1}$. The results of this calculation[8] are presented in Fig. 3.

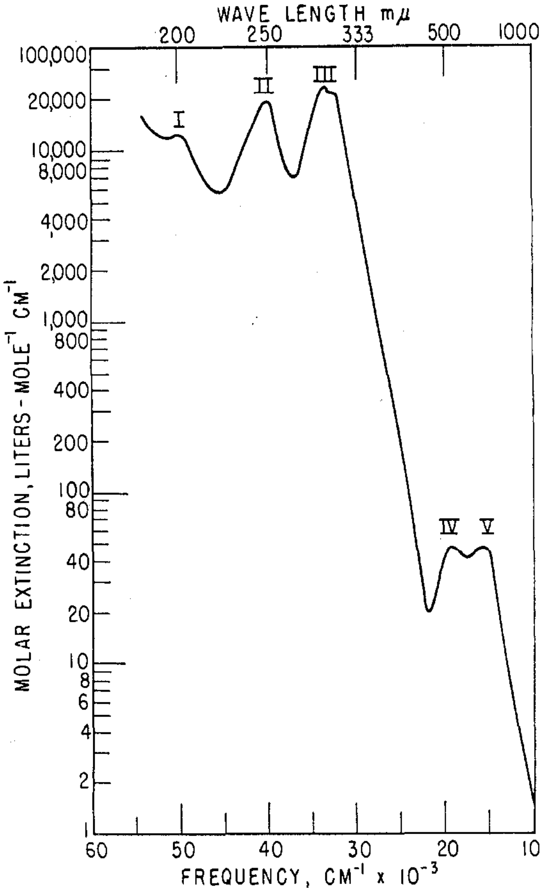

Fig. 1.—Electronic spectrum of bis-(2,2,6,6-tetramethyl-3,5-heptanediono)-copper(II) in cyclohexane.

The type of π interaction shown in Fig. 3 can have a profound influence on the electronic structure of the complex, but, in this case at least, hardly affects the metal–ligand bond energy. As the d_{xz} (b_{2g}) electrons are raised in energy by about the same amount that the π_3 (b_{2g}) electrons are lowered, no net stabilization is obtained.

Discussion

Bands I and III.—We shall attempt to show that these bands are most reasonably assigned as $\pi_3 \rightarrow \pi_5^*$ and $\pi_3 \rightarrow \pi_4^*$ transitions, respectively. The notation is defined by Fig. 3. For both bands the intensities imply that the transitions responsible are essentially allowed.

As will be shown later, it may be inferred from the energies of d–d transitions in bis-(acetylacetonato)-copper(II) that the correct ordinate value to be used

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(6) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).

(7) D. W. Barnum, *ibid.*, **22**, 183 (1961).

(8) It should be emphasized that this is a very naïve calculation and is intended only to provide a rough idea of how metal $d\pi$–ligand $p\pi$ interaction will affect the ligand π–π^* transitions in first order. We are aware of the neglect of the metal p_z orbital but believe this to be tolerable for present purposes. A more thorough calculation is being carried out by Mr. T. E. Haas, M.I.T.

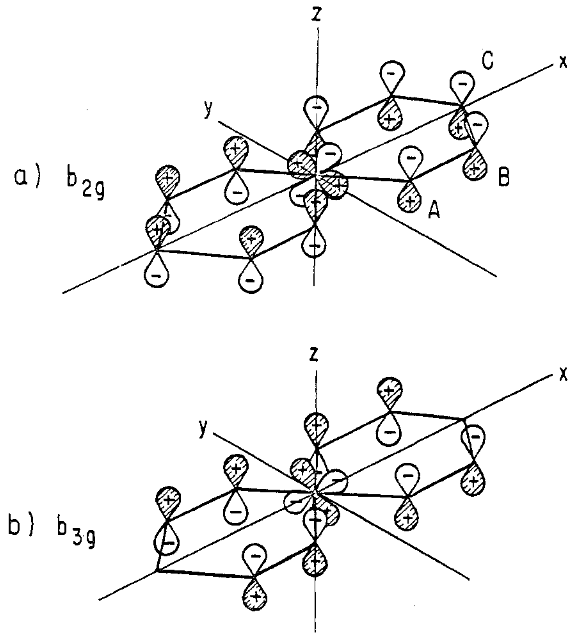

Fig. 2.—(a) First b_{2g} bonding π-orbital. The metal d_{xz} orbital is directed in between the oxygen pπ-orbitals. (b) First b_{3g} bonding π-orbital. The d_{yz} orbital connects the π systems of the two chelated ligands; positive lobes are shaded.

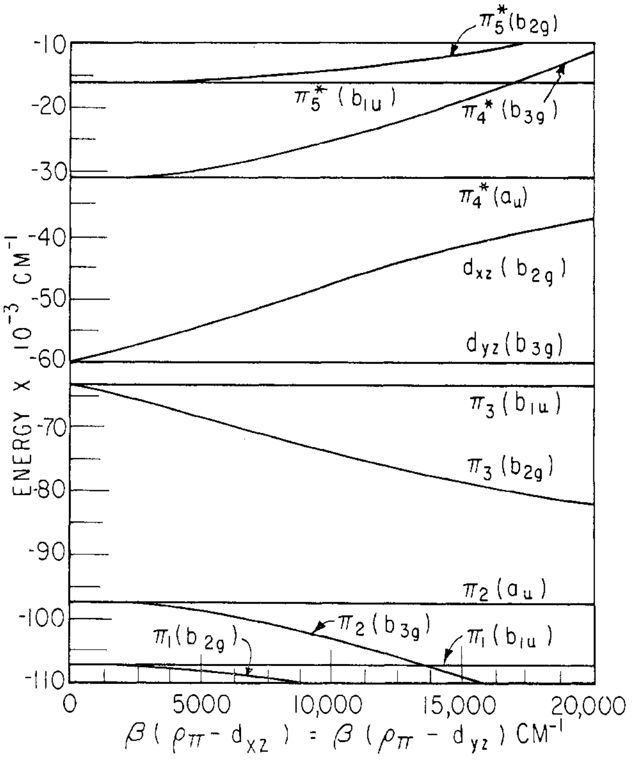

Fig. 3.—Effect of metal–oxygen π-bonding on energy levels of Cu(acac)$_2$.

in Fig. 3 is $\sim$2500 cm.$^{-1}$. With this ordinate, the allowed $\pi_3 \rightarrow \pi_4^*$ and $\pi_3 \rightarrow \pi_5^*$ transitions and their energies are

$$\pi_3 \longrightarrow \pi_4^* \left\{ \begin{array}{l} b_{2g} \longrightarrow a_u, \ \sim 36{,}000 \text{ cm.}^{-1} \\ b_{1u} \longrightarrow b_{3g}, \ \sim 33{,}000 \text{ cm.}^{-1} \end{array} \right.$$

$$\pi_3 \longrightarrow \pi_5^* \left\{ \begin{array}{l} b_{2g} \longrightarrow b_{1u}, \ \sim 51{,}000 \text{ cm.}^{-1} \\ b_{1u} \longrightarrow b_{2g}, \ \sim 48{,}000 \text{ cm.}^{-1} \end{array} \right.$$

Since bands I and III are observed at $\sim$48,000 and $\sim$33,000 cm.$^{-1}$, respectively, their assignments as $\pi_3 \rightarrow \pi_5^*$ and $\pi_3 \rightarrow \pi_4^*$ are indicated. Band I is observed only as a single peak, whereas the calculation predicts two components separated by $\sim$3000 cm.$^{-1}$. This inconsistency may be explained in many ways. (1) If the observed peak is assigned to the $b_{1u} \rightarrow b_{2g}$ component, and the calculation correctly assesses or underassesses the splitting, the $b_{2g} \rightarrow b_{1u}$ component would be beyond the range of observation. (2) The calculation may overestimate the separation of the components. They may be too close to permit resolution. (3) One component may be much weaker than the one observed. (4) The spectrum in this region is so poor, because of experimental difficulties, that *detailed* agreement with even precise calculations cannot be reasonably demanded.

Band III is observed in all cases to have a more or less conspicuous shoulder on the low energy side, some 1000–2000 cm.$^{-1}$ below the main maximum which generally occurs at $\sim$33,000 cm.$^{-1}$. This may be explained by assigning the main maximum to the $b_{2g} \rightarrow a_u$ component of the $\pi_3 \rightarrow \pi_4^*$ transition and the lower energy shoulder to the $b_{1u} \rightarrow b_{3g}$ component. Further evidence for the assignment of band III as a π–π^* transition is presented in part IV.[3]

The possibility that band I arises from an "atomic" transition in the copper(II) ion was considered but rejected. The lowest atomic transition in Cu^{2+}, $3d^9 \rightarrow 3d^8 4s$, occurs at energies greater than 60,000 cm.$^{-1}$. It does not seem likely that ligand field effects would lower this to below 40,000 cm.$^{-1}$ for concomitant with the rise in energy of some d orbitals will be a rise in energy of the s orbital. This question will, however, be re-examined later in the light of a more thorough calculation.[8]

The intensities of the bands causing the completely unresolved, weak shoulders at $\sim$400 mμ cannot be estimated with any accuracy but are obviously quite low. It was suggested in part I[2] that they are due either to a spin-forbidden π–π^* transition or to an n–π^* transition and these still appear to be the most probable assignments. It is not entirely impossible that they may be due to a d–d transition as has been proposed[5,9] but the weight of more recent evidence[10] is against this.

Bands IV and V.—There has been considerable discussion lately concerning the assignment of bands appearing in the visible region of the spectrum of bis(acetylacetonato)-copper(II). Solvent effects[11] and polarizations[9,10,12] as well as inferences from electron spin resonance data[13] have been invoked to make assignments. No final solution to the problem has yet appeared, but the paper of Piper and Belford[10] presents the current position. The data obtained in this

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(9) J. Ferguson, *J. Chem. Phys.*, **34**, 1609 (1961).

(10) T. S. Piper and R. L. Belford, *Mol. Phys.*, **5**, 169 (1962).

(11) R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).

(12) G. Basu, R. L. Belford, and R. E. Dickerson, *Inorg. Chem.*, **1**, 438 (1962).

(13) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 35 (1958).

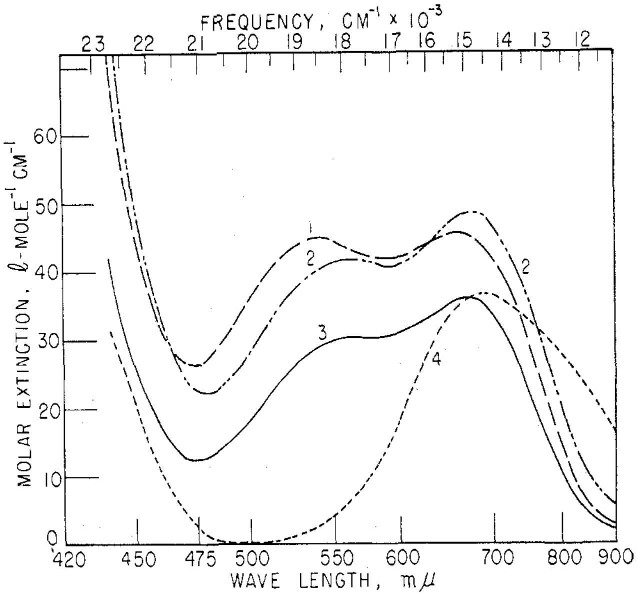

Fig. 4.—Visible spectra of symmetrical β-diketone complexes of copper(II) in chloroform: 1, bis-(2,2,4,4-tetramethyl-3,5-heptanediono)-copper(II); 2, bis-(2,4-dimethyl-3,5-heptanediono)-copper(II); 3, bis-(2,4-pentanediono)-copper(II); 4, bis-(1,1,1,5,5,5-hexafluoro-2,4-pentanediono)-copper(II).

work, in themselves, do not throw much further light on the question, though the shift of both bands, IV and V, to higher energies (see Fig. 4) with increasing inductive character of the α-substituents is consistent with the assumption that d_{xy} is the orbital of highest energy.

From the tentative assignment of Piper and Belford[10] we have inferred the value of $\beta(p_\pi\text{–}d_{xz})$ used in connection with the assignments of bands I and III.

Band II.—This band appears with varying but high intensity in the spectra of all β-diketonate complexes of copper(II) but it is not present in the spectra of metal acetylacetonates generally.[2] Barnum[7] has previously suggested that it may be a component of the $\pi_3 \rightarrow \pi_4^*$ transition. However, a more likely assignment now seems to be as a charge transfer band involving the jump of a σ-bonding or oxygen n electron to a metal orbital. Evidence supporting this general assignment and contributing to a more detailed description will now be summarized.

The only orbitals which seem likely as the acceptor orbitals on the copper ion are the vacant $4p_z$ and the half-filled $3d_{xy}$. If the former were the correct choice, solvent basicity would have a marked influence on the band energy, since any tendency of the complex to become five- or six-coördinate by attachment of solvent molecules would substantially raise the energy of the $4p_z$ orbital without any substantial effect on the ligand orbitals from which the electron originates. If, however, the acceptor orbital is $3d_{xy}$, no large solvent effect would be expected since this orbital will not be directly affected by the bonding of one or two solvent molecules.

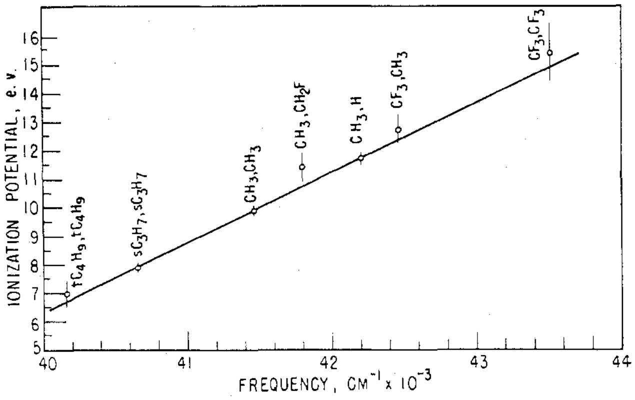

Fig. 5.—Shifts in frequencies of band II in methanol with changes in the ionization potentials of the α-substituents.

Experimentally, study of solvent effects on band II poses some problems because many donor solvents absorb appreciably in the same region. However, the comparison of spectra in chloroform and cyclohexane with those in methanol can be made. The band energy increases only slightly (0 to 1000 cm.$^{-1}$) from the non-coördinating solvents to methanol. This is taken as evidence that $3d_{xy}$ rather than $4p_z$ is the acceptor orbital.

The proposed assignment for band II also implies that on increasing the electron density at the oxygen atoms by increasing the inductive effect of the α-substituents a reduction in band energy should occur. The ionization potentials of the substituent radicals may be taken as a measure of their inductive effects.[14] As Fig. 5 shows, there is an excellent correlation between the energy of band II and the ionization potentials.[15] For the unsymmetrically substituted complexes, the resultant effect of the two different substituents has been taken as proportional to the average of their ionization potentials. This correlation supports the proposed assignment. Moreover, the absence of any pronounced effect of γ-substituents on the energy of band II (see part IV for details[3]) supports the proposal that the electron which is "transferred" originates in a σ or n orbital rather than a π orbital since γ-substitution has a marked effect upon π orbitals.

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[14] F. A. Matsen, in "Technique of Organic Chemistry," Vol. IX, "Chemical Applications of Spectroscopy," W. West, Ed., Interscience Publishers, New York, N. Y., 1956, pp. 686–687.

[15] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.