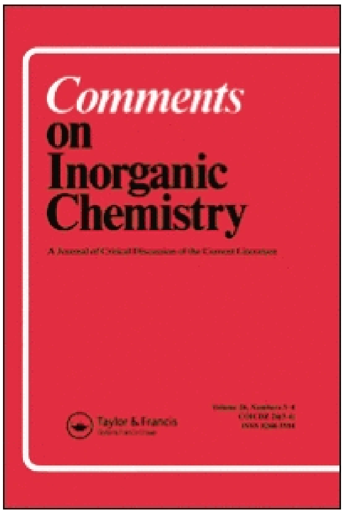

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Singly and Doubly Excited States of Exchange-Coupled Dimers

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Singly and Doubly Excited States of Exchange-Coupled Dimers

The optical absorption spectra of dimers of weakly coupled paramagnetic transition metal ions differ from those of monomeric complexes in several respects: They show additional splittings of absorption bands; intensities of spin-forbidden transitions may be enhanced by several orders of magnitude; the dimer absorptions may be strongly temperature dependent; new bands corresponding to the simultaneous excitation of both ions are observed. From an analysis of excited state exchange splittings, the orbital contributions to the exchange parameter J_{AB} can be deduced. The dimer excitations are intimately related to charge transfer transitions, which provide their intensities.

INTRODUCTION

The study of exchange-coupled polynuclear complexes remains an active area of research in coordination chemistry. A great number of new complexes has been synthesized in the past decade. Empiric correlations between structural and magnetic properties have been established.[1] A variety of theoretic models has been proposed for the treatment of "exchange interactions" in these weakly coupled systems.[1] The relevance of polynuclear transition metal sites in biologic systems has been demonstrated.[1]

Most of the work has been concerned with the electronic ground-state properties of this large class of compounds. Electronically excited states have received much less attention. Their study requires the use of optical spectroscopic techniques. In the present Comment some of the effects that are typical of exchange-coupled dimers will

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be illustrated and summarized. Optical spectroscopy provides a means to a more profound and detailed understanding of the nature of exchange interactions.

GENERAL OBSERVATIONS

One of the consequences of exchange interactions between paramagnetic ions in a polynuclear complex is an energetic splitting of electronic states. This is shown in Figure 1. The order of magnitude of these exchange splittings is given by J, the exchange parameter. The magnetic and caloric properties between room temperature and liquid helium temperature usually show some anomalies as a result of the ground-state splitting. Measurements of the magnetic susceptibility are routinely used to derive values for the ground-state exchange parameters. It is important to realize that this procedure always relies on a theoretic molecular model with a subsequent statistic treatment. The measurement of bulk thermodynamic properties does not provide a direct access to the molecular levels. Spectroscopic techniques, in principle, do not suffer from this restriction. (Far)-infrared and Raman spectroscopy cover the energy range of interest. However, an orbital mechanism is needed to obtain intensity in the absorption or scattering process of photons. In pure spin systems, therefore, transitions within the exchange-split ground-state manifold are forbidden. Optical spectroscopy has been used successfully to determine exchange splittings and thus exchange parameters in many different dimers.[2] Inelastic neutron scattering is another technique that has recently been used to probe exchange splittings.[3] In contrast to photons, neutrons can interact directly with the spin system. These aspects are discussed more thoroughly in Refs. 2 and 3.

Our main concern here is electronically excited states. As a consequence of the splittings shown in Figure 1, an electronic transition, which shows up as a single line in the absorption or luminescence spectrum of a monomeric complex, can be split into several components in the dimer spectrum. Both the ground- and excited-state splittings contribute to the observed spectral splittings. The two effects can easily be distinguished, the former being temperature dependent in absorption and the latter not; Figure 2 shows an example. Instead of two electronic R lines corresponding to ${}^4A_2 \rightarrow {}^2E$ transitions as in mononuclear chromium(III) complexes, the low-

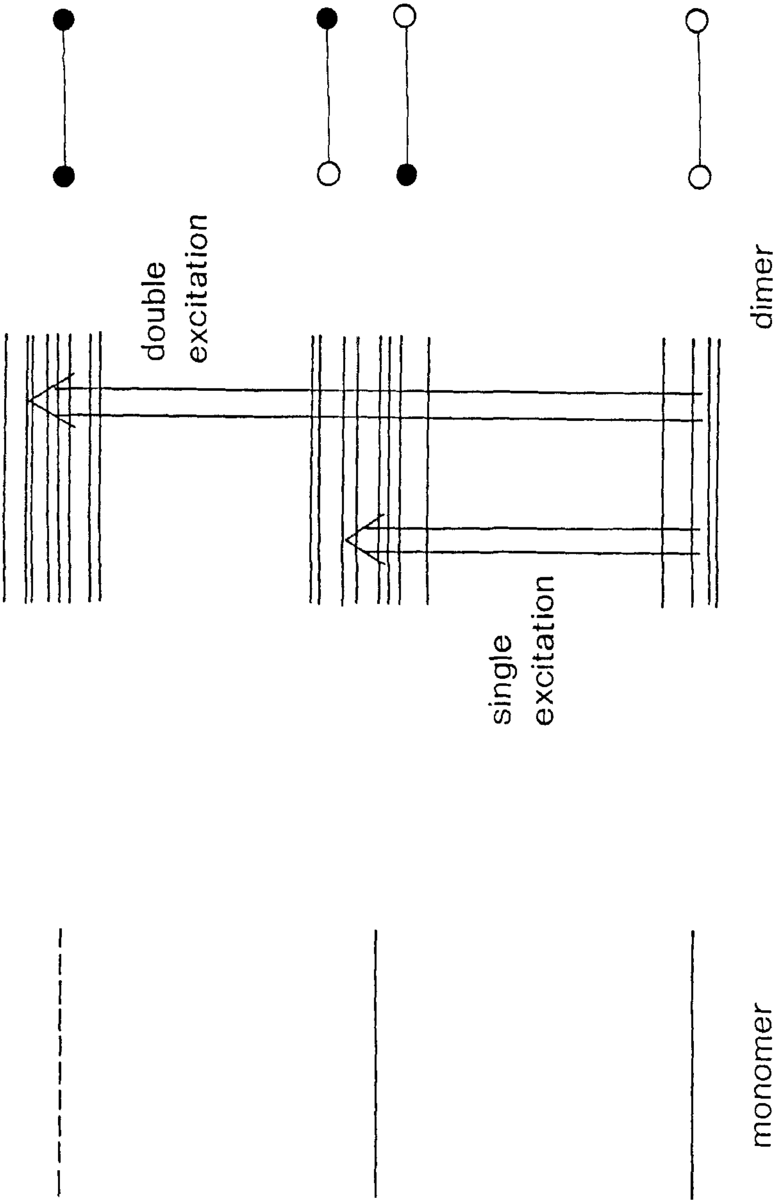

FIGURE 1 Energy splitting of electronic states in an exchange-coupled dimer (schematic). Single- and double-dimer excitations are indicated.

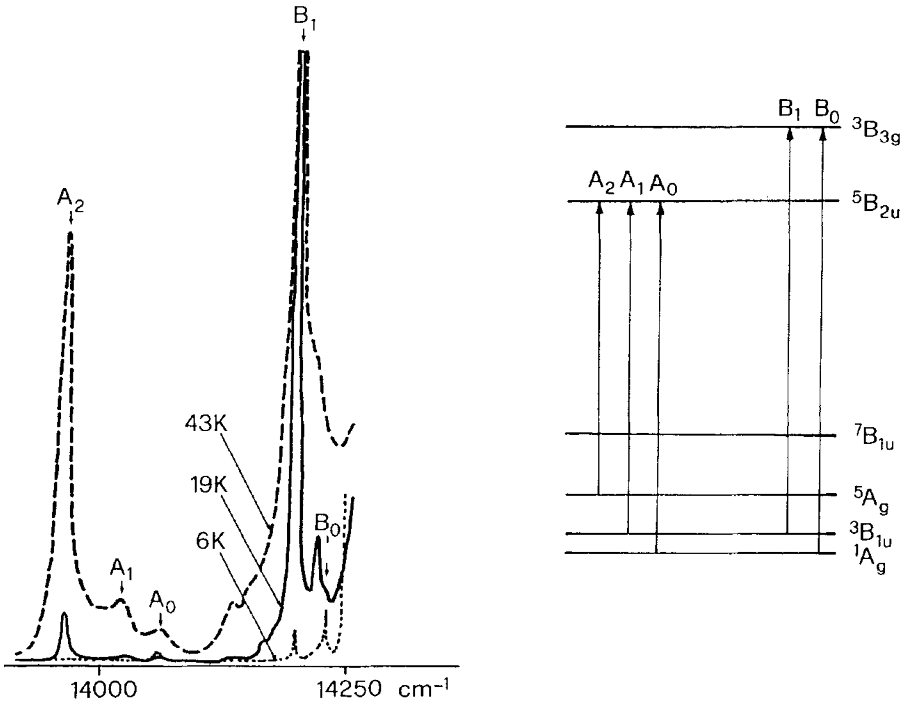

FIGURE 2 Low-energy part of ${}^4A_2 \rightarrow {}^2E$ dimer excitations in $[(en)_2Cr(OH)_2Cr(en)_2]$ $Br_4 \cdot 2H_2O$ and corresponding energy level diagram. (From Ref. 2.)

temperature crystal absorption spectrum of the complex $[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$ shows a larger number of electronic lines in this spectral region with pronounced temperature dependences.[2]

The most conspicuous features of a dimer spectrum are the absorption bands whose energy corresponds approximately to the sum of two single excitations. These so-called double excitations or simultaneous pair excitations (SPE) by a single photon are typical of exchange-coupled systems. They are also observed in compounds with extended exchange interactions. Examples are given in Figure 3 for the two classic chromium dimers $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$

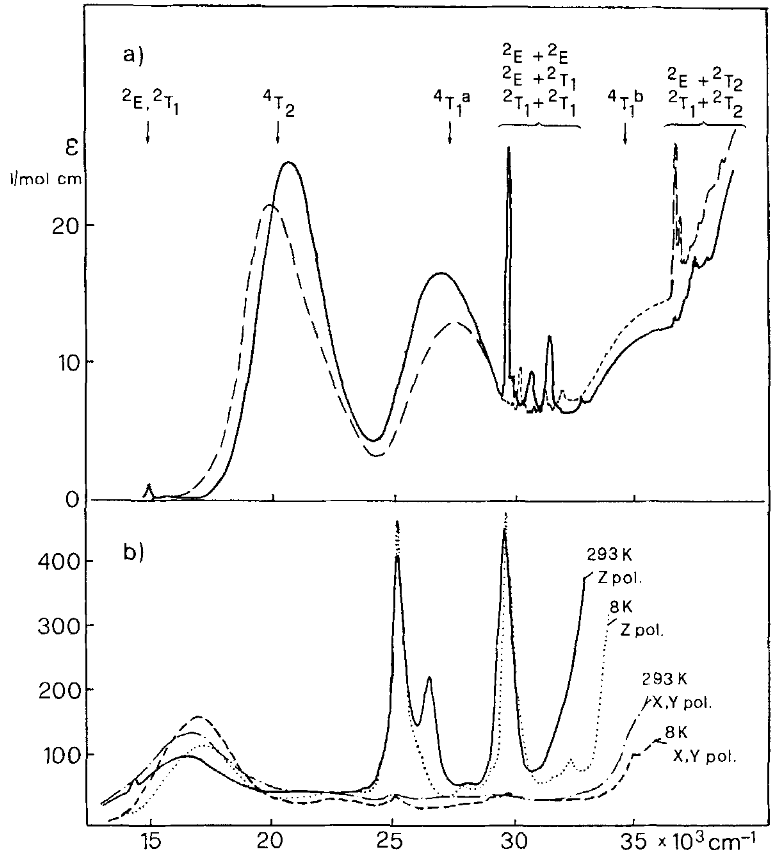

FIGURE 3 Polarized absorption spectra of (a) $[(NH_3)_5Cr(OH)Cr(NH_3)_5]\ Cl_5 \cdot 3H_2O$ (acid rhodo) and (b) $[(NH_3)_5CrOCr(NH_3)_5]\ (CO_4)_4$ (basic rhodo).

(acid rhodo)[2] and $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$ (basic rhodo).[4] Both complexes are coupled antiferromagnetically with $2J$ values of -30 and -450 cm^{-1}, respectively.[4,5] The double excitations of spin-forbidden (in the single ion) transitions are quite intense even in the weakly coupled acid rhodo complex. They are strongly polarized and temperature dependent. In the basic rhodo complex they are more intense than the formally spin-allowed (in the single ion) transitions and dominate the visible absorption spectrum.

Figure 3 also shows that the spin-allowed (in the single ion) transitions are not greatly affected by the exchange coupling. Spin-allowed *d–d* bands are generally broad because they involve $t_2 \longleftrightarrow e$ electron promotions. Exchange splittings are smaller than the bandwidths and remain unresolved. The intensities of spin-allowed *d–d* bands are approximately the same in mononuclear and polynuclear complexes. In contrast, spin-forbidden bands can be enhanced by several orders of magnitude in exchange-coupled systems.

INTENSITY MECHANISMS

Dexter, who was inspired by the observation of simultaneous excitations in a pair of praseodymium(III) ions, was the first to provide a theoretic framework for an understanding of double excitations.[6] In a zeroth-order approximation double excitations are forbidden because they correspond to two-electron processes. Dexter showed that this prohibition could be overcome by first-order perturbation theory, taking into account the electronic interaction between the ions but *neglecting the overlap* of the wavefunctions on centers A and B. In this perturbation approach the intensity of the double excitations is stolen from allowed electronic transitions on the individual constituents. There is a formal analogy between this treatment and the Dexter formalism for excitation energy transfer in coupled systems.[7] Since the formalism does not rely on any overlap between the wavefunctions on the two centers, it applies to any weakly coupled chromophore system. It has been successfully applied to SPE transitions in Yb_2O_3.[8]

Among the various theoretic models proposed for describing the chemical bonding in copper(II) acetate, the *weakly coupled chromophore* model by Hansen and Ballhausen[9] is basically closely related to the Dexter approach. *Overlap* between the constituents is *neglected*, and intensity for simultaneous pair excitations has to be obtained through configuration interaction. Charge transfer (CT) transitions are the most likely sources of intensity.

Tanabe and co-workers have developed a theoretic formalism to account for the observed enhancements, polarizations and temperature dependences of spin-forbidden *d–d* transitions in exchange-coupled transition metal dimers and extended magnetic materials.[10–12] This formalism relies heavily on overlap between the magnetic orbitals of the constituting centers.[13] Consequently, intensity enhancements of several orders of magnitude, as experimentally observed in many cases, can be accounted for. The interaction between a pair of spin-only ions and the electric vector of the radiation field is represented by[10–12]

$$\sum_{i,j} \Pi_{Ai\,Bj} \cdot \mathbf{E}(\mathbf{s}_{Ai} \cdot \mathbf{s}_{Bj}), \tag{1}$$

where i and j number the singly occupied orbitals on the ions A and B. The components of $\Pi_{Ai\,Bj}$ are related to the orbital exchange parameters $J_{Ai\,Bj}$ as follows:

$$\Pi^{\alpha}_{Ai\,Bj} = \left(\frac{\delta J_{Ai\,Bj}}{\delta E^{\alpha}}\right)_{E \to O}, \tag{2}$$

where $\alpha = x, y, z$.

Transitions that are spin forbidden in the single ion may become formally allowed by this mechanism. The relevant quantum numbers are those of the dimer spin (S, M_S), and the selection rules are $\Delta S = 0$, $\Delta M_S = 0$. Transitions that are symmetry forbidden in the single ion may also become allowed. The transformation properties of the $\Pi^{\alpha}_{Ai\,Bj}$ coefficients in the dimer point group determine the symmetry selection rules. If the dimer has a center of inversion in both the ground and excited states, all the terms contributing to $\Pi_{Ai\,Bj}$ are either zero or cancel out. Simultaneous excitations of the same transitions on both ions are therefore forbidden in centrosymmetric dimer. The main source of intensity for dimer transitions in this mechanism are metal (A) ⟷ metal (B) charge-transfer transitions (MMCT), as well as bridging ligand ⟷ metal charge-transfer (LMCT and MLCT) transitions. High intensities can be expected for transitions involving orbitals on the ions A and B, which, either directly or by superexchange, have some overlap. Many single- and double-pair excitations in dimers, and also in systems with extended interactions, have been successfully interpreted on the basis of this formalism.

Finally, we should not forget to consider the mechanism that is responsible for spin-forbidden intensity in monomeric complexes: spin-orbit coupling in conjunction with odd-parity crystal field components. This so-called single-ion intensity mechanism always contributes to the intensity of spin-forbidden (in the single ion) transitions in a dimer, since there can be no center of inversion at the single-ion site. With respect to the dimer spin, $\Delta S = \pm 1$ transitions can occur as well as $\Delta S = 0$ transitions.[14] This mechanism competes with the pair intensity mechanism in single excitations of weakly coupled systems ($|J| \leq 30\ \text{cm}^{-1}$).[15]

SINGLE EXCITATIONS

A Heisenberg–Dirac–van Vleck (HDvV)-type Hamiltonian,

$$H_{\text{g.s.}} = -2J_{AB}\,\mathbf{S}_A \cdot \mathbf{S}_B, \tag{3}$$

provides an adequate description of the exchange coupling in the electronic ground state of a spin-only dimer. If we now produce an electronically excited state by flipping the spin of one of the unpaired electrons on ion A or ion B, the appropriate expression for the exchange interaction is given by[10–12]

$$H_{\text{e.s.}} = -2\sum_{i,j} J_{Ai\,Bj}\,(\mathbf{S}_{Ai} \cdot \mathbf{S}_{Bj}). \tag{4}$$

The $J_{Ai\,Bj}$'s are orbital exchange parameters. And it is one of the principal aims of a study of excited pair states to determine, or at least estimate, those parameters. They contain information relating to exchange pathways and orbital mechanisms of exchange. Such information is not obtainable from a study of the ground-state properties alone. The ground-state exchange parameter J_{AB} is an average of the orbital parameters $J_{A_i B_j}$. A number of excited pair states has been successfully interpreted in terms of this model.[16] Dubicki's work on the acid erythro complex $[(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)]^{5+}$, represents a particularly nice example.[17] The corresponding $^4A_2 \rightarrow {}^2E$ dimer spectrum is reproduced in Figure 4. The formalism becomes considerably more complicated in the case of ions with orbitally degenerate states. Orbital angular momentum has to be taken into account.

Another point of interest concerns the question of whether we should view the excitation in singly excited pair states as localized or delocalized. Do the locally excited configurations $\circ\!-\!\bullet$ and $\bullet\!-\!\circ$ shown in Figure 1 represent eigenstates of the dimer? They do not, because off-diagonal matrix elements of the type

$$\langle \circ\!-\!\bullet \; |H_{\text{e.s.}}| \; \bullet\!-\!\circ \rangle \tag{5}$$

are usually nonzero.[2] Proper pair wavefunctions are then given by

$$\Phi_{\pm} = 1/\sqrt{2}\,[\, \circ\!-\!\bullet \;\pm\; \bullet\!-\!\circ \,]. \tag{6}$$

The energy difference between Φ_+ and Φ_- is $2\langle \circ\!-\!\bullet \; |H_{\text{e.s.}}| \; \bullet\!-\!\circ \rangle$. The matrix elements (5) are called *resonance* or *excitation transfer* integrals. This can be understood intuitively, since the operator takes the excitation from one center to the other. The excitation is thus shared by the two centers A and B.

DOUBLE EXCITATIONS

Simultaneous pair excitations of both spin-allowed and spin-forbidden (in the single ion) transitions have been reported in the literature. Spin-forbidden SPE transitions in chromium(III)[18,19] and manganese(II)[20,21] compounds have been particularly well investigated. The Tanabe formalism appears to provide a sound basis for their interpretation. Energy splittings as well as the temperature depend-

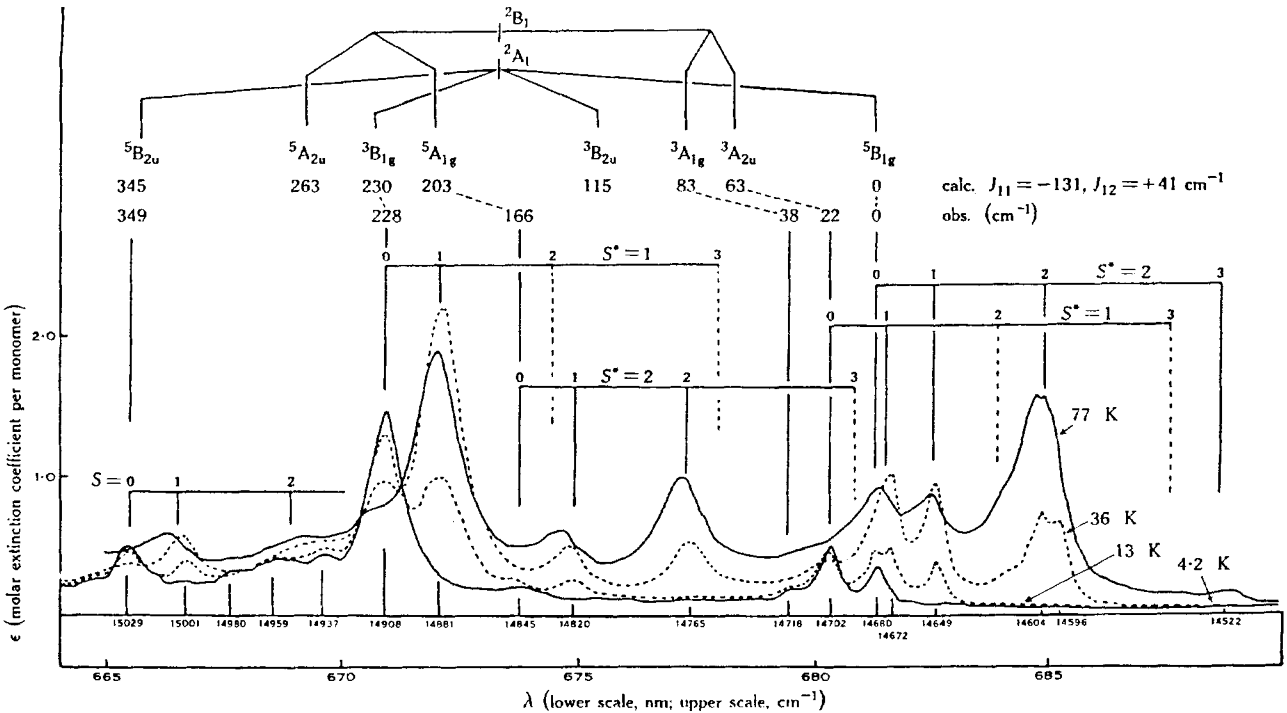

FIGURE 4 The temperature dependence of $^4A_{2g} \rightarrow {}^2E_g$ absorption of acid erythro chloride in A polarization. The full (broken) lines directly above the absorption represent the calculated positions of resolved (unresolved) members of electronic progressions. S and S^* are the total spin quantum numbers of the ground and excited states, respectively. The experimental energies (cm^{-1}) of the $S = 0$, 1 and 2 bands are given at 4.2, 13 and 36 K, respectively. The symmetry species apply to antisymmetrized pair states in D_{4h} point group. (From Ref. 17; reproduced by permission.)

ence and polarization of their intensities could be interpreted. It is interesting to note here that a pair model is often also adequate for extended systems in this case, in contrast to single excitations. As illustrated by the two dimeric chromium(III) complexes in Figure 3, there is usually a qualitative correlation between the strength of the exchange coupling (J_{AB} value) and the intensity of the double excitations. The reason being that the $J_{Ai\,Bj}$ parameters and the $\Pi^{\alpha}_{Ai\,Bj}$ coefficients are related to similar one-electron and two-electron integrals. In the basic rhodo complex it was possible to measure the CT absorption, which obviously acts as the main source of intensity for the double excitations.[4] It is polarized along the Cr–Cr axis and peaks at 36,000 cm^{-1}. Its intensity is approximately 40 times bigger than that of the double excitations. The CT character of the double excitations in the basic rhodo complex is therefore of the order of 2%. It is less than 0.1% in the acid rhodo complex. This estimate is revealing because it shows us that even in the basic rhodo complex we are dealing with a weakly coupled chromophore system, despite the relatively high intensity of the double excitations in the near ultraviolet (UV). The $2J$ value of -450 cm^{-1} is small compared with crystal field and intraionic electron repulsion energies.

Simultaneous excitations of oxo-bridged iron(III) dimers are partly responsible for the color of natural yellow sapphires. This was shown in a careful study of polarized single crystal spectra by Ferguson and Fielding.[22] Intense absorption bands in the near UV are also observed in "natural" oxo-bridged dimers. In the complex [HEDTA FeOFe HEDTA]$^{2-}$, those absorptions were assigned to double excitations.[23] The situation here is more complex than in the sapphire. The Fe–O distance is 1.80 Å, considerably shorter than Fe–O distances in mononuclear iron(III) complexes and very similar to the Cr–O distance in basic rhodo. In addition, the absorption bands in question have molar extinction coefficients of the order of 5000. Furthermore, oxygen → iron CT transitions are expected to occur in the same spectral range. It appears certain, therefore, that the bands have a great deal of allowed CT character. Oxo-bridged iron(III) dimers occur in a number of nonheme iron proteins. They also show some intense absorptions above 25,000 cm^{-1}.[24]

So far in our discussion we have only considered excitations that are spin forbidden in the single ion. The participation of excitations that are spin allowed in the single ion is not nearly as well understood.

Our first example involves a spin-allowed excitation, which is really a spin-forbidden excitation in disguise and, therefore, can still be discussed in terms of the mechanism 1. Simultaneous excitations in the dimer [$F_5Mn^{II}FNi^{II}F_5$] can be observed in the near UV spectrum of $KMgF_3$ and $KZnF_3$ crystals, which are doped simultaneously with manganese(II) and nickel(II). This is shown in Figure 5.[25] The two most prominent bands at 40,000 and 45,000 cm^{-1} are readily assigned, from their positions and their dependence on the manganese and nickel concentrations, to ${}^6A_{1g}$(Mn) ${}^3A_{2g}$(Ni) → ${}^4E_g^a$, ${}^4A_{1g}$(Mn)${}^1E_g$(Ni) and → ${}^4E_g^b$(Mn)${}^1E_g$(Ni) double excitations. They are very intense, which can be rationalized in terms of a pair mechanism, because they involve almost pure spin–flip single-ion transitions. The more interesting absorptions in the spectrum of Figure 5 are the structured band systems 1 and 2. They are displaced by equal amounts to lower energy from the intense double excitations, and their fine structures are comparable. A consistent and satisfactory analysis of band systems 1 and 2 was obtained by assigning them to ${}^6A_{1g}$(Mn) ${}^3A_{2g}$(Ni) → ${}^4E_g^a$, ${}^4A_{1g}$(Mn) ${}^3T_{1g}^a$(Ni) and ${}^4E_g^b$(Mn) ${}^3T_{1g}^a$(Ni), respectively. The involvement of the spin-allowed ${}^3A_{2g}$ → ${}^3T_{1g}^a$ nickel(II) excitation is very revealing. It turns out that of the four spin-orbit components of ${}^3T_{1g}^a$ only one, Γ_3 (O_h notation), has the proper symmetry to mix with ${}^1E_g$ under spin-orbit coupling. And this is the only component that shows up in the double excitations. It is, therefore, the ${}^1E_g$ character mixed into the Γ_3 component of ${}^3T_{1g}^a$ that is responsible for the absorptions 1 and 2. In others words, it is the spin-forbidden (in the single ion) character mixed into the spin-allowed (in the single ion) transition that allows it to participate in a double excitation. The Tanabe pair intensity mechanism is very efficient in this dimer, because there is no center of inversion. Metal → metal one-electron processes can directly contribute to the intensity, in contrast to centrosymmetric dimers.

Dimeric copper(II) complexes usually have absorption bands that are not found in monomeric complexes.[26,27] Figure 6 shows the region of "dimer bands" in copper(II) acetate, as reported by Dubicki.[26] The 28,000 cm^{-1} band corresponds approximately to the sum of two *d–d* single excitations. It is polarized along the Cu–Cu axis, and its molar extinction coefficient is somewhat lower than that of the single *d–d* excitations. Both SPE[8] and LMCT[26] assignments have been proposed for the dimer band.

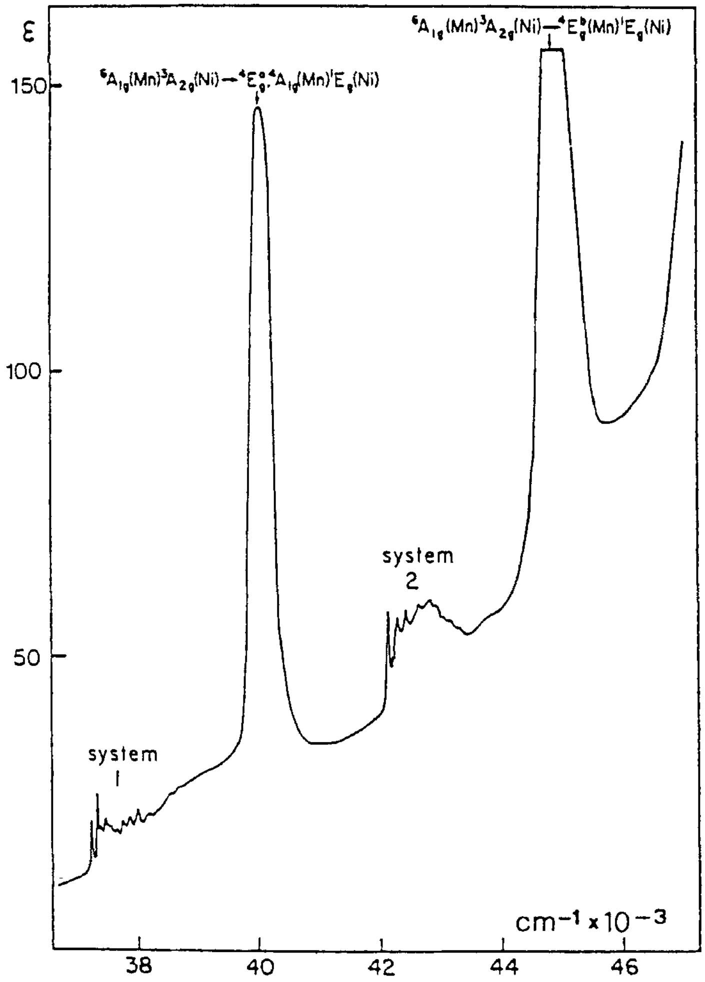

FIGURE 5 Near-UV absorption spectrum of [$F_5MnFNiF_5$] dimers in $KZnF_3$ doped simultaneously with manganese(II) and nickel(II). (From Ref. 20; reproduced by permission.)

The key to understanding the nature of this transition may lie in the pronounced temperature dependence of its intensity between helium and room temperature, for which neither of the proposed assignments immediately accounts. The observed cold band behavior appears to follow the population of the $S = 0$ ground level. Unless

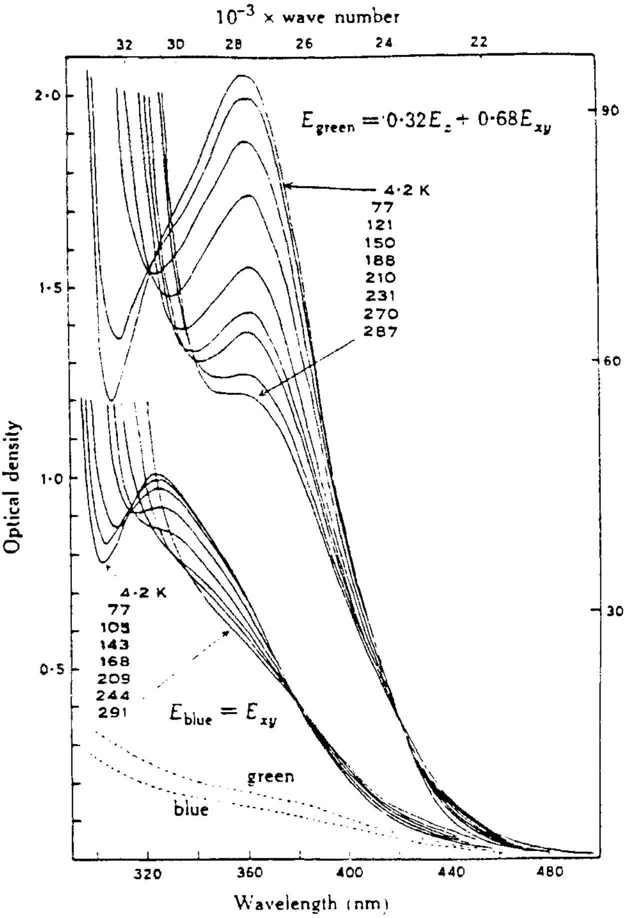

FIGURE 6 The near-UV spectrum of $Cu(CH_3CO_2)_2$, H_2O for $(20\bar{1})$ face. Broken lines represent the absorption of the sample pinhole with polarizer against a reference pinhole. Crystal thickness is 0.022 mm. (From Ref. 26; reproduced by permission.)

an unreasonably large singlet–triplet splitting of $> 2000\ cm^{-1}$ is assumed for the excited state, the triplet → triplet intensity must be very small compared to the singlet → singlet intensity. This indicates a *spin-dependent intensity mechanism.* It is tempting to conclude this Comment by speculation on its origin. Within the weakly coupled chromophore model,[9] SPE transitions may acquire intensity through configurational interaction with chromophore (A) → chromophore (B) electron transfer transitions. The latter are expected to lie above 40,000 cm^{-1}, and they have not been observed. The important point is, however, that the unpaired electron on copper (A) can only be transferred to copper (B) if its spin projection is antiparallel to that of the unpaired electron on copper (B).[28] This is shown in Figure 7. In an exchange-coupled copper(II) dimer, therefore, the lowest-energy copper (A) → copper (B) CT transition is a *pure singlet transition.* It is expected to be polarized along the copper(II)–copper(II) axis. The observed behavior of the 28,000 cm^{-1} band in copper(II) acetate suggests that it acquires its intensity from a chromophore (A) → chromophore (B) transition of the above type through configuration interaction. Symmetry considerations show that vibronic coupling is needed in addition to configurational mixing to obtain intensity. Symmetric double *d–d* excitations become *z* allowed if the enabling mode has a_{2u} symmetry in D_{4h}, thus removing the center of symmetry. A similar intensity mechanism was proposed to explain the double excitations in the basic rhodo complex.[4]

Progress in our understanding of the "dimer bands" in dinuclear copper(II) complexes will have to come from experiment. A study of the 40,000–100,000 cm^{-1} region might reveal the chromophore (A) → chromophore (B) electron transfer transitions. Resonance Raman studies with excitation energies corresponding to the "dimer

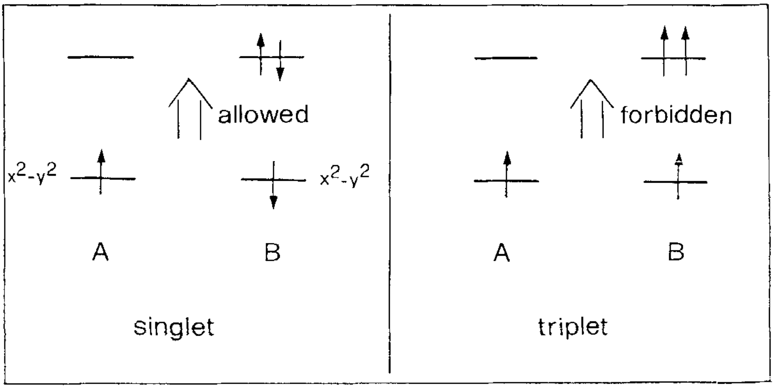

FIGURE 7 Schematic representation of chromophore (A) → chromophore (B) electron transfer transitions in dimeric copper(II) acetate.

band" might provide more information about the nature of these transitions.

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References

1. R. D. Willett (ed.), NATO ASI on Magneto-Structural Correlations in Exchange-Coupled Systems, Reidel, Amsterdam, 1984.
2. H. U. Güdel, Optical Spectroscopy in Ref. 1.
3. H. U. Güdel, Inelastic Neutron Scattering from Clusters in Ref. 1.
4. H. U. Güdel and L. Dubicki, Chem. Phys. **6**, 272 (1974).
5. J. Ferguson and H. U. Güdel, Aust. J. Chem. **26**, 505 (1973).
6. D. L. Dexter, Phys. Rev. **126**, 1962 (1962).
7. D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).
8. H. J. Schugar, E. I. Solomon, W. L. Cleveland and L. Goodman, J. Am. Chem. Soc. **97**, 6442 (1975).
9. A. E. Hansen and C. J. Ballhausen, Trans. Faraday Soc. **61**, 631 (1965).
10. Y. Tanabe, T. Moriya and S. Sugano, Phys. Rev. Lett. **15**, 1023 (1965).
11. J. Ferguson, H. J. Guggenheim, and Y. Tanabe, J. Phys. Soc. Japan **21**, 692 (1966).
12. K. I. Gondaira and Y. Tanabe, J. Phys. Soc. Japan **21**, 1527 (1966).
13. T. Fujiwara, J. Phys. Soc. Japan **34**, 1180 (1973).
14. M. Naito, J. Phys. Soc. Japan **34**, 1491 (1973).
15. S. Decurtins and H. U. Güdel, Inorg. Chem. **21**, 3598 (1982).
16. References 7, 8, 10–15 quoted in Ref. 12.
17. L. Dubicki, Aust. J. Chem. **25**, 739 (1972).
18. J. P. van der Ziel, J. Chem. Phys. **57**, 2442 (1972).
19. G. G. P. van Gorkom, J. C. M. Henning and R. P. van Stapele, Phys. Rev. B **8**, 955 (1973).
20. S. E. Stokowski and D. D. Sell, Phys. Rev. B **3**, 208 (1971).
21. T. Fujiwara, W. Gebhardt, K. Petanides and Y. Tanabe, J. Phys. Soc. Japan **33**, 39 (1972).
22. J. Ferguson and P. E. Fielding, Aust. J. Chem. **25**, 1371 (1972).
23. H. J. Schugar, G. R. Rossman, C. G. Barraclough and H. B. Gray, J. Am. Chem. Soc. **94**, 2683 (1972).
24. E. I. Solomon and D. E. Wilcox, Magneto-Structural Correlations in Bioinorganic Chemistry in Ref. 1.
25. J. Ferguson, H. U. Güdel and E. R. Krausz, Mol. Phys. **30**, 1139 (1975).
26. L. Dubicki, Aust. J. Chem. **25**, 1141 (1972).
27. S. R. Desjardins, D. E. Wilcox and E. I. Solomon, unpublished results.
28. P. A. Cox, Chem. Phys. Lett. **69**, 340 (1980).