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ABSTRACT

November 1959

The diatomic and linear triatomic molecules such as the oxides and halides of the "iron-group" elements are of importance in high temperature systems. Although the various high symmetry compounds of these elements, e. g. the solid oxides, hydrated complexes, etc., are sufficiently understood in terms of the present ligand-field theory, no semi-quantitative schemes have been utilized to understand and predict the spectroscopic and thermal properties of their simple, gaseous molecules. In this article, the observed dissociation energy vs. atomic no. curves for the linear gaseous oxides and the halides of the first transition series are compared with the corresponding energy curves of the solid oxides and the halides and the similarities are pointed out. It is shown that the double maximum stabilization curves observed in the gaseous molecules as well, can be understood in terms of the splitting of the (3d)-shell of the transition atoms in a linear (C_{oov} or D_{ooh} symmetry) ligand field with two independent splitting parameters one of which is small. A method for predicting the low-lying molecular spectral states is developed. The energies of the states depend on the splitting parameters and the electron interactions. The parameters are estimated from the first portion of the thermal data and used only for these elements. The electron interaction energy is obtained from the spectral terms of free atoms (ions). Unlike the case in the high symmetry applications, this procedure here takes into account "electronic correlation" (configuration interaction) effects. The generality of the treatment is revealed by comparing the results of the simple ionic and covalent models with those of the molecular orbital method. Calculations of spectral states are made for ScO, TiO, VO and CrO and experimental data discussed.

Ligand Field Theory of Linear Gaseous Molecules Involving the First Transition Series Elements

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Diatomic and linear triatomic gaseous molecules involving metals of the first transition series are of chemical and astrophysical interest. However there are no simple ways of predicting their spectroscopic states or dissociation energies. The usual semi-empirical molecular orbital method[1] has been applied to correlate spectral data of homonuclear and heteronuclear molecules of the first three periods; by analogy one can treat the states of similar heavier gaseous species when sufficient data exist for comparison. The success of this method has been due to two favorable circumstances; first as in the atomic case, light molecules have fewer low-lying states and have less complicated states than heavy molecules; second, the light molecules have been subjected

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[1] G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand, New York, 1950), Chap. 6

[*] Lawrence Radiation Laboratory, Postdoctoral Fellow 1959-60.

to a great deal of spectral investigation and analysis. As a result it has been possible to draw empirical correlation diagrams showing the crossing points of the energy levels in going from the "separated atoms" to the "united atom" configurations. Neither of these circumstances obtains for the gaseous species of the first transition series. The spectral data,[2] as is well known, are quite incomplete and many of the observed transitions remain unanalyzed because of their complexity. Even the ground states of the molecules are not established. The unfilled inner shells characteristic of the transition metals cause the greatest difficulty in applying a molecular orbital model, particularly in heteronuclear molecules such as oxides or halides.

The variation with atomic number of the heats of dissociation of the gaseous transition-metal compounds also shows interesting features (Figs. 1 and 2).[3] If bonding occurs among the outer electrons of the atoms one would expect for either covalent or ionic bonding a smooth, continuous variation in heats. In all

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[2] B. Rosen, ed., Donnees Spectroscopiques Concernant Les Molécules Diatomiques (Hermann and Cie, Paris, 1951)

[3] Professor Leo Brewer, private communication

cases for which data are available double-humped curves are obtained. Similar anomalous variation of binding energies have been observed for metals,[4] for a wide range of solid compounds[4] and for complexes in solution.[5]

For many years ligand field theory has been used to explain the magnetic and spectral properties of complexes in solution. Recently Orgel[6] and, independently, Griffith[7] have applied ligand field theory to solids and to aqueous complexes involving transition metals to explain the observed variation in stabilities across the

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[4] O. Krikorian, High Temperature Studies (Part I of Thesis) UCRL-2888, April 1955; L. Brewer and O. Krikorian, J. Electrochem. Soc. 103, 38, 701 (1956).

[5] M. Calvin and N. Melchior, J. Am. Chem. Soc. 70, 3270 (1948); L. E. Orgel, J. Chem. Soc. (London), 4756 (1952); H. Irving and R. J. P. Williams, ibid, 3192

[6] L. E. Orgel, J. Chem. Phys. 23, 1819 (1955).

[7] J. S. Griffith, J. Inorg. and Nuclear Chem. 2, 1 (1956), ibid. 2, 229 (1956), ibid. 3, 15 (1956).

periodic table. In the presence of electrostatic fields of symmetry commonly found in solid compounds and in complexes in solution, the five 3d-orbitals of the first transition series metals lose their degeneracy and in octahedral or tetrahedral fields, for example, they are split into two sublevels. The binding energy E will reflect the d-orbital splitting and may be understood as having three components,[6,7]

$$E = P' + \lambda\Delta + p \qquad (1)$$

P' represents the energy required to transform the free transition-metal atom into its valence state, the state in which presumably it exists in a compound. For example, in ionic compounds P' is the ionization potential with respect to the free atoms. Δ represents the difference in energy between the two d-sublevels in the ligand field. The first transition group elements display the properties of intermediate field splitting, in which the field splitting is large compared to spin-orbit coupling (which is neglected),[7] but comparable to the term separations in the free atom. p represents that part of the energy which is not very sensitive to the value of λ -- for example, the coulomb attractive energy in an ionic molecule -- and it will vary in some regular way across the periodic table.

This model has been used to explain the variation in binding energies for the whole spectrum of bond types, from metallic bonding to complex bonding in solution.[6,7] In metals, the d-electrons are delocalized; Δ is not important. The variation in bond energies depends on P'. In complexes which are of Pauling's "ionic" type,[8] P' is zero with respect to the free ion and Δ plays the dominant role. In all cases, however, a minimum is predicted at Mn, producing the characteristic double-humped curve.

The binding energies of the solid oxides and halides of the first transition series exhibit the double minimum behavior, as is shown in Figs. 1 and 2. According to the theory[6,7] outlined above the variation is due to the ligand field (i.e. Δ) effect. However it is quite striking that the stabilizations of these solids are very similar, both in magnitude and variation with Z, to those observed for the corresponding gaseous species in Figs. 1 and 2. This similarity might suggest that in both cases the stabilization is due to an essentially atomic quantity such as P', as is the case in metals,[7] rather than to a symmetry dependent ligand field. On the other hand, we might willfully set aside this possibility and consider whether the trend in dissociation energies of the gaseous molecules could be explained within the framework of the

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[8] L. Pauling, The Nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1940), p. 37

ligand field theory. We shall show that this may indeed be the case; then going one step further we may make full use of this framework towards a crude prediction of the spectroscopic ground state and first few excited molecular states of these species.

In the following we shall attempt to apply the ligand field theory as used by Griffith and Orgel[6,7] to the oxide, halide, etc., gaseous molecules of the first transition group towards some understanding of their spectroscopic and energy properties. We shall in addition consider the simple molecular orbital and valence-bond pictures of these molecules and discuss the relations between the various approaches.

Let us first give a description of a molecule such as MeO(g) or linear MeCl$_2$(g) strictly in terms of the usual ligand field theory, assuming that all the bonding or charge-transfer effects involve the outer 4s- and 4p- orbitals of the metal atom and the $(3d)^n$ subshell remains essentially as in the free ion. Later we shall consider the complications that would arise from various types of bonding and consider the result of a general molecular orbital treatment. We assume, for the moment that the gas molecule is ionic (Me^{++}O^{--}) and the ligand field seen by the $(3d)^n$ subshell is comparable in strength to that in the solid. In diatomic and linear triatomic molecules (symmetry group $C_{\infty v}$ or $D_{\infty h}$) the 3d levels of the metal atom will split into 3 subshells as in Fig. 3.

The naming of the orbitals assumes that the z-axis lies along the internuclear axis. The splitting is subject to the following constraint,[9] and so there are only two independent

$$2\Delta_3 = 2\Delta_1 + \Delta_2 \qquad (2)$$

splitting parameters. The splitting pattern, which can be derived from group theory, is due to the spatial properties of the d-orbitals, which are of two types. Three (d_{xy}, d_{xz}, d_{yz}) have charge densities between the Cartesian coordinate axes and two ($d_{x^2-y^2}$, d_{z^2}) have charge densities along the axes. If we imagine bringing the charge cloud associated with another atom along the internuclear (z) axis into the neighborhood of an atom with stable d-orbitals, d_{z^2} will feel most strongly the coulomb repulsion and as a result its energy will increase. $d_{x^2-y^2}$ and d_{xy} will be least affected by the presence of negative charge along the z-axis, while d_{xz} and d_{yz} will experience moderate repulsion. In this way the main features of the splitting diagram presented in Fig. 3 are explained.

If localized 3d-orbitals and intermediate field strength as defined above are assumed, the 3d-sublevels will not be overlapped by any other energy levels in the molecule. Then, the

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[9] See, for example, H. A. Bethe, *Ann. Phys.* (5) 3, 182-188 (1929).

splitting scheme is more general than strictly for the $Me^{++}O^{=}$ structure. Mixing with other configurations, such as $Me^{+}O^{-}$ or MeO, will give qualitatively the same result so long as these effects are confined to the 4s- and 4p-electrons of the metal. This is because the electron cloud of the ligand will remain symmetrically disposed about the internuclear axis and continue to provide a field of $C_{\infty v}$ symmetry.

In a general molecular orbital treatment one would combine the 2p-electrons of O with the metal 4s, 4p, and 3d-electrons of the same symmetry. Because there are more available orbitals on the metal than can be used to bond with O there will be several anti- and nonbonding orbitals in addition to the nonbonding 3d-orbitals. This is in contrast to the situation with high (tetrahedral or octahedral) coordination,[10] in which the only nonbonding orbital is 3d and thus is obviously the lowest orbital available for 3d-electrons in a complex or compound. Although the situation in the gaseous species is somewhat more ambiguous, the molecular orbitals for that case can be reasonably ordered so as to give the same qualitative result as the ligand field splitting.

We can now apply energy considerations to the shape of the graph of dissociation energies. Although we are ultimately interested in dissociations of the type

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[10] J. W. Linnett, *Discussions Faraday Soc.* No. 26, 7 (1958).

$$\mathrm{MeO}\ (g) \longrightarrow \mathrm{Me}\ (g) + \mathrm{O}\ (g) \qquad (3)$$

the ionic model suggests that we consider the reaction

$$\mathrm{MeO}\ (g) \longrightarrow \mathrm{Me}^{++}\ (g) + \mathrm{O}\ (g). \qquad (4)$$

We ignore the reaction

$$\mathrm{O}\ (g) \longrightarrow \mathrm{O}^{=}\ (g) \qquad (5)$$

because its effect is constant. The energies of these dissociations are plotted in Fig. 1.

For the ground state molecules, P' of Eq. (1) is the ionization potential of the metal and has already been accounted for in the data presented in Figs. 1 and 2. p represents the coulomb interaction in the case of ($\mathrm{Me}^{++}\mathrm{O}^{--}$) and will increase linearly or with a slightly negative curvature across the first transition series. In the more general case of mixed ionic-covalent bonding as in $\mathrm{Me}^{+}\mathrm{O}^{-}$, P' may still be retained as the total ionization potential, whereas the effect of 4s-4p bonding may be incorporated into p since this will vary uniformly with Z. From the nature of the field splitting we expect a double-humped curve with maxima at $d^2(\mathrm{Ti}^{++})$ and $d^7(\mathrm{Co}^{++})$ and minima at $d^0(\mathrm{Ca}^{++})$, $d^5(\mathrm{Mn}^{++})$ and $d^{10}(\mathrm{Zn}^{++})$. For the solids (Figs. 1 and 2) octahedral splitting will produce maxima at d^3 and d^8. The data are not sufficiently complete to illustrate this difference between the two cases; however there is no contradiction in the data to that assumption. We cannot hope to evaluate Δ_1, Δ_2 and Δ_3 for the gaseous case from the rather limited data. Furthermore, Williams[11] observes that even in an octahedral field the single splitting parameter is not constant for all the transition metals. However we can attempt a rough approximation of Δ_3 from Ca, Sc, and Ti points and of Δ_1 from V and Cr points. The ligand field splitting is taken as the difference from the smooth base curve. For the gaseous diatomic oxides

$$\Delta_3 \sim 35 \text{ Kcal}$$

$$\Delta_1 \sim 10 \text{ Kcal} \quad .$$

The value of Δ_3 has been obtained from only two points; Δ_1, from two independent differences, is about constant, so that the variation of splitting parameters between the first few neighboring elements is apparently small. Furthermore, these splitting parameters which have been approximated from the thermodynamic data for the first few transition oxides will be applied later only to these same species. Since Δ_1 is small the ligand field result has been reduced to essentially one independent parameter for the first few transition elements as in the octahedral

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[11] R. J. P. Williams, Discussions Faraday Soc. No. 26, 125 (1958)

field in the solid. For the solid we obtain

$$\frac{2}{5}\Delta \sim 20 \text{ Kcal}$$

where Δ is the energy difference between the 3d-sublevels in the octahedral field. This corresponds to Δ_5 in the gaseous case and is comparable in magnitude. Under the restriction that Ca, Mn, and Zn must show zero field stabilization any d-orbital splitting schemes for which the first sublevels are depressed from those of the free atom by approximately the same energy will show similar stabilizations in the first portions of each hump. The field stabilizations in the halides are less than in the oxide, which is in agreement with the spectrochemical series. Interpreting this effect on an ionic model, for simplicity, one can imagine that in the halides only one 4s-electron is transferred to the ligand, leaving one on the transition metal to shield the d-electrons from the ligand field.

Now that the ligand field theory has proved suitable for rationalizing the behavior of the dissociation energies, it seems worthwhile to extend the model to try to account for the order of electronic states in the molecule, as was suggested earlier in the introduction.

The ground molecular state is determined by the order of available orbitals in the ligand field. In the general molecular orbital treatment mentioned above it is found that the bonding orbitals (σ and Π) are filled by the valence electrons associated with the ligand (oxygen) and the outer 4s shell of the transition metal. The first orbitals available for 3d-electrons are a group of three nonbonding orbitals of designation, δ, Π, and σ. These originate, in part, from 3d atomic levels and correspond in designation and relative energy to the 3d-sublevels arising from the simple ligand field treatment depicted in Fig. 3. So long as the 3d-orbitals are essentially localized on the transition metal, the energy level order will remain in spite of charge transfer in the outer atomic orbitals. Specifically, in going from a general molecular orbital picture to ionic structures such as Me^+O^- or $Me^{++}O^=$, the order of the inner 3d-electron levels will not change.

Of course, in going from a "separated atoms" to a "united atom" framework the energy levels will cross in unpredictable ways. The spectra of the transition metal hydrides can be described by analogy to a united atom.[1] However for the oxides and halides discussed here the ligand is assumed to be sufficiently far from the metal atom that the molecular orbitals have not altered from the "separated atoms" case. This is a restatement of our previous assumption of localized 3d-orbitals.

Because it is so convenient to use an ionic model for purposes of description we will relate the molecular orbitals of the gaseous molecule to the ionic structure $Me^{++}O^=$. However, it should be noted that the result is not limited to an ionic model.

For that structure, then, we consider $O^{=}$ produced in a ^1S state. Since a spherically symmetric state makes no contribution to net angular momentum or spin we can identify the angular momentum designations of the transition metal orbitals in the $C_{\infty v}$ splitting scheme as those of the molecular orbitals of the diatomic molecule. We are specifically interested in the 3d transition metal orbitals.

Molecular states are obtained by assigning the d-electrons to the lower d-sublevels of Fig. 3. We represent the electron configuration as in the following example of a TiO state: $2^+ - 2^+$ refers to the configuration with two d-electrons in δ orbitals with angular momenta opposed and spins parallel. The resultant state is $^3\Sigma$. In this way, the designations of all possible low-lying states can be obtained.

The next problem is to arrange the molecular states in order of their energies. There are two separate contributions to the energy of a state: a ligand field term, and the energy of electron interaction, commonly called pairing energy although strictly it includes terms in addition to those due to electron spin pairing. The ligand field energy is given in terms of Δ. We assume that the electron interaction, or "pairing" energy is approximately the same as in the free atom (ion) and can be obtained from the free atom (ion) terms.[12] There is no one-to-one correspondence between

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[12] C. E. Moore, Atomic Energy Levels (National Bureau of Standards, Circular 467, 1949)

states of atoms and of molecules with the same number of d-electrons. Any one molecular state with resultant angular momentum Λ corresponds to all these atomic (free ion) states of the same spin that have a component of angular momentum $M_L = \Lambda$. The "pairing" energy difference between two molecular states of configuration $(3d)^n$ is taken as the difference in energy between the lowest atomic (ionic) $(3d)^n$ terms with the same spin and M_L, respectively. For multiplet atomic states the center of energy is taken.

This device corresponds to a calculation of configuration interaction among all states of the molecule with the same angular momentum designation Λ. The same situation obtains in the free ion and the result of the corresponding "calculation" is, indeed, given by the separation of the ionic term values. Furthermore, the difference in ionic terms gives not only the "spin pairing" energy[6,7] but a complete electron interaction energy of $(3d)^n$ including electron correlation.

The simplification in calculation, which results from the direct relation between the molecular Λ and M_L of the atom, is not possible in octahedral or tetrahedral fields. For these cases, individual coulomb and exchange integrals must be determined and essentially configuration interaction neglected.

The results of calculations of low-lying molecular states of the diatomic gaseous oxides are given in Table I. We have attempted to define only the ground state and first few excited states. Higher excitation would involve orbitals other than those of the 3d-electrons. The tabulation is limited to the first four transition series oxides, which are the species for which values of the splitting parameters Δ_3 and Δ_1 have already been approximated. Of course the method could readily be extended to other members of the transition series oxides and to diatomic halides, if Δ's were available for them. The states of ScO, with one d-electron are the simplest to determine, and the number and complexity of low-lying states increases as more d-electrons are added. However, because of the selection rules for molecular transitions, few transitions among the low-lying levels of any one species would be possible. In Table II some of the observed transitions are listed. The state that is presumably the ground state is indicated by X. In the following paragraphs we will consider these observations in light of the predictions of the theory developed above.

For ScO, the observed ${}^2\Pi \rightleftarrows {}^2\Sigma$ transition may arise from the first two predicted excited states. However, in that case, the order of relative energy is reversed; ${}^2\Pi$ would be lower. Since the spectrum is fairly complicated and the analyses are not complete it is possible that the relative order of the states has been reversed. The differences between ${}^2\Sigma \longrightarrow {}^2\Pi$ and ${}^2\Pi \longrightarrow {}^2\Sigma$ are slight[13] -- different rotational lines would be missing at the

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[13] Reference 1, Chapter 5.

beginning of the rotational branches in the two cases. Also there would be differences in relative intensities of the branches. Accurate analysis would require high dispersion and careful study of levels of low rotational quantum number. It is possible that the $^2\Pi \rightleftarrows X\ ^2\Sigma$ transitions observed in BO and AlO, which do not have unfilled inner shells, have served as misleading clues in the assignment of the ScO spectrum.

The $^3\Sigma \rightleftarrows {}^3\Pi$ transition of TiO may correspond to the first two predicted states. However, again the order of levels would have to be reversed and for the same reasons as given above for ScO. $^3\Sigma$ would be lower.

The parentheses in Table II for the states of VO indicate that their true designation is highly in question. However, one of the $^2\Delta$ may correspond to the predicted ground state $^2\Delta$. A quartet transition ($^4\Delta \rightleftarrows {}^4\Pi$) would also be expected in the visible region as well as another doublet transition ($^2\Sigma \rightleftarrows {}^2\Pi$).

We would expect $^5\Pi \rightleftarrows X\ ^5\Sigma$ for CrO instead of $^5\Pi \rightleftarrows X\ ^5\Pi$ according to the analysis of Ninomiya. In addition we would expect low-lying triplet and singlet states with transitions $^1\Pi - {}^1\Pi$ and $^3\Pi - {}^3\Pi$ in the range of 3000 A.

From these few comparisons it is apparent that at present the spectroscopic data are not sufficiently complete nor are the available analyses sufficiently reliable for a meaningful comparison with the predictions of the model presented above. The model has many limitations; nevertheless it is hoped that as data become available they might serve as a useful guide to correlate spectroscopic information. Eventually it may be possible to obtain the stabilization energies along the transition series from the splitting parameters obtained from the spectral terms, and thus have a means for interpolating and filling in missing thermodynamic data.

We are indebted to Professors Leo Brewer and Kenneth Pitzer for helpful discussions during the course of this work. Professor Brewer has also provided the data presented in Figs. 1 and 2 prior to publication. This work was carried out under the auspices of the U. S. Atomic Energy Commission.

Table I

First few predicted states of diatomic oxides and their energies

Molecule	d-electron Configuration	State Designation	Energy[a]	Energy (cm^{-1})	Ground State (?)
ScO	2^+	${}^2\Delta$	-	0.00	X
	1^+	${}^2\Pi$	$\Delta_3+\Delta_1=\Delta$	$\Delta(\sim 16{,}000)$	
	0^+	${}^2\Sigma$	$\Delta_3 + \Delta_2$	$\sim 30{,}000$	
TiO	$2^+ - 2^+$	${}^3\Sigma$	-	0.00	X
	$2^+ - 1^+$	${}^3\Pi$	Δ	$\Delta(\sim 16{,}000)$	
	$2^+\ 1^+$	${}^3\Phi$	Δ	Δ	
	$2^+ - 2^-$	${}^1\Sigma$	${}^1D - {}^3F$	$\sim 8{,}300$	
	$2^+\ 2^-$	${}^1\Gamma$	${}^1G - {}^3F$	$\sim 14{,}200$	
VO	$2^+ - 2^+\ 1^+$	${}^4\Pi$	-	0.00	
	$2^+\ 1^+ - 1^+$	${}^4\Delta$	Δ	Δ	
	$2^+ - 2^+\ 2^-$	${}^2\Delta$	$({}^2G - {}^4F)-\Delta$	$\sim 11{,}700-\Delta$	X
	$2^+ - 2^+\ 1^-$	${}^2\Pi$	${}^2P - {}^4F$	$\sim 11{,}000$	
	$2^+ - 1^+ - 1^-$	${}^2\Sigma$	$({}^2P - {}^4F)+\Delta$	$\sim 11{,}000+\Delta$	
CrO	$2^+ - 2^+\ 1^+ - 1^+$	${}^5\Sigma$	-	0.00	X
	$2^+ - 2^+ - 1^+\ 0^+$	${}^5\Pi$	$\Delta_2 - \Delta_1=\Delta'$	$\Delta'(\sim 14{,}000)$	
	$2^+ - 2^+\ 2^- - 1^+$	${}^3\Pi$	$({}^3P - {}^5\Delta)-\Delta$	$\sim 16{,}800-\Delta$	X
	$2^+ - 2^+ - 2^- - 1^+$	${}^3\Phi$	$({}^3H - {}^5\Delta)-\Delta$	$\sim 17{,}000-\Delta$	X
	$2^+ - 2^+ - 1^-\ 0^+$	${}^3\Pi$	$({}^3P - {}^5D)+\Delta'$	$\sim 16{,}800+\Delta'$	
	$2^+ - 2^+\ 2^- - 1^-$	${}^1\Pi$	$({}^1F - {}^5D)-\Delta$	$\sim 41{,}000-\Delta$	
	$2^+ - 2^+ - 2^- - 1^-$	${}^1\Phi$	$({}^1F - {}^5D)-\Delta$	$\sim 41{,}000-\Delta$	
	$2^+ - 2^+\ 1^-\ 0^-$	${}^1\Pi$	$({}^1F - {}^5D)+\Delta'$	$\sim 39{,}000+\Delta'$	

[a] Electron interaction energies are obtained from the observed[12] term values of the free ions, Me^{++}.

Table II

First few observed transitions in the oxides[a]

Molecule	Observed Transitions	Observed Energy Difference (cm^{-1})
ScO	$A^2\Pi \rightleftarrows X^2\Sigma$	16,500
	$B^2\Sigma \rightleftarrows X^2\Sigma$	20,650
TiO	Triplet states only:	
	$B^3\Sigma \rightleftarrows X^3\Pi$	14,200
	$C^3\Pi \rightleftarrows X^3\Pi$	19,500
VO	$(^2\Delta) \rightleftarrows X(^2\Delta)$	17,500
CrO	$A^5\Pi \rightleftarrows X^5\Pi$ [b]	16,600

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[a] Data from Rosen, ed., *Donnees Spectroscopiques Concernant Les Molécules Diatomiques* (Hermann and Cie, Paris, 1951)

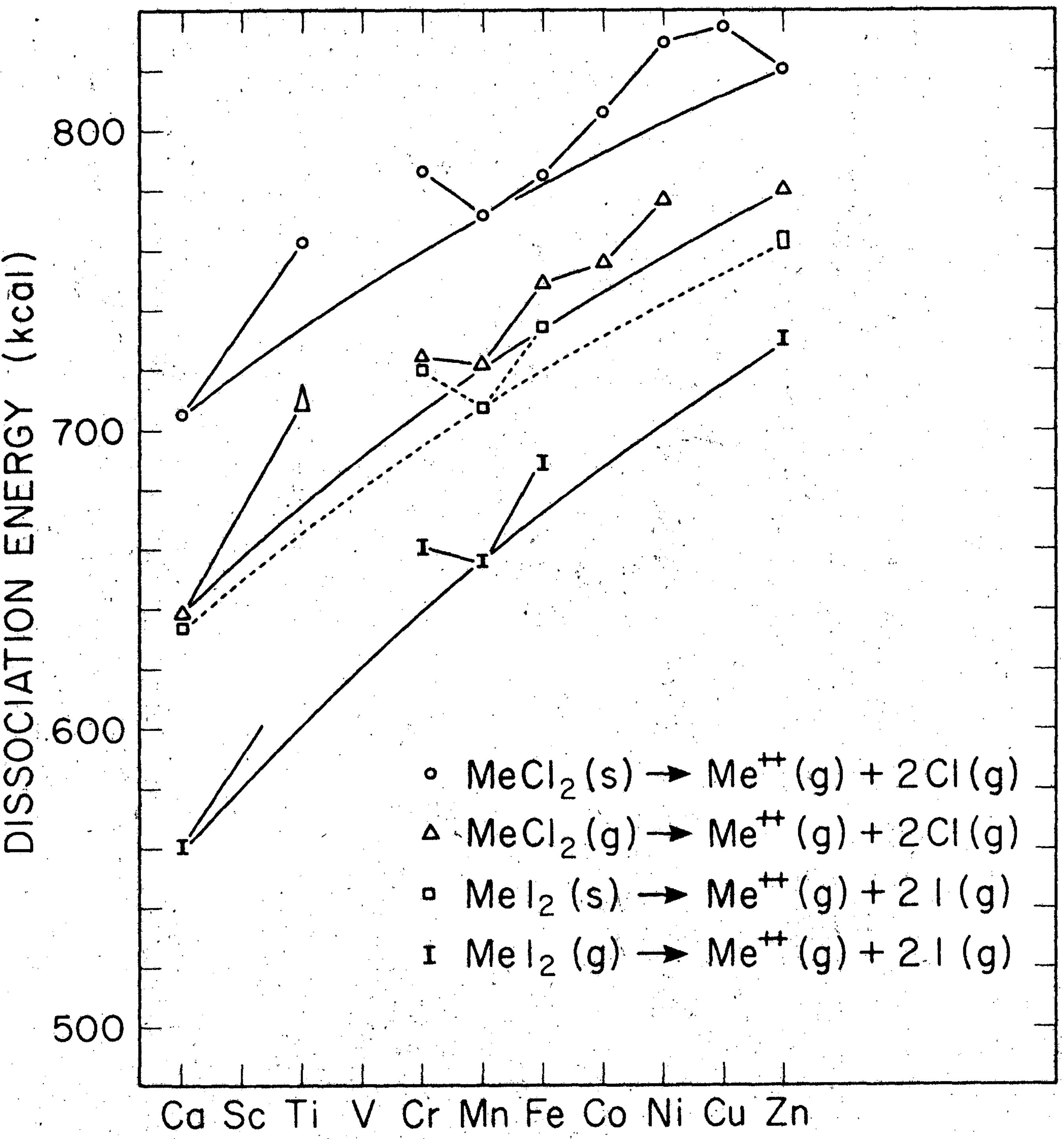
[b] See also M. Ninomiya, J. Phys. Soc. Japan 10, 829 (1955).

Figure Captions

Fig. 1 - Dissociation energies of solid and gaseous diatomic oxides

Fig. 2 - Dissociation energies of solid and gaseous chlorides and iodides

Fig. 3 - d-orbital splitting in diatomic and linear triatomic molecules. Symmetry group $C_{\infty v}$ and $D_{\infty h}$


DISSOCIATION ENERGY (kcal)
800
700
600
500
Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn
○ $MeCl_2(s) \rightarrow Me^{++}(g) + 2Cl(g)$
△ $MeCl_2(g) \rightarrow Me^{++}(g) + 2Cl(g)$
□ $MeI_2(s) \rightarrow Me^{++}(g) + 2I(g)$
I $MeI_2(g) \rightarrow Me^{++}(g) + 2I(g)$

721

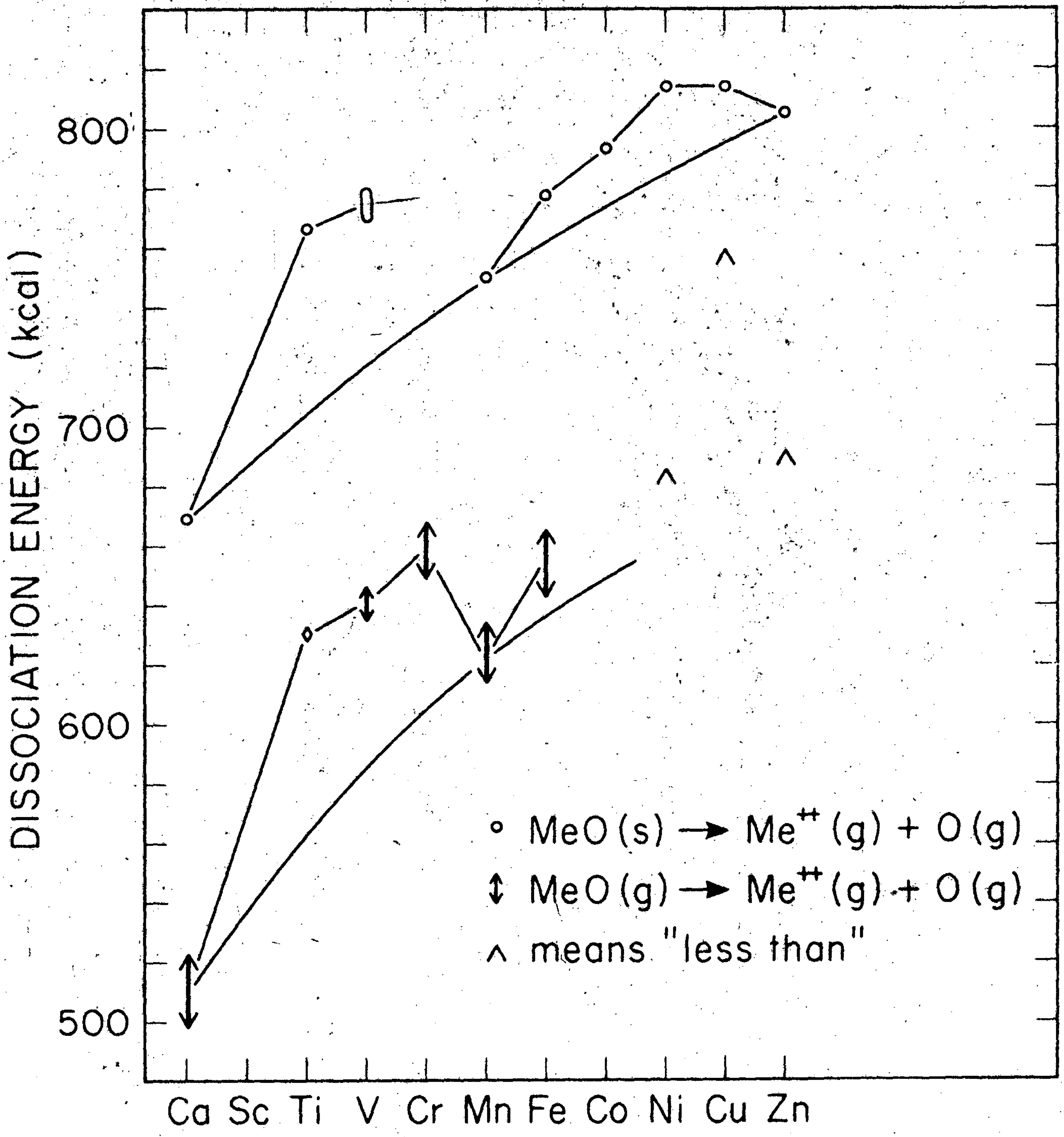

DISSOCIATION ENERGY (kcal)
800
700
600
500
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
○ MeO(s) → Me⁺⁺(g) + O(g)
↕ MeO(g) → Me⁺⁺(g) + O(g)
^ means "less than"

Fig 2

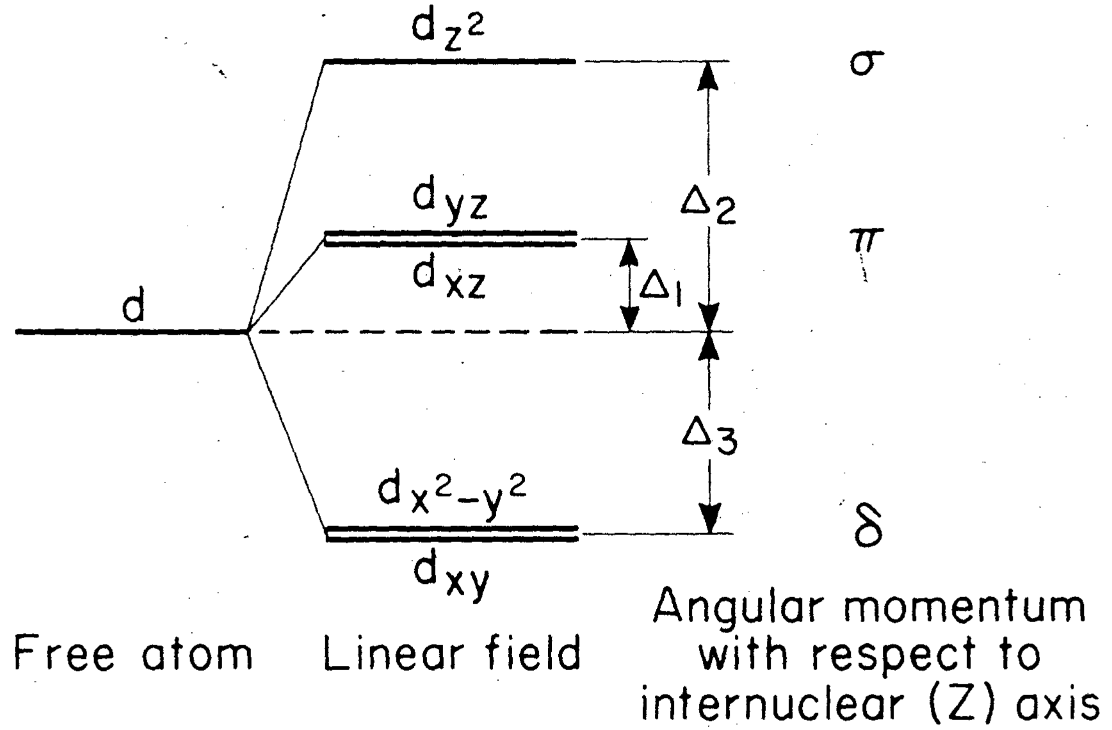

d_{z^2}
σ
d_{yz}
Δ_2
π
d_{xz}
Δ_1
d
Δ_3
$d_{x^2-y^2}$
δ
d_{xy}
Free atom
Linear field
Angular momentum with respect to internuclear (Z) axis

Fig 3