



# HOKKAIDO UNIVERSITY

Title	POLARIZATION FRACTIONS FOR CHEMISORPTION AND CATALYSIS FROM ENERGY LEVELS OF METAL IONS
Author(s)	GARDNER, R. A.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 15(3), 228-238
Issue Date	1968-02
Doc URL	<a href="https://hdl.handle.net/2115/24840">https://hdl.handle.net/2115/24840</a>
Type	departmental bulletin paper
File Information	15(3)_P228-238.pdf



## POLARIZATION FRACTIONS FOR CHEMISORPTION AND CATALYSIS FROM ENERGY LEVELS OF METAL IONS

By

R. A. GARDNER\*<sup>2</sup>

(Received December 15, 1967)

### Abstract

The vibration frequencies of chemisorbed intermediates are determined by the "polarization fraction", a constant which depends on the metal and its oxidation state in the adsorbent compound. This provides a method for assigning the numerical chemical oxidation state of a metal in a catalyst at the moment of the catalytic reaction. The polarization fractions of several metals were calculated from the spectra of chemisorbed carbon monoxide. The origin of the polarization fraction from fundamental properties of the metal is indicated by its relationship to the electronic energy levels of metal ions. It is inversely proportional to the accessibility of low-lying spin-orbit states of the gaseous metal ions. This relationship is used to calculate the polarization fractions of many metals that have not yet been studied by infrared spectroscopy as adsorbents for CO. Having the metal in the appropriate compound so that it has a polarization fraction is one criterion of catalysis, at least, of catalysis of reactions of intermediates. The necessary compound may be one which produces from the metal, at the surface, a non-bonding orbital having an electronic configuration identical to one of the gaseous metal ions which has low-lying accessible electronic states.

### Introduction

Molecules in contact with adsorbents produce bands in the infrared spectra at frequencies different from their gas phase frequencies. This change in vibration frequency could be used as a measure of the influence of the adsorbent on the chemisorbed molecule. This would not be very useful since a certain change in the vibration frequency of one molecule would be meaningless when considering another molecule. A more useful expression of the influence of the adsorbent has been in terms of numbers of valence electrons associated with the adsorbate molecule. These numbers of electrons may be related to the vibration frequencies of bonds of the adsorbate by suitable equations.<sup>1)</sup> While the change in vibration frequency is not equivalent from

\*) The Standard Oil Company (Ohio) Research Department, Cleveland, Ohio, U.S.A.

*Chemisorption and Catalysis from Energy Levels of Metal Ions*

one adsorbate to another, the change in numbers of valence electrons is equivalent for a class of adsorbates known as "intermedions".<sup>2)</sup>

Generally, the numbers of electrons which correspond to the vibration frequencies of chemisorbed species are non-integral, that is, numbers composed of an integer and a fraction. Certain chemisorbed species are distinguished by the fact that their vibration frequencies correspond to non-integral numbers (of electrons) whose fraction is a constant characteristic of the metallic component of the adsorbent compound. These species are "intermedions" and the fraction is known as the "polarization fraction" of the metal. It is considered to be the fractional part of the polarization exerted on any intermedion by the metallic component of the adsorbent compound. The possibility that these fractions have fundamental significance is suggested by a relationship between the polarization fractions determined from spectra of chemisorbed carbon monoxide and the electronic energy levels of gaseous metal ions. These are the ions which have low lying excited electronic states that are close in energy to the ground state. This relationship is used to calculate the polarization fractions of many metals which have not been studied spectroscopically as adsorbents for CO. Contrary to previous concepts,<sup>1)</sup> these calculations indicate that the polarization fraction of a metal is not a singular, unique constant for each metal, but may be different for certain oxidation states. This provides a means for the assignment of the specific oxidation state of the metal at the moment of the catalysis of a reaction of intermedions. It also establishes as a criterion for catalysis (at least for catalysis of reactions between intermedions) the certain oxidation states of metals which correspond to metal ions that have low-lying electronic energy levels.

### Discussion

Analyses of infrared spectra of chemisorbed CO may be based on the following equation<sup>1)</sup> which relates the vibration frequency " $\nu$ " of CO intermedions, to their number " $E$ " of valence electrons,

$$[\nu(\text{CO}) - 2,269.96] [E(\text{CO}) - 12.1182] = 268.309 \text{ cm}^{-1}. \quad (1)$$

According to this equation, the vibration frequencies of chemisorbed CO intermedions correspond to non-integral numbers of electrons. This might suggest that some electron sharing takes place between the adsorbate and the surface and might imply that a strong bond has been formed. Instead, intermedions are found to be weakly held on the surface and readily removed by evacuation. Yet they cannot be considered to be physically adsorbed. The energy required to remove one electron from CO to form the positive ion is 15 eV. This

R. A. GARDNER

changes the vibration frequency from  $2,143.27^{3)}$  to  $2,183.90\text{ cm}^{-1}$ .<sup>4)</sup> The CO stretching vibration frequencies of carbonyls vary from  $2,164\text{ cm}^{-1}$  for  $\text{H}_3\text{BCO}$ <sup>5)</sup> to  $1,738\text{ cm}^{-1}$  for  $\text{H}_2\text{CO}$ .<sup>6)</sup> Infrared bands that may be attributed to chemisorbed CO intermediations have been reported from  $2,203\text{ cm}^{-1}$  on an adsorbent containing chromium<sup>7)</sup> to  $1,230\text{ cm}^{-1}$  on a silica supported nickel oxide.<sup>8)</sup> A change of frequency of this magnitude, namely  $900\text{ cm}^{-1}$ , accompanied by such weak bonding might result from the deformation of the electron cloud of the adsorbate by an intense highly localized center of charge at the adsorbent surface without covalent bonding. It is considered that actual electron exchange does not take place between the surface and the chemisorbed intermedion. This view is consistent with the description of chemisorbed intermediations by equations derived entirely from the vibration frequencies of gaseous species – the neutral molecule and ions. Chemisorbed intermediations are considered to be neutral atoms and molecules which are polarized so that they have the vibration frequencies and perhaps other properties that they would have if electron sharing or transfer had occurred. This view is supported by analyses of the infrared spectra of chemisorbed carbon dioxide.<sup>2)</sup> Carbon dioxide intermediations which are polarized by an apparent acceptance of 1.90 anti-bonding electrons – equivalent to a change of  $700\text{ cm}^{-1}$  – have become bent, yet are so weakly held to the surface that they are rotating. To emphasize that the assignment of non-integral numbers of electrons to chemisorbed intermediations is considered a useful artifice, these will be generally referred to as “apparent” electron transfers in the remaining discussion.

On the basis of the conventional representation of cupric copper as  $3d^9$ , adsorbates could appear to accept one or donate one electron. Chemisorbed CO intermediations on  $3d^9$  cupric copper would then appear to have 11 and 9 valence electrons. According to Eq. (1), these would have vibration frequencies of  $2,030$  and  $2,184\text{ cm}^{-1}$  respectively. Instead, the chemisorbed CO intermediations on adsorbents containing copper had vibration frequencies of  $2,174$  and  $2,121\text{ cm}^{-1}$ .<sup>1)</sup> According to Eq. (1) these correspond to CO intermediations with 9.32 and 10.32 valence electrons. The chemisorbed CO intermedion with a vibration frequency equivalent to 9.32 electrons has made an apparent donation of 0.68 electrons to the metal. If this apparent electron transfer is to fill a partially filled orbital of the metal, then that orbital must have contained 1.32 electrons. The chemisorbed CO intermedion with a vibration frequency equivalent to 10.32 electrons has made an apparent acceptance of 0.32 electrons from the metal. If this is to empty an orbital, then that orbital must have contained 0.32 electrons. Rather than an orbital configuration of  $3d^9$ , these two copper species might be represented as  $3d^{8.32}$  and  $3d^{9.32}$ . Instead of filling

*Chemisorption and Catalysis from Energy Levels of Metal Ions*

only the levels of the ground state there is some population of upper levels. The probability that an electron will be in levels above the ground state is proportional to the sum " $U$ " of the Maxwell-Boltzmann factors for electronic states *above* the ground state, namely,

$$U = \sum_{n=1}^{n=\infty} (2J_n + 1) \exp\left(-\frac{hc\bar{\nu}_n}{kT}\right) \quad (2)$$

where " $2J+1$ " is the multiplicity, " $\bar{\nu}$ " is the energy level in  $\text{cm}^{-1}$  and " $n=1$ " is the first electronic state above the ground state. Values of " $J$ " and " $\bar{\nu}_n$ " are given in the Atomic Energy Level Tables<sup>9)</sup> for gaseous atoms and ions.

Metal ions may be placed in an order according to the accessibility of energy states above the ground state. For example, the first electronic level above the ground state of singly ionized chromium (Cr II) is at an energy of  $11,962 \text{ cm}^{-1}$ . This level is not very accessible when compared with the first electronic level of doubly ionized chromium (Cr III) at an energy of  $60 \text{ cm}^{-1}$ . The numerical values of  $U$  are proportional to the accessibility of upper states. The larger values of  $U$  correspond to states of lower energy and greater multiplicity. Although  $U$  must be evaluated at a given temperature for Eq. (2), the accessibility of the upper states is a function of the energies and multiplicities of these states and independent of the temperature. (Since these data are tabulated in the Atomic Energy Level Tables in terms of the physicists' notation, we shall use the same notation for the Roman numerals, that is, the atom is I, the first positive ion II, *etc.*)

A previous note<sup>10)</sup> presented a relationship of the polarization fractions of several metals to  $\log_{10} U$  of their ions. The sums,  $U$ , were calculated for gaseous ions of metals whose polarization fraction had been determined from spectra of chemisorbed CO. The least positive ion having low-lying energy levels was chosen for each metal. These were Cr III, Fe II, Co II, and Ni III. The relationship between the polarization fraction ( $PF$ ) for these metals and  $\log_{10} U$  for these ions is:

$$PF = -0.2714 \log_{10} U_{298} + 0.3112 \quad (3)$$

for  $U$  calculated from Eq. (2) at  $T=298^\circ\text{K}$ . The sum,  $U$ , may be calculated for other metal ions and used in Eq. (3) to obtain the polarization fractions of those metals whose ions have low-lying states. These are listed in Table I along with the polarization fractions from CO chemisorption for those metals that do not have ions with low lying levels listed in the Atomic Energy Level Tables. Since all of the polarization fractions are derived directly or indirectly from the spectra of chemisorbed CO, there may be some uncertainty associated with the third decimal place. This is indicated by the small figures in Table I.

R. A. GARDNER

TABLE I. Polarization Fractions and Corresponding Gaseous Ions

Gaseous Ions	Metal	Polariz'n Fraction	Gaseous Ions	Metal	Polariz'n Fraction	Gaseous Ions	Metal	Polariz'n Fraction
II	V	0.04 <sub>2</sub>	IV	Co	0.26 <sub>2</sub>	II	Y	0.59 <sub>7</sub>
II	Ti	0.06 <sub>4</sub>	V	Mn	0.28 <sub>4</sub>	II	+Co	0.62 <sub>0</sub>
II	Sc	0.08 <sub>8</sub>	III	Fe	0.30 <sub>8</sub>	II	La	0.64 <sub>8</sub>
III	+Cr	0.09 <sub>9</sub>		*Cu	0.32	IV	Nb	0.70 <sub>5</sub>
III	V	0.11 <sub>9</sub>	IV	Ti	0.32 <sub>1</sub>	II	Ta	0.71 <sub>2</sub>
III	Ti	0.14 <sub>7</sub>	V	Cr	0.36 <sub>8</sub>	III	Ru	0.74 <sub>5</sub>
IV	Mn	0.15 <sub>3</sub>	III	Nb	0.38 <sub>8</sub>		#Rh	0.78
IV	Cr	0.20 <sub>5</sub>	III	Zr	0.46 <sub>8</sub>		#Ir	0.80
III	Sc	0.21 <sub>3</sub>	III	Y	0.51 <sub>4</sub>		**Pd	0.81
II	Nb	0.22 <sub>0</sub>	VI	Mn	0.53 <sub>4</sub>	IV	Zr	0.81 <sub>6</sub>
IV	V	0.24 <sub>5</sub>		*Ag	0.54		**Pt	0.81 <sub>7</sub>
II	+Fe	0.25 <sub>7</sub>	III	Co	0.54 <sub>3</sub>	III	+Ni	0.85 <sub>7</sub>
II	Zr	0.26 <sub>1</sub>	IV	Mo	0.54 <sub>4</sub>	II	Ru	0.94 <sub>2</sub>

(No Mark) from electronic energy levels of ion.

\* from infrared spectra of chemisorbed CO.<sup>11)</sup>+ from both CO spectra and energy levels of ions.<sup>10)</sup># from reactions known to be catalyzed by this metal.<sup>11)</sup>

However, it should be possible to determine the polarization fractions entirely from the accessibility of the energy levels of the metal ions without reference to chemisorption. Unfortunately, the necessary relationships are not known at this time.

The test of these polarization fractions by analyses of reactions catalyzed by these metals will be a part of those papers which deal with the specific reactions. The accompanying paper<sup>12)</sup> concerns catalyzed reactions of hydrogen and oxygen-forming water.

The new polarization fractions shown in Table I have not only greatly expanded the number of metals which may be considered as catalysts in the Intermedion Theory but also provided the following relationship between ionization states and chemical oxidation states. At the beginning of the Discussion, two copper species were proposed to account for the apparent electron transfers to form chemisorbed carbon monoxide intermedions. Partially filled orbitals that differ by a total of one electron were suggested for these two species. It seems natural to associate these with the "ic" and "ous" oxidation states conventionally assigned to metal species. By analogy with these assignments for copper, there should be two oxidation states for each polarization fraction

*Chemisorption and Catalysis from Energy Levels of Metal Ions*

of any metal. Thus, those gaseous metal ions or ionization states which correspond to a polarization fraction will also correspond to two oxidation states. Those ionization states which do not correspond to a polarization fraction (because they do not have low lying accessible energy states) are thought to correspond to a single chemical oxidation state. Finally, the gaseous atom, designated on the physicists' scale by "I", is equated with the zero chemical oxidation state. The following description of the oxidation and ionization states of manganese is summarized in Table II. The ionization state (of the

TABLE II. Ionization and Oxidation States of Manganese

Polarization Fractions	Corresponding Gaseous Ions	Chemical Oxidation States
	I Mn	Mn 0
	II Mn	Mn 1+
	III Mn	Mn 2+
0.153	IV Mn ous	Mn 3+
	IV Mn ic	Mn 4+
0.284	V Mn ous	Mn 5+
	V Mn ic	Mn 6+
0.534	VI Mn ous	Mn 7+
	VI Mn ic	*Mn 8+

\*) Mn 8+ may not exist.

corresponding gaseous metal ion) is expressed on the physicists' scale by the Roman numeral preceding the atomic symbol. The chemical oxidation state is noted by the Arabic numeral following the chemical symbol. The manganese atom, I Mn, corresponds to Mn "0". The first electronic level above the positive ion of manganese is at an energy of  $9,473 \text{ cm}^{-1}$ . Since this is not a low lying, accessible level, II Mn does not have a polarization fraction. It, therefore, corresponds to Mn 1+. (Energy levels below  $1,500$  or  $2,000 \text{ cm}^{-1}$ , depending on the multiplicity, are accessible because the quantity " $U$ " in Eq. (3) is different from zero for these levels.) The first excited electronic state of the III Mn ion is at  $26,824 \text{ cm}^{-1}$ . Thus III Mn corresponds to Mn 2+. The IV Mn ion has accessible levels, the first of which is at  $92 \text{ cm}^{-1}$ . According to Eqs. (2) and (3), IV Mn corresponds to Mn 3+ and the "ic" state of IV Mn corresponds to Mn 4+. The fourth and fifth positive ions of manganese also have accessible electronic levels. The oxidation states corresponding to these ionization states are shown in Table II. A summary of the relationship of ionization states and oxidation states is presented in Table



*Chemisorption and Catalysis from Energy Levels of Metal Ions*

forming water<sup>12)</sup> indicate that Ag 4+ and Cu 4+ are the catalytically active species. It is the "ic" state of silver that satisfies the requirements for catalysis of a reaction of OH and H<sub>2</sub> intermediations. This is the reaction which leads to the precipitation of silver from aqueous solutions of silver nitrate in the presence of hydrogen. The II Ag and III Ag ions do not have low lying excited electronic levels. Data is not presented in the Atomic Energy Level Tables<sup>9)</sup> for IV Ag. If IV Ag is the first ion having low lying levels, then it corresponds to the polarization fraction of 0.54. The relationship of ionization states and oxidation states of Ag are then the same as shown in Table II for Mn. Although silver was traditionally thought of as having only the 1+ oxidation state, the 2+ oxidation state has become recognized, especially in AgO. More recently, Ag 3+ has been proposed by several investigators<sup>13)14)</sup> to interpret their observations. The prediction of Ag 4+ in aqueous solutions of silver nitrate is an unexpected result of the Intermedion Theory. It is dependent on IV Ag being the first positive ion having low-lying excited electronic states. The presence of Ag 4+ in aqueous silver nitrate solutions and the catalysis of this reaction may require the higher solute concentrations.

The similar problem arises in the assignment of the oxidation state of copper which catalyzes the synthesis of water. It is the "ic" state of copper that satisfies the requirements for catalysis of a reaction between H<sub>2</sub> molecule and O atom intermediations to form water.<sup>12)</sup> As in the case of silver, the Atomic Energy Level Tables do not show accessible excited electronic states for II Cu and III Cu and no levels are listed for IV Cu. If IV Cu is the first positive ion with low lying accessible electronic states then, as with manganese, the "ous" state of IV Cu corresponds to Cu 3+ and IV Cu "ic" corresponds to Cu 4+. The 1+ and probably the 2+ oxidation states may exist on certain lattice faces of metals in the metallic state. (The density of atoms in the (111) face of face centered cubic metals is approximately 5 times that of the (321) face. The larger number of bonds in the (111) face would give it a higher oxidation state than the (321) face.) The 3+ and 4+ oxidation states would seem to require an anion. As an example, the catalytic activity of copper oxide for the synthesis of water decreases above 300°C. at the higher concentrations of hydrogen in the reacting gas mixture.<sup>15)</sup> This decrease in activity may be the result of a reduction of the copper oxide on the active lattice face from 4+ to a lower oxidation state at these conditions. The determination of the low-lying electronic levels of IV Ag and IV Cu should clarify these assignments.

In conclusion, some qualitative suggestions may be made concerning the origin and location of the polarization fraction. The quantity "U" is pro-

R. A. GARDNER

portional to the probability of electron occupancy of upper electronic states in the gaseous metal ion. The inverse relationship between  $U$  or  $\log_{10} U$  and the polarization fraction suggests that this fraction appears in the non-integral number of electrons corresponding to a chemisorbed intermedion as a result of the apparent filling or emptying of a lower electronic level of the metal in a compound. The larger the occupation of the upper levels, the larger the vacancy in the lower level and the smaller the occupation of the lower level. The larger values of  $U$  correspond to the smaller polarization fractions. This suggests that the polarization fraction found by CO chemisorption is directly related to the fractional electron population remaining on a time averaged basis, in the lower level.

In the adsorbent compound, a non-bonding orbital which has retained its configuration from the metal ion is most likely responsible for the polarization fraction. For most of the metals in Table I, the low-lying electronic states correspond to various values of the " $J$ " quantum number within a single "d" orbital of the ion. These closely spaced "spin-orbit" states make a significant contribution to  $U$  in Eq. (2) only when their energy is less than 1,500 or 2,000  $\text{cm}^{-1}$ . The polarization fraction is, therefore, quite sensitive to small variations in these electronic states. Whereas atomic orbitals must be changed to form bonding and antibonding molecular orbitals, Eq. (3) indicates that this non-bonding orbital remains identical in the metal compound to the corresponding orbital of the gaseous metal ion. It appears that the wave function of the electron in this non-bonding d-orbital includes these spin-orbit states which were excited states in the gaseous metal ion. The electron density in the lowest spin-orbit state of the metal in a compound seems to resemble a highly localized charge in its effect on the adsorbate. Meanwhile the electron density in the upper spin-orbit states seems to be delocalized and without effect on the adsorbate.

The polarization fraction may be thought of as an "unsaturation" of the metal (in a compound) due to the electrons spending some time in states different from the state that was the ground state in the gaseous metal ion. The formation of intermedions appears to provide a method for satisfying this "unsaturation" by transferring it to the adsorbate. Thus it would seem that each intermedion is associated with one metal species. A catalytic site would then be composed of at least, two metal species. The formation of any sort of metal-to-metal bond would cause both metal species to reach the same oxidation state. As suggested in the accompanying paper, this would require that both intermedions correspond to the same oxidation state.

A non-bonding orbital of the adsorbent compound would seem appropriate

*Chemisorption and Catalysis from Energy Levels of Metal Ions*

for interaction with an adsorbate molecule to form a chemisorbed intermedion. Since this orbital is not interacting with other atoms in the adsorbent, it is available for the polarization of the intermedion. This orbital might be present on the surface of only certain compounds of the metal at certain conditions of temperature, pressure, and composition. The chemisorbed intermedion and the surface may represent a meta-stable reversible complex which changes with time to a stable surface compound. Then, the polarization is replaced by orbital overlap and electron exchange with the formation of the strongly bonded surface compounds reported by many investigators. There seems to be some coincidence with the concept of the d-orbital vacancy traditionally associated with the chemisorptive and catalytic activity of transition metals. The relationships presented suggest that the d-orbital is not vacant but that the wave function of the electron included the various possible  $J$ -states within that orbital in proportion to their accessibility.

In the past, chemisorption and catalysis have been attributed to dangling bonds, partial valences and delocalized orbitals. The relationships drawn from the data in this and preceding papers are in qualitative agreement with those concepts. The polarization necessary for chemisorption and catalysis (at least for intermedions) seems to be the result of an intense highly localized center of charge in an orbital of the metal component of the adsorbent or catalyst compound. The electrons in this orbital may be considered as partly delocalized since they occupy states which were excited states in the gaseous metal ion. Since the energies and multiplicities of these states in the metal compound are identical to their energies and multiplicities in the gaseous ion, it is likely that this is a non-bonding orbital.

#### Acknowledgment

The author wishes to acknowledge the assistance of Mrs. M. KRIZAN and to thank The Standard Oil Company (Ohio) for permission to publish this work.

#### References

- 1) R. A. GARDNER and R. H. PETRUCCI, *J. Phys. Chem.* **67**, 1376 (1963).
- 2) R. A. GARDNER, "The Infrared Spectra of Chemisorbed  $\text{CO}_2$ ", *J. Catalysis*, submitted.
- 3) E. K. PLYLER, L. R. BLAINE and W. S. CONNER, *J. Opt. Soc. Am.* **45**, 102 (1955).
- 4) G. HERZBERG, "*Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*", D. Van Nostrand Co., Inc., Princeton, N. J. 1955, p. 522.
- 5) R. D. COWAN, *J. Chem. Phys.* **18**, 1101 (1950).
- 6) P. COSSEE and J. J. SCHACHTSCHNEIDER, *J. Chem. Phys.* **44**, 97 (1966).

## R. A. GARDNER

- 7) L. H. LITTLE and C. H. AMBERG, *Can. J. Chem.* **40**, 1997 (1962).
- 8) C. E. O'NEILL and D. YATES, *J. C. Spectrochim. Acta* **17**, 953 (1961).
- 9) C. E. MOORE, *Natl. Bur. Std. Circ. No. 467*, **1** (1949); **2** (1952); **3** (1958).
- 10) R. A. GARDNER and T. B. SELOVER, Jr., *J. Catalysis* **3**, 105 (1964).
- 11) R. A. GARDNER, *J. Catalysis* **3**, 7 (1964).
- 12) R. A., GARDNER, *J. Catalysis*, **10** (1968), in press.
- 13) E. J. CASEY and W. J. MOROZ, *Can. J. Chem.* **43**, 1199 (1965).
- 14) J. A. ALLEN, *Proc. Australian Conf. Electrochem., 1st, Sydney, Hobart, Australia* 1963, 72 (1965).
- 15) V. V. POPOVSKII and G. K. BORESKOV, *Problemy Kinetiki i Kataliza, Akad. Nauk S.S.S.R.* 1960, No. 10, pp. 67-72.