JOURNAL OF CATALYSIS **65**, 84–94 (1980)

Chemisorption of Diatomic Molecules (H_2, N_2, CO) on Transition *d*-Metals

EIZO MIYAZAKI

Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

Received November 1, 1979; revised February 13, 1980

The interaction energies of diatomic molecules, H_2, N_2, and CO with transition *d*-metal surfaces are empirically calculated using a bond energy bond order (BEBO) approach developed in earlier papers. The two problems, i.e., (i) does a molecule chemisorb on a given surface and (ii) whether the adsorbed species is in a molecular form or dissociative form, are examined from the potential energy curves obtained. The metals are then classified approximately into four groups, A, B, C, and D. The A group metals, which consist mainly of IV_B, V_B, and VI_B group metals in the periodic table of the elements, strongly chemisorb all the above gases including O_2 and NO molecules in a dissociative form at room temperature. The group D metals consisting of noble *d*-metals, on the other hand, chemisorb NO and CO in a molecular form and do not decompose CO and N_2 molecules. The group B (Fe, Re) and C (Co, Ni, Tc) metals which are known as main elements of catalysts for the reactions of Fischer–Tropsch and ammonia syntheses have intermediate adsorption properties between the A and D group metals. These qualitative and quantitative results of heats of dissociative and nondissociative adsorption are summarized in tables and compared with the experiments.

I. INTRODUCTION

The chemisorption of diatomic molecules such as H_2, O_2, N_2, CO, and NO is a fundamental problem for understanding heterogeneous catalysis. Dissociative chemisorption of CO or N_2 molecules, for instance, has been implicated as a step in catalytic methanation or ammonia synthesis on transition metals, respectively. Therefore it might be important to evaluate the activation barriers for dissociation of these molecules on a given surface. However, there are still many difficulties in evaluating quantitatively the interaction energies between gas molecules and solid surfaces to be required for computing the barriers. The available results by rigorous theoretical calculations so far are very limited and the agreement with experiments is not satisfactory. Thereby, it is currently desirable to find some empirical methods which can describe the experimental results more precisely and the interactions more generally in the available form for many kinds of metals.

For chemical reactions including heterogeneous catalytic reactions, "bond order" is an important parameter for representing the extent of the interaction between atoms in a molecule, since proceeding of a chemical reaction can be described by one particular bond splitting and another bond formation. The "Bond Energy Bond Order (BEBO)" model, which was first used by Johnston (*1*) for calculations of gas phase reactions, has recently been combined with a "Crystal Field Surface Orbital (CFSO)" concept (*2*) by Weinberg *et al.* (*3, 4*) and applied to the description of several surface reactions of simple molecules on Pt or Ni metals. As indicated in Weinberg's paper (*4*) and also commented upon by Knor (*5*), however, there are several difficulties in this model. One of them is arbitrariness of the results arising from using the CFSO concept and the other is the uncertainty in the values of "single (order) bond energy" between a metal surface and adsorbed species to be used in calculating the gas molecule–surface bond energy. These difficulties are main sources of calculational

0021-9517/80/090084-11$02.00/0

errors, and they also seem to prevent the general applications of the model by Weinberg to other kinds of metal systems.

In earlier papers (*6*, *7*) we developed an empirical approach in which one or two parameters were introduced into Pauling–Eley's formulation of the single bond energy and calculated the atom–surface single bond energies for oxygen, nitrogen, and hydrogen as well as heats of dissociative adsorption of these molecules. In addition, using these values of the single bond energies, the potential energy curves were calculated for the chemisorption of O_2 and NO molecules in the framework of the BEBO model without using the CFSO concept (*8*). The agreement of the results thus calculated by "BEBO + parameterized Pauling–Eley's equation" with experimental data was found to be very encouraging and this approach seemed to have a predictive power for the chemisorption properties of the molecules.

In the present paper, further calculations by similar method are performed for the chemisorption of H_2, N_2, and CO molecules on transition *d*-metals, which are important in the study of many catalytic reactions including ammonia and Fischer–Tropsch syntheses. Agreement of qualitative and quantitative results with experiments is also found to be encouraging. The calculated results are tabulated with the previous ones of O_2 and NO chemisorption and discussed comparatively.

II. CALCULATIONS

We consider a reaction process of a diatomic molecule (AB) on a metal surface (M_s) as

$$M_s + AB \rightarrow M_s \cdots A \cdots B \cdots M_s \rightarrow M_s\text{–}A + M_s\text{–}B \quad (1)$$

where $M_s \cdots A \cdots B \cdots M_s$ represents a molecularly adsorbed state of AB which leads to the dissociative state, M_s–A + M_s–B, on the surface in the final stage of the reaction. Now we draw attention to the energy difference between the initial state and adsorbate state; the interaction energy between the molecule AB and metal surface M_s, V_{AB} may be written as

$$V_{AB} = D_{AB} - E_{A-B,sur} - E_{M_s-A} - E_{M_s-B} \quad (2)$$

where D_{AB} is the dissociation energy of the molecule AB in gas phase which is known spectroscopically. $E_{A-B,sur}$ is the total energy in the A–B bond of the adsorbing molecule on the surface and the values may be given by BEBO relation as a function of the corresponding bond order, n_{A-B}: The empirical relations for N_2 and CO molecules were found to be represented, respectively, by the following cubic equations

$$E_{N-N,sur} = 6.667 n_{N-N}^3 - 8 n_{N-N}^2 + 39.333 n_{N-N} \quad (3)$$

and

$$E_{C-O,sur} = -13.333 n_{C-O}^3 + 56 n_{C-O}^2 + 37.334 n_{C-O} \quad (4)$$

where the coefficients were determined using the known BEBO data (*1*), i.e., $E_{N-N,sur}$ = 226, 100, and 38 kcal/mol for n_{N-N} = 3, 2, and 1, respectively, and $E_{C-O,sur}$ = 256, 192, and 80 kcal/mol for n_{C-O} = 3, 2, and 1, respectively. These BEBO relations are shown in Fig. 1

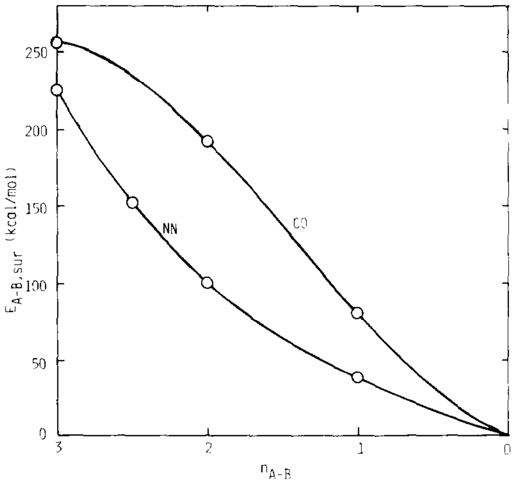

FIG. 1. Correlation between bond energy ($E_{A-B,sur}$) and bond order (n_{A-B}).

where solid lines designate calculated values using Eqs. (3) and (4). With H_2 molecule, the following relation is employed (*1*);

$$E_{\mathrm{H-H,sur}} = D_{\mathrm{H_2}} n_{\mathrm{H-H}}^{1.041}. \tag{5}$$

Further, $E_{\mathrm{M_s}-X}$ (X = A or B), the total energy in the bond formed between the surface metal and adsorbing atom, is assumed in the framework of the present BEBO model to be proportional to the corresponding bond order, $n_{\mathrm{M_s}-X}$ as

$$E_{\mathrm{M_s}-X} = E_{\mathrm{M_s}-X,\mathrm{s}} n_{\mathrm{M_s}-X} \tag{6}$$

where $E_{\mathrm{M_s}-X,\mathrm{s}}$ is the single bond energy of $\mathrm{M_s}$-X bond. We now introduce the following relation

$$n_{\mathrm{M_s-A}} + n_{\mathrm{M_s-B}} = \lambda(n_{\mathrm{A-B}}^0 - n_{\mathrm{A-B}}) \tag{7}$$

where $n_{\mathrm{A-B}}^0$ is the bond order of gaseous molecule AB at ground state and λ is a constant representing the ratio of the forming bond order, $n_{\mathrm{M_s-A}} + n_{\mathrm{M_s-B}}$, to the losing bond order, $n_{\mathrm{A-B}}^0 - n_{\mathrm{A-B}}$, during the surface reaction, (1); the relation (7) is essentially equivalent to that derived by using "bond order conservation rule" (*1*, *3*). In the present calculations, the constant λ is determined by assuming that when the molecule AB dissociates completely into $\mathrm{M_s}$–A and $\mathrm{M_s}$–B, namely, at $n_{\mathrm{A-B}} = 0$, the $n_{\mathrm{M_s-A}}$ and $n_{\mathrm{M_s-B}}$ should be equal to the bond order of the respective gas molecules, A_2 and B_2. Thus obtained λ values are summarized with those of O_2 and NO in Table 1 where the maximum bond order of carbon is taken to be 3 by referring to acetylene molecule. Using Eqs. (2), (6), and (7) one obtains

$$V_{\mathrm{AB}} = D_{\mathrm{AB}} - E_{\mathrm{A-B,sur}} - \lambda E_{\mathrm{M_s-A,s}}(n_{\mathrm{A-B}}^0 - n_{\mathrm{A-B}}) + (E_{\mathrm{M_s-A,s}} - E_{\mathrm{M_s-B,s}}) n_{\mathrm{M_s-B}}, \tag{8}$$

and

$$V_{\mathrm{AB}} = D_{\mathrm{AB}} - E_{\mathrm{A-B,sur}} - \lambda E_{\mathrm{M_s-A,s}}(n_{\mathrm{A-B}}^0 - n_{\mathrm{A-B}}) \tag{9}$$

for homonuclear diatomic molecules such as H_2, O_2, and N_2 from the relation $E_{\mathrm{M_s-A,s}} = E_{\mathrm{M_s-B,s}}$, and also for the process where the interaction of the surface with the atom B is negligible, i.e., $n_{\mathrm{M_s-B}} = 0$. Therefore, if the single bond energies between a metal and atoms A and B are known, the interaction energies due to the chemisorption may be computed using Eqs. (3)–(9). Values of these single bond energies for H, O, N, and C atoms, as the surface coverages approach zero, are listed for the 21 transition *d*-metals in Table 2. The listed values, except for the carbon atom, are the algebraical average values between $E_{\mathrm{M_s-A,s}}^{\mathrm{I}}$ and $E_{\mathrm{M_s-A,s}}^{\mathrm{II}}$ A: N, O, and H) which were evaluated previously (*6*, *7*), and they are given by

$$E_{\mathrm{M_s-A,s}}^{\mathrm{I}} = (\beta E_{\mathrm{M-M}} + E_{\mathrm{A-A,s}})/2 + 23[\gamma(X_{\mathrm{M}} - X_{\mathrm{A}})]^2, \tag{10}$$

$$E_{\mathrm{M_s-A,s}}^{\mathrm{II}} = \delta[(E_{\mathrm{M-M}} + E_{\mathrm{A-A,s}})/2 + 23(X_{\mathrm{M}} - X_{\mathrm{A}})^2]. \tag{11}$$

TABLE 1

Bond Energies, Bond Orders, and λ

Molecules AB	Bond energy D_{AB} (kcal/mol)	Bond order $n_{\mathrm{A-B}}^0$	Bond order of $\mathrm{M_s}$–A at $n_{\mathrm{A-B}} = 0$		λ
			$n_{\mathrm{M_s-A}}$	$n_{\mathrm{M_s-B}}$	
O_2	118	2	2	2	2
NO	151	2.5	3	2	2
H_2	103.2	1	1	1	2
N_2	226	3	3	3	2
CO	256	3	3	2	1.667

TABLE 2

Single Bond Energies of Metal-Adatom, $E_{M_s-A,s}$ (kcal/mol)

Metal	$E_{M_s-N,s}$	$E_{M_s-O,s}$	$E_{M_s-H,s}$	$E_{M_s-C,s}$
Ti	58.0	74.8	72.3	65.0
V	56.3	74.5	74.8	66.5
Cr	54.5	71.8	71.4	63.4
Mn	57.5	74.0	71.3	64.1
Fe	46.3	62.8	67.0	56.2
Co	44.2	59.3	63.1	52.9
Ni	44.2	59.5	63.2	53.0
Zr	64.7	82.5	79.0	71.9
Nb	59.5	80.0	80.9	72.1
Mo	50.0	68.8	74.1	63.0
Tc	42.8	59.0	66.2	55.2
Ru	33.2	47.3	64.8	49.3
Rh	32.3	45.5	63.2	47.7
Pd	30.7	42.8	59.8	44.6
Hf	70.7	89.3	84.8	77.7
Ta	65.0	86.5	86.0	77.6
W	56.8	77.8	81.7	71.8
Re	44.0	61.0	68.5	57.4
Os	34.7	49.3	67.6	51.8
Ir	33.5	47.5	66.5	49.7
Pt	32.5	46.0	63.4	47.9

Here β, γ, and δ are newly introduced parameters into Pauling–Eley's equation for single bond energy and were determined using available experimental data of adsorption heats of H_2, O_2, and N_2 molecules; they have values, respectively, of 1.0, 0.70, and 0.66 for oxygen, 0.30, 0.85, and 0.71 for nitrogen, and 0.94, 1.28, and 1.02 for hydrogen. The energy of the bond between the metal atoms, E_{M-M}, is evaluated by dividing the sublimation energy of the metals by 4 for bcc metals and by 6 for the other, and the X's are Pauling's electronegativities. On the other hand, the single bond energies of M_s–C bond have been calculated using Eq. (11) with $\delta = 0.90$ which has been determined by employing Brennan and Hayes' experimental data (*9*) of CO adsorption; the data used for the determination are in italics in Table 3, since CO is known to decompose into C and O atoms on these metals at room temperature and low CO coverage (see Section III, 3). As seen in the table, the agreement of calculated dissociative heats of adsorption of CO using $\delta = 0.90$ with the experimental ones is satisfactory except for Ti.

III. RESULTS AND DISCUSSION

1. Chemisorption of Hydrogen

In this case, using Eq. (9) and Table 1, the interaction energy V_{H_2} is given as a function of n_{H-H} by

$$V_{H_2} = 103.2(1 - n_{H-H}^{1.041}) - 2(1 - n_{H-H})E_{M_s-H,s} \quad (12)$$

for $1 \geq n_{H-H} \geq 0$, where $E_{M_s-H,s}$ is given in Table 2. Calculated results for the metals are shown in Fig. 2. The shape of the potential energy curves is similar to that of oxygen chemisorption (*8*); i.e., there is no activation energy for adsorption and also no stable molecular adsorption state for this molecule since there is no potential well throughout the bond order change, $1 \geq n_{H-H} \geq 0$, indicating that a H_2 molecule

TABLE 3

Experimental and Calculated Heats of Adsorption of CO and Calculated Stretching Frequencies (ν_{C-O}) and Bond Length (R_{C-O}) of Molecularly Adsorbed CO

Metal	Q_{exp}	Q^{C+O}_{calc} (kcal/mol)	$Q^{CO}_{calc}(E_d{}^{CO})$	ν_{C-O} (cm^{-1})	R_{C-O} (Å)
Ti	*153*	88	—	—	—
V		92	—	—	—
Cr		77	—	—	—
Mn	*78*	84	—	—	—
Fe	46	38	30	1826	1.151
Co	47	21	26	1877	1.146
Ni	42	22	26	1877	1.146
Zr	*150*	124	—	—	—
Nb	*125*	120	—	—	—
Mo	*74*	70	—	—	—
Tc		27	29	1843	1.149
Ru		−13	21	1921	1.141
Rh	46	−21	19	1941	1.140
Pd	43	−36	16	1976	1.137
Hf		155	—	—	—
Ta	*134*	150	—	—	—
W	*128*	115	—	—	—
Re		38	32	1802	1.153
Os		−1	24	1894	1.144
Ir		−11	22	1916	1.142
Pt	48	−20	20	1936	1.140

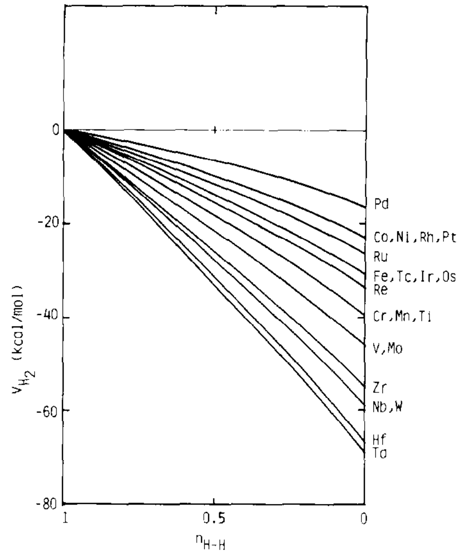

FIG. 2. Interaction energy between a H_2 molecule and a transition metal surface, V_{H_2} as a function of bond order, n_{H-H}.

easily adsorbs and dissociates on these metals. The values of the heats of dissociative adsorption, namely, the values of V_{H_2} at $n_{H-H} = 0$, are in good agreement with the experimental data (*7, 10*) as described in the previous paper (*7*).

2. *Chemisorption of Nitrogen*

The interaction energy of nitrogen with the transition metals, V_{N_2} is computed from Eq. (9) and Table 1 as a function of n_{N-N} as

$$V_{N_2} = 226 - E_{N-N,s} - 2(3 - n_{N-N})E_{M_s-N,s} \quad (13)$$

for $3 \geq n_{N-N} \geq 0$, where $E_{N-N,sur}$ and $E_{M_s-N,s}$ are given by Eq. (3) and Table 2, respectively. Calculated results are shown in Fig. 3. As may be seen in the figure, there is activation energy for nitrogen adsorption, particularly high-activation energy on Group VIII d-metals and it decreases as one goes to the left in the periodic table. Further, there is no stable molecularly adsorbed state for this molecule, since there is no potential minimum in the curves, which is similar to hydrogen or oxygen adsorption (*8*). In addition, the figure shows that the heat of dissociative adsorption is endothermic for the noble metals since the values of V_{N_2} at $n_{N-N} = 0$ are positive for these metals. These results suggest that the dissociative adsorption of molecular nitrogen is difficult at room temperature on most of the metals except a few metals such as Hf, Zr, Ta, W, Ti, Nb, V, and Cr, for which the activation energies for the adsorption are rather small (<20 kcal/mol). This prediction is qualitatively in agreement with the experiments and, as discussed by Brodén *et al.* (*11*), with the general experience from catalysis, i.e., Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, and Fe chemisorb molecular nitrogen whereas the other metals are inert: The measurements under well-defined surface conditions also seem to support this picture; polycrystalline Ti (*12–17*), Cr (*16*), Mo (*13, 18*), Ta (*19, 20*), and W (*21, 22*) as well as single crystals with various planes of Fe (*23, 24*), Mo (*25*), and W (*26, 27*) chemisorb molecular nitrogen to dissociate near room temperature.

On the other hand, nitrogen is known to be adsorbed in a molecular form when it is exposed at low temperature to such metals as Ni (*28, 29*), Pt (*30, 31*), Ru (*32*), W

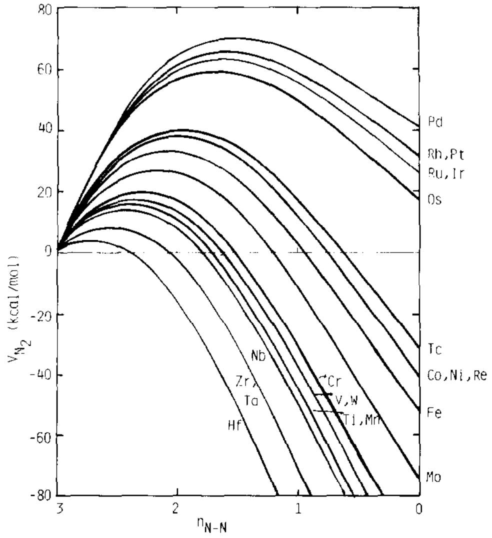

FIG. 3. Interaction energy between a N_2 molecule and a transition metal surface, V_{N_2} as a function of bond order, n_{N-N}.

(*33*), and Fe (*34*). However, such a molecular nitrogen adsorbed at low temperature usually desorbs almost completely below room temperature (*29, 34*), suggesting that this adsorption state is an unstable or a physisorbed state and not the chemisorbed one leading to the dissociation of the molecule on the surfaces.

3. Chemisorption of Carbon Monoxide

CO molecule has a 3σ and degenerated 1π molecular orbitals which contribute to the formation of the C–O bond. It also has a 5σ nonbonding orbital where the electrons are located on the C atom (*35*). Recent experimental and theoretical results indicate that molecularly adsorbed CO is initially attached through the C atom to d-metal surface, i.e., an end-on interaction through the C atom with the molecular axis perpendicular to the surface (*36–42*), followed by the dissociation of the C–O bond on some metals due to direct interaction of the O atom in the CO with the surface. Considering these facts, the following scheme consisting of two steps, (A) and (B), will be reasonably assumed for the chemisorption of CO;

$$\mathrm{M_s + CO \rightarrow M_s{\equiv}C{-}O} \qquad \text{(A)}$$

for $0 \leq n_{\mathrm{M_s-C}} \leq 3$ and $3 \geq n_{\mathrm{C-O}} \geq 1.2$, and

$$\mathrm{M_s{\equiv}C{-}O + M_s \rightarrow M_x{\equiv}C + M_s{=}O} \text{(B)}$$

for $0 \leq n_{\mathrm{M_s-O}} \leq 2$ and $1.2\ n_{\mathrm{C-O}} \geq 0$, where the change in the $n_{\mathrm{M_s-O}}$ or $n_{\mathrm{M_s-C}}$ is taken to be zero during the reaction of the step (A) and (B), respectively. The value 1.2 is a "critical value" of $n_{\mathrm{C-O}}$ at which point the effective interaction of the O atom with the surface begins to operate and it is determined from Eq. (7). The interaction energies corresponding to these steps are then given by

$$V_{\mathrm{CO}} = 256 - E_{\mathrm{C-O,sur}} - 1.667(3 - n_{\mathrm{C-O}})E_{\mathrm{M_s-C,s}} \qquad (14)$$

for step (A), and

$$V_{\mathrm{CO}} = 256 - E_{\mathrm{C-O,sur}} - 3E_{\mathrm{M_s-C,s}} - 1.667(1.2 - n_{\mathrm{C-O}})E_{\mathrm{M_s-O,s}} \qquad (15)$$

for step (B), where the $E_{\mathrm{M_s-C,s}}$ and $E_{\mathrm{M_s-O,s}}$ are given in Table 2. Calculated results using these equations are shown in Fig. 4. The shape of the potential energy curves is similar on the whole to that in the case of NO chemisorption (*8*); there is a potential well in a position of $n_{\mathrm{C-O}} = 2.5 - 2.0$ for most of the metals except Zr, Nb, W, Hf, and Ta, indicating that the chemisorption leading to a stable or metastable molecular adsorption state may occur on these metals without any activation energy. In particular, a stable molecularly adsorbed state may exist for the noble metals such as Pd, Rh, Pt, Ru, and Ir, since for these metals the values of the activation energy for the dissociation of the adsorbed CO into $\mathrm{M_s{-}C + M_s{-}O}$, $E_{\mathrm{a}}^{\mathrm{C+O}}$, measured from the position of the potential well are much

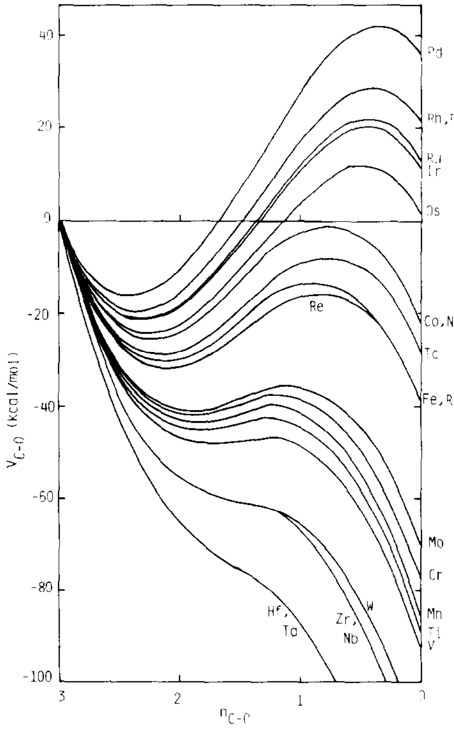

FIG. 4. Interaction energy between a CO molecule and a transition metal surface, V_{CO} as a function of bond order, $n_{\mathrm{C-O}}$.

larger than those of the activation energy of CO desorption from the molecularly adsorbed state, E_d^{CO}. The E_d^{CO} is, in the present case, equivalent to the heat of adsorption of CO in the molecular form, Q_{calc}^{CO}. In addition, it is suggested from the figure that dissociation of CO is negligible on the noble metal surfaces since the values of the V_{CO} at $n_{C-O} = 0$ are positive, which is similar to the above case of N_2 chemisorption on the same group metals. However, as seen in Fig. 4, the E_a^{C+O} decreases with increase in E_d^{CO}, and these two values become comparable for the cases of Ni and Co. Therefore, it is expected that both states, dissociative and nondissociative, may exist on these metals and the ratio of each type will depend on adsorption temperature and pressure, surface coverage (*99*), etc. The dissociaiton will be more feasible on Fe and Re metals than Ni and Co since the E_a^{C+O} in the former metals is obviously smaller than these in the latter ones. In addition, CO molecule will almost completely dissociate on the metals such as Mo, Cr, Mn, Ti, and V as well as Zr, Nb, W, Hf, and Ta, since the values of the E_a^{C+O} for these metals are very small or zero.

It is of interest to compare these predicted features of CO chemisorption with reported experimental results: It is generally agreed that CO is adsorbed in a molecular form at room temperature on noble *d*-metals such as Ru (*43–52*), Rh (*53–60*), Pd (*46, 61–70*), Ir (*11, 71, 72*), and Pt (*70, 71, 74–79*). But the behavior on clean surfaces of the metals such as Ti (*9, 12, 14, 17*), Nb (*9, 80*), Ta (*9, 80, 81*), W (*9, 82, 83*), Mo (*84–86*), and Mn (*9, 87*) is different, i.e., CO is completely or nearly completely decomposed into C and O atoms on these metals at room temperature and low surface coverage. The chemisorption properties of Fe, Co, Ni, and Re metals are known to be more complex; there both dissociative and nondissociative adsorbed states can coexist near room temperature. The ratio of these states is sensitive to the adsorption temperature (*88–90, 97*), degree of surface coverage (*41, 91*), or surface geometry (*11, 88, 92*); for instance, Joyner and Roberts (*89*) provided evidence that CO adsorbs in a molecular form at 290°K on Ni surface but dissociates at 400°K and they proposed that a heat of adsorption value 70 kcal/mol is required for CO dissociation. Kishi and Roberts (*90*) also studied this problem for Fe films and found that dissociation occurs slowly at 290°K but proceeds rapidly at 623°K. Yu *et al.* (*93*) reported similar results, i.e., CO exists nondissociatively on Fe at 117°K but it dissociates at room temperature. Thus, qualitative features of CO chemisorption seem to be in good agreement with the above predictions. Quantitative comparison between calculated and experimental (*9*) heats of adsorption is given in Table 3: It reveals good agreement in dissociative heats of adsorption on metals as Mn, Zr, Nb, Mo, Ta, and W except Ti, but some differences in nondissociative heats of adsorption, i.e., most of the calculated values are less than the experimental ones. The latter values obtained more recently are, however, more encouraging, namely, 26.5 (*94*), 30 (*95–97*) kcal/mol for Ni, 30 kcal/mol (*76*) for Pt, 31.6 kcal/mol (*58*) for Rh, etc., which are somewhat less than those by Brennan *et al.* and thereby are closer to the calculated values.

In addition, it is possible to evaluate empirically stretching frequencies (ν_{C-O}, cm^{-1}) and bond length (R_{C-O}, Å) of molecularly adsorbed CO at the potential well in Fig. 4 by using the following relationships between the bond energy of C–O, E_{C-O} and ν_{C-O} and R_{C-O}:

$$\nu_{C-O} = 520 + 6.35E_{C-O} \tag{16}$$

and

$$R_{C-O} = 6.608 - 4.388\log E_{C-O} + 0.877(\log E_{C-O})^2. \tag{17}$$

The relations (16) and (17) are obtained empirically from the known data of C–O bond, i.e., E_{C-O} = 256, 192, and 80 kcal/mol for ν_{C-O} = 2143, 1738, and 1030

cm^{-1} and for R_{C-O} = 1.128, 1.162, and 1.434 Å, respectively (*1*). The calculated results which are obtained by replacing the E_{C-O} in Eqs. (16) and (17) with the $E_{C-O,sur}$ at the potential well are given in Table 3. Calculated stretching frequencies of adsorbed CO are mostly in the range of 1800–2000 cm^{-1}, increasing as one proceeds to the right in the periodic table; this trend is agreeable with our general experience of ir spectra of adsorbed CO on the surfaces of the transition d-metals or transition monometal monocarbonyls (*98*). In addition, Passler *et al.* (*37*) have recently determined the bond length of adsorbed CO on Ni[100] surface by LEED and UPS analyses to be 1.15 Å which is very close to the present calculated value, 1.146 Å.

4. *Classification of the Metals*

So far we have considered the adsorption properties of clean transition *d*-metal surfaces for several diatomic molecules, focusing particularly on the two problems which arise when the molecules are exposed to the surfaces; i.e., (i) does the molecule chemisorb on the surface and (ii) whether the adsorbed species is in a molecular form or dissociative form. These are important problems for catalytic chemical reactions; as described above, methanation reaction can possibly take place by more than one mechanism depending on whether CO is either associatively or dissociatively adsorbed on the metal, further, Rabo *et al.* recently found that the metals which are active in promoting CO dissociation are also good methanation catalysts (*46*). The results described qualitatively in the previous sections for the above problems are summarized in Table 4, where the earlier results of O_2 and NO chemisorption are also included. The behavior of the metals considered here seems to enable them to be divided approximately into four categories, A, B, C, and D groups. The groups and the metals in each group are designated in order of decreasing dissociative heat of adsorption, but the order is changeable for the metals being near the borderlines between the groups depending on kind of the adsorbed molecule, particularly for the case of hydrogen (see Table 2).

The A group metals consisting of mainly IV_B, V_B, and VI_B group metals in the periodic table strongly chemisorb all the gases in dissociative form and hardly chemisorb in the molecular form at room temperature. On the contrary, the group D metals consisting of noble *d*-metals do not decompose CO and N_2 molecules and chemisorb heteronuclear diatomic molecules (CO and

TABLE 4

Classification of Transition *d*-Metals Based on Adsorption Properties

Group	Metals	Adsorption state									
		Dissociative form					Nondissociative form				
		H_2	O_2	N_2	NO	CO	H_2	O_2	N_2	NO	CO
A	Hf, Ta, Zr, Nb, W, Ti, V, Mn, Cr, Mo	+	+	+	+	+	−	−	−	−	−
B	Fe, Re	+	+	+	+	+	−	−	−	+	+
C	Ni, Co, Tc	+	+	−	+	+	−	−	−	+	+
D	Os, Ir, Ru, Pt, Rh, Pd	+	+	−	+	−	−	−	−	+	+

Note. + indicates possible, − impossible.

NO) in the molecular form. The group B and C metals, which are known as main elements of catalysts for the reactions of Fischer–Tropsch (*101*) and ammonia syntheses, have intermediate adsorption properties between the A and D group metals and the former metals are closer rather to the A group metals and the latter to the D group ones. It is, however, of note that the present classification is not rigid particularly for "intermediate metals" or group B and C metals and also for the metals located near the borderlines between the groups, on which the adsorption properties strongly depend upon adsorption temperature, surface coverage (*99*), geometry of exposed surface, etc.

Finally, this classification mostly agrees with that based on experimental data due to Brennan *et al.* (*100*) and also with a recent classification or criterion due to Brodén *et al.* (*11*) that the ability of transition metals to dissociate adsorbed diatomic molecules increases in general as one goes to the left in the periodic table.

Thus, the BEBO model combined with parameterized Pauling–Eley's equation seems to give an answer to the above problems of chemisorption, and the present quantitative and qualitative results are expected to be useful for the studies of heterogeneous catalytic reactions as well as chemisorption of gases (*102*).

REFERENCES

1. Johnston, H. S., "Gas Phase Reaction Rate Theory." Ronald Press, New York, 1966.

2. Bond, G. C., *Disc. Faraday Soc.* **41,** 200 (1966).

3. Weinberg, W. H., and Merrill, R. P., *Surface Sci.* **33,** 493 (1972); **39,** 206 (1973); **41,** 312 (1974); *J. Catal.* **40,** 268 (1975); Weinberg, W. H., *J. Catal.* **28,** 459 (1973).

4. Weinberg, W. H., *J. Vacuum Sci. Technol.* **10,** 89 (1973).

5. Knor. Z., *J. Catal.* **47,** 140 (1977).

6. Miyazaki, E., and Yasumori, I., *Surface Sci.* **55,** 747 (1976).

7. Miyazaki, E., *Surface Sci.* **71,** 741 (1978).

8. Miyazaki, E., and Yasumori, I., *Surface Sci.* **57,** 755 (1976).

9. Brennan, D., and Hayes, F. H., *Proc. Roy. Soc.* **A 258,** 347 (1965).

10. Cerný, S., Ponec, V., and Hladek, L., *J. Catal.* **5,** 27 (1966).

11. Brodén, G., Rhodin, T. N., Brucker, C., Benbow, R., and Hurych, Z., *Surface Sci.* **59,** 593 (1976).

12. Brearley, W., and Surplice, N. A., *Surface Sci.* **64,** 372 (1977).

13. Fromm, E., *Proc. 3rd Int. Congr. Surface Sci.* **II,** 889 (1977).

14. Shih, H. D., Jona, F., Jepsen, D. W., and Marcus, P. M., *Phys. Rev. Lett.* **36,** 798 (1976).

15. Nagasaka, M., and Yamashina, T., *J. Vac. Sci. Technol.* **9,** 543 (1971).

16. Andersson, S., and Nyberg, C., *Surface Sci.* **52,** 489 (1975).

17. Eastman, D. E., *Solid State Commun.* **10,** 933 (1972).

18. Kunimori, K., Kawai, T., Kondow, T., Onishi, T., and Tamaru, K., *Surface Sci.* **54,** 525 (1976).

19. Bauer, U., and Fromm, E., *Surface Sci.* **52,** 415 (1975).

20. Gasser, R. P. H., Lawrence, C. P., and Newman, D. G., *Trans. Faraday Soc.* **62,** 2916 (1966).

21. Yates, J. T., Jr., and Madey, T. E., *J. Chem. Phys.* **43,** 1055 (1975).

22. Oguri, T., *J. Phys. Soc. Japan* **18,** 1280 (1963).

23. Bozso, F., Ertl, G., and Weiss, M., *J. Catal.* **50,** 519 (1977).

24. Bozso, F., Ertl, G., Grunze, M., and Weiss, M., *J. Catal.* **49,** 18 (1977).

25. Han, H. R., and Schmidt, L. D., *J. Phys. Chem.* **75,** 227 (1971).

26. Housley, M., and King, D. A., *Surface Sci.* **62,** 93 (1977).

27. Adams, D. L., and Gomer, L. H., *Surface Sci.* **26,** 109 (1971).

28. Kirby, R. E., McKee, C. S., and Roberts, M. W., *Surface Sci.* **55,** 725 (1976).

29. King, D. A., *Surface Sci.* **9,** 375 (1968).

30. Wilf, M., and Dawson, P. T., *Surface Sci.* **60,** 561 (1976).

31. Shigeishi, P. A. and King, D. A., *Surface Sci.* **62,** 379 (1977).

32. Danielson, L. R., Dresser, M. J., Donaldson, E. E., and Dickinson, J. T., *Surface Sci.* **71,** 599 (1978).

33. Fuggle, J. C., and Menzel, D., *Proc. 3rd Int. Congr. Surf. Sci.* **II,** 1003 (1977).

34. Kishi, K., and Roberts, M. W., *Surface Sci.* **62,** 252 (1977).

35. Ransil, B. L., *Rev. Mod. Phys.* **32,** 245 (1960).

36. Li, C. H., and Tong, S. Y., *Phys. Rev. Lett.* **43,** 526 (1979).

37. Passler, M., Ignatiev, A., Jona, F., Jepsen, D. W., and Marcus, P. M., *Phys. Rev. Lett.* **43,** 360 (1979).

38. Andersson, S., and Pendry, J. B., *Phys. Rev. Lett.* **43,** 363 (1979).

39. Erley, W., Wagner, H., and Ibach, H., *Surface Sci.* **80,** 612 (1979).
40. Madey, T. E., *Surface Sci.* **77,** 575 (1978).
41. Fleisch, T., Otto, G. L., Delgass, W. N., and Winograd, N., *Surface Sci.* **81,** 1 (1979).
42. Smith, R. T., Anderson, J., and Lapeyre, G. J., *Phys. Rev. Lett.* **37,** 1081 (1976); Apai, G., Wehner P. S., Williams, R. S., Stohr, J., and Shirley, D. A., *Phys. Rev. Lett.* **37,** 1497 (1976).
43. Kobayashi, M., and Shirasaki, T., *J. Catal.* **32,** 254 (1974).
44. Dalla Betta, R. A., and Shelef, M., *J. Catal.* **48,** 111 (1977).
45. McCarty, J. G., and Wise, H., *Chem. Phys. Lett.* **61,** 323 (1979).
46. Rabo, J. A., Risch, A. P., and Poutsma, M. L., *J. Catal.* **53,** 295 (1978).
47. Sachtler, J. W. A., Kool, J. M., and Ponec, V., *J. Catal.* **56,** 284 (1979).
48. Klein, R., *Surface Sci.* **20,** 1 (1970).
49. Brown, M. F., and Gonzalez, R. D., *J. Phys. Chem.* **80,** 1731 (1976).
50. Goodman, D. W., Madey, T. E., Ono, M., and Yates, J. T., Jr., *J. Catal.* **50,** 279 (1977).
51. Thomas, G. E., and Wienberg, W. H., *J. Chem. Phys.* **70,** 954 (1978); **70,** 1437 (1978).
52. Kaemer, K., and Menzel, D., *Ber. Bunsen Gesellschaft* **79,** 649 (1977).
53. Wells, M. G., Cant, N. W., and Greenler, R. G., *Surface Sci.* **67,** 541 (1977).
54. Sexton, B. A., and Somorjai, G. A., *J. Catal.* **46,** 167 (1977).
55. Eckstrom, H. C., Possley, G. G., Hannum, S. E., and Smith, W. H., *J. Chem. Phys.* **52,** 5435 (1970).
56. Castner, D. G., Sexton, B. A., and Somorjai, G. A., *Surface Sci.* **71,** 519 (1978).
57. Klein, J., Leger, A., de Cheveigne, S., Guinet, C., Belin, M., and Defourneau, D., *Surface Sci.* **82,** L288 (1979).
58. Thiel, P. A., Williams, E. D., Yates, J. T., Jr., and Weinberg, W. H., *Surface Sci.* **84,** 54 (1979).
59. Cambell, C. T., and White, J. M., *J. Catal.* **54,** 289 (1978).
60. Yates, J. T., Jr., Worley, S. D., Duncan, T. M., and Vaughan, P. W., *J. Chem. Phys.* **70,** 1219 (1978).
61. Conrad, H., Ertl, G., and Latta, E. E., *J. Catal.* **35,** 363 (1974).
62. Palazov, A., Chang, C. C., and Kokes, R. J., *J. Catal.* **36,** 338 (1975).
63. Bradshaw, A. M., and Hoffmann, F. M., *Surface Sci.* **72,** 513 (1978).
64. Stephan, J. J., Franke, P. L., and Ponec, V., *J. Catal.* **44,** 359 (1976).
65. Soma-Noto, Y., and Sachtler, W. M. H., *J. Catal.* **32,** 315 (1974).
66. Conrad, H., Ertl, G., Koch, J., and Latta, E. E., *Surface Sci.* **43,** 462 (1974).
67. Tracy, J. C., and Palmberg, P. W., *J. Chem. Phys.* **51,** 4852 (1969).
68. Bader, S. D., Blakely, J. M., Brodsky, M. B., Friddle, R. J., and Panosk, R. L., *Surface Sci.* **74,** 405 (1978).
69. Conrad, H., Ertl, G., and Kuppers, J., *Surface Sci.* **76,** 323 (1978).
70. Hoffmann, F. M., and Bradshaw, A. M., *J. Catal.* **44,** 328 (1976).
71. Zhdan, P. A., Boreskov, G. K., Boronin, A. I., Schepelin, A. P., Egelhoff, W. F., Jr., and Weinberg, W. H., *Surface Sci.* **71,** 267 (1978).
72. Nieuwenhuys, B. E., and Somorjai, G. A., *Surface Sci.* **72,** 8 (1978).
73. McCabe, R. W., and Schmidt, L. D., *Surface Sci.* **66,** 101 (1977).
74. Bernsek, S. L., and Somorjai, G. A., *Surface Sci.* **48,** 204 (1975).
75. Brodén, G., Pirug, G., and Bonzel, H. P., *Surface Sci.* **72,** 513 (1978).
76. Kelemen, S. R., Fischer, T. E., and Schwarz, J. A., *Surface Sci.* **81,** 440 (1979).
77. Netzer, F. P., and Mathew, J. A. D., *Surface Sci.* **81,** L651 (1979).
78. Norton, P. R., Goodale, J. W., and Selkirk, E. B., *Surface Sci.* **83,** 189 (1979).
79. Matsushima, T., *J. Catal.* 55, 337 (1978).
80. Haas, T. W., Grant, J. T., and Dooley, G. J., "Adsorption and Desorption Phenomena" (F. Ricca, Ed.), p. 359. Academic Press, New York, 1972.
81. Belov, V. D., Ustinov, Y. K., and Komar, A. P., *Surface Sci.* **72,** 390 (1978).
82. Baker, J. M., and Eastman, D. E., *J. Vac. Sci. Technol.* **10,** 223 (1973).
83. Adnot, A., and Carette, J. D., *Surface Sci.* **75,** 109 (1978).
84. Felter, T. E., and Estrup, P. J., *Surface Sci.* **54,** 179 (1976).
85. Dawson, P. H., *Surface Sci.* **71,** 247 (1978); **76,** 464 (1978).
86. Petersson, L. G., Melander, R., and Hagstrom, S. B. M., *Chem. Phys. Lett.* **61,** 127 (1979).
87. Bickley, R. I., Roberts, M. W., and Storey, W. C., *J. Chem. Soc.* (A) 2774 (1971).
88. Erley, W., Ibach, H., Lehwald, S., and Wagner, H., *Surface Sci.* **83,** 585 (1979).
89. Joyner, R. W., and Roberts, M. W., *Chem. Phys. Lett.* **29,** 447 (1974).
90. Kishi, K., and Roberts, M. W., *J. Chem. Soc. Faraday I* **71,** 1715 (1975).
91. McCoy, E. F., and Smart, R. ST. C., *Surface Sci.* **39,** 109 (1973).
92. Mason, R., and Somorjai, G. A., *Chem. Phys. Lett.* **44,** 468 (1976).
93. Yu, K. Y., Spicer, W. E., Lindau, I., Pianetta, P., and Lin, S. F., *Surface Sci.* **57,** 157 (1976).
94. Christmann, K., Schober, O., and Ertl, G., *J. Chem. Phys.* **60,** 4716 (1974).

95. Wedler, G., Parr, H., and Schroll, G., *Surface Sci.* **44,** 463 (1974).

96. Tracy, J. C., *J. Chem. Phys.* **56,** 2736 (1972).

97. Madden, H. H., Küppers, J., and Ertl, G., *J. Chem. Phys.* **58,** 3401 (1973).

98. Ozin, G. A., *Acc. Chem. Res.* **10,** 21 (1977).

99. Miyazaki, E., *J. Catal.* **33,** 57 (1974); *3rd Int. Congr. Surf. Sci.* **I,** 801 (1977); *J. Math. Phys.* **20,** 184 (1979).

100. Brennan, D., Hayward, D. O., and Trapnell, B. M. W., *Proc. Roy. Soc.* **A256,** 81 (1960); Hayward, D. O., "Chemisorption and Reactions on Metallic Films" (J. R. Anderson Ed.), Vol. I. Academic Press, New York, 1971; Bond, G. C., "Catalysis by Metals," p. 66. Academic Press, New York; 1962.

101. Vannice, M. A., *Catal. Rev.* **14,** 153 (1976); Ponec, V., *Catal. Rev.* **18,** 151 (1978).

102. Haydock, R., and Wilson, A. J., *Surface Sci.* **82,** 425 (1979).