

Springer Series in Surface Sciences 1

H.J. Kreuzer · Z.W. Gortel

Physisorption Kinetics



Springer Verlag
Berlin Heidelberg New York Tokyo

6044167

H.J. Kreuzer
Z.W. Gortel

Physisorption Kinetics

With 133 Figures



Springer-Verlag
Berlin Heidelberg New York Tokyo

Professor Dr. Hans Jürgen Kreuzer

Department of Physics, Dalhousie University
Halifax, Nova Scotia, Canada B3H 3J5

Professor Dr. Zbigniew Wojciech Gortel

Department of Physics, University of Alberta
Edmonton, Alberta, Canada T6G 2J1

Guest Editor

Professor Dr. J. Peter Toennies

Max-Planck-Institut für Strömungsforschung, Böttingerstraße 6–8
D-3400 Göttingen, Fed. Rep. of Germany

Series Editors

Professor Dr. Gerhard Ertl

Institut für Physikalische Chemie, Universität München, Sophienstraße 11
D-8000 München, Fed. Rep. of Germany

Professor Robert Gomer

The James Franck Institute, The University of Chicago, 5640 Ellis Avenue,
Chicago, IL 60637, USA

ISBN 3-540-16176-7 Springer-Verlag Berlin Heidelberg New York Tokyo
ISBN 0-387-16176-7 Springer-Verlag New York Heidelberg Berlin Tokyo

Library of Congress Cataloging-in-Publication Data. Kreuzer, H.J. (Hans J.) Physisorption kinetics. (Springer series in surface sciences ; v. 1) Bibliography: p. Includes index. 1. Adsorption. I. Gortel, Z.W. (Zbigniew Wojciech), 1944-. II. Title. III. Series: Springer series in surface sciences ; 1. QD547.K74 1986 541.3'453 85-30307

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically those of translation, reprinting, reuse of illustrations, broadcasting, reproduction by photocopying machine or similar means, and storage in data banks. Under § 54 of the German Copyright Law where copies are made for other than private use, a fee is payable to "Verwertungsgesellschaft Wort", Munich.

© Springer-Verlag Berlin Heidelberg 1986
Printed in Germany

The use of registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Offsetprinting: Beltz Offsetdruck, 6944 Hemsbach/Bergstr. Bookbinding: J. Schäffer OHG, 6718 Grünstadt 2153/3150-543210

Springer Series in
Surface Sciences

Guest Editor: J. Peter Toennies

Springer Series in **Surface Sciences**

Editors: Gerhard Ertl and Robert Gomer

Volume 1: Physisorption Kinetics

By H. J. Kreuzer, Z. W. Gortel

Volume 2: The Structure of Surfaces

Editors: M. A. Van Hove, S. Y. Tong

Volume 3: Dynamical Phenomena at Surfaces, Interfaces and Superlattices

Editors: F. Nizzoli, K.-H. Rieder, R. F. Willis

Volume 4: Desorption Induced by Electronic Transitions, DIET II

Editors: W. Brenig, D. Menzel

Volume 5: Chemistry and Physics of Solid Surfaces, VI

Editors: R. Vanselow, R. Howe

Volume 6: Secondary Ion Mass Spectrometry SIMS V

Editors: R. J. Colton, D. S. Simons,
A. Benninghoven, H. W. Werner

Preface

This monograph deals with the kinetics of adsorption and desorption of molecules physisorbed on solid surfaces. Although frequent and detailed reference is made to experiment, it is mainly concerned with the theory of the subject. In this, we have attempted to present a unified picture based on the master equation approach. Physisorption kinetics is by no means a closed and mature subject; rather, in writing this monograph we intended to survey a field very much in flux, to assess its achievements so far, and to give a reasonable basis from which further developments can take off. For this reason we have included many papers in the bibliography that are not referred to in the text but are of relevance to physisorption.

To keep this monograph to a reasonable size, and also to allow for some unity in the presentation of the material, we had to omit a number of topics related to physisorption kinetics. We have not covered to any extent the equilibrium properties of physisorbed layers such as structures, phase transitions and thermodynamic properties in general. A number of excellent review articles, listed in the bibliography, cover this material. Likewise, little is said about scattering off solid surfaces; this subject is again covered in several books and many review articles. Lastly, little is said about chemisorption kinetics, for which microscopic theories and models have not been fully developed but are still at a rather early exploratory stage. It is the hope of the eternal optimists that we might learn something from physisorption kinetics to continue the task.

Halifax and Edmonton,
Canada, 1985

H.J. Kreuzer
Z.W. Gortel

1. Introduction	1
1.1 Adsorption Phenomena: a Brief Survey	1
1.2 Survey of Experimental Methods	17
2. Gas-Solid Interaction	23
2.1 The Static Surface Potential $V_S(r)$	23
2.2 Mean-Field Surface Potential at Finite Coverage	43
2.3 The Dynamic Atom-Solid Interaction	55
2.4 Phonon Dynamics of a Solid	64
2.5 The Gas-Solid Hamiltonian	86
3. The Master Equation	89
3.1 The Mesoscopic Approach to the Master Equation	89
3.2 The Master Equation for Physisorption Kinetics	96
3.3 The Microscopic Approach to the Master Equation	103
3.4 The Master Equation at Finite Coverage	107
4. Transition Probabilities in the Master Equation	112
4.1 One-phonon Processes at Low Coverage	112
4.2 Multi-phonon Processes and Correlation Functions	122
4.3 Soft Cube Model and Phenomenological Models at Low Coverage	133
4.4 Mean-Field Theory at Finite Coverage	141
5. Desorption Times	142
5.1 Model System with Two Bound States	143
5.2 Systems with a Few Shallow Bound States	146
5.3 Perturbation Theory of the Master Equation	150
5.4 Desorption Kinetics Mediated by Surface Phonons	157
5.5 Inclusion of Parallel Phonon Momentum for Mobile Desorption	159
5.6 Desorption from a Localized Adsorbate	164

5.7	Cole-Toigo Corrections	173
5.8	Multiphonon Contributions	176
5.9	Multilayer Desorption	181
5.10	Adsorbent Cooling in Thermal Desorption	186
5.11	Flash Desorption and Thermalization	190
6.	Time of Flight Spectra	198
6.1	Experiments	198
6.2	Flux of Desorbed Particles	207
6.3	One-phonon Processes	213
6.4	Classical Models	220
7.	Sticking and Accommodation	223
7.1	Experimental Results	223
7.1.1	Sticking Coefficient	223
7.1.2	Accommodation Coefficient	227
7.2	Theory	229
7.2.1	Sticking	229
7.2.1(a)	Quantum Theories of Sticking	229
7.2.1(b)	Classical Theories of Sticking	242
7.2.2	Energy Accommodation	251
7.2.2(a)	Quantum Theories of Accommodation	251
7.2.2(b)	Classical Theories of Accommodation	256
8.	Kramers Equation	259
8.1	Derivation from the Master Equation	261
8.2	Macroscopic Laws	269
8.3	Friction Coefficient	276
8.4	Hydrodynamics of Adsorption	277
9.	Summary and Outlook	282
9.1	Progress and Problems	282
9.2	Related Topics I: Photodesorption	283
9.3	Related Topics II: Electron-Stimulated Desorption	285
9.4	Approaches to Chemisorption Kinetics	286
References	293
Subject Index	317

1. Introduction

1.1 Adsorption Phenomena: a Brief Survey

Adsorption is the result of the interaction of a gas with a solid. Gas particles approaching the surface of a solid experience, at distances of a few angstroms above the surface, a net attraction that changes over to a strong repulsion closer in. If a gas particle can rid itself of enough energy, it will be bound to the surface: it is said to be part of the adsorbate. To understand the structure and the dynamics of an adsorbate, one must conceive the gas phase and the adsorbate as two coupled systems open to exchange of energy and particles, coupled in addition to the solid for energy exchange, and sometimes particle exchange, e.g., when gas particles or products thereof diffuse into the solid, or when surface reactions like oxidation of the solid take place. The term adsorption was, according to Kayser (1881), introduced by du Bois-Reymond.

The interaction between a gas and a solid is, of course, electromagnetic in nature. To develop a meaningful picture that incorporates its salient features, we follow Lennard-Jones (1932) and start with an isolated solid and an atom far away from its surface. For the present discussion, we consider a metal for which we adopt the Sommerfeld model of free electrons in which the lattice of ionic cores is smeared out into a uniform positively charged "jellium" background. The conduction band is filled with electrons up to the Fermi level E_F as indicated on the left of Fig. 1.1. The work function ϕ of the metal is the energy required to remove an electron at the Fermi level from inside the metal to infinity. On the far right of Fig. 1.1 we depict the electronic potential well of a free atom far from the surface. Its ionization energy E_I is the energy required to remove the most weakly bound electron from the atom or molecule; the affinity level E_A is the energy gained by attaching an electron to the particle to create a negative ion; typical values are given in Table 1.1. Let us now adiabatically bring the atom or molecule close to the surface and eventually into an adsorption site. As a result of the interaction between the electrons of the particle and those of the metal, the ionization and affinity levels will

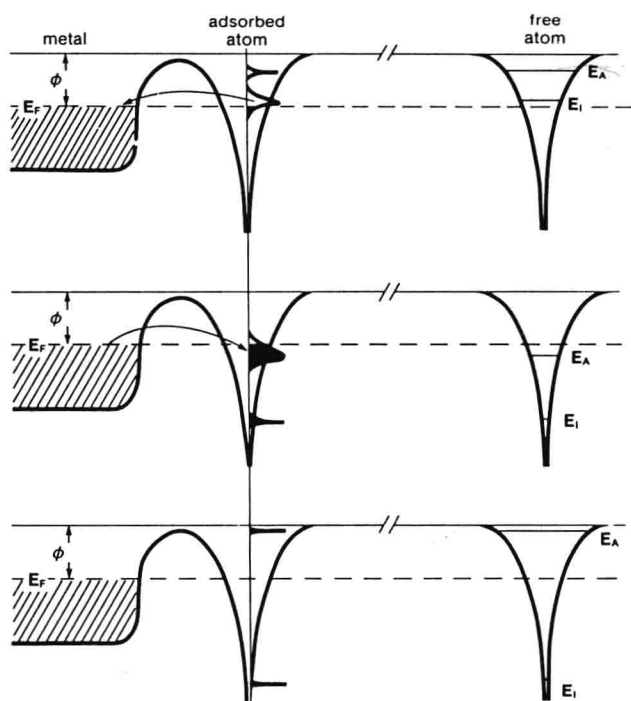


Fig. 1.1. The Lennard-Jones model of atomic adsorption on a metal. E_F = Fermi energy; ϕ = work function; E_I = ionisation energy; E_A = affinity level. Also indicated is the electronic density of states on the adsorbed atom. Arrows indicate charge transfer.

Table 1.1. Ionization energies E_I and electron affinities E_A for isolated atoms and molecules (Franklin and Harland 1974) and work functions ϕ of some metals (Hölzl and Schulte 1979).

	E_I [eV]	E_A [eV]	Metal	ϕ [eV]
H	13.59	0.76	Al	4.06-4.41
He	24.48	0.08	Mg	3.66
Li	5.39	0.65	Na	2.36-2.46
C	11.27	1.2	K	2.01-2.55
O	13.61	1.5	Cu	4.48-5.10
F	17.42	3.4	Ag	4.0 -4.74
O ₂	12.06	≥0.45	Au	5.1 -5.47
S	10.36	2.07	W	4.3 -5.22
Cl	13.01	3.6	Pt	5.12-5.93
W	7.98	0.5	Ru	4.71
N ₂ O	12.89	≤1.5	Fe	4.5 -4.81

shift and broaden into resonances as Gurney pointed out in 1935. Depending on the relative positions of E_I and E_A with respect to E_F , we can distinguish several broad areas of adsorption phenomena, depending on the charge transfer and the kind of bonds established.

If, in the adsorbed particle, the ionization energy E_I is above the Fermi energy, one typically encounters a positively charged adsorbate resulting from electron transfer to the metal. This is the case, for example, for alkalis on most metals. If E_A , on the other hand, is below the Fermi level, electrons are transferred to the adsorbate as happens for halogens on transition metals. For E_A above and E_I below the Fermi level, neutral adsorbates are encountered that for $|E_A - E_F|$ and $|E_I - E_F|$ small, as in the case of Si on metals, establish covalent bonds. Gurney (1935) emphasized that, whereas E_I and E_A correspond to sharp energy levels in the isolated molecule, they broaden into resonances upon adsorption, indicated in Fig. 1.1 by the density of states localized on the adparticle. Depending on the Fermi energy E_F of the metal, these resonances might be partially occupied, leading to a fractionally charged adsorbate. As the latter now makes up an electrical double layer, the work function of the metal is effectively changed as a function of the amount of gas adsorbed. In all three of the above situations, we speak of chemisorption: rearrangement of electronic orbitals possibly accompanied by charge transfer, results in net energy gains upon adsorption, i.e., in heats of adsorption, of the order of electron volts. Because bonding orbitals are established between the adsorbate and the solid, chemisorption is usually restricted to less than a monolayer, with often several adsorption sites present on the various surface planes of a crystal that may change their characteristics as a monolayer fills up. That adsorption can be likened to chemical reactions, was emphasized by Langmuir (1916); earlier speculations are due to Bone and Wheeler (1906) (see also Bone 1922) and Haber (1914a and b). The term chemisorption was, according to Lennard-Jones (1932), coined by Benton and White (1931), although in that reference they refer to primary and secondary adsorption. It took another 40 years until the picture of chemisorption sketched in Fig. 1.1 was quantitatively worked out in the functional density approach (e.g., Lang and Williams 1978) and in Anderson-type models (e.g., Newns 1969; Einstein 1975).

Returning to the discussion of Fig. 1.1, we lastly look at a situation where the electron affinity of the adsorbing molecule is very small or even negative and its ionization energy E_I is large compared to the work function ϕ of the metal. In such systems, the electronic configuration of the

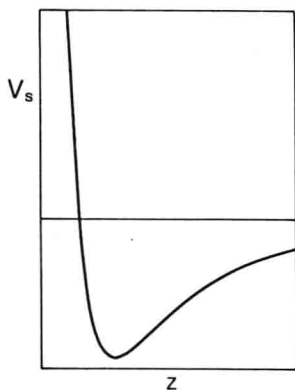


Fig.1.2. The surface potential of physisorption.

adsorbing particle is but slightly changed, i.e., only to the extent of an overall polarization producing an induced dipole that interacts with its image in the metal. This interaction can be modeled by an attractive van der Waals-type potential, acting on the (pointlike) adsorbate particle. Asymptotically far from the surface, it decreases as z^{-3} where z is the distance of the molecule from the surface. Closer to the surface, electron overlap produces strong repulsion. The resulting surface potential is sketched in Fig. 1.2. Particles adsorbed by this van der Waals mechanism are said to be physically adsorbed or physisorbed. Most typical are rare gases on metals, on alkali halides, and on graphite. A list of physisorbed systems, for which at least some kinetic data are available, is given in Table 1.2 where we also give the heat of adsorption (which is roughly the depth of the surface potential) and various kinetic data to be discussed later. In addition to rare gases, Table 1.2 lists rather inert molecules like CH_4 that physisorb on metals, and a number of other molecules, such as N_2O , that either chemisorb or physisorb on metals. Indeed, as indicated in our short discussion on chemisorption, once all "dangling" bonds have been used up at a surface for chemisorption, additional molecules will only be subject to dispersion forces of the van der Waals type, i.e., get physisorbed, unless bulklike condensation in the adsorbate takes place.

Before Langmuir (1916) stressed the monolayer character of chemisorption, it was generally believed that adsorption of a gas results in a transition layer which Eucken (1914) treated as a kind of miniature atmosphere through which particles must diffuse to react with the surface. At the 1932 Faraday Discussion "On the Adsorption of Gases and on Theories of the Adsorption of Gases", a clear distinction between physical adsorption due to weak van der Waals forces and chemical adsorption due to bonding forces was worked out [see articles by Lennard-Jones (1932) and Polanyi (1932)].

Table 1.2. Kinetic data for physisorbed gas-solid systems. Numbers in parentheses are estimates. References are given by first author only.

Gas	Solid	T [K]	θ_0 [10^{14}cm^{-2}]	θ/θ_0	E_d [kJ mole $^{-1}$]	ν [s $^{-1}$]	S	Reference
He	Ar	3.25	--	--	1.26 \pm 0.06	--	0.48	Lee(1974)
He	Kr	3.20	--	--	1.27 \pm 0.06	--	0.38	"
He	Xe	3.40	--	--	1.54 \pm 0.08	--	0.37	"
He	Nichrome	1.5-3.75	--	≤ 1	0.17-0.54	(0.67-10) $\times 10^9$	--	Sinvani et al.(19872)
He		3.6	--	0 and 0.7	--	--	>0.66	Sinvani et al.(1983)
He	Constantan	3.5-3.8	--	≤ 1	0.49-0.36	(2.5-51) $\times 10^9$	--	"
He	Sapphire	3.6	--	0 and 0.7	--	--	>0.66	"
Xe	C(0001)	85-102	6.35	0.002-0.08	20-23	--	--	Suzanne et al.(1973,1974)
		74-80	5.7	0.3-0.9	25.1 \pm 1.7	--	0.65	Bienfait, Venables(1977)
Xe	Ni(100)	30-100	5.65	0.5	23.01	(1-2) $\times 10^{12}$	--	Christmann, Demuth(1982)
		30	5.65	≤ 1	18.83	(10 12)	--	"
		30-100	5.65	0.05-0.8	25.10-18.83	--	1-0.5	"
Xe	Cu(311)	77-130	5.85	≈ 1	19 ± 2	--	--	Papp, Pritchard(1975)
Xe	Cu(211)	77	5.9	0.2-0.8	18 ± 2	--	--	Roberts, Pritchard(1976)
Xe	Cu(100)	77-83	5.7	<0.8	--	--	0.9	Glachant, Bardi(1979)
		77-80	5.7	<0.9	25.1 \pm 2.9	--	--	"
Xe	Ru(0001)	100	5.9	0-0.09	35.6-31.0	(10 13)	--	Wandelt et al.(1981)
		100	5.9	0.09-0.9	24.3-16.7	(10 13)	1	"
		107.4	5.9	0.1	(21.0)	6 $\times 10^{12}$	(1)	"

Table 1.2 (continued)

Gas	Solid	T [K]	θ_0 [10^{14}cm^{-2}]	θ/θ_0	E_d [kJ mole $^{-1}$]	ν [s $^{-1}$]	S	Reference
Xe	Pd(100)	77	5.8	0-1	31.8-27.0	--	1	Palmberg(1971)
Xe	Pd(110)	100	5.8	0-0.6	--	--	1	Küppers et al.(1979)
		100	5.8	0.1	46.9	(10^{15})	--	"
		100	5.8	0.1	41.4	(10^{15})	--	"
		100	5.8	1	41.4	(10^{15})	--	"
		100	5.8	1	36.0	(10^{15})	--	"
Xe	Ag(111)	66-123	5.65	--	18±1	--	--	McElhiney et al.(1976)
		75-90	5.86	1	27±3	--	--	Cohen et al.(1976)
		60	6.14	0.92	28±1	--	--	Unguris et al.(1979)
		60	6.14	0.99	21±1	--	--	"
		60	6.14	0.96	21.7±0.5	--	--	"
		60	6.14	1	16.7±0.5	--	--	"
Xe	W(111)	104	(6)	0.1-1	38.9±5.6	10^{15}	0.5	Dresser et al.(1974)
		104	(6)	0.0025-0.1	42.8-38.9	10^{15}	0.5	"
		120	(6)	0-0.7	--	--	1	Yates, Erickson(1974)
		120	(6)	0.1-0.3	38.9±5.6	--	--	"
Xe	W(100)	60	5.5	0-1	--	--	1	Wang, Gomer(1979)
		65	4.2	0-1	--	--	1	"
		62	--	--	22.2	(10^{15})	--	Wang, Gomer(1980)
		20	--	>1	--	--	1	"

Gas	Solid	T [K]	θ_0 [10^{14}cm^{-2}]	θ/θ_0	E_d [kJ mole $^{-1}$]	ν [s $^{-1}$]	S	Reference
Xe	W(110)	62	5.5	0-1	--	--	1	Wang, Gomer(1979)
		62	5.5	1	25.9	(10^{15})	--	Wang, Gomer(1980)
		20	5.5	>1	--	--	1	"
		27	(6.6)	0-0.25	18.0	1×10^{12}	--	Opila, Gomer(1981)
		27	(6.6)	0-0.25	16.3	4×10^{10}	--	"
		27	(6.6)	1-1.25	13.8	6×10^{12}	--	"
		27	(6.6)	1-1.25	11.7	3×10^{10}	--	"
		27	(6.6)	2-2.25	10.5	1.5×10^{10}	--	"
		78-125	5.9	1	27.2 ± 0.8	($k_B T/h$)	--	Nieuwenhuis(1974)
		78-125	5.9	1	31.4 ± 0.8	($k_B T/h$)	--	"
		78-125	5.9	1	26.4 ± 0.8	($k_B T/h$)	--	"
		78-125	5.9	<<1	29.3 ± 0.8	($k_B T/h$)	--	"
		78-125	5.9	1	28.0 ± 0.8	($k_B T/h$)	--	"
		78-125	5.9	<<1	30.1 ± 0.8	($k_B T/h$)	--	"
Xe	Ir(111) and (100) Ir(110)	78-125	5.9	1	29.3 ± 0.8	($k_B T/h$)	--	"
		78-125	5.9	<<1	30.1 ± 0.8	($k_B T/h$)	--	"
		78-125	5.9	1	32.6 ± 0.8	($k_B T/h$)	--	"
		78-125	5.9	<<1	27.2 ± 0.8	($k_B T/h$)	--	"
		78-125	5.9	<<1	30.1 ± 0.8	($k_B T/h$)	--	"
		78-125	5.9	1	28.0 ± 0.8	($k_B T/h$)	--	"
		78-125	5.9	<<1	30.1 ± 0.8	($k_B T/h$)	--	"
Xe	Ir(531)- (731)	78-125	5.9	<<1	30.1 ± 0.8	($k_B T/h$)	--	"
		78-125	5.9	<<1	30.1 ± 0.8	($k_B T/h$)	--	"

Table 1.2 (continued)

Gas	Solid	T [K]	θ_0 [10^{14}cm^{-2}]	θ/θ_0	E_d [kJ mole $^{-1}$]	ν [s $^{-1}$]	S	Reference
Xe	Au(100)	81-112	--	1	22 \pm 2	--	--	McElhiney et al.(1976)
Xe	ZnO	120-130	12.2	10^{-4}	24.1	--	--	Esser, Göpel(1980)
H ₂	Graphite	90-140	--	<0.1	5.4	--	--	Constabaris et al.(1961)
D ₂	Graphite	90-140	--	<0.1	5.6	--	--	"
H ₂	Si	3	(10)	0-1	4.2-0.9	--	0.1-0.8	Govers, et al.(1980)
D ₂	Si	3	(10)	0-1	4.7-1.1	--	0.26-0.9	"
H ₂	ZnO	95-196	12.2	0.0001	3.5	--	--	Esser, Göpel(1980)
CH ₄	Graphite	90-140	--	<0.1	12.7	--	--	Constabaris et al.(1961)
CD ₄	Graphite	90-140	--	<0.1	12.6	--	--	"
CH ₄	W(110)	110	--	--	29.1 \pm 4.2	3×10^{12}	--	Yates, Madey(1971)
CH ₄	W(111)	125	--	--	33.9 \pm 4.2	3×10^{12}	--	Madey(1972)
CH ₄	W(poly)	78	--	--	(33-50)	--	1	Shigelshi(1975)
CH ₄	NaCl	83-90	--	0.25-1	14-16	--	--	Ross(1954)
NH ₃	Al(poly)	128	(5.2)	0-1	37.7 \pm 8.4	--	0.13 \pm 0.08	Rogers, et al.(1980)
NH ₃	Ru(0001)	100	3.0	0-1	30.5	(10^{13})	0.2	Danielson et al.(1978)
		100	3.0	0-1	44.4	(10^{13})	0.2	"
NH ₃	Pt(111)	95-100	--	--	36 \pm 3	--	--	Gland, Kollin(1981)
N ₂	K(film)	75	--	--	17.2 \pm 2.1	10^{11} - 10^{12}	--	Mennicke et al.(1973)
N ₂	Ni(110)	140	11.0	0-0.47	42	10^{13}	1	Grunze(1984)
N ₂	Ni(110)	140	11.0	05-0.7	20	--	0.4 \pm 0.3	"

Gas	Solid	T (K)	θ_0 (10^{14}cm^{-2})	θ/θ_0	E_d (kJ/mole)	ν (s^{-1})	S	Reference
N_2	Fe(111)	85	---	---	24	10^{13}	0.7	Grunze(1984)
CO	ZnO	137-161	12.2	10^{-2}	26	---	---	Esser et al.(1980)
O_2	ZnO	127-241	12.2	10^{-2}	22.3	---	---	"
CH_3OH	Pd(100)	77	6	≤ 1	45.2	(10^{14})	---	Christmann, Demuth(1982)
		77	6	1-2	37.7	(10^{14})	---	"
		77	6	> 2	30.1	---	---	"
CO_2	ZnO	209-235	(12.2)	10^{-2}	44.9	---	---	Esser, Göpel(1980)
SF_6	Ru(001)	80	(5.3)	1	21.1	(3×10^{12})	1	Fisher et al.(1977)