Optical Preparation of Aligned Reagents

R. N. Zare

Department of Chemistry, Stanford University, Stanford, California 94305, USA

Apparate und Methoden / Atom- und Molekularstrahlen / Reaktionskinetik

Expressions are derived for the degree of alignment caused when a target molecule undergoes an electric-dipole-allowed transition induced by the absorption of plane polarized light.

1. Introduction

With the advent of quantum mechanics in the late 1920's, it became possible to investigate quantitatively the formation of molecules. The simplest of such reactions is the hydrogen-atom hydrogen-molecule bimolecular exchange reaction

$$H + H_2 \rightarrow H_2 + H \,.$$

For this three-electron system, London [1] wrote down without proof in 1929 an equation describing the energy of the H_3 configuration which reduced to a simplified form of the Heitler-London expression [2] when one of the H atoms is removed to infinity. In his laboratory at the Fritz-Haber-Institut in Berlin, Eyring and Polanyi [3] developed in 1931 a semi-empirical treatment of the H_3 potential energy surface, based on the London equation, which proved to be rather accurate because of partially cancelling errors. This event, which we have come together to celebrate, was a turning point in the development of chemical kinetics – for it caused chemists not only to study the rates of reactions in the bulk with increasing interest but to attempt to relate them to the dynamics of individual reactive encounters [4 – 6].

There are several properties of the London potential for H_3 which are worth noting. First, the H_3 potential surface has a barrier; energy is required to cross over from the reactants' to the products' regions of the potential energy surface. Second, there is a prediction that there is a potential well at the top of the barrier, suggesting the possible formation of a long-lived H_3 collision complex. However, this feature does not appear in the best ab initio calculations nor is there any experimental evidence to support its existence [7]. Third, the height of the barrier varies with reactant approach geometry, being at a minimum when the three H atoms are in a straight line (collinear). This last feature, which is confirmed by the best quantum calculations [7], easily fits into chemical expectations as a simple manifestation of the directed nature of chemical bonding.

For the most part, geometric constraints on chemical reactivity are inferred from indirect evidence. For example, in the calculation of bimolecular rate constants from the kinetic theory of gases, a steric factor p is introduced, based on the idea that some collisions are more effective than others in promoting reaction [8]. The value of the steric factor is adjusted to bring experiment in accord with the hard-sphere collision model. While for some reactions a simple geometrical interpretation might be advanced for p, there are many other reactions for which p is so small that the value of p must be regarded more as a measure of the failure of the hard-sphere collision model, although the reaction orientational requirements it describes are

well accepted [8, 9]. More sophisticated theories of reaction rate constants also must confront the question of what role reagent approach geometry plays, but this is usually hidden in the assumed structure of the transition state and the term called the entropy of activation [8 – 10]. Clearly, a need exists for experiments that measure directly the geometric requirements for reaction.

Reagents are usually oriented using external electric and magnetic fields [11 – 13]. This technique has been applied with great success to salt molecules, such as TlF [14 – 16], CsF [16, 17], and LiF [18], to polar symmetric top molecules, such as CH_3I [19 – 26] and CF_3I [20, 27, 28], to paramagnetic molecules, such as NO [29 – 35], and using molecular beam magnetic resonance techniques to H_2 [35, 37]. For other systems, orientation is much less convenient. Moreover, even in the best circumstances, external field orientation often leads to a poor degree of spatial control whose exact characterization often presents difficulties. In this paper an alternative method for studying collisions having controlled reagent approach geometry is considered, namely, the absorption of plane polarized light by reagent molecules to produce aligned excited targets. Already one preliminary experiment has been carried out with this technique [38]; it is hoped that as tunable laser sources become more available the study of many additional reactive scattering systems will become accessible by this means. In what follows a simple derivation is presented for the degree of alignment that can be achieved as a function of the rotational quantum state, J, of the target. Special attention is given to the high-J limit, which so often describes molecular systems under practical conditions.

2. Procedure

2.1. The Angular Distribution of Axes of a Rigid Rotor Following Absorption of Plane Polarized Light

The wavefunction of a rigid rotor is characterized by the total angular momentum J and its projection M on the axis of quantization, i.e., by $|JM\rangle$. It has the explicit form

$$|JM\rangle = Y_{JM}(\theta, \phi) \tag{1}$$

where θ, ϕ are the polar and azimuthal angles. Thus the probability $P_{JM}(\theta, \phi)$ of finding the rotor axis pointing into the solid angle element $d\Omega = \sin\theta \, d\theta \, d\phi$ when the rotor is in the state $|JM\rangle$ is given by

$$P_{JM}(\theta) = |Y_{JM}(\theta, \phi)|^2 \sin\theta \, d\theta \, d\phi \,, \tag{2}$$

which is seen to be independent of the azimuthal angle ϕ. Note that this is normalized, i.e.,

$$\int d\Omega |Y_{JM}(\theta, \phi)|^2 = 1 \,. \tag{3}$$

The probability *amplitude* of finding the rigid rotor in the state $|JM\rangle$ following the dipole absorption of plane polarized radiation ($j_{ph} = 1$, $m_{ph} = 0$) is proportional to the Wigner coefficient (Clebsch-Gordan coefficient) $(J''M'', 10|JM)$ where $|J''M''\rangle$ is the initial state of the rotor. Thus the distribution of rigid rotor axes for this particular M state is

$$P_{JM}(\theta) = (J''M'', 10|JM)^2|Y_{JM}(\theta, \phi)|^2$$

(which has not been normalized). The M'' states are assumed to be equally populated with no phase relations (meaning random phase relations) among them. Thus the total probability is obtained by simply summing over all initial M'' states, giving

$$P_J(\theta) = \sum_{M''} (J''M'', 10|JM)^2|Y_{JM}(\theta, \phi)|^2. \tag{4}$$

The evaluation of Eq. (4) is considered in detail in the Appendix [39]. There it is shown that Eq. (4) reduces to

$$P_J(\theta) = (J''1, 1-1|J0)^2|Y_{1-1}(\theta, \phi)|^2 + (J''0, 10|J0)^2|Y_{10}(\theta, \phi)|^2$$
$$+ (J'' -1, 11|J0)^2|Y_{11}(\theta, \phi)|^2. \tag{5}$$

Using explicit expressions for the Wigner coefficients and the identities

$$|Y_{11}(\theta, \phi)|^2 = |Y_{1-1}(\theta, \phi)|^2 = (3/8\pi)\sin^2\theta$$

$$|Y_{10}(\theta, \phi)|^2 = (6/8\pi)\cos^2\theta \tag{6}$$

$P_J(\theta)$ can be recast into the familiar form

$$P_J(\theta) = [1 + \mathscr{A}_0(J)P_2(\cos\theta)]/4\pi \tag{7}$$

where

$$P_2(\cos\theta) = (3\cos^2\theta - 1)/2 \tag{8}$$

is the second order Legendre polynomial, and $\mathscr{A}_0$ is the so-called *alignment parameter* [40–44], ranging in value from $+2$ for a pure $\cos^2\theta$ distribution to -1 for a pure $\sin^2\theta$ distribution. For $\mathscr{A}_0 = 0$, the distribution is isotropic. Note that the alignment parameter $\mathscr{A}_0$ plays the same role as the asymmetry parameter β does in describing photofragment angular distributions [44].

For a P branch transition in which $J = J'' - 1$

$$\mathscr{A}_0^P(J'') = (J'' - 1)/(2J'' + 1) \tag{9}$$

while for an R branch transition in which $J = J'' + 1$
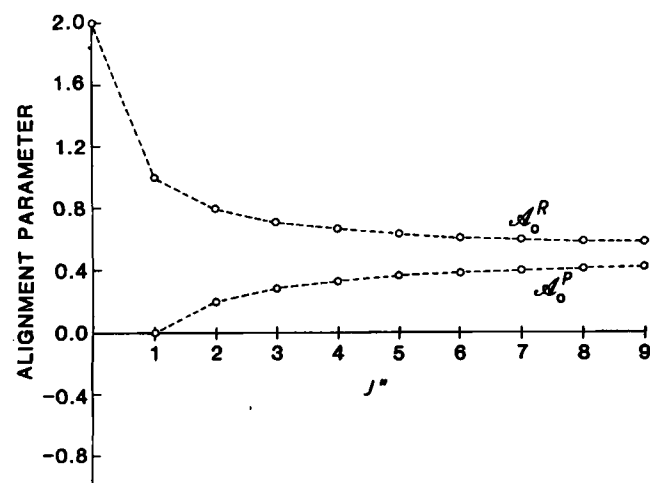
$$\mathscr{A}_0^R(J'') = (J'' + 2)/(2J'' + 1). \tag{10}$$

Fig. 1

The alignment parameters $\mathscr{A}_0^R(J'')$ and $\mathscr{A}_0^P(J'')$ as a function of J'' for a rigid rotor transition $J'' \to J$, where $J = J'' + 1$ for the R branch and $J = J'' - 1$ for the P branch

Of course, a rigid rotor cannot have Q branch transitions in which $J = J''$. Fig. 1 plots the alignment parameter as a function of the initial rotational quantum number J''. It is apparent that for low

rotational quantum numbers it is much more favorable to pump the members of the R branch than the P branch in order to align the excited state. However, as J'' increases, $\mathscr{A}_0^P(J'')$ and $\mathscr{A}_0^R(J'')$ approach the same limit, namely,

$$\mathscr{A}_0^{P,R}(\text{classical}) = \tfrac{1}{2}. \tag{11}$$

The degree of alignment can be judged by how much $\mathscr{A}_0$ differs from zero. Even in the high-J'' limit the degree of alignment produced by this optical pumping scheme is found to be significant; $P_J(\theta)$ has the form $(3/8\pi)(1 + \cos^2\theta)$.

A $^1\Sigma - {}^1\Sigma$ transition is well-described as a rigid rotor transition; Eqs. (9)–(11) characterize the distribution of axes when a diatomic molecule in a $^1\Sigma$ state absorbs a plane polarized infrared photon (or a more energetic photon to make an electronic $^1\Sigma - {}^1\Sigma$ transition). For the purposes of making subsequent collisions infrared pumping has the obvious advantage that the radiative lifetime of the prepared state is so much longer.

2.2. The Angular Distribution of Axes of a Symmetric Top Following Absorption of Plane Polarized Light

The wavefunction of a symmetric top is characterized by the total angular momentum $\mathbf{J}$, its projection K on the top axis (also called the figure axis), and its projection M on the space-fixed axis of quantization, i.e., by $|JKM\rangle$. It has the explicit form

$$|JKM\rangle = \left[\frac{2J+1}{8\pi^2}\right]^{1/2} D_{KM}^{J*}(\phi, \theta, \chi) \tag{12}$$

where D_{KM}^J is a rotation matrix and ϕ, θ, χ are the three Euler angles relating the body-fixed and space-fixed frames. Thus the probability $P_{JKM}(\phi, \theta, \chi)$ of finding the top axis pointing into the solid angle element $d\Omega = d\phi\sin\theta d\theta d\chi$ when the top is in the state $|JKM\rangle$ is given by

$$P_{JKM}(\theta) = |D_{KM}^J(\phi, \theta, \chi)|^2 d\phi\sin\theta d\theta d\chi \tag{13}$$

which is seen to be independent of the angles ϕ and χ. Once again this clearly satisfies the normalization

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\chi \langle JKM|JKM\rangle = 1. \tag{14}$$

The selection rules for infrared (or microwave) dipole transitions between nondegenerate vibrational levels of a symmetric top are $\Delta J = 0$, ± 1 and $\Delta K = 0$ if $K \neq 0$, $\Delta J = \pm 1$, $\Delta K = 0$ if $K = 0$, since the change in the dipole moment (as well as the permanent dipole moment) is along the direction of the top axis [45]. This is called a $\|$band. Then the probability amplitude of finding the symmetric top in the state $|JKM\rangle$ following the dipole absorption of plane polarized radiation ($j_{ph} = 1$, $m_{ph} = 0$) is proportional to the product of Wigner coefficients $(J''M'', 10|JM)(J''K'', 10|JK)$, where $|J''K''M''\rangle$ is the initial state of the symmetric top. Thus the (unnormalized) angular distribution of top axes is given by

$$P_{JK}(\theta) = \sum_{M''} (J''M'', 10|JM)^2(J''K'', 10|JK)^2|D_{MK}^J(\phi, \theta, \chi)|^2 \tag{15}$$

where once again a sum is performed over the initial M'' states, which are assumed to have a random distribution. Eq. (15) is evaluated explicitly in the Appendix in which it is shown that

$$P_{JK}(\theta) = (J''K'', 11|JK'' + 1)^2|D_{10}^1(\phi, \theta, \chi)|^2$$
$$+ (J''K'', 10|JK'')^2|D_{00}^1(\phi, \theta, \chi)|^2$$
$$+ (J''K'', 1-1|JK'' - 1)^2|D_{-10}^1(\phi, \theta, \chi)|^2. \tag{16}$$

Using explicit expressions for the Wigner coefficients and the identities

$$|D_{10}^1(\phi, \theta, \chi)|^2 = |D_{-10}^1(\phi, \theta, \chi)|^2 = \tfrac{1}{2}\sin^2\theta$$

$$|D_{00}^1(\phi, \theta, \chi)|^2 = \cos^2\theta \tag{17}$$

$P_{JK}(\theta)$ can be recast once again into the form of Eq. (7).

For a P branch transition in which $J'' = J - 1$ the alignment parameter is

$$\mathscr{A}_0^P(J'', K'') = \frac{J''(J'' - 1) - 3K''^2}{J''(J'' + 1)}, \tag{18}$$

for a Q branch transition in which $J'' = J$

$$\mathscr{A}_0^Q(J'', K'') = -\frac{J''(J''+1) - 3K''^2}{J''(J''+1)}, \qquad (19)$$

and for an R branch transition in which $J'' = J + 1$

$$\mathscr{A}_0^R(J'', K'') = \frac{(J''+1)(J''+2) - 3K''^2}{(J''+1)(2J''+1)}. \qquad (20)$$

Eqs. (18) and (20) reduce to Eqs. (9) and (10), respectively, when $K'' = 0$. Eq. (19) only holds for $K'' \neq 0$; moreover, it shows that when $J'' \gg K''$ pumping of the Q branch can produce a high degree of alignment but with an opposite sign as that of P or R branch pumping.

The above results apply to a parallel band of a pure symmetric top. It is an easy matter to obtain the corresponding expressions for a perpendicular band in which the changing dipole moment is perpendicular to the top axis, as is the case for a Σ-Π transition in a diatomic molecule (or linear polyatomic molecule) for example. It is also possible to generalize this treatment (a) by considering dipole transitions between asymmetric top states or (b) by taking into account resolved or unresolved hyperfine structure. However, these extensions of the theory seem presently like exercises in angular momentum coupling and are deferred until experiments calling for their use are completed.

3. Discussion

The above treatment has demonstrated that absorption of plane polarized light may be used to prepare target molecular systems with known alignment whose degree of alignment can often be chosen to be high. It has been assumed that the ground state of the target is characterized by magnetic sublevels having equal population and random phase relations. Moreover, it has been assumed that the optical pumping process is not so strong that this characterization is disturbed. Of course, the latter need not be the case and it is also possible to align target molecular systems by strong optical pumping [46 – 49]. It should also be pointed out that the above treatment is restricted to absorption of a single photon by the target system. However, sequential absorption of photons may also be used to advantage to cause target alignment, and the first such experiments have just been carried out [50]. Because polarized light sources, particularly lasers, are so convenient to operate and to control, it may be anticipated that optical alignment of reagents will become often the method of choice in future experiments that investigate the "stereodynamics" of elastic, inelastic, and reactive scattering events.

Appendix

The problem is to evaluate the sum

$$S(J'', K'') = \sum_{M''} (J''M'', j_{\text{ph}} = 1 m_{\text{ph}} = 0|JM)^2 |D_{KM}^J|^2. \qquad (A-1)$$

This is readily accomplished using a form of the inverse Clebsch-Gordan series [51]

$$(j_1 m_1, j_2 m_2|j_3 m_3) D_{k_3 m_3}^{j_3} = \sum_{k_1} (j_1 k_1, j_2 k_3 - k_1|j_3 k_3) D_{k_1 m_1}^{j_1} D_{k_3 - k_1, m_2}^{j_2}. \qquad (A-2)$$

With the identification

$$\begin{aligned}
&j_1 = J'' \quad m_1 = M'' \quad k_1 = K'' \\
&j_2 = 1 \quad\; m_2 = 0 \quad\;\; k_2 = K - K'' \qquad (A-3) \\
&j_3 = J \quad\; m_3 = M \quad\; k_3 = K.
\end{aligned}$$

Eq. (A-2) becomes

$$(J''M'', 10|JM) D_{KM}^J = \sum_{K''} (J''K'', 1K - K''|JK) D_{K''M''}^{J''} D_{K-K'',0}^1. \qquad (A-4)$$

Squaring both sides of Eq. (A-4) and summing over M'' yields

$$\begin{aligned}
\sum_{M''} (J''M'', 10|JM)^2 |D_{KM}^J|^2 \\
= \sum_{M''} \left[\sum_{K''} (J''K'', 1K - K''|JK) D_{K''M''}^{J''} D_{K-K'',0}^1\right]^* \qquad (A-5) \\
\left[\sum_{K'} (J''K', K - K'|JK) D_{K'M''}^{J''} D_{K-K',0}^1\right]
\end{aligned}$$

The lefthand side of Eq. (A-5) is recognized as $S(J'', K'')$, the sum to be evaluated. By unitarity of the rotation matrices

$$\sum_{M''} D_{K-K'',M''}^{J''*} D_{K-K',M''}^{J''} = \delta_{K''K'}, \qquad (A-6)$$

and the righthand side of Eq. (A-5) simplifies:

$$S(J'', K'') = \sum_{K''} (J''K'', 1K - K''|JK)^2 |D_{K-K'',0}^1|^2 \qquad (A-7)$$

where the sum over K'' is from $K - 1$ to $K + 1$. Thus Eq. (A-7) has the explicit value

$$\begin{aligned}
S(J'', K'') = (J''K - 1, 11|JK)^2 |D_{10}^1|^2 + (J''K, 10|JK)^2 |D_{00}^1|^2 \\
+ (J''K + 1, 1 - 1|JK)^2 |D_{-10}^1|^2, \qquad (A-8)
\end{aligned}$$

which is identical to Eq. (16). Furthermore, when $K = 0$ and $|D_{m0}^j|^2$ is equated to $[4\pi/(2j+1)]|Y_{jm}|^2$, Eq. (A-8) reduces to Eq. (5), ignoring a constant of proportionality.

In evaluating Eqs. (5) and (16) $P(\theta)$ may be readily expressed as

$$P(\theta) = a\sin^2\theta + b\cos^2\theta. \qquad (A-9)$$

This can be put into the form of Eq. (7) using the identity

$$\mathscr{A}_0' = \frac{2(b-a)}{2a+b} \qquad (A-10)$$

to relate the alignment parameter $\mathscr{A}_0'$ to the coefficients a and b.

References

[1] F. London, Z. Elektrochem. *35*, 552 (1929).
[2] W. Heitler and F. London, Z. Phys. *44*, 455 (1927).
[3] H. Eyring and M. Polanyi, Z. Phys. Chem. *B12*, 279 (1931).
[4] M. A. Eliason and J. O. Hirschfelder, J. Chem Phys. *30*, 1426 (1959).
[5] J. C. Polanyi and J. J. Schreiber, The Dynamics of Bimolecular Reactions, in: Physical Chemistry, An Advanced Treatise, ed. W. Jost, Vol. VIA, pp. 383 – 487, Academic Press, New York 1974.
[6] R. D. Levine and R. B. Bernstein, Molecular Reaction Dynamics, Oxford University Press, New York 1974.
[7] D. G. Truhlar and R. E. Wyatt, Ann. Rev. Phys. Chem. *27*, 1 (1976).
[8] I. W. M. Smith, Kinetics and Dynamics of Elementary Gas Reactions, Butterworths, London 1980.
[9] D. L. Bunker, Theory of Elementary Gas Reaction Rates, Pergamon Press, Oxford 1966.
[10] R. E. Weston, Jr. and H. A. Schwartz, Chemical Kinetics, Prentice Hall, Englewood Cliffs 1972.
[11] J. P. Toennies, Molecular Beam Scattering Experiments on Elastic, Inelastic and Reactive Collisions, in: Physical Chemistry, An Advanced Treatise, ed. W. Jost, Vol. VIA, pp. 227 – 381, Academic Press, New York 1974.
[12] J. Reuss, Adv. Chem. Phys. *30*, 389 (1975).
[13] P. R. Brooks, Science *193*, 11 (1976).
[14] H. G. Bennewitz, K. H. Kramer, W. Paul, and J. P. Toennies, Z. Phys. *177*, 84 (1964).
[15] J. P. Toennies, Z. Phys. *182*, 257 (1965).

[16] H. G. Bennewitz, R. Gegenbach, R. Haerten, and G. Müller, Z. Phys. *226*, 279 (1969).

[17] U. Borkenhagen, H. Malthan, and J. P. Toennies, Chem. Phys. Lett. *41*, 222 (1976).

[18] L. Y. Tsou, D. Auerbach, and L. Wharton, Phys. Rev. Lett. *38*, 20 (1977).

[19] P. R. Brooks and E. M. Jones, J. Chem. Phys. *45*, 3449 (1966).

[20] P. R. Brooks, E. M. Jones, and K. Smith, J. Chem. Phys. *51*, 3073 (1969).

[21] G. Marcelin and P. R. Brooks, J. Am. Chem. Soc. *95*, 7885 (1973); *97*, 1710 (1975).

[22] K. H. Kramer and R. B. Bernstein, J. Chem. Phys. *42*, 767 (1965).

[23] R. J. Beuhler, Jr., R. B. Bernstein, and K. H. Kramer, J. Am. Chem. Soc. *88*, 5331 (1966).

[24] R. J. Beuhler, Jr. and R. B. Bernstein, Chem. Phys. Lett. *2*, 166 (1968); *3*, 118 (1969).

[25] R. J. Beuhler and R. B. Bernstein, J. Chem. Phys. *51*, 5305 (1969).

[26] D. H. Parker, K. K. Chakravorty, and R. B. Bernstein, J. Phys. Chem. *85*, 466 (1981); Chem. Phys. Lett. (in press).

[27] P. R. Brooks, J. Chem. Phys. *50*, 5031 (1969).

[28] P. R. Brooks, J. S. McKillop, and H. G. Pippin, Chem. Phys. Lett. *66*, 144 (1979).

[29] S. Stolte, J. Reuss, and H. L. Schwartz, Physica *57*, 254 (1972).

[30] H. L. Schwartz, S. Stolte, and J. Reuss, Chem. Phys. *2*, 1 (1973).

[31] S. Stolte, J. Reuss, and H. L. Schwartz, Physica *66*, 211 (1973).

[32] H. P. M. Kessener and J. Reuss, Chem. Phys. Lett. *31*, 212 (1975).

[33] H. Thuis, S. Stolte, and J. Reuss, Chem. Phys. *43*, 351 (1979).

[34] S. L. Anderson, P. R. Brooks, J. D. Fite, and O. VanNguyen, J. Chem. Phys. *72*, 6521 (1980).

[35] D. van den Ende and S. Stolte, Chem. Phys. Lett. *76*, 13 (1980).

[36] H. Moerkerken, M. Prior, and J. Reuss, Physica *50*, 499 (1970).

[37] H. Moerkerken, L. Zandee, and J. Reuss, Chem. Phys. *11*, 87 (1975).

[38] Z. Karny, R. C. Estler, and R. N. Zare, J. Chem. Phys. *69*, 5199 (1978).

[39] This material is taken from R. N. Zare, Ph. D. Thesis, Harvard University, Cambridge, Massachusetts, 1964.

[40] U. Fano and J. H. Macek, Rev. Mod. Phys. *45*,553 (1973).

[41] J. H. Macek and I. V. Hertel, J. Phys. *B7*, 2173 (1974).

[42] J. Macek and D. Burns, in: Topics in Current Physics. Vol. I, Beam Foil Spectroscopy, pp. 237 – 264, S. Bashkin, ed., Springer-Verlag, New York 1976.

[43] I. V. Hertel and W. Stoll, Adv. At. Mol. Phys. *13*, 113 (1978).

[44] C. H. Greene and R. N. Zare, Ann. Rev. Phys. Chem. *32* (1982).

[45] G. Herzberg, Molecular Spectra and Molecular Structure, Vol. II, pp. 414 – 424, Van Nostrand, Princeton 1945.

[46] H. G. Dehmelt and K. B. Jefferts, Phys. Rev. *125*, 1318 (1962).

[47] C. B. Richardson, K. B. Jefferts, and H. G. Dehmelt, Phys. Rev. *165*, 80 (1968).

[48] K. B. Jefferts, Phys. Rev. Lett. *20*, 39 (1968); *23*, 1476 (1969).

[49] R. E. Drullinger and R. N. Zare, J. Chem. Phys. *51*, 5532 (1969); *59*, 4225 (1973).

[50] E. W. Rothe, F. Ranjbar, and D. Sinha, Chem. Phys. Lett. *78*, 16 (1981); *81*, 175 (1981).

[51] See Eq. (3.188) of L. C. Biedenharn and J. D. Louck, Angular Momentum in Quantum Physics, p. 85, Addison-Wesley Publishing Co., Reading, Massachusetts, 1981.

E 5129

Chemical Dynamics in Surface Reactions

G. Ertl

Institut für Physikalische Chemie, Universität München

Adsorption / Katalyse / Oberflächenerscheinungen

Chemical interactions of gaseous molecules with solid surfaces may proceed with or without bond-breaking (dissociative and non-dissociative chemisorption, respectively). The formation of new molecules via surface reactions of these species forms the basis of heterogeneous catalysis. Experimentally accessible information on the processes involved will be briefly outlined by means of a few selected examples.

I. Introduction

The atoms in the surface of a solid are missing a part of their nearest neighbors and are therefore potentially able to form chemical bonds (of strength $\gtrsim$ 1 eV) with suitable molecules arriving from the gas phase. The individual steps which may be involved in processes of this kind are illustrated schematically by Fig. 1. The interaction with the surface may be associated with bond dissociation within the molecule or not (dissociative and non-dissociative chemisorption, respectively), the adsorbed particles may migrate across the surface and after a certain lifetime desorb (eventually via mutual recombination). The appearance of new molecules in the gas phase as the consequence of such processes forms the basis for heterogeneous catalysis.

For the present discussion the surface is considered to consist of a two-dimensional periodic arrangement of identical atoms which can experimentally be approached e.g. by the use of well-defined metal single crystal surfaces. It has to be kept in mind, however, that even such systems will not be completely defect-free and that 'real' surfaces (as applied in practical catalysis) are usually much more complex. In the case of strong interactions with the adsorbate the lateral positions of the surface atoms may be altered (reconstructive chemisorption) which effect, however, will be of no importance with the examples discussed in the following.
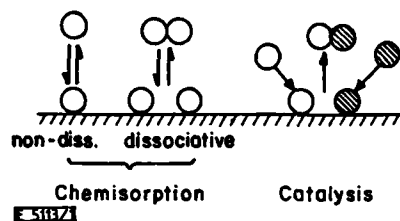

Fig. 1
Chemical processes at surfaces (schematic)

We are still very far away from a theoretical evaluation of the energy hyperfaces for gas-solid interactions as well as of the cross-sections determining transitions between different states.