

Quantum-dynamical model for thermal desorption of gases from solid surfaces

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The Montroll-Shuler model for the kinetics of dissociation of a diatomic molecule in a heat bath is adapted to thermal desorption of gases from solid surfaces. The rate constant k_{MS} is compared with that predicted by transition-state theory, k_{TST} , and that extracted from experimental data for the system Xe/W. A central feature of the present model is that k_{MS} shows a strong explicit dependence (θ_D^{-3} in the Debye approximation) upon the lattice dynamics, whereas k_{TST} has none at all.

I. INTRODUCTION

The kinetics of thermal desorption of gases from solid surfaces is conventionally interpreted in terms of transition-state theory¹ (TST). Assuming that the adsorbed atoms (adatoms) do not interact with each other, we can approximate the real system as a single atom (A) interacting with a surface (see Fig. 1). Taking the "reaction coordinate" to be the distance (r) of A from the equilibrium position of the surface atom (S) in the free solid and assuming the "transition state" to include all configurations of the system with r in the range δ , we can express the desorption rate constant as

$$k_{TST}(T) = (\beta h)^{-1} Z^\ddagger(\beta) \exp(-\beta D) / Z(\beta), \quad (1)$$

where

$$\beta \equiv (k_B T)^{-1},$$

k_B is Boltzmann's constant, T is the absolute temperature, Z^\ddagger and Z are partition functions for the solid (transition state) and solid plus adatom ("reactants"), respectively, and D is the barrier to activation. Note that the transmission coefficient has been set to unity. Now invoking the harmonic approximation and assuming that the adatom perturbs the solid negligibly, we can express the density of modes of the system as

$$\rho(\omega) \approx \rho_s(\omega) + \delta(\omega - \omega_0), \quad (2)$$

where ρ_s is the density of modes of the free solid and ω_0 is the fundamental frequency of oscillation of A in the field of S. Under the approximation (2), Eq. (1) becomes

$$k_{TST}(T) = (\beta h)^{-1} [1 - \exp(-\beta \hbar \omega_0)] \exp(\beta \hbar \omega_0 / 2) \times \exp(-\beta D). \quad (3)$$

Note that k_{TST} given by Eq. (3) is independent of the lattice dynamics of the solid. This feature of TST seems surprising in view of the great sensitivity of computed gas-solid collisional energy-transfer probabilities to the dynamical properties of the solid.²⁻⁵ It is tempting to conjecture that the strong influence of the lattice on the dynamics of detailed microscopic events is suppressed essentially by thermal averaging. This supposition is partially supported by a recent study⁶ of the microcanonical transition-state (i.e., RRKM⁷) rate constant. The microcanonical rate constant, a less averaged quantity than k_{TST} , exhibits a very strong dependence on the lattice dynamics of the solid (e.g., the

Debye temperature $\theta_D = \hbar \omega_D / k_B$, where ω_D is the Debye cutoff frequency) which is washed out upon canonically averaging to give k_{TST} .

In an early series of papers, Lennard-Jones and co-workers⁸⁻¹⁰ developed a quantum-mechanical model for desorption which, in fact, does give rise to explicit lattice-dynamical dependence of the rate constant. The model, recently elaborated by Bendow and Ying,¹¹ takes the adatom-lattice coupling to be linear in the normal coordinates of the lattice. The adatom escapes the surface by absorbing a single phonon to undergo a direct transition from a bound level to the continuum. Using the distorted-wave-Born approximation, one calculates the transition rate (i.e., the desorption rate constant), finding a θ_D^{-3} dependence. A very important restriction of the Lennard-Jones model, which is a direct consequence of the one-phonon mechanism, is that in order for adatoms in the lowest (and consequently most populated) levels to evaporate, the following inequality must hold:

$$D \leq k_B \theta_D. \quad (4)$$

Unfortunately, condition (4) is satisfied only in the case of very weakly bound physisorbed atoms. A "multiphonon" mechanism thus seems to be required in order to handle properly the majority of physically realizable systems.

We present here an adaptation of the Montroll-Shuler^{12,13} (MS) model to the kinetics of thermal desorption. This model, originally applied to the dissociation of a diatomic molecule immersed in a thermal bath, is based on the assumption that the vibrational energy "ladder" of the diatomic is climbed by a sequence of uncorrelated

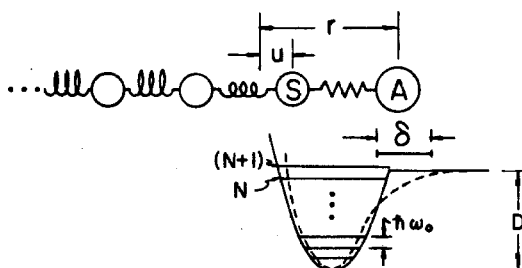


FIG. 1. Schematic diagram of atom (A) adsorbed on a surface. The dashed curve denotes the true interaction between A and the surface atom S. The solid curve is the truncated harmonic approximation of the Montroll-Shuler model. The region δ locates the transition state.

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one-quantum steps. The applicability of the MS model to desorption has been qualitatively discussed by Péterman.^{1a} To the best of our knowledge, however, no quantitative treatment has previously been given.

The plan of the remainder of this paper is as follows. In Sec. II we develop the model and briefly derive an expression for the rate constant, k_{MS} . In Sec. III we compare the predictions of our MS model with those of TST and with available experimental results. We also explore in detail the lattice-dynamical dependence of k_{MS} . Finally, in Sec. IV we summarize and discuss our results.

II. THEORY

In our adaptation of the Montroll-Shuler (MS) model, the adatom A plays the role of the diatomic molecule in the original theory¹² and the solid lattice that of the thermal bath. An adatom initially in a bound level eventually escapes from the surface by sequentially absorbing phonons until it reaches the continuum. The potential curve binding A to the surface is taken to be a truncated harmonic oscillator having $N+1$ bound levels ($0 \leq n \leq N$), which are assumed to be the same as those of the corresponding untruncated oscillator. The continuum is represented by the level $n=N+1$ of the untruncated oscillator. Hence, an adatom originally in a bound level $n \leq N$ is assumed to have evaporated once it reaches level $N+1$. We take the rate constant for the MS model to be simply the reciprocal of the *mean first passage time*, \bar{t} , which is the time required for A to reach level $N+1$ for the first time. If only transitions between adjacent levels are allowed and the adatom is initially in the lowest level ($n=0$), then \bar{t} can be simply expressed¹² in terms of the rate of transition $W_{n \rightarrow n+1}$ between levels n and $n+1$. Hence, we shall be concerned in the remainder of this section principally with deriving an expression for $W_{n \rightarrow n+1}$.

In the following formal developments, we retain essentially the same physical picture (see Fig. 1) upon which the TST treatment¹ is based. The zero-order Hamiltonian of the system corresponds to the unperturbed solid and the adatom (A) moving in the field of the surface atom (S) fixed at its equilibrium position ($u=0$). We consider only motion of A perpendicular to the surface, although we shall later treat the solid as three dimensional. We approximate the A-S interaction by the truncated harmonic potential

$$V = \begin{cases} \frac{1}{2} k(r-u-r_0)^2 - D & r-u \leq \sigma \\ 0 & r-u \leq \sigma, \end{cases} \quad (5)$$

where k is the force constant, which is related to the fundamental frequency (ω_0) of oscillation of A by

$$\omega_0 = (k/m_A)^{1/2}, \quad (6)$$

where m_A is the mass of the adatom.

According to Eq. (5) the perturbation coupling A to the solid is

$$V' = -kru. \quad (7)$$

Note that in first-order perturbation theory the form of V' dictates that A undergoes only single-quantum ($n \rightarrow n \pm 1$) transitions by absorption (or emission) of a single phonon.

The rate of transition between levels n and $n+1$ of A can be expressed in the thermally averaged "golden-rule" form

$$\begin{aligned} W_{n \rightarrow n+1} &= 2\pi\hbar^{-1} \sum_{\nu} p(\nu) \sum_{\nu'} |\langle n, \nu | V' | n+1, \nu' \rangle|^2 \\ &\quad \times \delta(\epsilon_{n, \nu} - \epsilon_{n+1, \nu'}) \\ &= 2\pi\hbar^{-1} k^2 |\langle n | r | n+1 \rangle|^2 \sum_{\nu} p(\nu) \\ &\quad \times \sum_{\nu'} |\langle \nu | u | \nu' \rangle|^2 \delta(\hbar\omega_0 - \epsilon(\nu) + \epsilon(\nu')), \end{aligned} \quad (8)$$

the second line of Eq. (8) following from Eq. (7). In Eq. (8), ν denotes the set of phonon occupation numbers required to specify a state of the solid lattice $|\nu\rangle$ having energy $\epsilon(\nu)$ and probability $p(\nu)$ of being observed. Treating the surface atom S as one in the bulk of the solid, we have

$$\begin{aligned} I &\equiv \sum_{\nu} p(\nu) \sum_{\nu'} |\langle \nu | u | \nu' \rangle|^2 \delta(\hbar\omega_0 + \epsilon(\nu') - \epsilon(\nu)) \\ &= \sum_{\mathbf{k}\lambda} \hbar(2N_0 m_s \omega_{\mathbf{k}})^{-1} |\hat{\mathbf{e}}_{\mathbf{k}} \cdot \hat{\mathbf{e}}_{\mathbf{k}\lambda}|^2 \bar{n}_{\mathbf{k}\lambda}(\omega_{\mathbf{k}}) \delta(\hbar\omega_0 - \hbar\omega_{\mathbf{k}}), \end{aligned} \quad (9)$$

where N_0 is Avogadro's number; $k\lambda$ denotes a mode of the lattice having wave vector \mathbf{k} , polarization $\hat{\mathbf{e}}_{\mathbf{k}\lambda}$ and frequency $\omega_{\mathbf{k}}$; $\bar{n}_{\mathbf{k}\lambda}$ is the expected occupation number of the mode, given explicitly by

$$\bar{n}_{\mathbf{k}\lambda}(\omega_{\mathbf{k}}) = [\exp(\beta\hbar\omega_{\mathbf{k}}) - 1]^{-1}; \quad (10)$$

m_s is the mass of the solid (surface) atom; and $\hat{\mathbf{e}}_{\mathbf{k}}$ is a unit vector parallel to the displacement of S (u), which we have implicitly restricted to be perpendicular to the surface. Taking the solid to be an isotropic continuum (Debye model), we replace the discrete sum in Eq. (9) by an integral, which is easily evaluated to give

$$I = 3\omega_0 \bar{n}(\omega_0) / (2m_s \omega_D^3). \quad (11)$$

Finally, combining Eqs. (8), (9), and (10), along with the standard relation

$$\langle n | r | n+1 \rangle = (\hbar/2m_A \omega_0)^{1/2} (n+1)^{1/2}, \quad (12)$$

we get

$$W_{n \rightarrow n+1} = \kappa(n+1), \quad (13a)$$

where

$$\begin{aligned} \kappa &\equiv (3\pi/2) (m_A/m_s) (\omega_0^4/\omega_D^3) \\ &\quad \times [\exp(\beta\hbar\omega_0) - 1]^{-1} \theta(\omega_D - \omega_0), \end{aligned} \quad (13b)$$

and θ is the Heaviside (unit step) function. Note from Eq. (13b) that the single-phonon mechanism in the MS model requires that

$$\omega_0 \leq \omega_D, \quad (14)$$

which is, in general, not nearly so restrictive as Eq. (4) for the Lennard-Jones direct one-phonon mechanism.

If we approximate the transition rate from the highest

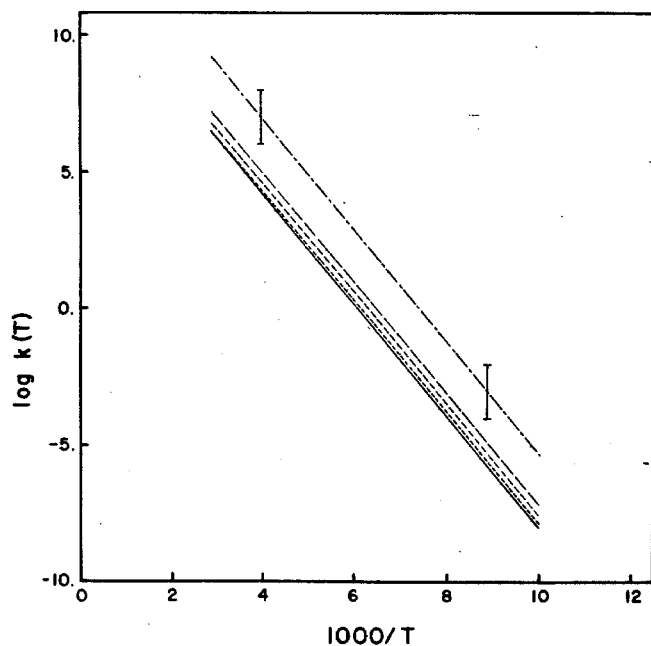


FIG. 2. $\log k$ vs $10^3/T$ for the system Xe/W at various Debye temperatures θ_D (----, 500 K; - · -, 400 K; —, 300 K). The solid curve refers to the TST and (— · —) to experiment (Ref. 14).

bound level (N) to the continuum by W_{N-N+1} and assume that T is sufficiently low that

$$\exp(-\beta N\hbar\omega) \approx 0, \quad (15)$$

\bar{t}^{-1} (and hence the rate constant for our model) can be evaluated as

$$k_{\text{MS}} = \bar{t}^{-1} = \kappa \left(\sum_{n=1}^{N+1} n^{-1} [\exp(\beta n\hbar\omega_0) - 1] [1 - \exp(-\beta n\hbar\omega_0)] \right)^{-1} \times [1 - \exp(\beta\hbar\omega_0)]. \quad (16)$$

III. APPLICATION

Figure 2 displays plots of $\log k$ vs $10^3/T$ for the Xe/W system. The experimental curve, determined by Dresser, Madey, and Yates,¹⁴ is given explicitly by

$$k = 10^{15} \exp(-4680 \text{ K}/T) \text{ sec}^{-1}. \quad (17)$$

The parameters required to evaluate the theoretical expressions (3) and (16) are ω_0 , D , and θ_D . In accord with experiment,¹⁴ we take the binding energy of the adatom to be $D = 4680$ K. For tungsten, $\theta_D \approx 400$ K.¹⁵ We estimate the fundamental frequency ω_0 using a procedure suggested by Lin and Wolken.¹⁶

We note (see Fig. 2) that both the MS and TST theoretical curves fall below the empirical one. However, as indicated by the error bars, the experimental curve is uncertain to at least ± 1 unit. Moreover, the estimated value of ω_0 could itself be uncertain by a factor within the range 1–2. Thus, the MS curve [see Eqs. (13b) and (16)] could be low by 1.2 units, the TST curve [see Eq. (3)] by 0.3 units.

We note that both k_{MS} and k_{TST} show Arrhenius behavior. The slopes of the plots (see Fig. 2), and hence the calculated activation energies, are approximately equal

and independent of lattice-dynamical properties. The activation energy in the MS model is essentially determined by the dominant term of the sum in expression (16), namely,

$$\exp[-\beta(N+1)\hbar\omega_0].$$

But D is related to N by (see Fig. 1)

$$N\hbar\omega_0 \leq D \leq (N+1)\hbar\omega_0,$$

and thus, for $N \gg 1$, the activation energy is

$$D \approx N\hbar\omega_0,$$

in agreement with that of TST [see Eq. (3)].

In Fig. 2 are also shown plots of $\log k_{\text{MS}}$ vs $10^3/T$ for $\theta_D = 300$ K and 500 K. Of course, it seems impracticable to vary θ_D independently of ω_0 and N (although one can imagine exotic experiments to accomplish such a feat, e.g., desorption from ⁶Li and ⁷Li metal surfaces). We do so artificially in order to illustrate graphically the dependence of k_{MS} upon the dynamical properties of the lattice. We see that the plots of k_{MS} are displaced vertically by varying amounts (depending on θ_D) from that of k_{TST} . This displacement, which arises solely from the ω_D^3 dependence in k_{MS} [see Eq. (13b)] and is characteristic of a one-phonon mechanism, has the following interpretation. As θ_D (and hence ω_D) increases, the density of lattice modes at frequency ω_0 decreases as ω_D^{-3} and hence the rate of desorption falls off accordingly. The same effect is observed in earlier one-phonon models.^{8–11}

In addition to showing a lattice-dynamical effect vastly different from that of TST (which, in fact, has none), the MS model predicts a slightly different isotopic dependence for the adatom. If the temperature is sufficiently high that

$$\exp(\pm\beta\hbar\omega_0) \approx 1 \pm \beta\hbar\omega_0,$$

then

$$k_{\text{MS}} \propto m_A^{-1},$$

whereas

$$k_{\text{TST}} \propto m_A^{-1/2}.$$

In principle, this disparity in isotopic dependence provides a basis on which to assess the validity of the two rate expressions. However, conventional thermal desorption experiments are not sufficiently sensitive to the pre-exponential factor in the rate constant to observe this isotopic dependence, i.e., the pre-exponential factors, as fit by experiment, are typically in error by 1 or 2 orders of magnitude (see Fig. 2). Even for the most favorable isotopic pair, H and D, the rate changes by a factor of only 2 for MS or $\sqrt{2}$ for TST. Such a small difference is virtually undetectable.

IV. SUMMARY AND DISCUSSION

By adapting the model of Montroll and Shuler (MS) for the kinetics of unimolecular dissociation of a diatomic molecule in a heat bath, we have formulated a quantum-dynamical model for thermal desorption of gases from solid surfaces. We have derived an explicit expression

[Eq. (16)] for the desorption rate constant and applied it to the system Xe/W, comparing the predictions of the MS model with those of transition state theory (TST) [Eq. (3)] and with experimental results.¹⁴

The fundamental mechanism of desorption in the MS picture is the following. Adatoms initially trapped in bound levels on the surface absorb single phonons from the solid lattice to undergo successive (uncorrelated) transitions to the next higher level, eventually reaching the continuum. We have noted that one-phonon quantum-dynamical models have previously been proposed.⁸⁻¹¹ However, these models assume that adatoms initially in bound levels desorb via direct transitions into the continuum and hence are restricted to systems obeying the inequality (4). The MS model is more widely applicable.

Recall that the MS and TST models are based on the same physical picture; both models assume the unperturbed mode density [Eq. (2)]. However, k_{MS} [Eq. (16)] depends upon lattice-dynamical properties, whereas k_{TST} [Eq. (3)] does not. Only if the mode density were perturbed would the general TST expression (1) give a k_{TST} depending upon lattice dynamics. There is additional evidence that the desorption rate constant should depend on lattice dynamics. Quite convincing is Kramers¹⁷ analysis of the one-dimensional Brownian motion of a particle crossing a barrier in a viscous solvent. This problem provides a simple general picture for the influence of solvent on rates of reaction (or relaxation, in general). Kramers finds that the barrier-crossing (i.e., reaction) rate constant $k_x(T)$ depends on the solvent dynamics through the friction coefficient η . In the limit $\eta \rightarrow 0$, $k_x(T)$ coincides essentially with the k_{TST} . As $\eta \rightarrow \infty$, $k_x(T) \propto \eta^{-1}$; the reaction becomes diffusion controlled.

Although the MS model accounts to some extent for the dynamical role played by the lattice in thermal desorption, it is by no means rigorous and definitive. One should recall that, in addition to the assumption inherent in the weak-coupling master equation, the MS model rests upon the following approximations:

(i) Perturbation theory is valid; the zero-order Hamiltonian is the unperturbed solid lattice plus the adatom (A) in the field of the surface atom (S) fixed at its equilibrium position;

(ii) The A-S interaction potential is a truncated harmonic oscillator;

(iii) The true continuum of A is replaced by the level $n = N + 1$ of the (untruncated) oscillator;

(iv) The lattice is an isotropic continuum; S is treated as a bulk atom.

It is difficult to estimate the relative importance of these various assumptions. More refined experiments or molecular dynamics simulations could provide suffi-

ciently detailed information to justify the effort required to relax some of them. Indeed, extant quantum-mechanical close-coupling calculations¹⁸ on gas-solid energy transfer suggest that it may be necessary to take into account strong (i.e., anharmonic) A-S interactions in zero order, to account for detailed features (e.g., energy and angular distributions) of thermal desorption.

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¹For recent reviews of thermal desorption, see for example (a) L. A. Péterman, in *Progress in Surface Science*, edited by S. G. Davison (Pergamon, New York, 1972), Vol. 3, Part 1, p. 1; (b) V. N. Ageen and N. I. Ionov, *ibid.*, Vol. 5, Part 1, p. 1 (1974); (c) D. Menzel in *Interactions on Metal Surfaces*, edited by R. Gomer (Springer, Heidelberg, 1975), Chap. 7; (d) D. A. King, *Surf. Sci.* **47**, 384 (1975).

²S. A. Adelman and J. D. Doll, *J. Chem. Phys.* **64**, 2375 (1976); S. A. Adelman and B. J. Garrison, *J. Chem. Phys.* **65**, 3751 (1976).

³J. D. Doll and D. R. Dion, *J. Chem. Phys.* **65**, 3762 (1976).

⁴B. J. Garrison and S. A. Adelman, *Surf. Sci.* **66**, 253 (1977).

⁵M. Shugard, J. C. Tully, and A. Nitzan, *J. Chem. Phys.* **66**, 2534 (1977).

⁶B. J. Garrison and S. A. Adelman, *J. Chem. Phys.* **67**, 2379 (1977).

⁷See P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley-Interscience, London, 1972) and references therein, especially R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.* **55**, 894 (1951), and R. A. Marcus, *J. Chem. Phys.* **20**, 359 (1952).

⁸J. E. Lennard-Jones and C. Strachan, *Proc. R. Soc. London Ser. A* **150**, 442 (1935).

⁹C. Strachan, *Proc. R. Soc. London Ser. A* **150**, 456 (1935).

¹⁰J. E. Lennard-Jones and A. F. Devonshire, *Proc. R. Soc. London Ser. A* **156**, 6 (1936).

¹¹B. Bendow and S.-C. Ying, *Phys. Rev. B* **7**, 622 (1973); S.-C. Ying and B. Bendow, *Phys. Rev. B* **7**, 637 (1973).

¹²E. W. Montroll and K. E. Shuler, *Adv. Chem. Phys.* **1**, 361 (1958).

¹³S. K. Kim, *J. Chem. Phys.* **28**, 1057 (1958).

¹⁴M. J. Dresser, T. E. Madey, and J. T. Yates, Jr., *Surf. Sci.* **42**, 533 (1974).

¹⁵C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1971), p. 219.

¹⁶Y.-W. Lin and G. Wolken, *Int. J. Quantum Chem.* (to be published). The fundamental frequency ω_0 is calculated from the curvature at the bottom of a Morse potential, $\omega_0^2 = 2\beta^2 D/m_A$, where β is the Morse parameter. The parameter β is chosen to give about the same width of the potential well at $\frac{1}{2}D$ as given by an LJ(6,12) potential using the same D and r_0 , where r_0 is the sum of the van der Waals radii of A and S.

¹⁷H. A. Kramers, *Physica (Utrecht)* **7**, 284 (1940); S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1943).

¹⁸Y.-W. Lin and S. A. Adelman (private communication).