

Figure 7. Schematic diagram of the mechanisms of $O(^3P)$ atom reactions.

the antibonding halogen-halogen or iodine-carbon σ orbital in a manner similar to the reaction of an F or Cl atom which has only a single unpaired p electron. In the reaction of $O(^3P)$ atoms with H_2 molecules this results²² in a collinear O-H-H transition state of $^3\Pi$ symmetry, and this situation also applies²³ to the abstraction of H atoms from hydrocarbon molecules by $O(^3P)$ atoms. Although interaction of the other unpaired p electron on the O atom with the Π electrons of the halogen or fluoroalkyl iodide molecule may result in a bent transition state of either $^3A'$ or $^3A''$ symmetry, this general picture would suffice to explain the dynamics of these reactions via the triplet potential-energy surface.

The triplet surfaces for the halogen reactions are more attractive than for the fluoroalkyl iodides and indeed result in a long-lived collision complex for the $O + ICl, I_2$ reactions.^{4,24} Herschbach has suggested⁴

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that the lowest triplet state in the collinear configuration has $^3\Sigma^-$ symmetry. Although this would initially require an O atom lone pair projected toward the halogen molecule and imply strong reactant repulsion, it might be accessible from a strongly bent initial configuration. Our results on the $O + Cl_2, Br_2$ reactions indicate that the potential-energy wells on these triplet surfaces are shallower than those for $O + ICl, I_2$. This accords with the electronegativity ordering rule proposed by Herschbach⁴ whereby the least electronegative atom occupies the central location for the most stable O-X-Y complex. Additional experiments are presently under way to study the dynamics of the $O + ICl$ reaction at high initial translational energy in order to resolve this question further.

Conclusions

Recent improvements in the techniques of crossed molecular beam reactive scattering now permit the measurement of differential reaction cross sections as a function of initial translational energy for a wide range of oxygen atom reactions. The dynamics of $O(^3P)$ atom reactions present more complexities than many other atom reactions which have been studied in molecular beams, due to the interaction of triplet and singlet electronic states. The results which have been gained so far give some indication of the electronic structure of the potential-energy surfaces involved. However more experimental measurements and electronic structure calculations will be required before a complete picture of oxygen atom reaction dynamics is obtained.

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Translational and Internal Energy Accommodation of Molecular Gases with Solid Surfaces

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The nature and degree of energy equilibration when molecular gases interact with solid surfaces, both reactively and passively, are important in gas-surface chemical kinetics and affect many areas of science and technology. Gas-surface energy occurs in processes

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ranging from coal gasification to heterogeneous catalysis, from supersonic and high-altitude flight to the fabrication of sophisticated solid-state electronic and optical devices, from energy conversion to materials fabrication. Gas-surface energy transfer is an initial step in vapor condensation to grow solid materials. It plays a role in the evaporation of solids to form complex molecular entities. It plays a similar role in corrosion and volatilization in high-temperature environments. Indeed, most reactions and interactions between gases and solid surfaces involve, as a first step, and perhaps as a last step, some degree of equilibration between the gaseous molecules and the surface. It is not surprising

that efforts to understand the dynamics and mechanism of chemical reactions which occur in whole or in part on solid surfaces have led to interest in the degree to which gaseous molecules impinging on a solid surface equilibrate with that surface in both their translational and internal degrees of freedom.

As with most other problems in surface science, no single experimental technique yields all the information desired for understanding the degree to which gaseous molecules exchange energy with solids. Classical hot-wire energy accommodation measurements have yielded much information on translational energy transfer, particularly of atomic gases.¹ In recent years, understanding has been greatly extended by atomic-beam scattering.¹⁻⁴ Information on internal energy accommodation of molecular gases has come from molecular beam scattering^{5,6} and from spectroscopy^{7,8} and has been inferred from chemical kinetic studies.⁹ These molecular techniques have inherent restrictions and, in consequence, have been applied to only a limited number of systems.

This Account focuses on measurements, made in the author's laboratory during the past few years, which have been concerned with molecular trends in translational and internal energy accommodation when relatively simple molecules interact with seasoned, room-temperature surfaces. The measurements have been made by a technique in which solid surfaces are vibrated at high velocity in a rarefied gas and the temperature increase of the oscillating surface is measured.¹⁰ The method differs from other experimental approaches to the study of gas-surface energy transfer and, because of this, can give information not readily obtained by other methods, but it also has limitations compared to other methods. The technique is described briefly in the following section so that the reader can understand the nature of the results being discussed. A major feature of the experiments is that one obtains, simultaneously and under identical conditions, relative values for energy transfer involving internal modes and for translational energy transfer.¹¹

The emphasis in this Account is on the *gas* molecular characteristics which affect translational and internal energy exchange. The gases studied cover a range of molecular structure and complexity and of surface residence time. The interaction is with substrates covered with absorbed layers of oxygen and/or test gas,

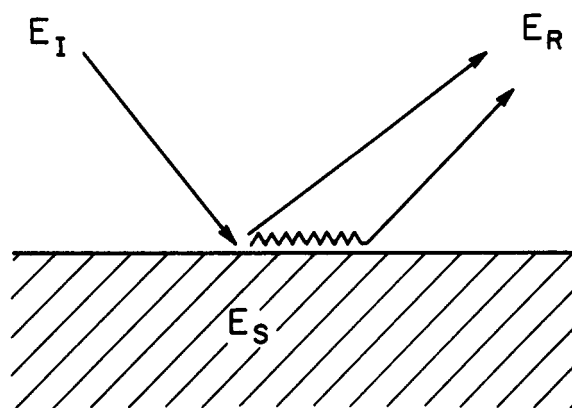


Figure 1. Gas-surface collision, schematic diagram.

not with atomically clean surfaces. In the systems studied, there is extensive trapping. Thus, the results to be discussed are not examples of the use of gas-surface interactions as a probe of atomically clean surfaces but rather are concerned with the systematics, from the standpoint of gas characteristics, of gas-surface energy exchange as it occurs in various branches of gas-surface chemical kinetics.

Accommodation Coefficients from the Vibrating Surface Method

Energy equilibration of gas molecules incident upon and subsequently emitted from a solid surface may be described by an accommodation coefficient (see Figure 1). Translational energy accommodation coefficients are defined by

$$\gamma_{\text{trans}} = \frac{E_{tI} - E_{tR}}{E_{tI} - E_{tS}} \quad (1)$$

where E_{tI} represents the average translational (*t*) energy of molecules incident (I) on the surface, E_{tR} the average translational energy of molecules reemitted (R) from the surface, and E_{tS} the average translational energy of molecules in thermal equilibrium with the surface (S). In a similar manner, one may define accommodation coefficients for internal energy γ_{int} or separately for rotational γ_{rot} , vibrational γ_{vib} , and electronic γ_{elec} energy exchange. Values of γ for a Maxwellian incident distribution are between 0 ($E_R = E_I$, no gas-surface energy exchange) and 1 ($E_R = E_S$, complete equilibration before reemission).

The vibrating surface method¹⁰ is a perturbation technique which gives γ when surface and gas are very close to equilibrium. In these experiments, the surface, initially in thermal equilibrium with a gas at reduced pressure, is vibrated at high velocity. The temperature of the rapidly moving surface increases, because as the surface moves into the gas, both the number and relative velocity of gas-surface collisions are increased over those for a stationary surface. Similarly, during the recession half of a cycle, both the number and relative velocity of gas-surface collisions are decreased compared to the stationary surface. The net effect is an enhancement of E_{tI} for molecules incident on the vibrating surface. The magnitude of E_{tI} and E_{tS} may be calculated by kinetic theory.¹²

Because E_{tI} is enhanced, gas-surface energy exchange causes the temperature of the moving surface to in-

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crease. The magnitude of the temperature rise depends upon the velocity of the oscillation and the gas pressure. It also depends upon γ_{trans} . In addition, the steady-state temperature rise is affected by other energy-transfer processes at the surface. These are of two types: gas-surface energy transfer involving internal modes of the gas molecules and energy transfer from the surface not involving the gas. The latter is described by an effective surface emittance ϵ' , as it is found empirically to be primarily radiation, secondarily conduction.¹¹

Energy exchange between molecular internal modes and the surface decreases the extent to which the surface temperature increases upon vibration. This is because the relative internal energy of gaseous molecules is unaffected by the surface motion. At steady state, when the surface has warmed up somewhat because of translational surface energy exchange, incident gas molecules are, on the average, translationally warm but internally cool relative to the moving surface. Internal-energy transfer in these experiments is a second-order effect which varies as pressure squared, in contrast to translational-energy transfer which varies directly with pressure.¹¹ The pressure-squared dependence arises because the amount of internal energy exchanged depends upon the incident gas flux, upon the maximum internal energy which could be transferred per collision, and upon the fraction γ_{int} of that maximum energy exchange which actually occurs. The maximum internal energy which could be transferred depends upon the steady-state temperature difference between the surface and the gas. That temperature difference is produced by translational energy transfer, the amount of which is proportional to incident gas flux. The result is that the total amount of internal energy exchanged increases with the square of the incident flux.

The different flux dependencies allow one to extract both $\gamma_{\text{trans}}/\epsilon'$ and $\gamma_{\text{int}}/\gamma_{\text{trans}}$ from measurements of the temperature increase ΔT as a function of gas pressure.¹¹ An important feature of the method is that the ratio $\gamma_{\text{int}}/\gamma_{\text{trans}}$ is obtained directly and that this ratio is independent of ϵ' and of most potential systematic errors in the measurements. Because the impinging gas is in internal equilibrium, the internal-energy accommodation coefficient obtained is weighted according to the thermal distribution of internal modes at the experimental temperature, i.e.,

$$\gamma_{\text{int}}C_{\text{int}} = \gamma_{\text{rot}}C_{\text{rot}} + \gamma_{\text{vib}}C_{\text{vib}} \quad (2)$$

where the internal heat capacity $C_{\text{int}} = C_{\text{rot}} + C_{\text{vib}} = C_p - (5/2)R$ (assuming $C_{\text{elec}} \approx 0$).

When making measurements, a thin sample is bonded to the end of an ultrasonic transducer and immersed in a gas at 10^{-4} to 0.05 torr. When the transducer is powered, the surface oscillates at a root-mean-square velocity in the range 16–35 m/s; the steady-state temperature rise, 0.05–1.0 °C, obtained in a few seconds, is measured with a differential thermocouple. A disadvantage of the technique, not uncommon in chemical kinetic studies, is that the substrate surfaces are covered with an ill-defined layer or layers of test and/or background gas.

Translational Energy Accommodation

Table I shows room temperature, energy accommodation coefficients of nitrogen obtained on a number

Table I
Room-Temperature Energy
Accommodation Coefficients of N₂

substrate	method	$\gamma_{\text{trans}}/\epsilon'$	$\gamma_{\text{rot}}/\gamma_{\text{trans}}$	γ_{trans}	ref
Ni	vibration	11.5	(0.17)	0.52	11
Cu	vibration	21.6	0.10	0.43	11
Pt	vibration	13.2	0.11	0.49	11
Ti alloy	vibration	3.13	0.13	0.46	23
Sb(111)	vibration	1.74	0.12	0.49	15
W	hot filament			0.53	14
Ni	N ₂ ⁺ fluorescence		0.19	0.58	8

of substrates by the vibrating surface method along with examples of results obtained by other techniques. We focus first on the results for γ_{trans} .

Experimental values of $\gamma_{\text{trans}}/\epsilon'$, the quantity obtained directly from the surface-temperature increase, vary by more than a factor of 10 because of the different radiative emittances of the different substrates. After multiplying the measured values by radiative emittances ϵ obtained independently,¹³ one obtains values for γ_{trans} which are, within experimental uncertainty, independent of the substrate, as illustrated by the results in Table I. Similar values of γ_{trans} are obtained by other workers using different techniques and substrates under similar experimental conditions.¹⁴ The constancy of the results, along with the experimental conditions employed, suggests that, from the viewpoint of the gas-surface interaction, all of the substrates in Table I are the same. The interaction is between the gas (N₂) and a surface covered by background and/or test gas (probably by O₂ or CO). Very similar results, also independent of substrate, are obtained with O₂ ($\gamma_{\text{trans}} \approx 0.56$)¹⁵ and Ar ($\gamma_{\text{trans}} \approx 0.65$).¹⁰ The values of γ_{trans} for N₂ (Table I) are at the low end of values measured under these experimental conditions (room temperature, covered surfaces) and are the lowest values to be discussed in this paper. Nonetheless, they are quite high, ~ 0.5 .

Comparison with theory^{16–20} suggests that, under these conditions, such high values of γ probably arise from a major part of the gas-surface equilibration occurring by molecules being trapped (physisorbed on the surface long enough to make a few gas-surface vibrations). Kinetic energy exchange between a gas and a surface at thermal energies may be qualitatively described as falling into four merging regimes: (1) elastic or nearly elastic collisions; (2) direct inelastic collisions, that is, energy exchange in single gas-surface collisions; (3) trapping or physisorption of the gas on the surface for a relatively short time, so that there are multiple collisions between gas and surface atoms but gas molecules leave the surface before complete thermal equilibration; (4) physisorption on the surface for a long

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enough time that gas molecules desorb with an energy and spatial distribution characteristic of thermal equilibrium at the surface temperature.

Clearly, the one extreme of elastic scattering corresponds to $\gamma = 0$ and the other extreme of long-residence-time trapping corresponds to $\gamma = 1$. However, the intermediate values of γ which are normally encountered probably correspond to some mixture of these qualitatively distinguishable processes. Under some conditions the different processes can be resolved in atomic-beam scattering studies.^{21,22}

Energy transfer in direct collisions is often discussed by comparison with hard-sphere or hard-cube model calculations;¹ in general, such models give upper limits to the energy transfer which takes place in single direct collisions. For example, more realistic Langevin equation, Monte Carlo calculations for He on tungsten, where there is no trapping, yield $\gamma \approx 0.01$, which is about an order of magnitude below the limit given by the hard-sphere model.^{16,19} Perhaps the highest value of γ arising unambiguously from direct collisions is the value $\gamma = 0.15$ – 0.20 found in the scattering of Ar atomic beams from clean polycrystalline tungsten surfaces.⁴ Observation of an energy accommodation coefficient greater than ~ 0.25 would appear to be an experimental indication that trapping is important in that energy-transfer process.²³

Theoretical considerations have shown that trapping—the inability of the gas particle to escape the potential after initial collision—is a sensitive function of incident gas energy. Below a certain incident energy almost everything traps on a cold surface, and above this energy almost nothing traps.^{16,19,24} For clarity, we define trapping to include all molecules which change the direction of their normal momentum more than once.¹⁸ Trapping appears to be a precursor to the detailed atomistic coupling of the gases' degrees of freedom to the solid excitations which are necessary for equilibration.^{18,20} At room temperature where, for the heavier inert gases and most molecular gases, trapping plays a significant role in energy accommodation, it appears that the translational energy accommodation coefficient is somewhat less than the fraction δ of gas particles initially trapped on the surface.^{17,18,20} Monte Carlo simulations of the energy distribution of reemitted gas particles as a function of the time the particles spend on the surface show that particles with short residence times, one or a very few perpendicular vibrations, accommodate little energy. But as the residence time increases, the energies of the emitted gas particles level off to an energy characteristic of the surface temperature.^{17,19,24}

For example, considering Ar on tungsten which has been the subject of extensive theoretical and experimental efforts, Langevin equation simulations¹⁸ indicate that at room temperature the fraction trapped $\delta = 0.5$ – 0.8 , depending upon model parameters. Over the same range of parameters, $\gamma_{\text{trans}} = 0.3$ – 0.6 and $\gamma_{\text{trans}}/\delta = 0.3$ – 0.8 .¹⁸ Direct analysis of molecular-beam scattering data indicates that at room temperature the

fraction trapped and equilibrated is 0.3 – 0.5 .⁴ A soft cube (hard cube plus attractive well) analysis of those same data indicates similar but slightly higher values for the fraction initially trapped.²⁵

In summary, considering the room-temperature interaction of molecular gases with contaminated surfaces, it appears that values of γ_{trans} greater than 0.5 arise from the major part of the energy transfer occurring via a trapping mechanism. Under these conditions it is likely that the magnitude of γ_{trans} is intermediate between the fraction of the molecules trapped initially and those physisorbed on the surface long enough to equilibrate.

Values of γ_{trans} somewhat lower than those in Table I are obtained for N_2 ($\gamma_{\text{trans}} = 0.34$) and O_2 ($\gamma_{\text{trans}} = 0.39$) on arsenic single-crystal cleavage surfaces.¹⁵ These values reflect the fact that the arsenic (111) cleavage surfaces are somewhat different, presumably cleaner, than the substrates in Table I. Accommodation coefficients usually change when surfaces are covered by chemisorbed gas layers, and for gases which do not themselves interact strongly with the surface, γ_{trans} is usually lower on a cleaner metal surface.¹ The lower values of γ_{trans} for N_2 and O_2 on arsenic (111) imply that a slightly smaller fraction of the incident molecules are trapped on the arsenic surface than on the other substrates in Table I.

Before leaving the subject of translational energy transfer, we turn briefly to results on a rather different kind of system, gaseous As_4 on arsenic (111). Tetrahedral As_4 is the major vapor species over arsenic. However, the solid does not consist of As_4 tetrahedral units, and the phase transition requires extensive changes in the electronic structure and atomic geometry of the arsenic atoms. Because of this, there are kinetic barriers to the evaporation of As_4 from arsenic or to the condensation and incorporation of As_4 on arsenic.^{26,27} The condensation coefficient for As_4 on arsenic (111) is below 10^{-4} at 550 K. Measurements of the energy accommodation coefficient, in contrast, yield $\gamma_{\text{trans}} \approx 1$.²⁸ The energy accommodation results indicate that impinging As_4 molecules are trapped on the surface for relatively long times, forming a two-dimensional gas-like layer, and that the retarded incorporation of As_4 molecules into the crystal lattice is associated with limited interchange between this layer and the underlying bulk solid. This result is in accord with detailed studies of the mechanisms of vaporization and condensation of As_4 from arsenic.^{26,27} Interestingly, in the case of arsenic, the surface residence time is long enough (a rough estimate is $\tau \approx 10^{-7}$ s)²⁹ that one finds chemical equilibrium between As_4 and As_2 molecules in this two-dimensional layer, even when these molecules are not in chemical equilibrium with the underlying bulk solid.³⁰

Rotational Energy Accommodation of N_2 and O_2

For N_2 , O_2 , and most other diatomics at room temperature, $C_{\text{int}} = C_{\text{rot}} = R$ and thus, from eq 2, vibrat-

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ing-surface measurements of γ_{int} yield γ_{rot} . The most striking feature about the internal-energy accommodation results in Table I is the relatively low value of $\gamma_{\text{rot}}/\gamma_{\text{trans}}$, 0.1–0.2. When $\gamma_{\text{rot}}/\gamma_{\text{trans}}$ is compared with the measured values of γ_{trans} and systematic and statistical experimental uncertainties are considered, for N_2 at room temperature $\gamma_{\text{rot}} \approx 0.03$ –0.11. Very similar values of $\gamma_{\text{rot}}/\gamma_{\text{trans}}$ and of γ_{rot} are measured for O_2 .¹⁵

The measured values of γ_{trans} for N_2 (and also O_2), along with experimental^{4,10} and theoretical^{18,19,25} results for Ar described in the preceding section, imply that the fraction of the incident N_2 molecules initially trapped on the surface is in the range 0.4–0.8 and that the fraction trapped and translationally thermally equilibrated is in the range 0.3–0.6. Thus, the low values of $\gamma_{\text{rot}}/\gamma_{\text{trans}}$ measured for N_2 and O_2 imply that, *even though a significant fraction of the incident N_2 and O_2 molecules are trapped, most of those trapped continue to rotate relatively freely in the sense that only 10–20% of those trapped equilibrate directly with the surface in their rotational degrees of freedom.* The small rotational energy accommodation coefficients appear to result from a combination of two factors:

(1) Relatively short residence times on the surface. If one crudely estimates the gas–surface interaction potential for these gas-contaminated surfaces from the heat of vaporization of the gas^{23,31} for N_2 with $\Delta H_{\text{vap}} = 1.3$ kcal/mol, one estimates a surface residence time³² at room temperature of $\tau/\tau_0 = \exp(\Delta H_{\text{vap}}/RT) \approx 10$ perpendicular vibrations. For Ar and O_2 , similar estimations yield $\tau/\tau_0 \approx 15$ perpendicular vibrations.

(2) Little angular anisotropy in the interaction potential between the molecules and the surface. Gas-covered metal surfaces are relatively smooth: close-packed metal surfaces themselves are relatively smooth compared to ionic crystals or semiconductors and gas coverings tend to smooth out heterogeneities. The factors which give rise to torques in molecule–surface interactions—shape or elliptical axial ratio at the van der Waals distance, molecular quadrupole moment, polarizability anisotropy—are not particularly large for N_2 . Analysis of the behavior of the physisorbed phase of N_2 on graphite indicates that, in this system, N_2 behaves as a free or nearly free rotor above 80 K.³³ Similarly, both three-dimensional and two-dimensional second virial coefficients for N_2 are not indicative of large torques on this molecule.³⁴

The energy accommodation measurements indicate that rotational energy equilibrates with surface phonons about a factor of 10 less efficiently than translational energy equilibrates with the surface phonons—for N_2 and O_2 at surface conditions which may not be too dissimilar to those encountered in heterogeneous reactions. It is tempting to compare these results with those from molecular-beam scattering of H_2 , D_2 , and HD from clean MgO and LiF. The molecular beam studies^{5,6} show high probabilities of translational–rotational energy interchange in single elastic scattering events. The experiments differ in the gases investigated (N_2 vs. H_2), in the surfaces examined (oxygenated

metals vs. ionic crystals), and in the degree of surface cleanliness and coverage. Of these, the change from a metal surface to an ionic crystal may be particularly significant. Rotational–translational interchanges are found to be at least a factor of 10 less probable in H_2 scattering from a close-packed metal surface, Ag(111), than from LiF and MgO.³⁵

However, in addition to the differences in the systems investigated, the quantities measured in the two types of experiments differ sufficiently that comparison is difficult. The vibrating surface experiments give information on rotational–surface ($r \leftrightarrow v_s$) and translational–surface ($t \leftrightarrow v_s$) energy exchange separately. In contrast, molecular-beam diffraction yields information on molecular rotational–translational ($r \leftrightarrow t$) interchange for the condition where there is no energy exchange with the surface. Depending upon the detailed mechanism of energy accommodation and rates of intramolecular energy transfer, $r \leftrightarrow t$ collisional interchanges might or might not affect γ_{trans} and γ_{rot} values. The results in Table I show that $t \leftrightarrow r$ interchange in N_2 does not occur on the surfaces studied in such a manner as to increase $\gamma_{\text{rot}}/\gamma_{\text{trans}}$ significantly above 0.1–0.2. However, this does not rule out the possibility that $t \leftrightarrow r$ interchanges occur to an appreciable extent or that they play a role in the mechanism of rotational energy equilibration.

The energy accommodation experiments also differ from the molecular beam experiments in that energy accommodation coefficients describe *net* degrees of equilibration. Equilibration requires many state–state changes, since these occur in opposite directions and to a degree compensate.

Without further experiments, one cannot say whether molecular-beam results imply that $\gamma_{\text{rot}}/\gamma_{\text{trans}}$ is higher for H_2 on MgO or LiF than it is for N_2 on gas-covered or semimetal¹⁵ surfaces. However, if γ_{rot} for H_2 on LiF is indeed greater than γ_{rot} for N_2 on gas-covered metal, this probably arises from differences in the surfaces not differences in the gases. Theoretical investigations ascribe rotational transitions to interactions between molecular shape asymmetry and surface corrugation amplitude^{36,37} and to interactions between molecular quadrupole moments and the electric field gradient above an ionic crystal.³⁸ All these effects are larger with an ionic crystal than with a gas-covered or close-packed metal. On the other hand, the electric quadrupole moment of N_2 is about twice that of H_2 ,³⁹ N_2 is slightly more anisotropic in shape, axial ratio perhaps ~ 1.3 ⁴⁰ compared to ~ 1.1 ;³⁷ N_2 also has a somewhat larger polarizability anisotropy and derivative than does H_2 .⁴¹ Thus all factors which give rise to molecular torques are increased for N_2 relative to H_2 . Spectroscopic studies of rotational-state changes upon scattering of N_2 from ionic and metallic surfaces might be enlightening (N_2 is too heavy for good diffraction in beam scattering).

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Table II
Room-Temperature Energy Accommodation
Coefficients of a Number of Molecular Gases
on Gas-Covered Polycrystalline Metal Substrates²³

gas	substrates	γ_{trans}/e'	$\gamma_{\text{int}}/\gamma_{\text{trans}}$	γ_{trans}
CH ₄	Fe	6.89	0.94	0.55
C ₂ H ₆	Fe	8.10	0.82	0.65
C ₂ H ₂	Cu	(31.3) ^a	0.86 ^a	(0.63) ^a
C ₃ H ₆	Fe	9.40	0.84	0.75
C ₃ H ₈	Fe	9.47	0.85	0.76
<i>n</i> -C ₄ H ₁₀	Fe	10.5	0.87	0.84
<i>neo</i> -C ₅ H ₁₂	Fe	10.8	0.86	0.87
<i>n</i> -C ₅ H ₁₂	Fe	11.1	0.91	0.88
<i>n</i> -C ₆ H ₁₄	Fe	11.1	0.91	0.88
<i>n</i> -C ₇ H ₁₆	Fe	11.5	0.96	0.92
<i>n</i> -C ₈ H ₁₈	Fe	11.8	0.96	0.95

^a From ref 11. Numbers in parentheses are more uncertain than the other measurements.

Polyatomic Molecules. Molecular Trends in Energy Accommodation

When one turns from gases like N₂, Ar, and O₂ to gases such as Cl₂ and NH₃, which have higher heats of vaporization and interact more strongly, and probably more specifically, with seasoned metal substrates at room temperature, values of γ_{trans} increase to ~ 0.9 and of $\gamma_{\text{int}}/\gamma_{\text{trans}}$ to ~ 1 .²³ (Because of the neglect of thermal conductivity from the surface in the vibrating surface measurements, energy accommodation coefficients from that method may be systematically up to 10% low;¹¹ this does not affect values of $\gamma_{\text{int}}/\gamma_{\text{trans}}$, however.) Thus, for strongly interacting molecules with relatively long surface residence times, γ_{trans} is close to 1 and $\gamma_{\text{rot}} \approx \gamma_{\text{trans}}$.

For CO₂, vibrating surface measurements yield $\gamma_{\text{int}}/\gamma_{\text{trans}} \approx 0.75$.³³ However, for CO₂ and for the hydrocarbons to be discussed below (except CH₄), interpretation is complicated by the fact that at room temperature there is a significant amount of internal energy in vibrational degrees of freedom as well as in rotational degrees of freedom. By analogy with gas-phase energy transfer⁴² and considering the size of the quanta involved, one anticipates that in gas-surface energy transfer also, $\gamma_{\text{trans}} \geq \gamma_{\text{rot}} \geq \gamma_{\text{vib}}$. This hierarchy is supported by spectroscopic measurements for N₂ on glass, which yield $\gamma_{\text{vib}} \approx 5 \times 10^{-4}$.⁷

The hierarchy, along with eq 2, can be used to compute upper and lower limits to γ_{rot} and γ_{vib} from the measured values of $\gamma_{\text{int}}/\gamma_{\text{trans}}$ and γ_{trans} . For CO₂, one obtains in this way $\gamma_{\text{trans}} = 0.7$, $\gamma_{\text{rot}} = 0.5-0.7$, and $\gamma_{\text{vib}} = 0.2-0.5$.²³ Furthermore, considering the results for γ_{trans} and γ_{rot} for N₂ and Cl₂ and their interpretation (discussed above), one anticipates that for a molecule like CO₂, for which one roughly estimates $\tau/\tau_0 \approx 1000$ surface vibrations from the heat of vaporization, $\gamma_{\text{rot}} \approx \gamma_{\text{trans}}$. Thus γ_{vib} is probably near the lower limit (0.2) of the range obtained in this manner. Although the results may not be exactly comparable because of differences in the surfaces, a review⁷ of spectroscopic studies of γ_{vib} for CO₂ lists $\gamma_{\text{vib}} = 0.22$ for the bending mode, the mode primarily populated at room temperature, and 0.2-0.4 for the antisymmetric stretch.

Table II shows results of measurements on a series of hydrocarbons arranged in order of increasing ΔH_{vap} .

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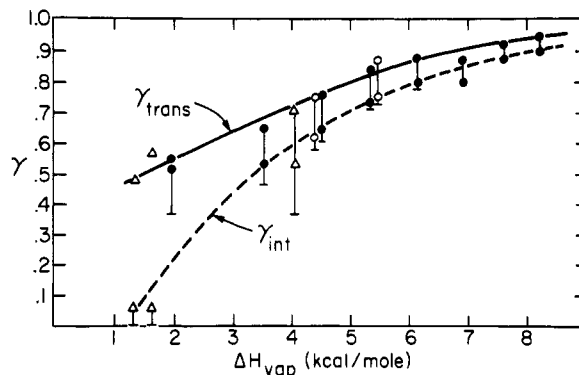


Figure 2. Room-temperature translational (upper points) and internal (lower points) energy accommodation coefficients of a number of molecular gases. From left to right: (●) *n*-C_mH_{2m+2} with *m* = 1-8; (○) C₃H₆, *neo*-C₅H₁₂; (Δ) N₂, O₂, CO₂. The extremities of the vertical lines represent upper limits to γ_{rot} and lower limits to γ_{vib} .

Values of γ_{trans} increase smoothly from 0.55 for CH₄ and 0.65 for C₂H₆ to 0.95 for *n*-C₈H₁₈.²³ (Recall that these values could be systematically up to 10% low.) Values of $\gamma_{\text{int}}/\gamma_{\text{trans}}$ rise smoothly from 0.82 for C₂H₆ to 0.96 for *n*-C₈H₁₈. For CH₄, however, $\gamma_{\text{int}}/\gamma_{\text{trans}} = 0.94 \pm 0.03$, an exception which is discussed further below. The high values of γ_{trans} imply that, under the experimental conditions, energy accommodation of all these gases is dominated by trapping.

The hydrocarbon results are plotted in Figure 2 as a function of ΔH_{vap} , along with results for N₂, O₂, and CO₂. The upper points represent experimental values of γ_{trans} ; the lower points represent experimental values of γ_{int} . The upper and lower extremities of the vertical lines represent, respectively, the upper limits to γ_{rot} and the lower limits to γ_{vib} calculated from eq 2 and the assumed hierarchy $\gamma_{\text{trans}} \geq \gamma_{\text{rot}} \geq \gamma_{\text{vib}}$. With this hierarchy, for a given molecule, γ_{rot} must be between the lower point and the upper end of the vertical line and γ_{vib} must be between the lower point and the lower end of the vertical line. (Experimental uncertainties have not been included.)

The correlation between energy accommodation coefficients and ΔH_{vap} illustrated by Figure 2 is perhaps not surprising for energy accommodation dominated by trapping. Although the normal-hydrocarbon accommodation coefficients also correlate to a degree with molecular weight, it is not possible to include molecules other than the normal hydrocarbons satisfactorily in a plot of γ vs. molecular weight.

Not only do γ_{trans} and γ_{int} correlate with ΔH_{vap} but one does not see differences in translational or internal energy accommodation among the heavier hydrocarbons which reflect differences in molecular structure. For example, compare neopentane and normal pentane (Table II). Neopentane is more spherical than normal pentane, and one might anticipate that neopentane would accommodate rotational energy less efficiently than does normal pentane. The data, however, do not warrant such a conclusion. This is in contrast to the data for O₂ compared to CO₂; as described above, γ_{rot} for O₂ is considerably smaller than γ_{rot} for CO₂. Apparently, at room temperature, the surface residence time is too long, and too much of the total internal energy is in vibrational degrees of freedom, for one to see any indication that branched- and straight-chain

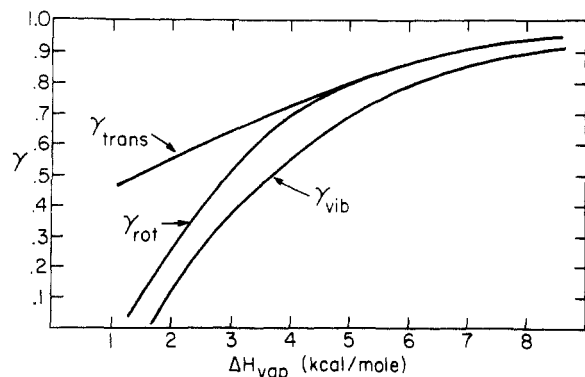


Figure 3. Trends in translational, rotational, and vibrational energy accommodation coefficients for molecular gases on seasoned surfaces at room temperature.

hydrocarbons differ significantly in either γ_{rot} or γ_{vib} . If such differences become significant at higher temperatures, where surface residence times are shorter, they could have implications for heterogeneous kinetic processes such as, for example, combustion in internal combustion engines.

Figure 3 summarizes trends in room-temperature translational, rotational, and vibrational molecular energy accommodation coefficients on seasoned surfaces, based upon the experimental results in Figure 2. The γ_{trans} line is the same as in figure 2. Following the CO_2 discussion above, the γ_{rot} line is sketched by assuming that γ_{rot} is near the upper limit of the range permitted by the measurements of γ_{trans} and $\gamma_{\text{int}}/\gamma_{\text{trans}}$. Correspondingly, the γ_{vib} line is sketched assuming that γ_{vib} is near the lower limit of the range permitted by the measurements. That is, γ_{rot} and γ_{vib} in Figure 3 are based upon the extremities of the vertical lines in Figure 2.

The data and the trends in Figure 3 are consistent with translational and internal energy accommodation being dominated by trapping and with rotational energy accommodation being a balance between surface residence time and molecular structure. γ_{rot} is small for molecules like N_2 and O_2 which have small values of ΔH_{vap} , are on the surface relatively short times, 10–20 perpendicular vibrations, and also have little angular anisotropy in their surface interaction potential. However, γ_{rot} approaches γ_{trans} for molecules like CO_2 , Cl_2 , NH_3 , plus C_2H_6 and larger hydrocarbons which are on the surface for relatively long times, >300 perpendicular vibrations. For these molecules, it appears that γ_{int} is less than γ_{trans} because of restrictions to vibrational energy accommodation.

The major exception to the qualitative trends in Figures 2 and 3 is γ_{int} for CH_4 . From $\Delta H_{\text{vap}}(\text{CH}_4) = 1.96$ kcal/mol, one would roughly estimate $\tau/\tau_0 \approx 30$ surface vibrations and would have expected $\gamma_{\text{int}}/\gamma_{\text{trans}} \approx 0.4$ by comparison with other data plotted in Figure 2. The measured value of γ_{trans} , 0.55, is that anticipated from ΔH_{vap} and the estimated τ/τ_0 . Methane is a relatively free rotor in the liquid state, and from its liquid-phase behavior⁴³ one would not expect CH_4 to be significantly less spherical than N_2 or O_2 . If one conjectures that

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vibrational-energy transfer is unusually efficient in CH_4 because it couples to rotational-energy transfer⁴⁴ (vibrational energy, however, is only 0.16 of the total internal energy at room temperature) and if one also adjusts for an unusually high rotational velocity in CH_4 ,⁴⁴ one predicts $\gamma_{\text{int}}/\gamma_{\text{trans}} \approx 0.6$ from comparison with other molecules, significantly below the measured value of 0.94. The reason for the apparently unusually high rotational-energy accommodation efficiency of CH_4 awaits further experiments. One possibility is that physisorbed CH_4 rotates freely about an axis perpendicular to the surface but that rotation about axes more or less parallel to the surface is hindered. Such appears to be the case for CH_4 adsorbed on graphite at low temperatures where interpretations of NMR,⁴⁵ neutron scattering,⁴⁶ and atom-atom potential calculations⁴⁶ indicate that, while isolated CH_4 molecules rotate relatively freely about an axis perpendicular to the surface, there is a barrier of 140–300 K for CH_4 rotation about axes more nearly parallel to the surface.

Concluding Remarks

Overall, it appears that molecular energy accommodation on seasoned surfaces at room temperature is dominated by trapping and is described by the hierarchy $\gamma_{\text{trans}} \geq \gamma_{\text{rot}} \gg \gamma_{\text{vib}}$. Under these conditions translational energy accommodation coefficients are greater than 0.5. Translational, rotational, and vibrational energy accommodation coefficients increase with surface residence time and correlate with ΔH_{vap} . It appears that γ_{rot} is close to γ_{trans} unless $\tau/\tau_0 \lesssim 100$ surface vibrations (one surface vibration ≈ 1 ps) and one is dealing with isotropic (spherical) molecules. In contrast, very long surface residence times, $\tau > 10^4$ ps, are required before γ_{vib} becomes approximately equal to γ_{trans} . At such long residence times $\gamma_{\text{trans}} \approx 0.9$. In addition, at such long residence times one may have two-dimensional chemical equilibrium among molecules in the physisorbed precursor state even when the two-dimensional gas phase is not in chemical equilibrium with the underlying bulk solid.

The above generalizations are to a degree just that, generalizations which gloss over a host of still-to-be-learned significant detail and to which there will probably be some interesting exceptions. In particular, the results discussed in this account apply to seasoned metal surfaces and may require substantial modification for surfaces of substantially different character, such as ionic surfaces or truly clean, bare surfaces. One also anticipates changes at high temperatures where incident energies are higher and surface residence times are considerably shorter.

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