

# Gas-Surface Interactions with Vibrationally Excited Molecules

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## I. Introduction

Energy transfer in gas-surface interactions is a field of importance to such practical areas as corrosion, plasma confinement, heat transfer, and catalysis. On the more fundamental level, measurements of the energy exchanged during the gas-solid interaction can provide information concerning the potential of interaction between the molecule and the surface. It was Maxwell<sup>1</sup> who first introduced the idea of an accommodation coefficient in his explanation of the observation by Kundt and Warburg<sup>2</sup> that the viscosity of a gas decreased with pressure at sufficiently low pressure. The viscosity decreased, he suggested, because of velocity "slip"; not all of the gas molecules incident on a surface are scattered in thermal equilibrium with the surface. Although his suggestion was made in the narrower context of momentum transfer, the idea that a fraction of collisions,  $\alpha$ , exchange energy completely with the surface while a fraction  $1 - \alpha$  are scattered without any exchange has been used for over a century to characterize the exchange of energy in gas-surface

collisions. The commonly defined energy accommodation coefficient  $\alpha$  is given by

$$\alpha = (E_f - E_i) / (E_s - E_i) \quad (1)$$

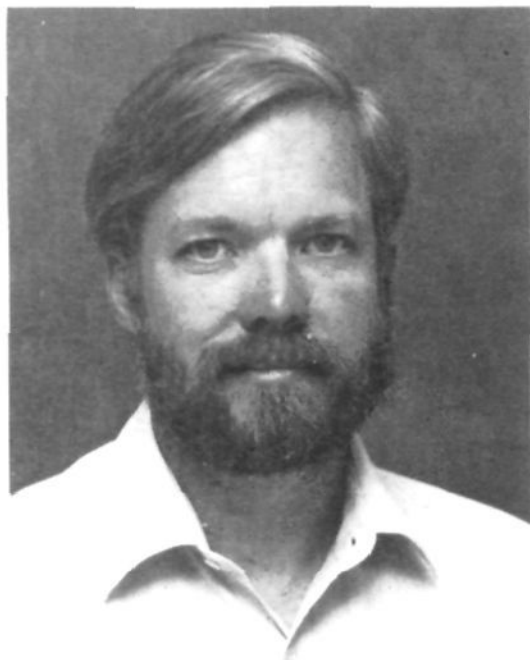
where  $E_f$  and  $E_i$  are the final and initial flux-averaged energies after and before the collision, respectively, and  $E_s$  is the flux-averaged energy for molecules scattered in thermal equilibrium with the surface. Thus, the energy accommodation coefficient falls in the range from zero to one. Note that if the distribution of energy is such that each energy is linearly proportional to a temperature with the same proportionality coefficient for the initial, final, and surface states, then we can also define  $\alpha$  as  $(T_f - T_i) / (T_s - T_i)$ .

By itself the energy accommodation coefficient is a rather crude measure of the exchange that can take place on collision with a surface. Yet it plays a key role in characterizing the gas-surface interaction. Important contributions to the measurement and interpretation of the accommodation coefficient have been summarized extensively.<sup>3-7</sup> More recently, attention has focused on what type of energy is transferred: translational, rotational, vibrational, or electronic. In a manner entirely analogous to eq 1, we can define an accommodation coefficient for each possible degree of freedom:

$$\alpha^j = (E_f^j - E_i^j) / (E_s^j - E_i^j) \quad (2)$$

where the superscript  $j$  represents the particular mode under consideration and  $E_f$  and  $E_i$  are the molecular energies in mode  $j$ . This review will be primarily concerned with the exchange of vibrational energy in gas-surface collisions and with the selective production or consumption of vibrational energy in elementary surface reactions. Thus, unless otherwise specified, we will refer to the vibrational accommodation coefficient  $\alpha^{\text{vib}}$  or  $\alpha^{\text{v}}$  simply as  $\alpha$ .

The exchange of vibrational energy is often characterized in the literature by one of two other parameters:  $\beta$ , the vibrational deactivation probability in a gas-surface collision, or SP  $\equiv (1 - \beta)$ , the survival probability for vibrational excitation. When the energy of the vibrational mode is large compared to the vibrational energy that molecules would have in equilibrium with the surface, then there is a straightforward relationship between  $\beta$  or SP and  $\alpha^{\text{v}}$ . Suppose that a vibrationally excited molecule with energy  $E_{\text{vib}}$  is incident on a surface. If the probability that the vibrational energy survives the collision is SP =  $1 - \beta$ , then the average vibrational energy of the scattered molecules will be  $(1 - \beta)E_{\text{vib}}$  if each deactivation produces only ground-state



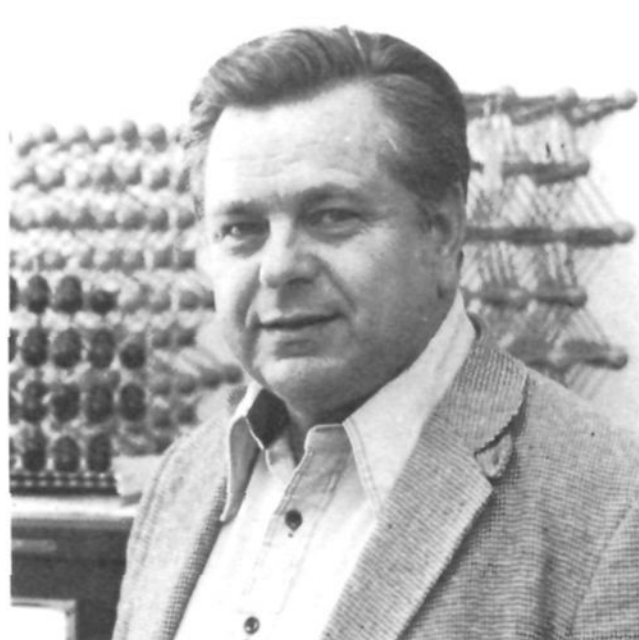
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molecules. From eq 2 for the vibrational degrees of freedom, we find that

$$\alpha^v = [E_{\text{vib}} - (1 - \beta)E_{\text{vib}}] / (E_{\text{vib}} - E_s) = \beta / (1 - E_s/E_{\text{vib}}) \quad (3)$$

Thus, if  $E_s \ll E_{\text{vib}}$ , which is typically true, then  $\alpha^v$  and  $\beta$  are the same, while for high surface temperatures or low vibrational frequencies  $\alpha^v > \beta$ .

Although early distinctions between the accommodation of translational and internal energy were made by Marsden,<sup>8</sup> by Tang et al.,<sup>9</sup> and by Kostoff et al.,<sup>10</sup> the first technique to study internal accommodation in a systematic way was developed by Rosenblatt and his colleagues in 1975<sup>11-13</sup> and is summarized in a recent account.<sup>14</sup> This "vibrating-surface method" is a perturbation technique that provides the accommodation coefficient when the gas and the surface are very close to equilibrium. The surface, which is originally at equilibrium with a low-pressure gas, is vibrated at a high velocity, and the temperature difference between the surface at rest and the vibrating surface is recorded as a function of the gas pressure. The technique sep-



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arates the overall accommodation coefficient into contributions from translation and internal energy in the following way. As the surface moves toward the gas both the number and relative velocity of gas-surface collisions increase compared to those for a stationary surface, whereas both decrease as the surface moves away from the gas. However, the net energy of translation, which is proportional to the square of the velocity, increases, so that the surface temperature will generally increase. The magnitude of the temperature increase will be directly related to the translational accommodation coefficient and will depend linearly on the pressure of the gas. Vibration of the surface does not change the internal energy of the incident molecules. However, because of the heating described above, the temperature of the surface becomes higher than the internal temperature of the impinging molecules, so energy flows from the surface to the internal degrees of freedom in proportion to the accommodation coefficient for these internal modes. The amount of surface heating is thus reduced from that expected if the internal energy accommodation were zero. The reduction is proportional to the product of the originally expected increase in temperature and the pressure of the gas, and since the originally expected increase is linear in the gas pressure, the reduction goes as the square of the pres-

sure. Thus, a careful study of the surface temperature change as a function of gas pressure can yield both the translational accommodation coefficient and the ratio of the internal energy accommodation coefficient to the translational accommodation coefficient.<sup>11,12</sup> Because the pressure of the sample gas needs to be relatively high to produce an observable temperature change, the surface is typically covered by background and/or test gas. This is a major disadvantage of the technique compared to those that provide an opportunity to control and measure the composition of the surface during the energy-exchange experiment.

A study of several hydrocarbons as well as simple gases such as CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> revealed some interesting qualitative trends.<sup>14</sup> For molecules with low heats of vaporization on a given surface, the internal accommodation coefficient was found to be substantially lower than the translational accommodation coefficient, but the two were nearly equal for molecules with relatively high heats of vaporization. In absolute magnitude, the internal accommodation coefficients ranged from about 0.2 to 1.0 for the gases studied. 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:

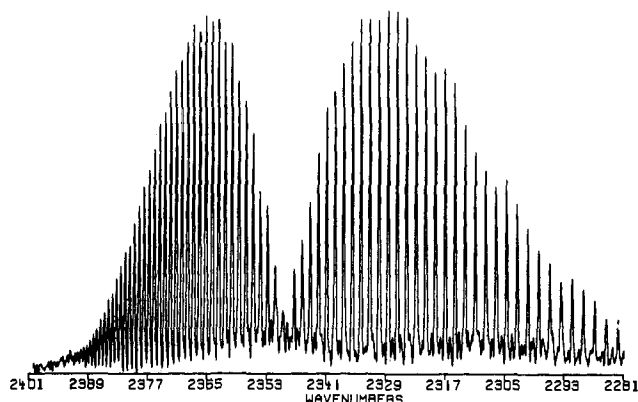
$$\alpha^{\text{int}}C_{\text{int}} = \alpha^{\text{rot}}C_{\text{rot}} + \alpha^{\text{vib}}C_{\text{vib}} \quad (4)$$

where  $C_i$  is the contribution to the heat capacity of the  $i$ th degree of freedom,  $C_{\text{int}}$  is the heat capacity of all internal degrees of freedom, and it has been assumed that  $C_{\text{elec}} = 0$ . If it is assumed that  $\alpha^{\text{rot}} > \alpha^{\text{vib}}$ , then this equation allows a determination of the upper limit to  $\alpha^{\text{rot}}$  and occasionally (for  $\alpha^{\text{rot}} = 1$ ) a lower limit to  $\alpha^{\text{vib}}$ . As will be shown below, however, there are several systems for which this inequality does not hold.

While the vibrating-surface method is of historical importance, the recent dramatic increase in the measurement of vibrational effects in gas-surface interactions has been caused by the incorporation of laser techniques into surface science. Some of the more important experimental results have been summarized in recent reviews,<sup>15-23</sup> while a very recent article in this journal has included a rather complete summary of the theoretical approaches to energy accommodation at surfaces.<sup>24</sup> However, this is the first review in the past 5 years to deal exclusively with the vibrational excitation and deactivation in surface interactions. Although it will focus primarily on experimental observations, references to the theory of vibrational energy transfer at surfaces will be included where particularly appropriate. The main part of the review is in four sections. Section II will describe vibrational excitation in gas-surface collisions, while section III will summarize vibrational excitation as a result of surface reactions. Sections IV and V will cover the complementary topics of vibrational deactivation in gas-surface collisions and the role of vibrational energy in surface reactivity, respectively. Conclusions and an outlook for the future are offered in sections VI and VII.

## II. Vibrational Excitation in Gas-Surface Collisions

In principle, the probability of vibrational excitation during a gas-surface collision can depend (1) on the



**Figure 1.** Infrared emission spectrum of the asymmetric stretch mode ( $00^0_1 \rightarrow 00^0_0$ ) from CO<sub>2</sub> excited during a collision with a 1450 K Pt foil. (From Mantell et al.,<sup>25</sup> with permission.)

properties of the molecule, including for example, the molecular charge distribution, the degree of internal excitation, the transition dipole moment, and the vibrational frequency, (2) on the properties of the surface, including its temperature, composition, and structure, and (3) on the relative properties of these two systems, such as the relative velocity and the orientation of the molecule at the moment of the collision and the position of impact. While recent experiments have made great progress in determining the vibrational excitation probability as a component separate from the accommodation of other degrees of freedom, the dependence of this probability on the above-mentioned parameters has not yet been systematically studied. Nonetheless, the development of several new techniques provides great promise for the future.

### A. FTIR Studies of Vibrational Excitation

Fenn and his coworkers<sup>25-27</sup> have used Fourier transform infrared (FTIR) emission spectroscopy to monitor the excitation of CO, CO<sub>2</sub>, NO, and OCS following collision of these molecules with a hot platinum foil. A free jet expansion of the gas of interest was intercepted at nearly normal incidence by a resistively heated platinum foil, and vibrational-rotational emission from the excited molecules was detected with ca. 0.2-cm<sup>-1</sup> resolution by an interferometer and an InSb detector. Because of the high molecular densities needed for the FTIR technique, it was not possible to perform the experiments under ultrahigh-vacuum (UHV) conditions, so that the exact nature of the surface was not determined.

An example of the emission spectra obtained is shown in Figure 1, which displays the spectral distribution of emission from the asymmetric stretching mode ( $00^0_1 \rightarrow 00^0_0$ )<sup>28</sup> of CO<sub>2</sub> following collision of this molecule with a 1450 K Pt surface. Each line in the spectrum can be related to the population of a particular rotational level in the  $00^0_1$  vibrational manifold. The rotational intensities can be analyzed to yield a rotational energy, which, when compared to the energy corresponding to the surface temperature, defines a rotational accommodation coefficient for the particular vibrational mode. A comparison of the integrated emission intensity for a particular band with that, for example, obtained from a nozzle heated so that the source gas has the same temperature as the surface

TABLE I. Accommodation Coefficients from FTIR Measurements

molecule	$\alpha$	$\alpha^v$	ref
CO <sub>2</sub>	0.6	0.22–0.16 ( $\nu_3$ )	22
CO	0.8 <sup>a</sup>	0.7	22
NO		0.88	23
OCS	0.65	1.00 ( $\nu_1$ )	24
		0.45 ( $\nu_2$ )	24

<sup>a</sup> Non-Boltzmann distribution.

provides an estimate of the vibrational temperature of the excited gas. From this latter temperature, a vibrational accommodation coefficient can be determined.

Accommodation coefficients for collisions of several molecular species with the Pt foil are summarized in Table I. For CO<sub>2</sub> the vibrational accommodation was 0.22 at 700 K and fell to 0.16 at 1500 K; a linear dependence between these two temperatures best fit the data. The vibrational accommodation was significantly higher for CO (0.7) and NO (0.88) than for CO<sub>2</sub> and was nearly complete for the  $\nu_1$  ("CO stretch") of OCS, although it was lower (0.45) for the bending mode of this molecule. A common trend was that the accommodation coefficient for rotation was lower than unity, even though the only molecules observed are those that have been vibrationally excited. One might expect that any surface collision intimate enough to produce vibrational excitation would also produce complete rotational accommodation. However, in agreement with other measurements,<sup>29</sup> the rotational temperature of a desorbing molecule was found not to have the same value as the surface temperature, even when the molecule has had a very long surface residence time.

## B. Excitation of NO on Pt(111)

Asscher, Somorjai, and their co-workers have coupled molecular beam scattering with state-resolved detection by multiphoton ionization to investigate collisions of NO with Pt(111).<sup>30–34</sup> A tunable ultraviolet laser was focused to a point in the scattering plane 2.5 cm from the platinum crystal. Two-photon ionization was induced by exciting the NO, first from selected rotational and vibrational levels of the ground X <sup>2</sup>Π state to the excited A <sup>2</sup>Σ state using wavelengths in the 225–236-nm range and then from the A state to the ionization continuum by a second photon from the same laser pulse. Positive ions were detected by an electron multiplier, and the resulting current signal was recorded as a function of laser wavelength to determine the population distribution of the vibrational and rotational levels.

Figure 2 displays the vibrational temperature of the scattered molecules as a function of surface temperature. The data shown by the crosses were obtained by measuring NO( $v = 1$ )/NO( $v = 0$ ) and determining from this ratio the final vibrational temperature  $T_f$ . Under the conditions for the supersonic expansion employed to form the molecular beam, it is expected that the vibrational distribution of the impinging NO should be characterized by a temperature of about  $T_i = 200$  K, so that given the vibrational quantum of 1876 cm<sup>-1</sup> there is very little NO( $v = 1$ ) in the incoming beam. The solid line depicts where the data points would lie if there were complete accommodation of the vibrational modes to the surface temperature. It is apparent from the figure that the vibrational accommodation

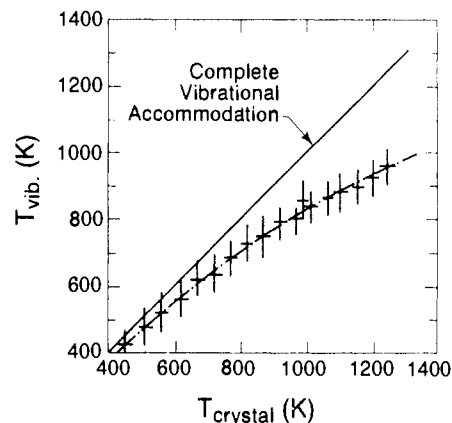
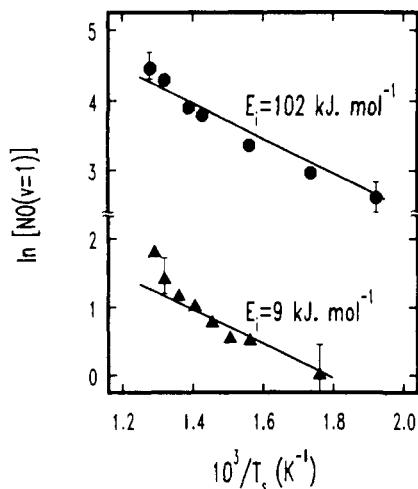


Figure 2. Vibrational temperature of scattered NO molecules as a function of the Pt(111) crystal temperature. The dashed-dotted line is the model prediction of the scattered vibrational temperature if  $\Delta E = 2.5$  kcal/mol. The crosses denote the experimental results. (From Asscher et al.,<sup>34</sup> with permission.)

coefficient is less than unity. Since for temperatures below about 1000 K the angular distribution of the scattered NO was closely described by a cosine law, it can be assumed that nearly all of the molecules detected have been trapped at the surface. At the highest surface temperature studied (around 1250 K), the vibrational accommodation coefficient was found to be roughly 0.74, in reasonable agreement with the value of 0.88 at 1430 K obtained by the FTIR method on a less well-characterized Pt surface.<sup>25</sup>

A simple model for the vibrational energy accommodation of NO on Pt(111) has been provided by Asscher, Pollak, and Somorjai.<sup>34</sup> The model supposes the existence of an extrinsic precursor state having a well depth  $E_\infty$  with respect to the gas phase and separated from the chemisorbed state by a barrier of height  $E_s$ . The probability for chemisorption from the precursor state is then simply given by  $p = k_1/(k_1 + k_2) = (1 + (k_1/k_2))^{-1}$ , where  $k_1$  is the rate constant for going from the precursor state to the chemisorbed state and  $k_2$  is the probability for desorption from the precursor state. If the preexponential factors for these two processes are assumed to be the same, then  $k_1/k_2 = \exp(-\Delta E/kT_s)$ , where  $\Delta E \equiv E_\infty - E_s$ , so that  $p = (1 + \exp(-\Delta E/kT_s))^{-1}$ . The model then assumes, perhaps unrealistically, that molecules desorbing from the precursor state retain their initial vibrational temperature ( $T_i = 200$  K) while those desorbing from the chemisorbed state acquire a vibrational temperature equal to  $T_s$ . Thus,  $T_f = pT_s + (1 - p)T_i$ . A plot of  $T_f$  as a function of  $T_s$  for  $\Delta E = 2.5$  kcal/mol is given by the dashed-dotted line in the figure and accurately reproduces the experimental data. Combination of the equations for  $T_f$  and  $p$  with the definition of the vibrational accommodation coefficient given by  $\alpha^v = (T_f - T_i)/(T_s - T_i)$  shows that  $\alpha^v = p = (1 + \exp(-\Delta E/kT_s))^{-1}$ . The vibrational accommodation coefficient can thus be interpreted as the probability of chemisorption from the precursor state. The mechanism by which chemisorbed molecules become vibrationally excited is unresolved in this model, since either a mechanism based on energy transfer from phonons or one based on electronic energy transfer would be expected to have a large enough rate constant to compete with the relatively slow desorption rate from the chemisorbed state.





**Figure 3.** Effect of surface temperature on the  $\text{NO}(v=1)/\text{NO}(v=0)$  scattering ratio for  $\text{Ag}(111)$ . The upper data points refer to a beam energy of  $102 \text{ kJ mol}^{-1}$ , while the lower ones were obtained at  $9 \text{ kJ mol}^{-1}$ , with  $\theta_i = 15^\circ$  in both cases. These two sets of data are arbitrarily scaled relative to each other. (From Rettner et al.,<sup>36</sup> with permission.)

### C. Excitation of NO on $\text{Ag}(111)$

Whereas the energy transfer described in the above experiments has concerned excitation following trapping, direct vibrational excitation on a single gas-surface encounter has been observed for the  $\text{NO}/\text{Ag}(111)$  system by Rettner et al.<sup>35,36</sup> In principle, such direct encounters can provide a more detailed probe of the excitation mechanism. A supersonic molecular beam of NO was directed at a single crystal of  $\text{Ag}(111)$  after passing through a high-speed chopper with a 1% duty cycle. Scattered NO molecules were detected by two-photon ionization as a function of internal energy level, scattering angle, surface temperature, and initial and final velocity. The initial beam energy  $E_i$  was varied between 0.1 and 1.0 eV, the initial angle  $\theta_i$  from  $15^\circ$  to  $65^\circ$ , the final angle  $\theta_f$  from  $0^\circ$  to  $75^\circ$ , and the surface temperature  $T_s$  from 155 to 760 K.

Vibrational excitation of the NO was found to depend almost exponentially on  $T_s^{-1}$ , as shown in Figure 3. The slope of the data in Figure 3, however, is not quite constant; it varies from a temperature such that  $kT$  is equal to the energy of the NO vibrational quantum at the highest temperatures to two-thirds of this value at lower temperatures. At all temperatures, the excitation depends linearly on the normal incident energy of the incoming beam,  $E_n = E_i \cos^2 \theta_i$ . The angular distributions of the scattered intensities are peaked near the specular angle. This observation and the dependence of the vibrational excitation on the incident beam conditions indicates that these experiments are dominated by direct scattering from the platinum surface. At the maximum surface temperature studied ( $T_s = 760 \text{ K}$ ) and the maximum incident energy ( $E_i = 120 \text{ kJ/mol}$ ), roughly 7% of the incident molecules were excited to their first vibrational level and less than 0.5% were excited to the second vibrational level. This is consistent with  $T_v = 1000 \text{ K}$ . In this direct-scattering regime, the scattered molecules do not approach thermal equilibrium distributions, and the simplified concepts inherent in the definition of accommodation coefficients are not applicable.

An electronic mechanism for the vibrational excitation is suggested by these data. While the alternative explanation of coupling to the phonons cannot be ruled out, such a mechanism would be unlikely to result in an excitation probability that factors into two independent terms, one dependent on  $E_n$  and one dependent on  $T_s$ . The electronic excitation might be the result of deexcitation of thermal electron-hole pairs in the metal, in which case the role of increasing  $E_n$  would be to allow the incident molecules to penetrate further into the electron cloud and increase the coupling. A rough calculation of the product of the density of filled and empty states separated by  $E_{\text{vib}}$  near the Fermi level gives a linear Arrhenius plot with an effective activation energy equal to  $E_{\text{vib}}$  over the temperature range explored by the experiment. Whether the actual coupling between the molecule and the electron-hole pairs is due to electron scattering or temporary negative molecular ion formation<sup>37</sup> is still a question to be answered, although a recent calculation favors the latter interpretation.<sup>38</sup>

### III. Vibrational Excitation as a Result of Surface Reactions

While investigation of the vibrational excitation that results from the collision of a molecule with the surface can provide information about the physics of the molecule-surface interaction, a problem of more chemical interest is how the potential between different atoms in a molecule is modified as a function of their interaction with the surface. Examination of the vibrational levels that are produced as two molecular fragments combine on a catalytic surface can provide a detailed picture of the transition state to molecule formation and of the exit channel for recombinative desorption.

#### A. CO Oxidation on Platinum

The oxidation of CO on platinum to produce  $\text{CO}_2$  is a reaction of just this sort. The reaction proceeds between chemisorbed CO and O atoms through a barrier situated about 24 kcal/mol above the gas-phase  $\text{CO}_2$  product at low coverage. Although the barrier decreases to about 12 kcal/mol at high coverages, the activation energy is still sufficiently high that there is a good possibility that the  $\text{CO}_2$  product, having surmounted the activation barrier, will acquire a considerable amount of excitation. Becker et al.<sup>39</sup> have performed time-of-flight velocity measurements and found that the translational energy of the product  $\text{CO}_2$  is substantially higher than that which would be expected for molecules in thermal equilibrium with the surface. Segner et al.<sup>40</sup> have found that the angular distribution of the desorbing  $\text{CO}_2$  is strongly peaked at the surface normal. A natural extension would be to enquire about the internal energy of the product. Because CO is linearly bonded to Pt at the carbon, the reaction between  $\text{CO}_a$  and  $\text{O}_a$  will produce an intermediate that is displaced in both the bonding and asymmetric stretching coordinates from the equilibrium positions of the symmetrical and linear  $\text{CO}_2$  product; vibrational excitation of these modes in the product would be a reasonable expectation.

**TABLE II. Internal Temperatures for CO Oxidation on Pt As Obtained by the FTIR Technique (in K)<sup>a</sup>**

$T_s$	$T_{ss}$	$T_b$	$T_{as}$	$T_r$
730	1300	1600	1500	1050
900	1700	1750	1600	1200

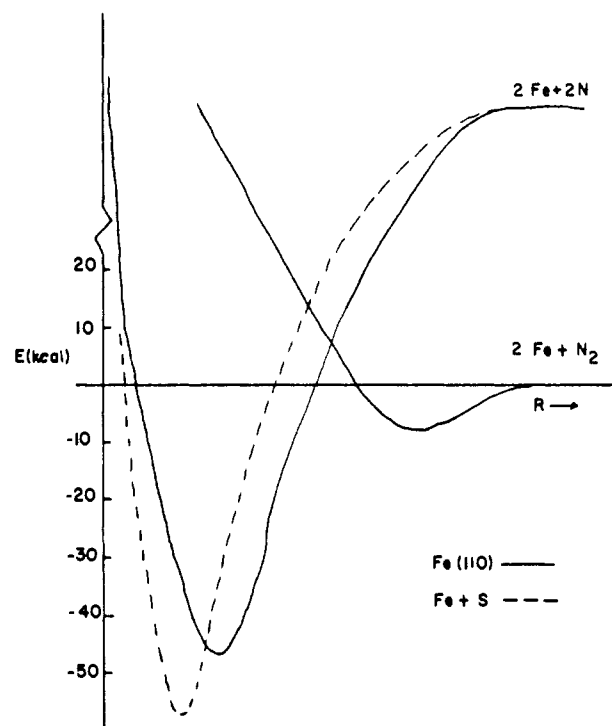
<sup>a</sup>Note: The subscripts s, ss, b, as, and r stand respectively for surface, symmetric stretch, bending, asymmetric stretch, and rotation. (From Mantell et al.<sup>45</sup>)

Bernasek and Leone<sup>41</sup> and Brown and Bernasek<sup>42</sup> detected infrared chemiluminescence from CO<sub>2</sub> produced by flowing CO and O<sub>2</sub> across a Pt gauze. An InSb detector was used in conjunction with narrow-band-pass interference filters that limited the detection to emission from those states that include one or more quanta of the 2349-cm<sup>-1</sup> asymmetric stretch of CO<sub>2</sub>. The extent of vibrational excitation, particularly in the asymmetric stretching mode, was found to decrease with increasing oxygen coverage on the catalytic surface.

The same reaction under similar conditions has been studied by Mantell et al.<sup>43-45</sup> using the FTIR method. Detailed analysis of the spectra showed that while there was equilibrium neither among the internal modes nor between these modes and the surface, Boltzmann equilibrium was obtained within a given mode. The results are summarized in Table II.<sup>45</sup> Note that all vibrational temperatures are greater than the corresponding surface temperatures and that all vibrational temperatures increase slightly with increasing  $T_s$  in this range except for the symmetric stretching temperature, which increases more dramatically. This more dramatic increase in  $T_{ss}$ , which correlated with increased oxygen coverage, was thought to be accompanied by a decrease in the excess translational energy, although the translational energy was not measured directly. This proposed decrease in translational energy is inconsistent with the results of Brown and Bernasek, where a similar increase in  $T_{ss}$  was observed under experimental conditions where the product translational energy cannot be changing. By coupling the FTIR method with a pulsed nozzle source for the CO reactant, Mantell, Ryali, and Haller demonstrated that for a constant surface temperature the vibrational excitation actually decreases with increasing oxygen coverage on Pt.<sup>44</sup> The authors suggest that an activated complex in which the CO<sub>2</sub> molecule sits at a 15° angle relative to the surface normal with the angle between the two CO bonds about 165° would account for the observed rotational and bending energies.

## B. Other Surface-Catalyzed Oxidations

Internal energy distributions for a few other products of catalytic oxidation reactions have also been reported in somewhat less detail. Lin and his co-workers have used laser-induced fluorescence of the OH product to study the activation energy for the OH desorption from Pt using the reaction of H<sub>2</sub> with a variety of oxidants.<sup>46-49</sup> The authors reported that the vibrational temperature of the OH was 1670 K for  $T_s = 1130$  K based on an OH( $\nu = 1$ )/OH( $\nu = 0$ ) ratio of  $0.04 \pm 0.03$ .<sup>49</sup> Kori and Halpern used the FTIR technique to study the CO vibrational distribution following oxidation of carbon atoms on Pt.<sup>50</sup> The catalytic oxidation was found to proceed via the reaction of adsorbed carbon



**Figure 4.** Potential energy of interaction for the nitrogen-iron adsorption system. The activation barrier for the recombinative desorption  $2N \rightarrow N_2$  is given by the crossing point of the atomic and molecular curves. (From Thorman and Bernasek,<sup>54</sup> with permission.)

and oxygen atoms to produce CO in vibrational levels up to  $\nu = 7$ . The vibrational distributions were substantially more excited than Boltzmann distributions at the corresponding surface temperature and agreed with a statistical model in which 2-3 platinum atoms participated in the reaction complex. Finally, Asscher et al. have studied the NO product formed from ammonia oxidation on Pt(111).<sup>51</sup> Both the vibrational and rotational distributions were found to be Boltzmann, but at temperatures below  $T_s$ . For example, for  $T_s = 804$  K, the NO( $\nu = 1$ )/NO( $\nu = 0$ ) ratio indicated a vibrational temperature of  $660 \pm 70$  K, while the rotational temperature was found to be  $340 \pm 60$  K.

## C. Nitrogen Recombination on Iron

An electron beam induced fluorescence technique<sup>52</sup> has been used by Bernasek and his co-workers to examine the vibrational distribution of N<sub>2</sub> desorbing after recombination on clean and sulfur-covered Fe.<sup>53-55</sup> A 0.025-cm-thick iron membrane was welded to the end of a stainless steel tube and heated to between 1050 and 1400 K. A pressure of roughly 1.3 atm of N<sub>2</sub> gas was introduced on one side of the membrane. Nitrogen from this high-pressure region atomically permeated the membrane and recombined on the low-pressure side. The product N<sub>2</sub> molecules desorbed from the surface and were excited on the  $N_2^+(B \ ^2\Sigma_u^+) \leftarrow N_2(X \ ^1\Sigma_g^+)$  transition by an electron beam of 2100 eV. Subsequent fluorescence on the  $N_2^+(B \ ^2\Sigma_u^+) \rightarrow N_2^+(X \ ^2\Sigma_g^+)$  transition was dispersed, detected, and analyzed to determine the internal energy distribution.

On clean iron surfaces the vibrational temperature of the desorbing N<sub>2</sub> was relatively constant at a temperature slightly higher than  $T_s$  for surface tempera-

tures ranging from 1086 to 1390 K. For sulfur-covered iron, on the other hand, a vibrational temperature of  $2600 \pm 200$  K was observed for  $T_s$  of 1150 K. Auger spectroscopy was used to demonstrate that the observed vibrational temperature was linearly dependent on sulfur coverage in the range from 1.0 to 1.8 S/Fe.

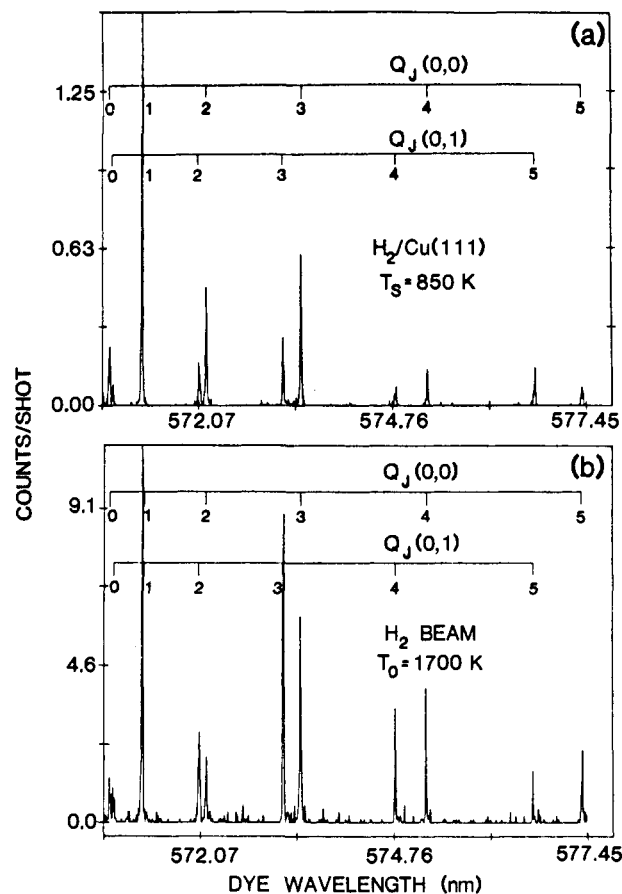
A qualitative explanation of the increased vibrational temperature for the sulfur-covered surfaces is based on changes in the location of the barrier to recombinative desorption as the sulfur coverage is increased. Electronegative sulfur withdraws electron density from the iron surface and makes the interaction between nitrogen and iron stronger, increasing the atomic well depth and moving the minimum closer to the surface, as shown in Figure 4. Note that the crossing point for the atomic and molecular interaction potentials is also shifted closer to the surface, thereby shifting the activation barrier further into the reactant channel for the process  $2\text{Fe} + 2\text{N} \rightarrow 2\text{Fe} + \text{N}_2$ . Early barriers are generally associated with vibrational excitation of the products, as shown by elegant gas-phase studies by Polanyi and his group.<sup>56</sup>

On the other hand it is known<sup>57</sup> that electronegative species increase the activation energy for  $\text{N}_2$  dissociation on Fe. This occurs, it is presumed, because the back-bonding into the  $\pi^*$  orbital of the  $\text{N}_2$  is inhibited, which decreases the binding energy of the chemisorbed molecule. This results in intersection between the repulsive molecular potential and the attractive atomic potential at higher energies, which are further out rather than closer in as suggested in Figure 4. The increase in vibrational excitation with sulfur would then be explained by recognizing that the transition-state barrier for recombinative desorption is increased with respect to the gas-phase  $\text{N}_2$  by sulfur doping, but still "early" enough to produce vibrationally excited species.

#### D. Hydrogen Recombination on Copper and Palladium

Kubiak, Sitz, and Zare have performed detailed studies of the recombinative desorption of  $\text{H}_2$  and  $\text{D}_2$  from clean  $\text{Cu}(110)$  and  $\text{Cu}(111)$ <sup>58,59</sup> and from sulfur-covered  $\text{Cu}(111)$ .<sup>60</sup> A 1–3-atm pressure differential across a 0.3-mm-thick disk caused  $\text{H}_2$  or  $\text{D}_2$  to permeate through the crystal, recombine on the low-pressure side of the disk, and desorb into the vacuum, where its internal energy distribution was determined by 2 + 1 resonant multiphoton ionization. Photons at roughly 193 and 211 nm were generated by Raman shifting a frequency-doubled dye laser in 5.5 atm of hydrogen. These two photons excited the  $\text{H}_2$  or  $\text{D}_2$  from specific vibrational and rotational levels of the ground state to the  $\text{E,F } ^1\Sigma_g^+$  state, from which a third photon of either wavelength could ionize the target gas.

Figure 5 displays a portion of the ionization spectra for (a)  $\text{H}_2$  recombinatively desorbing from a  $\text{Cu}(111)$  surface held at 850 K and (b)  $\text{H}_2$  expanded in a heated tungsten free jet at a source temperature of 1700 K and a source pressure of 1 atm. Under these free-jet conditions, the rotational and vibrational temperatures of expanded molecules are expected to be greater than 0.9 times the source temperature.<sup>61</sup> It is clear from the relative intensities of the labeled Q-branch transitions that the recombining hydrogen has substantial excitation, since the relative  $v = 1$  and  $v = 0$  intensities are



**Figure 5.** Examples of 2 + 1 resonance-enhanced multiphoton ionization spectra of  $\text{H}_2$ : (a) spectrum of  $\text{H}_2$  recombinatively desorbing from  $\text{Cu}(111)$  at  $T_s = 850$  K; (b) spectrum of  $\text{H}_2$  expanded in a free jet at  $T_0 = 1700$  K. If the spectrum in (a) corresponded to a Boltzmann distribution at 850 K, the relative strength of  $v'' = 1$  lines would be about 34 times less than those in (b). (From Kubiak, Sitz, and Zare,<sup>60</sup> with permission.)

similar to those for the 1700 K source. If the  $\text{H}_2$  molecules had desorbed in vibrational equilibrium with the surface temperature, the ratio of  $v = 1$  to  $v = 0$  intensity for any particular rotational line would have been some 34 times smaller than that observed for the 1700 K source.

A detailed analysis of spectra such as that in Figure 5 led to the following conclusions: (i) The desorbing  $\text{H}_2$  and  $\text{D}_2$  are vibrationally excited. The  $(v = 1)/(v = 0)$  ratio for  $\text{H}_2$  ( $\text{D}_2$ ) is  $0.052 \pm 0.041$  ( $0.24 \pm 0.20$ ) for desorption from  $\text{Cu}(110)$  and  $0.084 \pm 0.030$  ( $0.35 \pm 0.20$ ) for desorption from  $\text{Cu}(111)$ . Contamination by sulfur reduces the ratio on  $\text{Cu}(111)$  by a factor of 10–100. (ii) The  $\text{H}_2$  and  $\text{D}_2$  rotational distributions are not accurately represented by a temperature, although the deviation from Boltzmann behavior is not dramatic. (iii) The mean rotational energy is less than that expected for  $T_s$ . (iv) There is little difference in the rotational distributions between the  $\text{Cu}(111)$  and  $\text{Cu}(110)$  surfaces. Nor is there is substantial difference between the rotational distribution of  $\text{H}_2(v = 1)$  and  $\text{H}_2(v = 0)$ . (v) Ortho and para modifications of both  $\text{H}_2$  and  $\text{D}_2$  are statistically populated. (vi) The rotational distribution is not sensitive to the surface temperature in the range 850–960 K.

The qualitative effect that the rotational distribution is not strongly different from a Boltzmann distribution at  $T_s$  but that the vibrational distribution is substantially excited is in good agreement with the dynamical

predictions of Gelb and Cardillo,<sup>62</sup> who used classical trajectory calculations to study the reverse process. They concluded that the adsorption probability should be insensitive to rotational excitation but should increase dramatically with vibrational excitation. The fact that sulfur contamination *decreases* the vibrational excitation of H<sub>2</sub> desorbing from copper but *increases* the excitation of N<sub>2</sub> desorbing from iron (see above) deserves attention. An analogue to the model proposed by Gadzuk<sup>63-65</sup> may be relevant for the H<sub>2</sub>/Cu system. For clean copper it is supposed that the hydrogen atoms are partially negatively charged and that when they recombine they travel along the H<sub>2</sub><sup>-</sup>/Cu potential as the hydrogen leaves the surface. At a certain distance, the electron on the H<sub>2</sub><sup>-</sup> tunnels to unoccupied Cu levels above the Fermi level, leaving the H<sub>2</sub> in a stretched configuration and giving rise to vibrational excitation. In this view, the electronegative sulfur atoms might prevent the H<sub>2</sub> from carrying the negative charge and thereby lead to a diminution of the vibrational excitation.

Schröter, Zacharias, and David found qualitatively similar results for the recombinative desorption of D<sub>2</sub> from polycrystalline Pd covered with 1.0–1.5 monolayers of sulfur.<sup>66</sup> Deuterium atoms were supplied to the surface by permeation through a 1-mm-thick crystal, while the internal state distribution of the D<sub>2</sub> product was monitored by laser-induced fluorescence on the B <sup>1</sup>Σ<sub>u</sub><sup>+</sup> → X <sup>1</sup>Σ<sub>g</sub><sup>+</sup> Lyman transition using a tunable vacuum ultraviolet laser. In the temperature range T<sub>s</sub> = 550–1050 K the rotational temperature of the D<sub>2</sub> product was 450 K, nearly independent of T<sub>s</sub>, while the vibrational temperature was 1100 K, significantly higher than T<sub>s</sub>. A comparison of these results to those obtained on clean Pd would be highly interesting, but has not yet been reported.

#### IV. Vibrational Deactivation in Gas–Surface Collisions

##### A. Measurements of Vibrational Deactivation in Bulk Samples

Anderson et al.<sup>67</sup> were among the first to attempt the direct measurement of a vibrational deactivation probability for a gas–surface collision. In their experiment a continuous-wave CO<sub>2</sub> laser excited vibrationally SF<sub>6</sub>, CH<sub>3</sub>I, CH<sub>3</sub>OH, and cyclopropane at a pressure of 0.001–1.0 Torr. Excited molecules decayed partly by collisional deactivation with one another and partly due to collisions with a heated, polycrystalline molybdenum ribbon. The temperature change in the ribbon as a function of gas pressure (adsorbed energy) is used to calculate the vibrational accommodation coefficient. Since this experiment determines only the vibrational energy absorbed by the surface, however, it neglects vibrational deactivation into rotational and translational modes of the colliding molecule. Thus, the values of α<sup>v</sup> so determined are a lower limit to the total α<sup>v</sup> as defined in eq 2. Another disadvantage of this technique is that it is not possible to specify which vibrational mode is exchanging energy with the surface because there will be significant intramolecular vibrational scrambling due to the many gas-phase molecular collisions that occur before the surface collision.

TABLE III. Vibrational Energy Accommodation and Heats of Vaporization<sup>a</sup>

molecule	α <sup>v</sup>	ΔH <sub>vap</sub> , kcal/mol
CH <sub>3</sub> F	0.49	4.2
cyclopropane	0.53	4.8
SF <sub>6</sub>	0.61	5.6
CH <sub>3</sub> OH	0.81	8.6

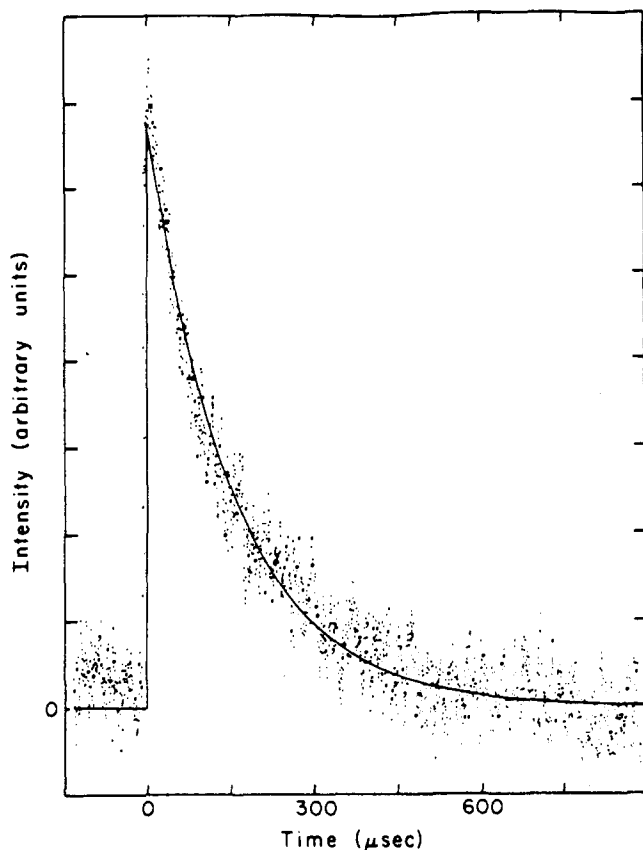
<sup>a</sup> From Anderson, Lee, Pildes, and Bernasek.<sup>67</sup>

In agreement with the qualitative correlation made by Rosenblatt (see section I), Anderson et al. found that the vibrational energy accommodation coefficient increased with increasing heat of vaporization of the colliding molecule. For physical adsorption the heat of adsorption usually correlates with the heat of vaporization of the adsorbate species. As the heat of adsorption increases, the residence time of the adsorbate on the surface is expected to increase, leading to an increase in energy exchange. The observed vibrational accommodation coefficients (±0.1) and the literature heats of vaporization (kcal/mol) are shown in Table III.

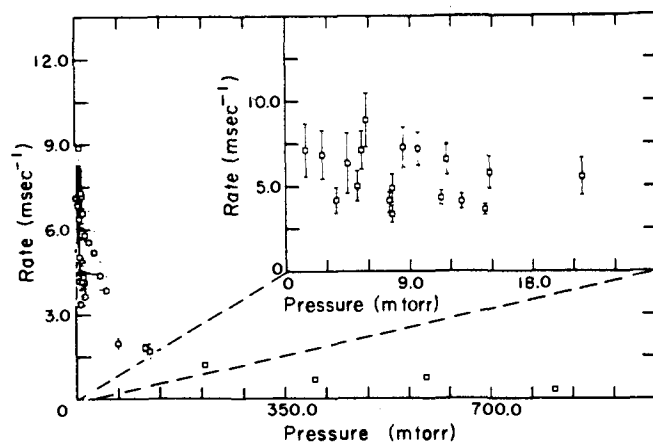
Our own group has investigated vibrational relaxation at Ag, Ni, Al, and Al<sub>2</sub>O<sub>3</sub> surfaces by directly observing the decay time of infrared fluorescence from individual vibrational modes excited by pulses of infrared laser radiation.<sup>68-70</sup> The principle of the technique is as follows. A cylindrical experimental cell is equipped with a tungsten filament wrapped with, for example, silver and mounted parallel to the walls of the cylinder but slightly off axis. Under UHV conditions, the filament is heated and the metal evaporates onto the inside walls of the cylinder. The gas of interest, for example CO or CO<sub>2</sub>, is then introduced at a pressure of 0.5–5 mTorr and excited to a desired vibrational level by a pulsed infrared laser. At these pressures the mean free path of the gas is larger than the inside diameter of the cylinder so that the excited molecules undergo many collisions with the surface of the cylinder before colliding with one another. The number of surface collisions per unit time can be calculated from gas-kinetic theory. Although most of the molecules will lose their vibrational excitation by collisions with the surface, a few molecules will emit infrared fluorescence, which can be imaged onto a detector and recorded as a function of the time delay following the excitation pulse. The exponential decay of fluorescence provides the mean vibrational lifetime of the excited molecules, and this time, when combined with the mean number of surface collisions per unit time, can be used to calculate the probability for deactivation per collision.

A typical signal for the 00<sup>0</sup>1 level of CO<sub>2</sub> is shown in Figure 6, while a plot of the measured lifetime as a function of CO<sub>2</sub> pressure is shown in Figure 7. The deactivation probability is obtained from the low-pressure extrapolation of the lifetime after very minor corrections for the radiative lifetime and diffusion of molecules out of the cylinder. For CO<sub>2</sub>(00<sup>0</sup>1) on silver, the deactivation probability is calculated to be 0.16, in reasonable agreement with the accommodation coefficient of 0.23 determined by the FTIR method for excitation of CO<sub>2</sub> by collisions with platinum (Table I; recall from section I that α = β for E<sub>s</sub> << E<sub>vib</sub>). The temperature dependence of the deactivation probability was examined by heating the cell in the range from 298





**Figure 6.** Fluorescence decay curve obtained for 10.5 mTorr of  $\text{CO}_2$  and a silver surface at 298 K. The signal (dots) is the average of 5000 laser shots, while the solid line is the fit of a single-exponential decay to the data. (From Misewich et al.,<sup>68</sup> with permission.)



**Figure 7.**  $\text{CO}_2$  fluorescence decay rate as a function of pressure for collisions with stainless steel at 298 K. At low pressures the diffusion rate to the surface of the cylinder increases. Since the excited molecules are deactivated primarily by surface collisions, the fluorescence decay rate increase with decreasing pressure below about 350 mTorr. (From Misewich et al.,<sup>68</sup> with permission.)

to 473 K. The deactivation probability for  $\text{CO}_2(00^01)$  was found to be nearly invariant to temperature in this range, while that for  $\text{CO}_2(10^01)$  fell from 0.72 at 300 K to 0.37 at 440 K. For  $\text{CO}(v=2)$  the probability fell from 0.33 at 300 K to 0.20 at 440 K.

The magnitudes for the deactivation probabilities and the temperature dependencies indicate that a dominant mechanism for relaxation involves trapping and subsequent deactivation by one or more of several mechanisms, including electron-hole pair formation,<sup>70</sup> vi-

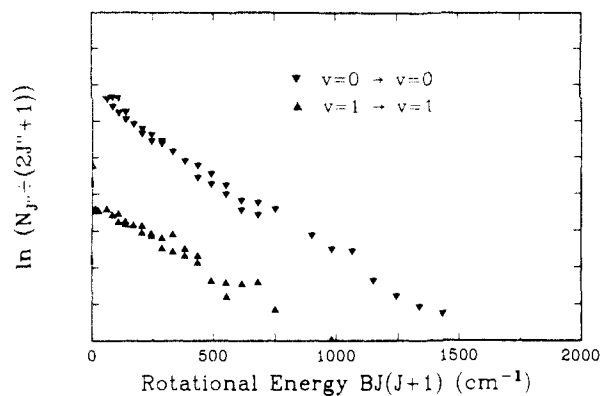
brational-to-rotational energy transfer,<sup>72-74</sup> vibrational-to-translational energy transfer, energy transfer between the oscillating dipole and the electrons of the surface,<sup>75</sup> or perhaps even transfer of energy to the surface phonons. In order to probe the mechanism more critically, we have recently compared the probability for vibrational relaxation of  $\text{CO}_2(00^01)$  on clean Al with that on  $\text{Al}_2\text{O}_3$ . If, as expected, the electronic degrees of freedom in the surface are important to the relaxation, we should find that the probability for deactivation on Al is higher than that on  $\text{Al}_2\text{O}_3$ . Indeed, our results indicate that the deactivation probability on Al is somewhat higher than that on  $\text{Al}_2\text{O}_3$ . However, it may be premature to conclude that the electrons of the metal play a key role, since the trapping probability of  $\text{CO}_2$  on these two surfaces has not yet been measured. Although trapping seems to be the dominant mechanism for the relaxation on Ag and Ni, large deactivation probabilities may also be present for the directly scattered component. The deactivation probability for  $\text{CO}_2(10^01)$  is larger than both the ground-state trapping probability and the deactivation probability for  $\text{CO}_2(10^00)$ .

One disadvantage of this technique is that it is difficult to characterize the surface on which the deactivation takes place. However, this drawback might be overcome by using a rectangular cell composed of single crystals rather than the cylinder. Current effort in our group is being directed toward testing this idea, first with a LiF surface and then with metallic crystals.

## B. Molecular Beam Measurements of Vibrational Deactivation

Extremely detailed measurements of vibrational deactivation have been reported by Loy and his co-workers at IBM.<sup>76-81</sup> This group used a tunable, pulsed infrared laser to excite vibrationally a small spatial segment of a molecular beam which then impinged on either a LiF or Ag crystal. State-specific multiphoton ionization using a tunable ultraviolet laser was used to characterize the molecular beam before and after scattering. Scanning of the ultraviolet laser wavelength allowed the determination of the vibrational, rotational, and electronic (spin-orbit) distribution of the probed molecules. State-resolved angular and velocity distributions were obtained by setting the probe laser frequency to detect a well-defined state and either rotating the intersection of the probe laser in the scattering plane for angular discrimination or scanning the delay between the exciting and probe laser pulses for velocity discrimination.

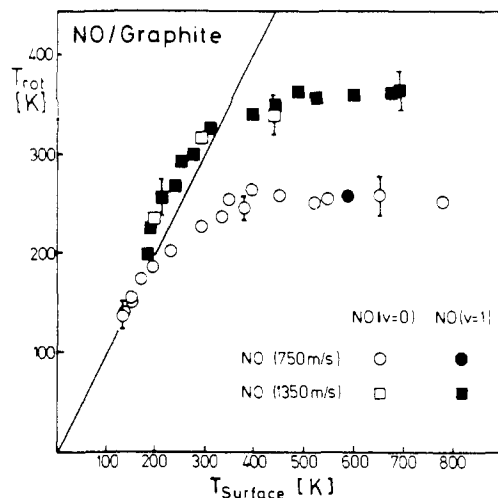
Results have been reported for the scattering of  $\text{NO}(v=1, J=3/2, \Omega=1/2)$  from optically polished LiF and  $\text{CaF}_2$ ,<sup>76</sup> from cleaved LiF(100),<sup>77,78,81</sup> from Ag(111),<sup>79-81</sup> and from Ag(110).<sup>80,81</sup> The results on LiF are perhaps the more interesting, since this is one of the few non-metallic surfaces from which molecular scattering has been studied in detail. For the purposes of the present discussion, the most important experimental observable is the survival probability ( $\text{SP} = 1 - \beta$ ) of vibrationally excited species. Unfortunately, this is also the most difficult observable to measure, since it involves integration over final rotational and electronic distributions as well as over scattering angles and velocities.



**Figure 8.** Rotational distributions for NO molecules scattered from  $v = 0 \rightarrow v = 0$  and from  $v = 1 \rightarrow v = 1$  on a LiF(100) surface at 300 K with an incident energy of 310 meV and an incident angle of  $45^\circ$ . (From Misewich et al.,<sup>77</sup> with permission.)

The original report for scattering of NO from a polished LiF surface came as somewhat of a shock to the surface science community, since a careful examination showed that the survival probability was zero; all of the NO( $v = 1$ ) was deactivated on collision with the surface. Because there are no appreciable electronic relaxation pathways in LiF, it was generally expected that the vibrational survival probability for collisions with this surface would be very high. In fact, quantum mechanical calculations by Bawagan et al.<sup>73</sup> at somewhat higher energy than the experimental one as well as classical mechanical calculations by Lucchese and Tully<sup>82</sup> using a generalized Langevin approach both predicted that the survival probability should be 0.9–1.0. The IBM group then repeated the experiments for a cleaved LiF(100) surface. For this surface a survival probability of 0.9 was observed, in good agreement with theory. The major difference between the two surfaces is that the cleaved LiF is atomically smooth, whereas the polished surface, though optically smooth, is quite rough on the atomic scale. Apparently, the rougher surface caused substantially more vibrational relaxation, perhaps because of increased trapping. On the cleaved LiF(100) surface, NO( $v = 1$ ) has a survival probability of 0.9 and is scattered into a nearly specular lobe characteristic of direct inelastic scattering. For  $T_s = 300$  K the surviving  $v = 1$  molecules are distributed both over spin-orbit components ( $T_{\text{elec}} = 200$  K) and over many rotational levels ( $T_r = 345$  K). For an initial translational energy of  $E_i = 310$  meV at  $\theta_i = 45^\circ$  ( $E_n = 155$  meV), both the normal and parallel components of the momentum are decreased by about 30% by the collision. Rotational and electronic distributions for  $v = 1 \rightarrow v = 1$  scattering were found to be identical with those for  $v = 0 \rightarrow v = 0$  scattering, indicating that for this system the vibrational motion is decoupled from the translational, electronic, and rotational degrees of freedom. Data describing the rotational distributions are reproduced in Figure 8. The angular and velocity distributions were insensitive to the rotational energy transfer for levels below  $J = 20.5$ .

It is interesting to contrast the results obtained for cleaved LiF(100) with those obtained on Ag(111) and Ag(110). The vibrational survival probability for both metal surfaces was also quite large,  $\geq 0.9$ , comparable with the result for LiF(100), and scattering was again peaked in the specular direction. Thus, for direct-

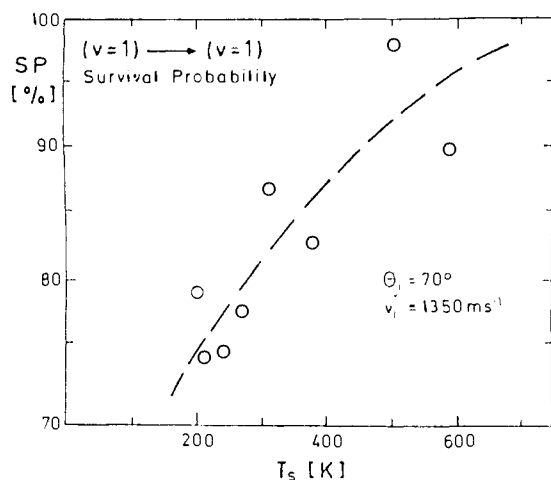


**Figure 9.** Rotational temperature  $T_{\text{rot}}$  of both  $v = 1 \rightarrow v = 1$  and  $v = 0 \rightarrow v = 0$  NO molecules specularly scattered from a graphite surface as a function of surface temperature. (From Vach et al.,<sup>85</sup> with permission.)

inelastic scattering of vibrationally excited molecules, large survival probabilities can be observed in scattering from metal surfaces despite the additional deactivation channel of electron-hole pair excitation. Since the rate of electron-hole pair excitation is a strong function of the distance of the vibrationally excited molecule from the surface<sup>71</sup> and since for direct-inelastic scattering the time spent during the surface collision is quite short, it may be that there is not enough time for deactivation unless the incoming molecule is trapped.

Vach et al.<sup>83–85</sup> have reported equally fascinating results for the scattering of NO( $v = 1$ ) from graphite surfaces. The method employed is similar to that used by the IBM group, except that a continuous-wave spin-flip Raman laser was used for the vibrational excitation. Final-state distributions were determined by multiphoton ionization, and velocity distributions were measured by surrounding the ionizing laser beam with a cylindrical grid held at ground potential. Ionization makes an immeasurable change in the velocity of the scattered NO, so that the time it takes for the ions to move from the center to the edge of the cylinder is characterized of the velocity of the NO( $v, J$ ) level selected by the probe laser. After passing through the edge of the cylindrical grid, the ions are rapidly accelerated to a particle multiplier. By rotating and translating the crystal it was possible to obtain angular distributions with both state and velocity selection. Both a specular component, due to direct-inelastic scattering, and a cosine component, due to trapping-desorption, were observed.

The results of these studies clearly demonstrated first a strong interaction between both molecular rotation and translation and the surface phonons and second a weak coupling between the vibrational degree of freedom and either the phonons or the molecular rotation and translation. Scattering of ground-state molecules that originated from a Boltzmann distribution of rotations and scattering of  $v = 1$  molecules that originated from a single rotational level resulted in nearly identical rotational distributions. Thus, the rotational distribution of the scattered molecules is almost independent of both the vibrational and rotational level of the incident molecules. (A minor exception to this conclusion



**Figure 10.** Survival probability of vibrational energy for seeded NO molecules scattered from a graphite surface as a function of surface temperature. (From Vach et al.,<sup>85</sup> with permission.)

will be noted below.) The coupling between incident kinetic energy and outgoing rotational energy, while present, was extremely weak, as shown in Figure 9. Furthermore, the velocity of the scattered molecules was nearly independent of their rotational level, so that scattered NO does not simply gain its rotational energy at the expense of translation. The cause of the rotational excitation must therefore be interaction with the surface phonons.

Vibrational survival probabilities were found to be high, in agreement with the predictions of Lucchese and Tully, and to be weakly dependent on  $T_s$ , as shown in Figure 10. The decrease in survival probability with decreasing surface temperature may be due to the increased residence time for low  $T_s$ . Interestingly, however, even the diffusely scattered NO had a high vibrational survival probability, although the fraction of diffuse scattering decreased with increasing  $T_s$ . In order to determine the mechanism for the vibrational deactivation, the authors studied whether the rotational distribution of the scattered  $v = 0$  molecules was influenced by the presence of vibrational excitation, an influence predicted by Gerber et al.<sup>72</sup> Although a 10% increase in the resonant NO( $v = 0, J = 63/2$ ) signal was observed, the amount of the increase was such that vibration-to-rotation energy transfer to this resonant channel could account for no more than 0.03% of the total relaxation. There was similarly no increase in the translational energy of the  $v = 0$  product molecules as a result of the vibrational excitation. Thus, it again appears that the small amount of vibrational relaxation observed is caused entirely by the interaction with surface phonons.

### V. Role of Vibrational Energy in Surface Reactivity

We have seen several examples in section III of recombinative desorptions in which the product molecules are observed to be vibrationally excited. It follows from microscopic reversibility that there are dissociative adsorption reactions that can be enhanced by vibrational excitation in the reactants. A recent review by Chuang<sup>86</sup> has discussed some of the possible excitation methods. One of the earliest attempts to observe en-

hanced reactivity due to vibrational excitation of the reactants was made by Bass and Fanchi,<sup>87</sup> who studied the decomposition of  $N_2O$  on Cu. Although a large enhancement was observed when the  $N_2O$  was excited by a laser in its asymmetric stretching vibrational mode, the experiments were performed under conditions where the Cu surface was certainly contaminated, and the evidence that the enhancement was not due to simple thermal heating of the sample was not totally convincing. A somewhat different technique was used by Prada-Silva et al.<sup>88</sup> to study the effect of vibrational excitation on the isomerization of cyclopropane to propylene on a mica surface. By varying the source temperature and seeding conditions, these authors produced molecular beams of the reactant with equivalent translational excitation but varying vibrational excitation. For a change of vibrational temperature from 700 to 820 K, they observed that the isomerization probability increased from  $3.4 \times 10^{-6}$  to  $5.4 \times 10^{-4}$ .

The most comprehensive study to date, however, is the methane chemisorption on tungsten, rhodium, and nickel. Stewart and Ehrlich<sup>89</sup> first observed for effusive beams of methane that heating the source to roughly 700 K led to a large increase in the sticking probability on rhodium. In addition, they observed that the sticking probability for  $CH_4$  was substantially higher than that for  $CD_4$  at the same source temperature. Because these two molecules have nearly the same translational energy distribution, Stewart and Ehrlich interpreted their results to indicate that the vibrational excitation at the higher source temperature was the cause of the increase in sticking probability.

Subsequently, Brass et al.<sup>90</sup> used a He/Ne laser to excite the incident beam and found that the sticking coefficient on Rh for  $CH_4$  excited to the  $\nu_3$  level is  $<10^{-4}$ , while that for the  $2\nu_3$  level is  $<7 \times 10^{-2}$ . In a similar experiment, Yates et al.<sup>91</sup> found that on Rh(111) the sticking probabilities for the excited  $\nu_3$  and  $2\nu_4$  levels were  $<5 \times 10^{-5}$ . Thus, vibrational excitation alone was not able to increase dramatically the probability of dissociative adsorption on these surfaces.

In an effort to resolve this controversy, Rettner, Pfnür, and Auerbach<sup>92</sup> undertook a study of the translational energy dependence of the sticking probability for  $CH_4$  on W(110). The method used was similar to that employed previously to study the sticking probabilities for  $N_2$  on W(110)<sup>93</sup> and for  $H_2$  on Cu.<sup>94</sup> Sticking probabilities were measured from the initial slopes of coverage vs exposure. The exposure was determined by controlling the dose time of a beam whose flux was calibrated. The coverage was determined by reacting any adsorbed carbon with oxygen and measuring the integrated area of the resulting CO thermal desorption peak. The results of this study showed that the sticking probability increased exponentially with the normal component of the kinetic energy. A five-order-of-magnitude increase was observed for variation of the beam energy between 10 and 100 kJ mol<sup>-1</sup>. A simple one-dimensional tunneling model, in accordance with the suggestion by Winters,<sup>95,96</sup> adequately explained the exponential dependence on  $E_n$  as well as the increased sticking probability for  $CH_4$  relative to  $CD_4$ .

In the course of these experiments the authors noted that the same beam velocity produced by two different source temperatures gave quite different sticking probabilities, where the larger sticking probability was

TABLE IV. Effect of Nozzle Temperature on Initial Sticking Probabilities of CH<sub>4</sub> on W(110)<sup>a</sup>

trans energy, eV	surf temp, K	nozzle temp, K	S <sub>0</sub>
0.11 ± 0.01	800	770	(2.5 ± 1.0) × 10 <sup>-5</sup>
0.11 ± 0.01	800	340	(5.0 ± 2.0) × 10 <sup>-6</sup>
0.23 ± 0.02	800	720	(4.0 ± 2.0) × 10 <sup>-5</sup>
0.23 ± 0.02	800	305	(7.0 ± 5.0) × 10 <sup>-6</sup>

<sup>a</sup> From Rettner, Pfnür, and Auerbach.<sup>98</sup>

associated with the higher source temperature. Since the beam velocities were the same to within experimental error and since the rotational degrees of freedom are substantially cooled by the expansion, the increase was most likely the effect of vibrational excitation. A more careful study<sup>97,98</sup> produced the data listed in Table IV.

Two possible limits for interpretation of these data are (1) that only one vibrational mode was responsible for the increase or (2) that all vibrational modes are equally effective in accelerating the dissociative adsorption. In the former case if, for example, it is assumed that the  $\nu_4$  mode is the effective motion, then placing 0.16 eV in this vibration leads to a sticking probability that is about 3 times larger than that which would be obtained by putting the same amount of energy into translation. In the latter limit, where all modes are assumed to be equally effective, the increase in sticking probability as a result of placing energy into vibration is almost exactly equal to that for placing the energy into translation.

The interpretation of Rettner, Pfnür, and Auerbach is completely consistent with all the previous measurements. In this interpretation the lack of effect of vibration observed by Brass et al.<sup>90</sup> and by Yates et al.<sup>91</sup> was caused not because vibration does not increase the sticking probability but because the velocities employed were so low that the combined effect of vibration and translation was not enough to produce an observable coverage. The results of Stewart and Ehrlich<sup>89</sup> can also be explained. If the cause of the isotope effect is tunneling and not necessarily vibration, then the increase in sticking coefficient with source temperature can be due, at least in part, to the higher translational energy at the higher source temperature.

Ceyer and her group have thoroughly investigated the dynamics of chemisorption of methane on Ni(111).<sup>99</sup> In addition to studying the absolute dissociation probabilities of CH<sub>4</sub> and CD<sub>4</sub> as a function of the normal component of the translational energy and the vibrational energy, they also used high-resolution electron energy loss spectroscopy to demonstrate that the nascent products of the chemisorption event are methyl radicals and hydrogen atoms. Dissociative chemisorption increases exponentially with the normal component of the translational energy. In the 12–17 kcal/mol range, vibrational energy, created by heating the nozzle source, is at least as effective as translational energy in promoting the chemisorption and may be as much as 4–5 times more effective as long as the total energy is at least 14 kcal/mol. There is a strong isotope effect: the probability of CH<sub>4</sub> dissociative chemisorption is about an order of magnitude larger than that of CD<sub>4</sub> for comparable normal components of the translational energy.

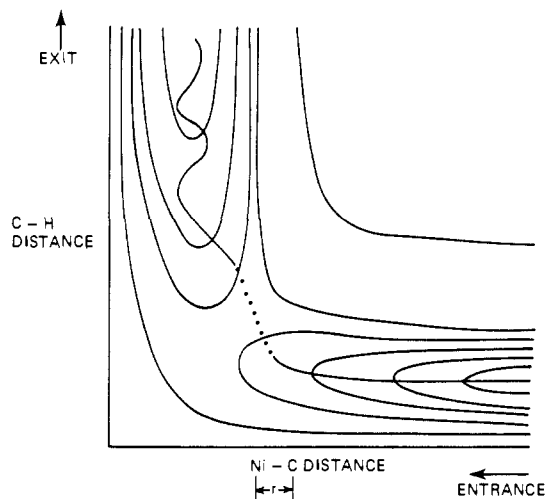


Figure 11. A schematic contour potential energy surface for the dissociative interaction of CH<sub>4</sub> with Ni(111). The C-H distance (exit channel) is plotted as a function of the Ni-C distance (entrance channel). The potential minimum at large Ni-C distance represents the equilibrium position of physisorbed methane. As the Ni-C distance is decreased, the interaction becomes repulsive and the extent of deformation grows. Complete deformation is not necessary for dissociation because at some Ni-C distance, the barrier is sufficiently narrow for the light hydrogen atom to tunnel through to the product channel. (From Lee, Yang, and Ceyer,<sup>99</sup> with permission.)

These observations were interpreted in terms of a model for the dissociative chemisorption in which the barrier to dissociation comes from the energy necessary to distort the tetrahedral configuration into one in which the carbon can approach the surface more closely so that Ni-C and Ni-H bonds can be formed as the C-H bond breaks. The deformation energy can come either from vibration, principally in the  $\nu_4$  and  $\nu_2$  modes, or from translation perpendicular to the surface. One possible scenario for the dissociation is that favorable collisions would have three of the methane hydrogen atoms pointed downward toward the surface. Translational or vibrational energy would then cause the carbon atom to move close enough to the surface so that, at the transition state, the plane containing the three hydrogen atoms would also include the carbon atom. The energy required for such a distortion is calculated to be 16.3 kcal/mol and is within the range of energies that causes significant dissociation experimentally. The reaction would be completed in this picture by extension of one of the three C-H bonds. Tunneling through the barrier along this C-H coordinate might well lead to the observed increase in the rate of CH<sub>4</sub> dissociation over that of CD<sub>4</sub>. A schematic contour potential energy surface for the reaction is shown in Figure 11, where the dotted line indicates the tunneling. In contrast to the results and interpretation of the dissociation on W(110) put forth by Rettner, Pfnür, and Auerbach, however, the results of Less, Yang, and Ceyer for Ni(111) show that a one-dimensional tunneling model does not correctly predict the differences in energy-dependent dissociative chemisorption between the CH<sub>4</sub> and CD<sub>4</sub>; the shape of the barrier must be somewhat more complicated. Nonetheless, the deformation model and tunneling by the lighter hydrogen atom are likely to account for the major features of methane dissociation. The experiments of Rettner, Pfnür, and Auerbach and of Lee,

Yang, and Ceyer have provided a new and detailed picture of this important decomposition reaction.

Some very recent work has begun to investigate the effect of vibrational excitation on the dissociative chemisorption of  $N_2$  on Fe(111).<sup>100</sup> The sticking probability for this system is low and rate determining for thermal beams at room temperature, but it can be increased to nearly 0.10 by translational excitation of the incoming beam to 0.5 eV. By studying the effect of nozzle temperature on the sticking probability at constant translational energy, the investigators have determined that vibrational excitation is also very effective, though perhaps not quite as effective as excitation with the same amount of energy in translation.

## VI. Outlook for the Future

Although the study of vibrational exchange in gas-surface collisions is still in its infancy, it is growing at a rapid rate, fed primarily by technical advances in such areas as Fourier transform infrared spectroscopy and laser detection/production of molecules in specific internal energy levels. Even in its infancy, this field has provided new insights into the energy exchange between a gas-phase molecule and the surface.

Vibrational excitation and deactivation in direct scattering at metal surfaces has demonstrated the importance of interactions with the electronic levels of the surface. More experiments probing the dependence of the exchange process on the band structure of the solid, on the vibrational frequency and mode of the gaseous molecule, on the velocity of the gaseous molecule, and on the surface temperature are desirable. It is likely that increased theoretical effort in this area will be necessary before a complete picture of vibrational energy exchange can be formulated.

Vibrational excitation as a result of surface reactions and vibrational consumption in gas-surface reactions have provided interesting glimpses of the exit and entrance channels in reactions of importance to catalysis. For example, the exit channel in the oxidation of CO and the entrance channel in the dissociative adsorption of methane have each been well characterized. Of course, further work could probe the coupling of  $CO_2$  translation and vibration or could provide more state-specific vibrational excitation of  $CH_4$ , but these experiments await technological improvements in the detection and excitation of specific molecules.

In the adolescence of this field, it is likely that detection and excitation of vibrationally excited molecules might well be accompanied by production or detection of molecular alignment or orientation. Indeed, preliminary experiments on the vibrationless levels of such molecules as NO and  $N_2$  have already been performed. The FTIR techniques have been applied entirely thus far to uncollimated nozzle sources and in systems with background pressures too high to permit careful surface characterization or control of surface composition. A wide variety of molecules can be studied in such experiments because the molecular fluxes are so large. It seems unlikely, however, that the FTIR methods can be applied for any molecule in a collimated molecular beam experiment at ultrahigh vacuum. Nearly all of the state-selected molecular beam scattering experiments reported to date have involved the NO molecule

because of its high cross sections for IR absorption, multiphoton ionization, and laser-induced fluorescence. Some work, however, is emerging with  $H_2$ ,  $N_2$ , CO,  $NH_3$ , NH, and OH. We can expect to see more studies with these and other molecules with low-lying electronic levels in the future. Among those that might be good candidates are SH, HCN, CN, SiH, GeH, SiCl, GeCl, and most metal and semiconductor monoxides.

While it is difficult to speculate on how this field will appear in full maturity without knowing in advance what technological improvements can be drawn from other areas, it is conceivable that many important surface reactions will be understood at a much more fundamental level by the introduction of state-specific techniques. It may never be economical to perform catalytic reactions on a commercial scale with state-selected reactants, but lithographic photoassisted gas-surface reactions at metal and semiconductor surfaces may play an important future role in commercial manufacture of electronic and optoelectronic devices. The increased understanding of the dynamics of the surface reaction, however, may be the most important product of such research, since it could point the way to great savings and innovative approaches to a variety of important practical problems.

## VII. Summary

Translational energy and momentum exchange in gas-solid collisions have long been characterized by the accommodation coefficient, which in more recent years has been applied also to rotational and vibrational exchange. The vibrating-surface technique has given values of the internal accommodation coefficient lower than the translational accommodation coefficient,  $\alpha^t$ , for molecules with low heats of vaporization and equal to  $\alpha^t$  for those with high heats of vaporization ( $0.2 < \alpha^{int} < 1$ ). These trends are in agreement with vibrational deactivation measurements made in bulk gas cells using the decay in IR emission from laser-excited gases.

In recent work direct determination of the internal states of scattered molecules has given more detailed information. Measurements of infrared emission in vibrational activation experiments on hot platinum surfaces show that  $CO_2$  has an  $\alpha^v$  of 0.22 for the asymmetric stretch, which is similar to the value obtained for  $\alpha^v$  in deactivation measurements on silver. The CO stretch in OCS has  $\alpha^v$  near unity on hot platinum but a lower value (0.45) for the bending mode. The values of  $\alpha^v$  for CO and NO are ca. 0.8 for activation on hot platinum, more than twice the value for deactivation of CO on silver. In vibrationally excited molecules  $\alpha^r$  was always less than unity.

Laser diagnostics have been employed, especially in connection with molecular beam techniques, to give even more complete measurements of energy and momentum exchange. Laser-induced fluorescence and multiphoton ionization have both been used to measure the internal state distributions of molecules scattered and emitted from single-crystal surfaces in ultrahigh-vacuum molecular beam systems. The vibrational temperature of NO, with initial  $T_v = 200$  K, is equal to the surface temperature when scattered from a Pt(111) surface near 400 K but becomes increasingly lower than  $T_s$  at elevated temperatures, even though the angular



distributions indicate that all of the molecules are initially trapped below 100 K. At 1250 K,  $\alpha^v$  is 0.74 compared to 0.88 on polycrystalline Pt at 1430 K.

By contrast, NO scattering from Ag(111) is dominated by direct scattering without trapping. The distributions of scattered molecules are not consistent with a fraction that has equilibrated with the surface and one with the characteristics of the incident beam, as the definition of accommodation coefficients imply. The excitation seems to occur via an electronic mechanism, either by electron/hole pair excitation or by the formation of a temporary molecular ion. The excitation probability depends independently on the temperature of the surface and the normal kinetic energy of the incident molecule and  $T_v$  is higher than  $T_s$ , even for vibrationally cold molecules.

Dramatic vibrational excitation has been observed in CO<sub>2</sub> produced from CO oxidation on platinum. The product CO<sub>2</sub> is formed from adsorbed CO and O and results in narrow angular distributions of emitted intensities and in  $T_v$  for CO<sub>2</sub> much greater than  $T_s$ . The "transition-state energy" for this reaction is 12–24 kcal/mol above the gas-phase value for free CO<sub>2</sub>, and a large fraction of this energy is carried away from the surface with the CO<sub>2</sub> product. The bending mode and both stretching modes have  $T_v$  greater than  $T_s$ . The values of  $T_v$  are different for each mode, but have Boltzmann-like distributions within each mode. The extent of excitation decreases with increasing oxygen coverage, especially for the asymmetric stretch. The excitation of all the vibrational modes increases with temperature, especially for the symmetric stretch.

Using a molecular beam of NO( $v = 1$ ), survival probabilities of 0.9 have been measured on cleaved LiF, Ag(100), and Ag(110), in general agreement with both quantum and classical calculations. Angular intensity distributions indicate that these systems are dominated by direct-inelastic scattering. Thus electronic channels for vibrational deactivation seem to be small for the short residence times associated with direct scattering. In the LiF work the electronic, rotational, and angular intensity distributions of scattered NO were the same for  $v = 1$  and  $v = 0$ .

In the scattering of NO from graphite velocity distributions of the scattered molecules were also correlated with the internal state distributions. The survival probabilities are high for  $v = 1$ , even for the diffusely scattered component. There is also little evidence of translation-to-rotation conversion, indicating that the internal modes and translation exhibit strong direct coupling with the phonon spectrum of the solid and are only weakly coupled to each other via the collision process.

Vibrational energy has been shown to be effective in causing dissociative adsorption. For methane on W-(110), vibration is 1–3 times as effective as excitation by the equivalent amount of energy in translation, while for N<sub>2</sub> on Fe(111) it appears to be somewhat less effective than translation. Further investigations of this phenomenon are certain to lead to an increased understanding of mechanism of adsorption and desorption.

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