

MECHANISM FOR BOND-SELECTIVE PROCESSES IN LASER DESORPTION

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A general mechanism for the occurrence of bond-selective processes in rapid desorption is proposed and discussed. A criterion for the required laser power is derived. The necessary conditions can be realized with current experimental capabilities.

1. Introduction

Laser-induced bond-selective processes have long been a goal in chemical reactivity [1–3]. It is usually not found possible to create a “hot spot” in a molecule which will not dissipate its energy on a time scale of chemical relevance. Consequently, it is expected that the weakest bond in the molecule will break even for short pulse excitation. Deviations from such statistical behavior require the existence of “bottlenecks” for intramolecular vibrational energy transfer. One possibility that has been considered [4–7] is a heavy atom “blocking effect”. The purpose of this Letter is to discuss an alternative general mechanism and to suggest that there is already experimental evidence in support of this proposal.

The mechanism will be discussed for laser-induced rapid desorption of molecules from surfaces [8]. This topic covers a wide variety of molecules and substrates, in particular, small molecules from metal surfaces [9–11] as well as large molecules from metal or insulator surfaces [12–18]. It should however be recognized that the essential physiochemical conditions can be realized in other types of systems, such as two molecules bound together by a weak van der Waals bond. We have in mind rapid heating-induced desorption in which the solid substrate on which the

molecules are adsorbed simply acts as a chromophore taking up the energy provided by the short, focused, laser pulse. Thermal diffusivity in most solids is sufficiently low that considerable local heating occurs during a short laser pulse. We assume that the adsorbate molecule does not receive energy directly from the laser radiation and concentrate our attention on the energy flow from the hot surface to the cold adsorbate species.

Labile molecules adsorbed on the surface can either desorb or dissociate. The latter process requires that energy flows from the surface to the adsorbate. Based on chemical activation studies as well as laser-induced processes in isolated molecules, it is commonly expected that such an intramolecular vibrational energy transfer is quite facile. A molecule physisorbed on a surface is bound by a weak, van der Waals type bond. The surface phonons will communicate well with this low frequency mode. During rapid laser heating the physisorption bond is thus expected to be readily pumped. A bottleneck may occur however in the energy flow from the surface-adsorbate van der Waals bond to the chemical bonds in the physisorbed molecule. The latter have far higher frequencies and are not well matched to be pumped via excitation of the physisorption bond. The energy flow out of this bond and into the mol-

ecule can therefore be slow and a relatively cold molecule will desorb, i.e. it is possible by rapid laser-induced thermal desorption to break the surface-adsorbate bond even if this is not the weakest bond in the free molecule. The existence of bottlenecks in rapid heating-induced desorption has been recognized previously by Lucchese and Tully [11] who carried out a quantitative calculation on the extent of disequilibrium achievable for NO molecule bound to cold LiF(100) using the stochastic trajectory technique. They point out that "various modes of the desorbing molecule can be thought of as thermometers which measure the surface temperature and which have different characteristic response times".

The essential point of our proposed mechanism is that the van der Waals bond between the chromophore and the rest of the system restricts the rate of energy flow out of the chromophore. This mechanism is obverse to the heavy atom blocking effect and may be regarded as the "sluggish responder" effect. Here it is the low force constant (rather than the high mass) which is responsible for the frequency mismatch.

In section 2 we consider the physical parameters which characterize the energy flow rate from a van der Waals to a higher frequency, chemical bond. For the purpose of delineating the major trend, a single reduced parameter (the so-called "exponential gap" or "adiabaticity parameter" ξ [1]) is deemed sufficient. The time scale in the problem is provided by the time τ required for the surface hot spot to transfer energy to the physisorption bond in excess of its dissociation energy D . The physisorption bond may however fail to dissociate after the time τ since energy will also flow from it to the internal molecular modes. Our conclusion (section 3) is that the molecule *will* desorb internally "lukewarm" if the heating rate is sufficiently rapid. The simple quantitative criterion is

$$\tau\nu \exp(-\xi) < 1, \quad (1)$$

where ν is the frequency of the physisorption bond (see fig. 1). If condition (1) is not satisfied, the molecules may still desorb (provided the energy per laser pulse is high enough) but energy in excess of the physisorption bond energy D will be carried by its internal degrees of freedom. In section 4 we discuss

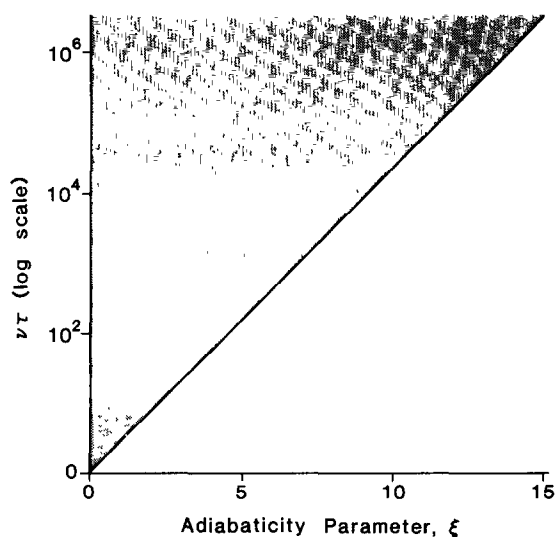


Fig. 1. The region ($\ln(\tau\nu) < \xi$, unshaded) where internally cold molecules desorb from a rapidly heated surface. τ is the time required to dissociate a physisorbed atom bound to the surface with the same potential as the molecule. ξ is the adiabaticity parameter for energy transfer into the molecule from the physisorbed mode of frequency ν . In a simple model where the van der Waals bond perpendicular to the surface is coupled to one chemical bond of the molecule of frequency ν' , $\xi = (D\Delta E)^{1/2}/\hbar\nu$ where $\Delta E \approx \hbar\nu'$ and D is the dissociation energy of the vdW bond. When this model yields $\xi \gg 1$, alternative couplings (with their own characteristic adiabaticity parameters) will provide the actual pathway for energy flow into the molecule.

further the implications of this model and suggest that experimental evidence in support of our criterion may already be available.

2. The bottleneck

Bonds of the van der Waals (vdW) type are weaker and considerably less stiff than ordinary chemical bonds. The frequency mismatch implies that energy will not readily flow from an excited chemical bond to the weaker vdW bond. Indeed, photodissociation of van der Waals adducts [19–22] where such flow occurs has been suggested [23] as an example of a non-statistical unimolecular fragmentation process*. One can then either develop a detailed microscopic

* Multiphoton dissociation of van der Waals dimers is one example where non-statistical effects can be experimentally realized [24].

theory [25–28] or introduce in a statistical theory explicit bottlenecks for energy transfer [29].

Here we consider an inverse effect: the inefficient transfer of energy from a van der Waals bond to a chemical bond. To compute the transfer rate from the vdW to a chemical bond, we shall appeal to microscopic reversibility and use the extensively studied [25–28] rates for the reverse process (i.e. chemical to vdW bond). The rate constant for energy depletion out of the chemical bond in a collinear three-atom arrangement is essentially of the form $\nu' \exp(-\text{gap})$. Here ν' is the vibrational frequency of the chemical bond and gap is the magnitude of the inertia of the van der Waals bond (vide infra). The density of states in the one-dimensional chemical bond is essentially $(h\nu')^{-1}$. Hence the rate of transfer per energy interval is just $\exp(-\text{gap})/h$ and this rate is equal to the rate of transfer in the opposite direction. To obtain the rate constant for transfer out of a vibrational state of the van der Waals bond we need to divide by the density of states $(h\nu)^{-1}$ in the vdW well, giving $\nu \exp(-\text{gap})$ where ν is the frequency of the vdW vibration. It is perhaps worth noting that in the absence of a bottleneck, i.e. when $\exp(-\text{gap}) \sim 1$, we recover the traditional RRR result of ν (per state per second).

The magnitude of the exponential gap is determined by the adiabaticity parameter ξ . In general [1,30], $\xi = |\Delta p|/\alpha h$ where Δp is the change in the momenta of the heavy particles and α is the range parameter of the coupling force (with dimensions of inverse length). The adiabaticity parameter is, in principle, symmetric in the two bonds. For the purpose of our simplistic discussion we shall consider an approximation that centers attention on the vdW bond. This will make $\xi \propto \nu'/\nu$ and since $\nu' \gg \nu$, this (and not the other, ν/ν' term) is the dominant contribution. It is possible to retain both terms, and this must be done when other aspects of the problem are also treated in a more accurate fashion. We thus put $\Delta E = p\Delta p/\mu$ where μ is the reduced mass for motion in the vdW well and ΔE is the energy transfer out of the bond. $\xi = \pi(2\mu\Delta E)^{1/2}/\hbar\alpha$ where α is the range parameter for the repulsive part of the vdW potential [25,28]. For a Morse potential α is related to the dissociation energy D and the frequency ν by $\nu = (\alpha/\pi)(D/2\mu)^{1/2}$. Hence an alternative form is

$$\xi = (D\Delta E)^{1/2}/\hbar\nu \quad (2)$$

showing that for a given ΔE , the vdW bond dissociation energy D and frequency ν have an opposite effect on the rate, which is $\nu \exp(-\xi)$. The energy uptake by the chemical bond, ΔE , is proportional to its frequency ν' .

The exponential gap factor that we quote is for a collinear three-atom arrangement. It can become exceedingly small, leading to very slow rates. Under such circumstances alternative coupling mechanisms (e.g., stretch to bend, etc.) will take over. A familiar example is vibration-to-rotation transfer which is dominant when vibration-to-translation is too slow because of the gap. Such alternative pathways are however equally governed by exponential gap considerations [23,30–32]. In particular, the restoring force for bending in a vdW well is typically quite weak, with a low frequency. The general form for the adiabaticity parameter is [1]

$$\xi = 2\pi(T/T') = 2\pi/\nu T',$$

where T is the characteristic time of the mode associated with the surface-adsorbate bond and T' the mode in the free molecule coupled to the former.

3. Kinetics of energy transfer

We need to estimate the time required to dissociate the physisorption bond and the amount of internal excitation in the desorbing molecule at the instant of dissociation. In order to have a result characteristic of the mechanism it is desirable to provide an estimate which does not refer explicitly to the temporal profile of the laser pulse. Of course, both the laser power and the spatial profile of the laser beam are very relevant but we shall attempt to lump all these aspects into one parameter. Necessarily, such a description will be a simplistic one, but one which hopefully focuses attention on the essence of the phenomenon.

There is an extensive literature dealing with laser heating of surfaces. From it (e.g., ref. [8]), we conclude that for a given thermal diffusivity κ and laser beam cross section πd^2 , there will be a surface hot spot for such times t that satisfy $4\kappa t \ll \pi d^2$. Since for the substrates of interest $\kappa < 0.1 \text{ cm}^2/\text{s}$ this condition

is satisfied over the time scale for rapid desorption. The temperature of the hot spot is inversely proportional to the thermal conductivity K and follows the temporal profile of the laser pulse with a slight lag time. The relevant reduced time variable is $y = \kappa t/d^2$, with a range $0 \leq y \ll 1$.

As an intermediate stage in the argument, consider an atom physisorbed on the surface and disregard for the moment the possibility of desorption. Since the frequency of the surface bond is comparable to the frequencies of the solid, we take it to be at the same temperature. If the atom is at the center of the laser beam, the energy $E_0(t)$ of the physisorption bond at the time t can be determined (see ref. [8]) to be

$$E_0(t) = (k_B d/\pi^{1/2} K) \int_0^y F(y-y') y'^{-1/2} dy', \quad (3)$$

where y is the dimensionless time variable, k_B Boltzmann's constant, K the thermal conductivity (of dimension energy per degree length time) and F the absorbed laser power per unit at the center of the beam. We reiterate that the estimate (3) is only valid for $y \ll 1$. The entire set of parameters in (3) is, for our purpose, equivalent to one time parameter τ , which is the time required for the atom to desorb:

$$E_0(\tau) = D, \quad (4)$$

where D is the bond energy of the atom to the surface.

The systems of interest is however a molecule which is bound to the surface. Energy which flows into the physisorption bond from the surface can also flow out of the physisorption bond into the molecular internal degrees of freedom. The energy balance for the physisorption bond of interest is then

$$\frac{dE(t)}{dt} = \frac{dE_0(t)}{dt} - kE(t), \quad (5)$$

where the first term on the right-hand side is the rate of energy gained if there were no flow to the rest of the molecule and the second term on the right-hand side is the loss term due to energy flow into the molecule (recall that k is the relevant rate constant, as discussed in section 2).

Eq. (5) can be analytically integrated to determine $E(t)$:

$$E(t) = \exp(-kt) \int_0^t \frac{dE_0(t')}{dt'} \exp(kt') dt'. \quad (6)$$

The reader may however object that the rate of loss of energy from the physisorption bond and into the molecule should increase faster than linearly with the excess energy. Hence eq. (6) overestimates the rate of energy accumulation in the surface bond. An underestimate of energy localization would be provided by a rate of loss which is exponential in the excess energy

$$\frac{dE(t)}{dt} = \frac{dE_0(t)}{dt} - kh\nu\{\exp[E(t)/h\nu] - 1\}. \quad (7)$$

Eq. (7) is also analytically integrable (by making the substitution $y(t) = \exp[-E(t)/h\nu]$).

To be certain that we have a conservative estimate, which allows as much energy as possible to be pumped out of the physisorption bond into the molecule we shall replace in the loss term (which is the gain term for the molecule) $E(t)$ by its upper bound of D . This allows for minimal energy accumulation in the physisorption bond for any physically realistic choice of the loss term. We expect the loss term to increase monotonically with $E(t)$; hence replacing $E(t)$ by D provides an overestimate of the gain of energy by the molecule. With this replacement the loss term becomes time-independent and integration of $dE(t)/dt$ is immediate

$$E(t) = E_0(t) - ktf(D), \quad (8)$$

where $f(D) = D$ or $h\nu[\exp(D/h\nu) - 1]$ for (5) or (7), respectively. In general $f(D)$ is monotonically increasing with D , that is, the more stable the physisorption bond the more energy flows into the molecule.

Energy gain by the molecule will be small (in units of D) for such early times t that $kt < 1$. If during such times sufficient energy flows into the surface bond, the molecule will desorb internally cold. The first (gain) term in (8) reaches the bond dissociation energy D at $t = \tau$. At that time, using $f(D) = D$, $E(\tau) = D(1 - k\tau)$. The double overestimate (using (7) and the replacement of $E(t)$ by D in the loss term) yields $E(\tau) \approx D\{1 - k\tau[\exp(N) - 1]\}$ where N is the number of bound states in the vdW well.

The simple operational criterion for the desorp-

tion of internally cold molecules is thus

$$k\tau < 1, \quad (9)$$

where τ is the time for desorption of an atom bound to the surface with the same dissociation energy as the molecule and $k = \nu \exp(-\xi)$ is the rate constant for energy transfer from the physisorption mode of frequency ν to the molecule. ξ is the adiabaticity parameter as discussed in section 2. To be overcautious one need replace (9) by $Nk\tau < 1$ where N is the number of bound states in the potential binding the molecule to the surface. Hence, for ordinary coupling between the surface mode and the molecule

$$\nu\tau < \exp \xi \quad (10a)$$

for desorption of cold molecules. For very efficient coupling

$$(D/h)\tau < \exp \xi \quad (10b)$$

is the operational regime for selective rapid desorption **.

It is quite possible for the molecule to desorb (i.e. for $E(t)$ to exceed D) even when the criteria are not satisfied. Under such circumstances however considerable (in units of D) energy has been pumped into the molecule. The fate of such an energy-rich molecule will depend on the specific chemical details of the experiment. If the molecules have a low threshold unimolecular isomerization or dissociation pathway, the failure of our criterion can be easily detected. In general, such energy-rich molecules are also more susceptible to undergo fragmentation or rearrangement on the surface. In the absence of a chemical marker for the excess energy, the desorbing molecules can also be probed by spectroscopic techniques.

4. Discussion

We propose that the physisorption bond may serve as a bottleneck for energy transfer from a rapidly heated surface to the internal degrees of freedom of

** Sometimes the laser pumping is characterized by a peak rate of heating α (dimension K s^{-1}). Using $\alpha = dE_0/dt$ in (5) one readily verifies that in terms of α , the criterion is $\alpha \geq (D/k_b)k$.

an adsorbed molecule. An operational criterion for the rate of heating has been derived in terms of the adiabaticity parameter, ξ , which represents the ability of the adsorbate molecule to resist changes in vibrational excitation. As expected, a low frequency surface mode coupled to high frequency molecular modes allows for the slowest heating rates.

Experimental evidence from the unimolecular decomposition of van der Waals adducts [19–22] suggests that values of $\exp \xi$ in excess of 10^5 (corresponding to $\xi > 11$) are not uncommon †. With $\xi > 10$, heating rates of 10^{11} – 10^{12} K s^{-1} can be used to desorb selectively even reasonably strongly bound molecules ($D \approx 1000$ cm^{-1}) so that the free molecules are “lukewarm” i.e. have a much smaller internal energy content than they would have if described by traditional slow heating rates (10 K s^{-1} or less). These rapid heating rates can be achieved with nanosecond laser pulses (or with laser pulses having nanosecond spikes). Indeed, surface heating rates as high as 10^{15} K s^{-1} have been reported with femtosecond laser pulses [33], suggesting the possibility of selectively desorbing molecules from even tighter-binding surfaces. Actually, the heating rates necessary for selective desorption of large molecules may be even less than 10^{11} – 10^{12} K s^{-1} for $D \approx 1000$ cm^{-1} bound molecules if the binding energy D is divided among n surface–adsorbate bonds (where n might be typically 6–12). In such a case a temperature rise of only about 100 K is required to break the contact between the molecule on the surface and the surface itself.

The value of the adiabatic parameter may also be inferred from the computational study by Lucchese and Tully [11] of NO desorbing from LiF which for a picosecond heating rate shows that the NO molecules desorb with much reduced vibrational excitation as compared to that for NO molecules scattered from a hot surface. From the potential energy sur-

† This is of critical importance since the operational criterion (eq. (10)) is more robust than the particular model used to estimate ξ . Put in other words, when our model predicts too high a value for ξ , an alternative energy transfer pathway with a lower value of ξ will take over. It is important therefore to establish from experiment that there are no pathways with very low values of ξ .

face used in that computation [34], we estimate^{††} $\xi > 10$. Hence a heating rate of less than a nanosecond would suffice to desorb NO molecules with vibrational energy content below D .

Is there any experimental evidence to support the claim that rapidly desorbed molecules come off the surface lukewarm? The answer is unequivocally yes. Experiments on the desorption of CH₃OH and C₂H₄ from metal surfaces with pulsed nanosecond lasers show that these simple, small molecules are desorbed intact whereas at much slower heating rates there is essentially complete fragmentation [10,14]. These observations have been interpreted previously as the competition between the rate of desorption, k_d , and the rate of reaction, k_r , where it has been assumed [10,14,35] that both k_d and k_r are represented by Arrhenius-type expressions ($k = \theta \nu \exp(-E/RT)$) with pre-exponential factors ν_d and ν_r and activation barriers E_d and E_r . Here θ is the adsorbate coverage. It is expected that $E_d > E_r$ but that $\nu_d > \nu_r$. Then at low temperatures, $k_r > k_d$, whereas at high temperatures k_d dominates. This treatment is based on being able to describe the physisorption bond and molecule as being at a (time-dependent) temperature. This implies facile energy flow between them. On the contrary, we suggest that sufficiently rapid surface heating causes non-equilibrium desorption.

The same type of behavior in which evaporation dominates over degradation has also been observed for large molecules desorbing from surfaces following pulsed laser heating [12–18]. For example, Engelke et al. [18] have examined the two-step laser desorption laser multiphoton ionization of 20 phenylthiohydantoin (PTH)-amino acids, and in almost every case the mass spectra are dominated by the parent ion peak. Here a pulsed CO₂ laser desorbs as neutrals the PTH-amino acid molecules adsorbed on a glass substrate which is heated by the CO₂ laser pulse. PTS-serine and PTH-threonine are known to be thermally labile, losing water upon heating above 400 K [36]. Nevertheless, the intact parent molecule

is observed as the base peak and no evidence is found in the mass spectrum for water elimination, although introduction of these molecules into a conventional mass spectrometer from a heated inlet shows extensive degradation. Indeed, this behavior applies to rapid surface heating by other means, such as by bombardment of the surface with MeV energy fission products of californium-252 [37] or by bombardment of the surface with primary ions in the keV energy range [38]. This has the practical consequence of providing a means of analyzing adsorbed molecules notorious for their non-volatility and/or thermal instability. The proposed mechanism provides an understanding necessary to plan experiments to exploit the dominance of desorption over reaction upon rapid laser heating of the surface substrate containing adsorbed species. Experiments are being formulated to examine the various facets of the criterion (eq. (10)) for selective desorption in detail.

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^{††} Two alternatives were used: (i) α estimated from the repulsive part of the potential; and (ii) the binding energy D (≈ 90 meV ≈ 1000 K) of NO to the surface combined with the vibrational frequency in the well. Note that the well used [34] contained not only dispersion forces but also an electrostatic term due to the interaction of the NO dipole with the charges on Li⁺ and F⁻.

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