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Mechanisms of activation of heterogeneous reactions by laser radiation

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We investigate theoretically the mechanisms whereby heterogeneous reactions are activated by IR laser radiation via selective pumping of the vibrational degrees of freedom of adsorbed molecules, and also via stimulation of electron migration between surface groups. The latter mechanism is used to explain the increased rate of decomposition of NH_2 groups on an aerosil [SiO_2] surface in the radiation field of a CO_2 laser.

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1. Problems connected with the action of laser radiation on physico-chemical processes are presently attracting considerable attention for perfectly understandable reasons.[1-4] One of the timely concomitant problems is the selective activation of adsorption and catalytic processes; a solution of this problem would provide the chemical industry and the material sciences with entirely new possibilities. Direct stimulation of surface reactions by laser radiation can be effected in two ways.1) The first is to activate gas-phase molecules that subsequently enter in surface reactions (see, e.g.,[5]). The second is activation of molecules adsorbed on a surface.[6] This method has certain distinguishing features worthy of a more detailed examination. Adsorption (and especially chemosorption) shifts the frequencies of the molecule absorption bands and gives rise to new IR spectral bands as a result of the change in the symmetry of the force field.[7,8] For the same reason, the isotopic shift of the frequency increases in a number of cases. This extends the possibilities of laser action.

At the same time, chemosorption is connected with the formation of chemical compounds of a new type, which do not exist in the gas phase and whose reactivity and mechanisms of interaction with other molecules differ from the analogous properties of the gas phase. We note also that by using adsorbents with developed surfaces it is possible effect chemical transformations at an appreciable density of the medium, something difficult to do in the gas phase in view of the collision line broadening and other factors.

Recent theoretical investigations of energy-exchange processes in an adsorbent + adsorbate system can be of partial help in the choice of the system or of the particular type of interaction,[4,9-11] although the complexity of heterogeneous systems makes rigorous deductions impossible. At the same time, it can be concluded from the results of these theoretical papers that in the case of excitation of vibrational degrees of freedom the activation of adsorbed molecules via buildup of a definite chemical bound by IR laser radiation is possible only if the relaxation of this vibration has low probability, since the effectiveness of the activation becomes noticeable at a pumping rate exceeding the relaxation rate. In the case of chemosorption at a radiation density ~100 W/cm² this condition imposes considerable limitations on the type of the activated surface structures; this will be discussed separately later on.

It should also be noted here that in many cases the obvious mechanisms of activation of surface reactions by laser radiation, such as acceleration of the molecule in the course of absorption, weakening of the chemical bond by vibrational pumping or by excitation of surface migration, and others, are insufficient in a number of cases for the understanding of the surface phenomena. One must not, for example, lose sight of processes connected with electron transfer between surface groups, accompanied by an energy change on the order of a vibrational quantum. A sharply inhomogeneous heating of the surface can also lead to an appreciable change of its properties, especially in the case of minutely dispersed samples. Therefore the interpretation of the experiment, even in the presence of a distinct resonance, calls for a thorough theoretical analysis of the possible mechanism whereby the reactivity is changed, and for at least order-of-magnitude estimates of the contributions of the various processes. We determine below the region of applicability of selective vibrational laser excitation of various surface groups, and demonstrate the importance of electron transfer between surface atoms. The numerical estimates obtained for the vibrational relaxation times of the adsorbed molecules demonstrate the feasibility of vibrational activation for only definite oscillation modes. In the case of laser-mediated decomposition of NH_2 groups on the surface SiO_2, a preferable activation mechanism is demonstrated, namely stimulation of the electron transfer by infrared radiation.

2. Some of us[6] have established an interesting fact—a sharp increase in the rate (by ~10^3 times) of the decomposition of NH_2 groups on the surface of aerosil (SiO_2) in the radiation field of a CO_2 laser ($I \sim 30$ W/cm^2) compared with the thermal reaction that takes place at the same temperature (~800 °C) as in the irradiation zone. Since the laser emission frequency $\gamma = 932$ cm^{-1} coincided with the maximum of the absorption band of the SI–N bond, it could be assumed that the reaction is accelerated by the pumping of this vibrational degree of freedom. However the estimates made in[6] of the lifetime of the oscillation, on the basis of the data of[12] and of the width of the absorption band, have led to a value $\tau_{\rm rel} \sim 10^{-11}$ sec. This value agrees also with the theoretical estimates presented below. At this lifetime, selective pumping of the Si–N oscillation is impossible, since the rate of thermal excitation of this bond exceeds by many orders of magnitude the rate of radiative excitation at a given radiation intensity. This conclusion agrees also with the fact that the rate of the decomposition is not strongly changed when the radiation frequency near 932 cm^{-1} is changed by an amount ~20 cm^{-1}.

Thus, to interpret these experiments we are forced to resort to several other concepts, although this entails certain difficulties due to the complexity of the system, the scarcity and ambiguity of the factual material, a situation generally typical of adsorption and catalytic systems.

3. The proportional increase of the concentration of the surface OH groups and of oxygen bridges, observed in experiments on the decomposition of NH_2 groups,[6,7] indicates that oxygen takes part in the decomposition reaction and apparently oxidizes partially the NH_2 groups to H_2 and N_2. On the other hand, there are data that indicate that surface reactions of this type proceed via formation of active surface states of oxygen: the radicals O^- and O_2^-,[13] the formation of which should be aided by the partial reduction of the surface, for example in chemosorption of ammonia. In addition, the radical O^- may possibly be produced by transfer of a proton from the OH group to a neighboring NH_2 group.

It is necessary to call attention next to the very low value constant of the thermal reaction $K_T \sim 10^{-4}$ sec^{-1}. Representing the reaction constant in the form

$$K_T = A \exp\{-E_a/RT\} \tag{1}$$

and substituting in (1) the values of K_T, $T \sim 100$ K, and the experimental value $E_a \sim 27$ kcal/mol, we obtain for the pre-exponential factor the anomalously low value $A \sim 0.2 \times 10^2$ sec^{-1} compared with the factor predicted on the basis of the classical kinetic concepts.[14] The obtained value corresponds to an effective steric factor$^{2)}$ ~10^{-10}. This indicates that the measured rate constant K_T can hardly pertain directly to the reaction of radicals of the type

$$O^- + NH_2 \rightarrow OH^- + NH. \tag{2}$$

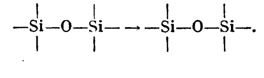
We also note that if the rates of reactions of type (2) were to limit the process, then K_T would take the form

$$K_T \sim \mathcal{K}[O^-], \tag{3}$$

where $\varkappa$ is the rate constant of the bimolecular reaction (2). This assumption also leads to an unreasonable concentration of the reacting particles, for example $[O^-] \sim 10^4$ molecules/cm^2, corresponding to one active particle per 10^6 globules of aerosil with dimensions ~100 Å. In addition, an activation energy 27 kcal/mol is patently high for the reaction of active particles such as O^-.[13]

At the same time, attention is called to the fact that the processes of formation and regeneration of active particles, as well as their migration over the surface to the reaction groups, are connected with the transfer of an electron between the different forms of the surface oxygen. Since quartz is a dielectric, one can expect these processes to be hindered. The estimate given below for the electron-transfer probability demonstrates that it can be stimulated by IR radiation. It is then possible to reconcile the orders of magnitude of the observed quantities. From the character of the derivation it will be seen that similar estimates can be used also for a number of other systems.[5,16]

4. We consider two oxygen atoms separated by a distance equal to the lattice period, i.e., ~5 Å. For the sake of argument, we consider the migration of the radical O^- on account of electron transfer:



$$\underset{|}{\overset{O^-}{\overset{|}{-Si}}}-O-\underset{|}{\overset{O}{\overset{|}{Si}}}- \rightarrow -\underset{|}{\overset{O}{\overset{|}{Si}}}-O-\underset{|}{\overset{O^-}{\overset{|}{Si}}}-. \tag{4}$$

Since the character of the bond of the oxygen with the silicon is altered by the electron transfer, it can be assumed, starting from general considerations,[17] that the electron transfer is connected with the electron-vibrational transition shown schematically in Fig. 1. The two left-hand terms on Fig. 1 pertain to the left-hand oxygen atom of (4), and the two right-hand terms to the right atom, respectively. The electron transfer is ac-

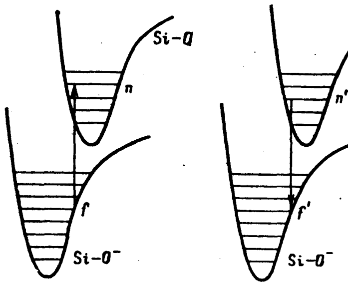


FIG. 1. Transfer of electron between two SiO surface groups.

companied simultaneously by the transitions marked by the arrows in Fig. 1. The shift of the minimum of the potential curve on going from Si–O to Si–O⁻ is apparently unknown, but in other analogous cases it is of the order of 0.2–0.3 Å.[18] Therefore, starting from the Franck-Condon principle, we can determine the order of the dimensionless Stokes losses and the activation energy of the process.[19] After elementary calculations we find that the transition probability is maximal for vibrational levels near $n\sim 10$, which corresponds to an activation energy of the order of 20–30 kcal/mol (the measured value is ~27 kcal/mol).

We turn next to an estimate of the electron-transfer probability. It is necessary here to single out resonant transfer of an electron between like vibrational levels of two absolutely identical Si–O groupings. The transfer rate is determined by the overlap of the electron wave functions at the different atoms. On the other hand, if the Si–O groupings are in unlike conditions, say one is alongside the NH_2 group, then the system of vibrational levels is shifted, and an excess (or deficit) of energy should be radiated (radiative transition) or scattered in the lattice (nonradiative transition) even in a transition between like vibrational levels. In these cases the transition probability depends also on the energy-disposal conditions.

Radiative transfer of an electron and the compensation of the resonance defect via radiation (or absorption) of field energy are connected with an interaction of the type

$$V_R\sim eE_0r\cos\omega_0t, \tag{5}$$

where E_0 is the amplitude of the electric field intensity, r is the electron coordinate (the electromagnetic wavelength is much larger in this case than the interatomic distance), and ω_0 is the radiation frequency. The wave functions of the system in the initial and final states are defined in the form

$$\Phi_1(r, R_1, R_2)=\Psi(r-R_1)\varphi_f(R_1)\chi_{n'}(R_2), \tag{6}$$

$$\Phi_2(r, R_1, R_2)=\Psi'(r-R_2)\chi_n(R_1)\varphi_{f'}(R_2), \tag{7}$$

where Ψ and Ψ' are the wave functions of the electron, R_1 and R_2 are the coordinates of the oxygen atoms, φ_f and $\varphi_{f'}$ are the nuclear wave functions for the lower terms, and χ_n and $\chi_{n'}$ are the wave functions for the upper terms (Fig. 1).

Using the estimate

$$\langle\Psi|r|\Psi'\rangle\sim b_0S, \tag{8}$$

where b_0 is the distance between atoms (~5 Å), S is the tunnel factor:

$$S\sim\exp\{-b_0(2m_e\varepsilon)^{1/2}/\hbar\}\sim 0{,}04, \tag{9}$$

m_e is the electron mass, and ϵ is the electron affinity of the O atom (~1.5 eV), we obtain formulas for the rate of electron transfer in the interaction with the thermal and laser radiations[3)]:

$$W_{R,T}\sim\frac{4\pi}{137\hbar}b_0^2S^2J_{fn}^2J_{f'n'}^2\frac{dI(\Delta\omega)}{d\omega}, \tag{10}$$

$$W_{R,L}\sim\frac{4\pi}{137\hbar}b_0^2S^2J_{fn}^2J_{f'n'}^2I_0\frac{\Gamma_{f'n}/2}{(\omega_0-\Delta\omega)^2+\Gamma_{f'n}^2/4}. \tag{11}$$

Here J_{fn} and $J_{f'n'}$ are the Franck-Condon factors, $dI/d\omega$ is the spectral density of the termal radiation as determined by the Planck formula, $\Gamma_{f'n}$ is the sum of the widths of the vibrational levels f' and n, and

$$\Delta\omega=\delta+\omega_f+\omega_{n'}-\omega_n-\omega_{f'}, \tag{12}$$

where δ is the small vibrational-level shift discussed above, and $\hbar\omega_f$ etc. are the energies of the corresponding levels. Since the Si–O vibration frequencies are ~1000 cm^{-1}, it is possible to make $\Delta\omega$ close enough to ω_0 by varying the levels.

According to estimates presented below, $\Gamma_{f'n}$ amounts to ~10^{11} sec^{-1}. In the case of exact resonance this leads to the following ratio for the velocities of the laser and thermal processes:

$$\frac{W_{R,L}}{W_{R,T}}\sim I_0/\Gamma_{f'n}\frac{dI}{d\omega}\sim 10^4. \tag{13}$$

Even at a line width ~100 cm^{-1} this ratio is ~10^2. In this case ω_0 can differ from Δ by ~100 cm^{-1} without affecting substantially the transfer rate. It should also be noted here that the presented estimates of the acceleration of the electron transfer by the laser radiation are valid for any other radiation process, since relation (13) contains only the spectral densities of the radiation.

The calculations performed agree with the observed acceleration of the decomposition of the NH_2 groups. The increment of $W_{R,T}$ at maximum overlap of the vibrational wave functions leads to a value $W_{R,T}\sim 10^2$ sec^{-1}, which agrees with the value of the pre-exponential factor in (1). The estimate of the pre-exponential factor in the case of nonradiative transitions (the perturbation was assumed to be the non-adiabaticity operator[17]) yielded the value

$$A\sim 10^2-10^3\ \text{sec}^{-1}. \tag{14}$$

This means that the nonradiative process is apprently in competition with the radiative-thermal electron-transfer process.

Thus, the described mechanism explains qualitatively the main singularities of the decomposition of the NH_2 groups on the surface of aerosil. It is characteristic here that the reaction rate increases not on account of the decrease of the activation energy (which remains the same), but on account of the increase of the pre-exponential factor. We are consequently dealing with the laser-thermal decomposition mechanism, which calls for the presence of both laser radiation and heating by thermal means.

The presence in the resonance denominator (11) of the quantity $\Delta\omega$, which is generally speaking sensitive to changes in the masses of the neighboring groups, offers definite hope for the presence of selectivity in such processes.

In conclusion, notice must be taken of the fact that the scheme presented above, while explaining and relating many experimental data, is by way of hypothesis, the experimental verification of which encounters difficulties of technical order.

5. For selective vibrational action of laser radiation on the reaction rate it is necessary that the rate of radiative excitation exceed noticeably the rate of the thermal excitation of this vibration. Taking into account the connection between the thermal excitation and the relaxation rate

$$\tau_{\text{rel}} W = \exp\{-\hbar\omega/K_B T\} \tag{15}$$

and the fact that the rate of radiative excitation at $I \sim 30\ \text{W/cm}^2$ is less than $10^7\ \text{sec}^{-1}$, we find that at $\hbar\omega$ not greatly exceeding $K_B T$ the lifetime of the vibrational excitation should be at least 10^{-8} sec. Therefore one of the important questions in the estimate of the effect of IR radiation on the reaction rate is that of the vibrational excitation (provided that excitation of this vibration contributes to the reaction) and the search for long-lived vibrations.

In connection with the foregoing, we consider several model problems that help explain some fundamental factors and estimate the order of the quantities of interest to us. We use for this purpose a procedure that has given good account of itself (see[9-11, 20-22]), according to which the dissipation of energy from the adsorbed atom into the lattice is due to the fact that the atom "jolts" that surface atom (or groups of atoms) from the lattice, with which it is directly bound (Fig. 2). The vibrations of the surface atom can be described as those of a local oscillator of Debye frequency ω_D. The fact that the surface atom interacts with other lattice atoms and that excitation is rapidly dissipated from it into the volume is taken into account by assuming the levels of the surface-oscillator levels to be completely smeared out, i.e., that the density of states of the n-th level (ρ_n) is $\sim (n\hbar\omega_D)^{-1}$. A more rigorous description is also possible, wherein the displacements of the surface atoms are resolved along the normal coordinates of the lattice, and the state density of the latter is described by a Debye distribution. This complication of the problem, however, does not lead to essentially new results or to a noticeable change of the orders of the obtained quantities.[22]

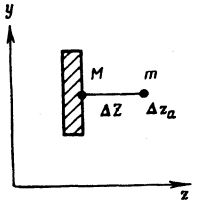


FIG. 2. Illustrating the derivation of the formula for the vibrational relation rates of the adsorbed atom.

Consider the oscillations of atoms with masses m and M (Fig. 2) along, say, the z axis. The interaction potential of the adsorbed atom, which depends on the distance between the atoms, is approximated by a Morse potential:

$$U_a = U(z_0+\Delta z_a+\Delta Z) = D_a\{\exp[-2k(\Delta z_a+\Delta Z)] - 2\exp[-k(\Delta z_a+\Delta Z)]\}, \tag{16}$$

where z_0 is the average distance between the atoms, Δz_0 is the displacement of the adsorbed atom from the equilibrium position, and ΔZ is the displacement of the surfact atom from the equilibrium position. Since the amplitudes of the atom vibrations are small compared with the interatomic distance, we can neglect in the zeroth approximation the coupling of the adsorbed-atom vibrations with those of the lattice atom, and write down the perturbation V that causes exchange of vibrational energy between the adsorbed atom and the lattice in the form

$$V = U(z_0+\Delta z_a+\Delta Z) - U(z_0+\Delta z_a). \tag{17}$$

If the energy of the vibrational quantum exceeds by n times the Debye energy of the lattice, then n-quantum excitation of the surface atoms takes place in the course of the relaxation, and the relaxation rate is estimated, in first-order perturbation theory, by the formula[22]

$$\Gamma_{1\to 0} \sim \frac{0.6\omega_a}{x_a n^{1/2}}\left(\frac{10.86 x_a m}{M}\right)^n, \tag{18}$$

where $\omega_a \approx n_D$ is the vibration frequency of the adsorbed atom, and x_a is the anharmonicity coefficient of the adsorption oscillator ($x_a = \hbar\omega_a/D_a$). In the presence of optical modes in the crystal, the latter also contribute to the displacements ΔZ of the surface atom:

$$\Delta Z = \Delta Z_{ac} + \Delta Z_{opt}. \tag{19}$$

In this case the rate of decay into l acoustic and $n-l$ optical phonons takes the form

$$\Gamma_{1\to 0} \sim \frac{\omega_a}{4x_a[l(n-l)]^{1/2}}\left(\frac{\omega_a}{l\omega_D}\right)^{l+1}\left(\frac{\omega_a}{(n-l)\omega_{opt}}\right)^{n-l}\left(\frac{m}{M_{ac}}\right)^{l}\left(\frac{m}{M_{opt}}\right)^{n-l}(10.86x_a)^n, \tag{20}$$

where ω_{opt} is the frequency of the optical phonon, M_{ac} is the mass connected with the acoustic vibrations, and M_{opt} is the mass connected with the optical vibrations, with $\omega_a \approx l\omega_D + (n-l)\omega_{\text{opt}}$.

In the case of relaxation of the Si–N vibration, energy considerations admit of the possible excitation of either three or four acoustic phonons (according to various data, ω_D for SiO_2 ranges from 275 to 390 cm^{-1}[24, 25]), or one optical phonon $\omega_{\text{opt}} \sim 500\ \text{cm}^{-1}$ and two acoustic ones. The latter is more probable and, substituting in (20) the necessary values $x_a \sim 5.7\times 10^{-3}$,[23] $M_{\text{ac}} \sim 60$ a.u., and $M_{\text{opt}} \sim 28$ a.u., we obtain $\Gamma_{\text{Si-N}} \sim 10^{11}\ \text{sec}^{-1}$, in agreement with measurements for similar systems.[6, 12] We note also that the relaxation rate of the Si–O vibration will be of the same order. On the other hand, the rate of radiative excitation of the vibrations is estimated from the formula

$$W_R \sim \frac{4\pi}{137}\frac{q^2}{m\omega_a}\frac{I_0}{\Gamma}, \tag{21}$$

where q is the effective charge at the ends of the dipole in units of e. From (21) we obtain for the Si–N bond the estimate $W_R \sim 10^4$ sec^{-1}, which is in no way comparable with the rate of thermal excitation $W_T \sim 10^{10}$ sec^{-1}. To make these quantities comparable, it is necessary in this case to increase I_0 by six or seven orders. Despite the pessimistic character of this estimate, there exist apparently many interesting adsorption systems where resonance buildup of the bonds in the adsorbed molecule may turn out to be the decisive factor.

6. The power of the required action on the chemical adsorption systems can be decreased only by increasing the lifetimes of the corresponding excited states. It is seen from (18) and (20) that this can be done by increasing the vibrational quantum $\hbar\omega_a$ or by decreasing the mass of the atom. In this sense an ideal system is made up of adsorbed hydrogen atoms, whose frequencies exceed by one order of magnitude the Debye frequency of the adsorbent.[26] In this case, however, it appears that a more probable process is the breakup of the vibration perpendicular to the surface into several quanta of lateral vibrations (i.e., along the y axis, see Fig. 2), with subsequent relaxation of the latter. The relaxation of the lateral vibrations is described by the same formulas (18) and (20). It is only necessary to recognize that the frequency of these vibrations is as a rule smaller by several times than the frequency of the normal vibrations, and that the relaxation rate is higher. In the case of hydrogen adsorbed, say, on platinum, we can put $n \sim 14$ in formula (18) ($\omega_a \sim 2000$ cm^{-1}, $\omega_D \sim 150$ cm^{-1}). At the anharmonicity constant $x_a \sim 2\times10^{-2}$ typical of hydrogen compounds, we obtain for the rate of direct relaxation the extremely small value $\Gamma \sim 10^{-26}$ sec^{-1}. We recognize further that the relaxation can proceed via breakup of a normal vibration into approximately five lateral-vibration quanta ($\omega_{ay} \sim 400$ cm^{-1}). To calculate the rate of relaxation via such a mechanism we must estimate the perturbation that causes the transition. Representing the potential of the interaction of the atom with the surface in the form (16), recognizing that D_a depends on y, and expanding $D_a(y)$ in powers of the displacement from the equilibrium position, we find that breakup of one normal-vibration quantum into five lateral-vibration quanta requires a perturbation of the type

$$\frac{1}{5!}k^5\frac{\partial^5 D_a}{\partial y^5}(\Delta z_a)^5 y^5.$$

The factor $\partial^5 D_a/\partial y^5$ can be estimated in analogy with the normal vibrations and is of the order of $D_a' k^5$, where D_a' is determined from the anharmonicity coefficient and from the frequency of the lateral vibrations. In this case D_a' is approximately one-fifth of D_a. Thus, by using the perturbation-theory formulas, we can write down an expression for the rate of decay of a normal vibration into p lateral-vibration quanta:

$$\tilde{\Gamma} \sim 2\pi\frac{p^p}{p!}\omega_{ay}^2 x_a^{p+1}\frac{\Gamma_{py}/2}{(\Delta\omega)^2+\Gamma_{py}^2/4} \tag{22}$$

where Γ_{py} is the rate of relaxation of the p-th lateral vibration quantum, and $\Delta\omega \approx \omega_a - p\,\omega_{ay}$ is the detuning from resonance.

In our case Γ_{5y} is estimated with the aid of (18) with $n = 411/150 \approx 3$, namely $\Gamma_{5y} \sim 5\times10^4$ sec^{-1}. Such low relaxation rates are due to the small mass ratio $m_H/M_{Pt} \approx 5\times10^{-2}$. It is seen from the foregoing estimate that the detuning from resonance in (22) patently exceeds Γ_{5y}. Assuming $\Delta\omega \sim 10$ cm^{-1} at $p \sim 5$, we obtain $\tilde{\Gamma} \sim 1$ sec^{-1}.

Thus, it is seen from the foregoing estimates that the lifetimes of the vibrations of the hydrogen atoms chemisorbed on platinum and similar adsorbents lie in the range 1–10^{-4} sec.4)

The situation in question arises, unfortunately, only for very light adsorbed atoms. On the other hand it is clear that the relaxation rate is proportional to the square of the amplitude of the vibration of the atom directly bound to the surface. In the case of adsorption of polyatomic molecules, the excitation of certain normal modes can lead to considerably lower vibration amplitudes of the atom directly bound to the surface, and hence to an increased lifetime of the vibrational excitation. We consider this question in somewhat greater detail using an OH surface group as an example.

7. We consider first the relaxation of the valence vibrations of OH ($\omega_{\nu\mathrm{H}} \approx 3750$ cm^{-1}). The light atom H vibrates near the heavy atom O and causes a tremor in the latter, with an amplitude approximately $m_\mathrm{H}/m_\mathrm{O}$ times smaller than the amplitude of the hydrogen-atom vibration. An approximate analysis of the normal vibrations of this system shows that the ratio of the amplitudes is of the order of

$$\alpha = \left|\frac{y_\mathrm{H}}{y_0}\right| \sim \frac{m_\mathrm{H}}{m_0}\frac{\omega_{\nu\mathrm{H}}^2}{\omega_{\nu\mathrm{H}}^2-\omega_{y\mathrm{O}}^2} \sim \frac{1}{16},$$

where $\omega_{y\mathrm{O}}$ is the frequency of the lateral vibrations of the oxygen atom: $\omega_{y\mathrm{O}} \ll \omega_{\nu\mathrm{H}}$. Using the formulas derived above, we can calculate the decay rate of the valence vibration of OH:

$$\Gamma_{\mathrm{OH}} \sim \alpha^2\frac{m_\mathrm{O}}{m_\mathrm{H}}\left(\frac{\omega_{y\mathrm{O}}}{\omega_{\nu\mathrm{H}}}\right)^{n+2}\Gamma_\mathrm{O}(n), \tag{23}$$

where α is the amplitude ratio, $\Gamma_\mathrm{O}(n)$ is the rate of relaxation of an adsorbed atom with parameters of the oxygen atoms and with vibration frequency 3750 cm^{-1}, and $n = 3750/390 \approx 10$ (in the case of decay into acoustic phonons). It is seen from (23) that the probability of the direct relaxation is quite small in this case. A more probable manner of relaxation is breakup of the valence vibration into approximately five quanta of the deformation vibration of hydrogen ($\omega_{y\mathrm{H}} \sim 870$ cm^{-1}). The rate of breakup of the deformation vibration is calculated from a formula similar to (23). Assuming here that $\alpha \sim 0.1$, we obtain for the relaxation rate of the deformation vi-

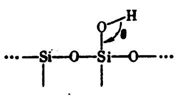


FIG. 3. Adsorbed OH group.

bration (with the optical phonons taken into account) a value ~10^{10} sec^{-1}. Using (22), we can estimate the rate of relaxation of the OH valence vibration via the mechanism in question, namely $\tilde{\Gamma}_{OH}$ ~ 10^6 sec^{-1}. Thus, excitation of the OH valence vibration can be used, according to the foregoing estimates for laser stimulation of the reaction.

The considered relaxation of the hydrogen vibrations in the OH group is the simplest example of relaxation of the vibrations of atoms that are not directly bound to the surface. Examination of the adsorption system shown in Fig. 4 explains that when a remote atom A_n. This in turn increases the lifetime of the given vibration. An interesting example of such a system is shown in Fig. 5, which shows a uranyl ion adsorbed on a silica-gel surface. The frequency of the indicated vibration in uranyl salts is ~930 cm^{-1}.[27] The amplitude of the uranium atoms that participate in this vibration is ~16/238 of the oxygen-atom amplitude. These uranium vibrations are transmitted in turn to the bridging oxygen atoms, whose deformation-vibration frequency is ~500 cm^{-1}. The vibration amplitude of the oxygen atoms is in this case of the order of the uranium atom vibration amplitude, and the relaxation rate is, according to (23), ~10^6 sec^{-1}. This raises definite hopes of feasibility of laser activation of adsorbed uranyl ions. (Activation of uranyl in solutions was recently observed in[28]).

8. We should thus draw from the foregoing the following conclusions: The mechanisms of activation of chemical reactions on a surface by IR laser emission can be connected both with excitation of long-lives vibrations of the adsorbed molecules and with the stimulation of simultaneous electron-vibrational transitions in neighboring adsorbed groups, due for example, to electron transfer. The last mechanism is preferable in the case of activation of the decomposition of NH_2 group on aerosil by CO_2-laser radiation.

Selective vibrational activation of chemosorbed molecules has a number of distinguishing features compared with activation in the gas phase, and its effectiveness is determined by the rate of breakup of the excited vibration into lower-frequency intramolecular vibrations and lattice vibrations of the adsorbent. The longest lifetimes are possessed apparently by valence vibrations of hydrogen in chemosorbed molecules (e.g., OH). The long relaxation times (τ ~ 10^{-6} sec) are possible also for molecules consisting of atoms with greatly differing masses, and upon excitation of groups far from the surface. The relaxation of vibrations of atoms directly bound to the surface is relatively rapid (with the exception of hydrogen), with relaxation times ~10^{-12} sec. The relaxation of the vibrations of chemosorbed hydrogen atoms is hindered by the low mass and the high frequency of the vibration of the latter. In this case estimates yield for the relaxation time of the valence vibrations value ~1 sec, and ~10^{-4} sec for deformation vibrations.

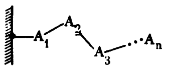


FIG. 4. Adsorbed chain of atoms.

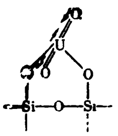


FIG. 5. Chemosorbed uranyl ion.

In connection with the foregoing, great interest can attach also to an experimental determination of the corresponding relaxation times and migration velocities of an electron.

[1] We do not dwell here on possible indirect stimuation techniques such as synthesis of new catalysts, which are used under the specific conditions created by laser radiation.

[2] Such low steric factors are observed for some reactions in solutions, and have apparently not been reliably explained to this day [14].

[3] Formulas (10) and (11) were written out for processes with absorption of radiation. Under the experimental conditions, however, the rates of the radiative processes turn out to be of the same order as (10) and (11).

[4] Horiuchi and Toya [26] estimated the relaxation rate from the width of the spectral lines of chemosorbed hydrogen. The observed line width can be due, however, to inhomogeneity of the surface, and a direct comparison is difficult here.

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Quantum motion of atoms in the resonant field of a standing light wave

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A quantum analysis is made of the motion of atoms in the resonant field of a standing light wave. The wave functions and the eigenstate spectrum of an atom in this field are found allowing only for stimulated atomic transitions in the field. The spectrum represents two infinite systems of allowed energy bands corresponding to two generally different stationary states of an atom in the field. The edges of all the allowed energy bands are found as a function of the field intensity and detuning of the field frequency from the resonant transition frequency. The wave functions are special functions of a new type and they are identical, for zero detuning, with the eigenvalues of the Mathieu equation. For some values of the field and detuning the spectra of an atom in a standing light wave are calculated numerically. A general analysis of the spectra of quantum motion and of the wave functions of stationary states is used in considering the influence of resonant spontaneous decay on the motion of an atom in the field. In the case of positive detuning such resonant spontaneous decay increases the energy of motion of an atom, whereas in the case of negative detuning such decay reduces the energy. In the latter case a steady-state distribution of field-cooled atoms between several of the first energy bands is established. It is shown that under the influence of a test field such cold atoms may undergo resonant transitions within and between allowed energy bands.

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1. INTRODUCTION. FORMULATION OF THE PROBLEM

The interaction of a free atom with a resonant light field is known to be always accompanied by a change in the internal state of the atom and also by a change in the motion of an atom as a whole. Thus, the emission (absorption) of one photon by an atom alters the atomic momentum by an amount equal to the momentum of a resonant photon and the energy of translational motion is reduced by the recoil energy. It is also known that such recoil usually has no significant influence on the spatial motion of atoms interacting with a resonant light field. Firstly, the absorption (emission) of one resonant photon alters the momentum of an atom by an amount $\Delta P = \hbar k$ (k is the wave vector of the field) which is between four and five orders of magnitude less than the average thermal momentum of an atom $\overline{P} = (2M\varkappa T)^{1/2}$ ($\varkappa$ is the Boltzmann constant). Secondly, collisions and spontaneous decay of atoms from the states involved in a resonant transition usually result in a very rapid loss of resonance between such atoms and the field so that the atoms can reemit only a small proportion of the resonant photons.

Nevertheless, in some cases the number of reemitted resonant photons may be so high that the total change in the energy and momentum of an atom due to its interaction with the field is comparable with the average thermal values of these quantities. For example, this