

Resonant action exerted on atoms on a surface and on atoms in molecules: selective oscillation buildup and selective reabsorption and adsorption; excitation of nonlinear oscillator by a set of resonant frequencies or by internal transitions

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We consider resonant oscillation buildup and detachment of atoms on the surface of a substance under the influence of an electromagnetic or a hypersonic field, a process that can be used to sort out atoms, to purify surfaces, to generate powerful hypersound, etc. We consider excitation of a nonlinear oscillator (atom in a molecule or on a surface) by a set of resonant frequencies and indicate the conditions under which this problem can be reduced to that of resonant excitation of a linear oscillator. The buildup of external oscillations by internal transitions is proposed. The possibility of separating definite atoms from adsorbed atoms with the aid of the tunnel effect is noted.

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Selective and multiple-step excitation and dissociation of molecules by an intense electromagnetic field were considered first in^[1,2], with different features and different methods of strong excitation of a nonlinear oscillator, and with the appearance of new buildup frequencies in intense fields (due to the polarization forces). This problem of selective excitation is of considerable interest for the realization and intensification of definite chemical reactions, for sorting out atoms, for selective biological action, etc.

In this paper we consider new possibilities of resonant buildup of nonlinear oscillators and of resonant action exerted on atoms on the surface of a substance. These processes, depending on the choice of conditions, make it possible to realize either high-power genera-

tion of coherent hypersound, or else realize selective reabsorption or adsorption of atoms of definite sorts.

1. *Adsorption of molecules and atoms* by surfaces is effected by interaction forces whose potential $U(x)$ makes possible buildup of oscillations of the adhered atoms. Inasmuch as at a specified $U(x)$ the resonant frequency (i.e., the distances between the levels) depends on the mass of the atoms, selectivity of the action is possible, especially in view of the possible very close equality of $U(x)$ for different isotopes and isomers of atoms *if the surface is highly homogeneous* and if the atoms select definite energy places at which they stick in the crystal-lattice cells (places corresponding to an energy minimum). If the adsorption is not uniform over the surface but in spots (two-dimensional crystals with

overwhelming majority of the atoms which are not located on the perimeter of the spots have the same binding potential, and are therefore suitable for selectivity.

Instead of an adsorption layer one can use for the resonant buildup a surface layer of atoms of the substance itself. These surface atoms have an oscillation frequency and a binding potential that are different from the frequency and binding of the atoms inside the volume. However, the frequencies in this case are higher and, most importantly, they cannot be altered without replacing the surface, whereas in the case of adsorption, replacement of the adsorbent changes the frequency but leaves the surface unchanged. In order of magnitude, the resonant frequencies of the oscillations of the atoms on the surface are $\omega \approx \sqrt{K/M} \sim 1/\sqrt{M} \sim 10^{12} - 10^{13} \text{ sec}^{-1}$, with $\Delta\omega/\omega \approx \Delta M/2M$.

The exciting force can be connected in the heteropolar case with the presence of a charge at the atom [$F \approx q_{\text{eff}}E$, where $q_{\text{eff}} \approx 0 + e$]. In the homopolar case it can be connected with the atom's dipole moment [$F = d_0(\partial E/\partial x)$] or with its polarization and interaction with the remaining part [$F \approx (\partial/\partial R)(d^2/R^3) \approx 3d^2/R^4$, where $d \approx dE$] and

$$E_{\text{eff}} = \frac{1}{q_{\text{eff}}} F = \frac{3d^2 E^2}{q_{\text{eff}} R^4} \sim \left[3 \left(\frac{a}{R} \right)^4 \frac{a^2 E}{q_{\text{eff}}} \right] E \gg (10^{-7} E) E$$

assuming a comparison with $q_{\text{eff}} \lesssim e$, where $\alpha \approx a^3$.

More effective may be excitation of homopolars by the inertial force $F \approx M\ddot{\xi}(t)$, where $\xi(t)$ is the amplitude of the surface oscillations (see below).

2. *Emission of hypersonic phonons* in resonant excitation of atoms on a surface. If the surface concentration of the adsorbed atoms is N_1 , their mass is M , their oscillation velocity is u , and their frequency is ω , then the amplitude of the hypersonic wave is $\Delta p_s \approx N_1 u M \omega$, and the density of the sound power is $I_s \approx (\Delta p_s)^2 / \rho c_s$, for example, at $N_1 \approx 10^{14} \text{ cm}^{-2}$, $M \approx 10^{-22} \text{ g}$, and $u \approx 10^4 \text{ cm/sec}$ we obtain $\Delta p_s \approx 3 \times 10^2 \text{ atm}$ and $I_s \approx 10^4 \text{ W/cm}^2$, which are colossal pulsed flux densities of hypersound of very high frequency, the adsorption of which is small only at very low temperatures.

Let us estimate the line widths of the oscillations due to the sound emission. The dissipation time is $\tau \approx N_1 M u^2 / I_s \approx \rho c_s / N_1 M \omega^2 \cdot 10^3 / N_1 \text{ sec}$, i.e., $\Delta\omega/\omega \sim 1/\tau\omega < \Delta M/M$ if we choose $N_1 \approx 10^{13} - 10^{14} \text{ cm}^{-2}$. To decrease the line width and to decrease the sound radiation by several orders of magnitude one can choose the substrate layer thickness such that the atoms stick to it in such a way that no phonons are emitted (small substrate thickness), or that the emitted phonons return and are absorbed but not with the same phase, for example, in such a way that the thickness subtends an odd number of quarters of the acoustic wave, $l \approx \lambda_s(2n+1)/4$, thereby ensuring reabsorption of the emitted phonon.

For strong excitation of oscillations in the molecule and for excitation of oscillations of adsorbed atoms, it

oscillator is excited.

3. *Excitation of nonlinear oscillator by a set of resonant frequencies.* If we specify the potential $U(x)$ that retains the atom and the force $F(t)$ that causes it to oscillate, then the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x^2} + U(x) + \pi F(t).$$

In the near-harmonic case we have $U(x) \approx (1/2)M\omega^2 x^2$, and the probability of exciting the n th level at a specified $F(t)$ is

$$w_n = \frac{1}{n!} \{ \epsilon(t) / \hbar\omega \}^n \exp \{ - \epsilon(t) / \hbar\omega \},$$

where $\epsilon(t)$ is the quasiclassical work performed on the oscillator. For example, at exact resonance, when $F \approx F_0 \cos \omega t$, this work is $\epsilon \approx (\int |F| dt)^2 / M \approx (F_0 t)^2 / M$.

However, the form of $U(x)$ can deviate significantly from harmonic. We present below conditions for the excitation of a strongly nonlinear oscillator by a set of frequencies and show when the excitation can become strong rapidly enough.

Assume that to know the energy levels E_n and the matrix elements of the transitions $g_{mn} = \int \psi_m^* x \psi_n dx$, where ψ_m and E_m are the values for the unperturbed Hamiltonian.

We seek the exciting field in the form $E = \sum_k (1/2) A_k \times \exp[i\omega_{k+1,k} t] + \text{c.c.}$, where $\omega_{k+1,k} = (E_{k+1} - E_k)/\hbar$, i.e., in the form of a set of resonant frequencies.

Specifying the prepared wave function in the form $\Psi = \sum_m C_m(t) \psi_m \exp(-E_m t/\hbar)$, and substituting it in the Schrödinger equation, we obtain $\dot{C}_m = (1/i\hbar) \sum_n g_{mn} \times \exp[i\omega_{mn} t] F(t) C_n$, or else specifying $F(t)$ in explicit form and retaining only the nonoscillating terms we have

$$\dot{C}_m = (q_{\text{eff}} / 2i\hbar) \{ g_{m, m+1} A_m C_{m+1} + g_{m, m-1} A_{m-1}^* C_{m-1} \}.$$

Choosing $qA_m = (F_0/i) [(m+1)\hbar/2M\omega]^{1/2} / g_{m, m+1}$, we obtain $\dot{C}_m = - (F_0/2\hbar) \{ [(m+1)\hbar/2M\omega]^{1/2} C_{m+1} - (m\hbar/2M\omega)^{1/2} C_{m-1} \}$, but such an equation describes the passage through the levels in the harmonic oscillator under the influence of resonant action $F_0 \cos \omega t$, thus confirming the strong action of the selected field. In addition to the set of resonant frequencies, it is possible to sweep the frequency^[1,2] in a way such as to trace the motion of the particles over the excited levels, and a set of successively or alternately switched-on frequencies.

Let us estimate the fields needed for a strong rapid buildup of oscillations of the n th level when the damping is suppressed. From the condition $(F_0 t)^2 / M \sim \epsilon_n \sim n\hbar\omega$ we obtain for the heteropolar bond $E \approx \sqrt{Mn\hbar\omega} / t g \approx V \text{ cm}$ for $n \approx 10$, $q \approx 0.1e$, and $t \approx 30 \mu\text{sec}$. For the homopolar bond, an equally effective action can be obtained by hypersonic oscillations with amplitude $\xi \approx F_0 / \omega^2 M$, i.e., at a sound flux density $I_s \approx (1/2)\xi^2 \omega^2 \rho c_s \approx F_0^2 \rho c_s / 2\omega^2 M^2$. Inasmuch as the pressure in the sound wave is $\Delta p_s \approx \rho c_s \xi \omega \approx \rho c_s F_0 / M\omega$, we obtain for $F_0 \approx \sqrt{Mn\hbar\omega} / t$ the value $\Delta p \approx \rho c_s \sqrt{n\hbar/M\omega} / t \sim 3 \times 10^{-4} \text{ atm}$, which corresponds to hypersound power densities $I_s \approx (\Delta p_s)^2 / \rho c_s \approx 10^{-8}$

W/cm^2 , the adsorption of which can be made small at low temperatures.

In the case of excitation of sound by the pressure of radio waves or light (shift of neighboring frequencies or modulation of the light at the frequency ω), the required power density is $I \approx \Delta p c \approx 3 \times 10^5 W/\text{cm}^2$, but excitation by the Lorentz force due to interaction with the surface current with an external constant magnetic field H^* yields $\Delta p_s \sim (1/c) J_s H^* \approx H_0 H^* / 8\pi$, i.e., the maximum field amplitude $H_0 \approx 8\pi \Delta p_s / H^* \approx 3 \times 10^{-2}$ Oe, corresponding to radio-emission flux densities $I \sim (H_0^2 / 4\pi) c \approx 0.3 W/\text{cm}^2$. The use of electromagnetic (or acoustic) resonators can decrease the necessary power further. It is possible to excite sound by acting on the opposite surface of the plate.

The resonant adsorption processes considered above can be realized both on the surface of a single crystal and on a large surface area comprising many small crystallites.

Resonant re-adsorption can be used not only to select atoms by types, but also to rid surfaces of adsorbents. It is easy to realize reversible conditions, under which selective adsorption takes place as a result of resonant adsorption of energy by the approaching atoms.

4. *The tunnel effect of atoms* under the influence of a field or inertia can also be used for mass separation, in view of the strong exponential mass dependence of the tunneling probability $W_{\text{tun}}(M)$. Indeed, $W_{\text{tun}}(M)$

$\approx \omega \exp[-K - (\Delta M/M)K]$, where $K \approx (2/\hbar) \int \sqrt{M(U-E)} dx$. Assuming $W_{\text{tun}} \leq 1/\tau_0 \approx 10^{-5}$, $K \geq 15$, and $\exp[(\Delta M/M)K] \approx 5 - 10$, we obtain a sufficient separation efficiency at not too small values of $\Delta M/M$. It is possible to combine resonant buildup on the first level followed by facilitated tunneling, or else detachment of the excited atoms by heating.

5. *Action on an oscillating two-level system.* If a system (atom, molecule, etc.) undergoes, under the influence of a resonant field $E_0 \sin \omega t$, transitions between two electronic or vibrational levels (for a two-level system these transitions are effected from one level to the other and back with a frequency $\Omega = 2d_{1,2}E_0/\hbar$, where $d_{1,2}$ is the dipole matrix element and E_0 is the amplitude of the resonant field), then these transitions can be used to cause the system to oscillate, as a unit, in another field, even a static one, if, for example, this system has different polarizabilities or dipole moments or interaction potentials while at different levels. In this case the matching of the buildup frequency to the resonant frequency, even in the case of a nonlinear coupling, is effected simply by time variation of the field amplitude $E_0(t)$ that changes $\Omega(t) \ll \omega$.

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