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E.V. Shuryak.

NONLINEAR MECHANICS
OF ATOMIC MOTION IN MOLECULES.

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Abstract.

The long time evolution of molecular vibration for both free molecules and those in the intense electromagnetic field, resonant to one of the modes, is discussed. The interaction between modes causes the decay of the initial excitation of one of the modes to others via the intermode resonances. The life time of the excitation is strongly dependent on the distribution of such resonances and a number of thresholds is predicted as a function of molecule nonlinearity or the external field intensity. The transition to complicated, statistical behaviour ^{of the} motion is studied and the boundary of this regime is found. In this regime molecule can gain energy from the field up to its dissociation. Some applications of the results to explanation of the data on collisionless dissociation in laser pulse are presented.

1. Introduction.

The problems we study in this paper are connected with the description of the atomic motion in molecules during the time which is much larger than the oscillation period but small compared to the collision rate. We discuss both the evolution of the initial excitation and the behaviour of molecules in the resonant electromagnetic field.

For such problems the traditional small vibration approximation or the linearization of the equation of motion can not be used. The nonlinear terms, although small numerically for not too large excitation energy, are crucial for these phenomena. The fact that the long time behaviour of the nonlinear systems is qualitatively different from that of the linear ones and the divergency of the perturbation theory in such problems is known for a long time. For example, under certain conditions the nonlinear systems behave in a very complicated and quasistochastic way, so that the initial excitation becomes equally distributed over all degrees of freedom. In other words the dissipation inside the molecule (without collisions) is possible. The similar behaviour in the oscillating field leads to increase in the molecular excitation energy up to collisionless dissociation, recently discovered experimentally /1/. As is shown in /2b/ there may be even ionization. The selectivity of such phenomena causes very interesting applications. One may think that with the progress in laser techniques and in our understanding of the nonlinear mechanics of the atomic motion the active control of the chemical reaction mechanism will be possible. But not only applications of these phenomena are important, but also they are of great theoretical interest for they are the example of the transition from the dynamical to statistical behaviour in systems with finite number of the degrees of freedom.

The intensive studies of these problems in many oscillatory systems - The Solar system, particle accelerators, plasma

oscillation and essentially the numerical experiments with nonlinear chains /6,7/ long ago initiated by Fermi, during the last years made significant progress in our understanding of such phenomena and now the general picture of the n-dimensional motion is somehow clarified./8/. The present paper is essentially based on the ideas and conclusions of this theory. As far as we know, this is its first applications to the motion in molecules.

The oscillation of the twoatomic molecule, which has only one vibrational mode, in the intense resonant electromagnetic field is just the problem of the nonlinear resonance, well known in the classical mechanics, see e.g. /9/. The discussion for the molecules in particular, but in classical framework, is made in /10/, where also the role of rotations is studied. In the author's work /11/ the problem is treated in quantum case. It is shown, that the variations of the oscillator amplitude are quantized themselves. For the calculation of the quasienergy /12/ spectrum and the corresponding wavefunctions both the perturbation and the quasiclassical methods are developed. The latter one is used in chapter 2 in the discussion of the twoatomic molecule behaviour in the resonant field. In particular, the interesting phenomenon of "tunneling" between two possible classical solutions is possible.

The evolution of the molecule excitation has been studied by many authors in connection with the so called monomolecular reactions or the spontaneous dissociation of the excited molecule. For their description the Slatter theory has been proposed /3/, in which the energy transfer between the linear modes is neglected, and also the statistical model of Kassel et al /4/ in which on the contrary, the intermolecule relaxation is assumed to be sufficiently fast. The numerical /5/ and also some "real" experiments have shown that for molecules larger than threeatomic ones the Kassel theory works well, while for the threeatomic case some anomalies are observed. But yet these

calculations present no clear explanations of the results and the understanding of the validity regions of these theories.

The interaction between modes we study in chapters 3 (classical description) and 4 (quantum case). Suppose we excite initially only one of the linear modes. How this initial state will "decay" into others and how long time it will need for it? The answer to this question essentially depends on the distribution of the resonances between the given mode and others and also on the strength of the coupling between modes. This dependence is not trivial and contains a number of thresholds at which more and more strong resonances become effective. Such phenomena have been also observed "experimentally" in numerical studies of the nonlinear chains /6,7/.

The twoatomic molecule in the resonant field can effectively gain energy from the field only if it can be transferred from the excited mode to others. So the possibility to observe at rather low intensity of the field of the collisionless dissociation also depend on the distribution of the intermode resonances. Because of this also the thresholds as a function of the field intensity appears. In chapter 6 we estimate the thresholds for several molecules and are able to explain why for Ba_3 , O_3O_4 , SF_6 this dissociation has been found and for OCS , CCl_4 not in experiments /1/ with the intensity not exceeding 10^9 Wt/cm².

In chapters 3,4 we describe the initial stage of the excitation "decay" via the unstable resonances. The further evolution of the system becomes complicated and its detailed description is difficult. But for large enough energy of the excitation this process finally becomes so complicated, that the statistical description becomes possible. These questions are discussed in chapter 5. Based on the so called Chirikov criterion of stochasticity /8/ we find the stochasticity boundary of motion in molecules, separating the regions of the dynamical and statistical behaviour. One of its consequences is the explanation of the above mentioned facts about the monomo-

lecular reactions. The other particular result is the estimation of the amount of energy gained by one molecule per one laser pulse. The result seems to agree with data /1/ in magnitude and dependence on the field intensity.

In the works /2/ the following explanation of the collisionless dissociation has been proposed. In manyatomic molecules the density of states increase rapidly with the increase in the excitation energy. So with the account of the finite width of the rotational band they are mixed into quasicontinuum of states rather soon. From this the conclusion is made that the consequent absorption of quanta is possible up to dissociation.

This explanation seems to us completely insufficient. This is clearly seen already from the fact that the nonlinearity of the system is not at all involved in it, while in the absence of the coupling between modes the large density of states is of no use since the dipole matrix elements into these states are equal to zero. And indeed, the experiments with the nonlinear chains found long time stability for the small nonlinearity case, that is no energy gain. The rotation of the molecules in the absence of collisions can not help, for the states with different angular momenta can not be mixed. In this respect the rotation is just like the translational movement: it makes the spectrum very dense, continuous, but it does not help for quanta absorption.

Our consideration also leads to the conclusion, that at high enough excitation energy of molecule the separate modes collapse into quasicontinuous spectrum and that in this region the quanta absorption is possible. But the condition for all this to take place, which is just the condition of the stochastic behaviour we mentioned above, is dependent on the intermode interaction and therefore is essentially determined by the nonlinearity parameters. The phenomenon of the infinite excitation in this regime is called the stochastic instability and is known in several systems.

In the end of the introduction let us say, that since we apply the ideas and terminology developed in the fields other than the molecular physics, we concentrate our attention to the explanation of their physical meaning. Therefore the presentation of the material is somehow simplified in sense that the particular examples and numerical estimates are presented rather than the formal derivation of the general formulae. We hope that this way is better for the understanding and further use of the discussing theory.

2. Twoatomic molecule in resonant field.

In this work we treat only the vibrational mode of the molecule and thus reduce the problem to that of nonlinear oscillator with the resonant exciting force which is studied in quantum case in the work /11/. The rotations of the molecule do not play an essential role in the problem, they can be taken into account by the change of the effective nonlinearity as it is done in /10/.

The usual and the best studied case for atoms and molecules in the external oscillating field is that when only two levels of the system are essentially involved in the transitions while the others are out of resonance. The molecule vibrations is the exception: for in this case the anharmonism is small and for high enough field amplitude many levels can contribute. This is the case we are going to discuss, for in it rather simple and transparent quasiclassical method can be used. It is discussed in details in /11/ and we do not repeat its derivation here. Let us only say, that it include as a first step the transition to such variables as the resonant phase $\alpha = \theta - \Omega \cdot t$ where θ is the angular variable of the oscillator, Ω is the frequency of the field, and to action variable I conjugated to α . The second important step is the consideration of only resonant part of the field influence. In this approximation the resonant Hamiltonian becomes time independent and its quantization give the quasienergy /12/ spectrum of the problem. The general form of the resonant Hamiltonian is

$$\tilde{H}(I, \alpha) = H_0(I) - \Omega \cdot I + U(I, \alpha) \quad (1)$$

where $H_0(I)$ is the unperturbed Hamiltonian of the oscillator, $U(I, \alpha)$ is the resonant part of the perturbation which depend on time only through α , $\Omega \cdot I$ is the "centrifugal" term for we are in the rotating frame with frequency Ω of the force. In /11/ mainly the case is considered when the width ΔI of the region where $U(I, \alpha)$ is important is small compared to the action resonant value I_0

$$\omega(I_0) \equiv \frac{dH_0(I_0)}{dI} = \Omega; \quad \Delta I \ll I_0 \quad (2)$$

so that (1) can be expanded near I_0 and simplified

$$\tilde{H}(I, \alpha) \approx \frac{\omega'}{2}(I - I_0)^2 + U(I_0, \alpha) + \text{const}; \quad \omega' \equiv \frac{d^2 H_0(I_0)}{dI^2} \quad (3)$$

As this Hamiltonian has the form of the sum of kinetic and potential energies its quantisation meets no difficulties. But this simple approximation can not be used if $I_0 \approx 0$. This is just the case, for the molecules are excited in reality from the ground state. This circumstance do not change the principal ideas of the method, but makes it more difficult to obtain results in the explicit form. Therefore we discuss this case separately here.

In this connection let us note, that in /10/ the equation of motion for action is reduced to the potential form $\ddot{I} = -dV(I)/dI$. But the potential $V(I)$ depend on the trajectory itself and therefore can not be used for quantization.

In the case of molecule excitation by resonant field the resonant Hamiltonian (1) may be parametrized as:

$$\tilde{H}(I, \alpha) = \varepsilon \cdot I + \frac{\omega'}{2} I^2 + f \sqrt{I} \cdot \cos \alpha \quad (4)$$

where $\varepsilon = \omega(I_0) - \Omega$ is the frequency shift with the first transition, $\omega' \equiv d^2 H_0(I_0)/dI^2$ is the nonlinearity of the mode, the constant $f = e \bar{E} / \sqrt{\hbar}$ where $e \bar{E}$ is the dipole matrix element of the first transition $v=0 \rightarrow v=1$, ε is the electric field of the wave.

The dynamics, determined by this Hamiltonian, can be understood in the more convenient way with the help of the so called phase portrait or the picture of the equipotentials on the phase surface. There may be different pictures depending on the parameters, in Fig.1 three main possibilities are shown: a) $\varepsilon > \varepsilon_0 = -\frac{3}{2} (\omega' f^2 / 2)^{1/3}$; b) $\varepsilon = \varepsilon_0$; c) $\varepsilon < 0$; $\omega' < 0$. One can see for example, that the rapid turn in of the field with the initial condition $I=0$ in case a) leads to the trajectory AB with $\tilde{E} = 0$. There is also another trajectory in this case with $\tilde{E} = 0$, CD, but in order to occupy it one needs, for example, to begin with the case c) and then change adiabatically the frequency of the force. The existence of two solutions is well known in the classical case, see e.g. /9/.

Proceeding to the quantization let us note, that no method is known for Hamiltonians with arbitrary dependence of coordinates and momenta. This problem is not even strictly determined. But in the quasiclassical approximation (we are interesting in) no difficulties arise for all derivatives act only to the strongly oscillating part of the wavefunction and thus "commute" with other functions of the coordinates. In /11/ the α -representation is used which is shown in several examples to lead to the results fast. But in our case the I -representation is better, in which the wavefunction is the superposition of the solutions of the type

$$\tilde{\Psi}(I) = \exp \left[-\frac{i}{\hbar} \int \alpha_{ef}(I') dI' \right] \quad (5)$$

where $\alpha_{ef}(I)$ are the solutions of the equation $\tilde{E} = \tilde{H}(I, \alpha_{ef})$:

$$\alpha_{ef} = \arccos \left(\frac{\tilde{E} - \varepsilon I - \frac{\omega'}{2} I^2}{f \cdot \sqrt{I}} \right) \quad (6)$$

The number of these solutions with real α_{ef} can be seen from Fig. 1. For example in the case a) α_{ef} is real in two regions (I_1, I_2) , (I_3, I_4) while in others it is complex. These two regions are of course the two classically accessible values of I . In quantum case these two solutions are not separate for the "tunneling" through the classically inaccessible region with probability

$$W = \exp \left[- \frac{2}{\hbar} \int_{I_2}^{I_3} \text{Im} \alpha_{ef}(I') dI' \right] \quad (7)$$

is possible. The quantisation condition as usual is the decrease of the wavefunction to both limits $I=0, \infty$. If we neglect the "tunneling" terms in spectrum, than the quantization condition is just the familiar one: the area between E_{n+1} and E_n equipotentials is Plank constant. As far as the quasienergy spectrum and the wavefunctions are found, the decomposition of any initial state can give its evolution at any time moment.

Note, that near the dissociation boundary the applicability conditions are violated (of the used approximations). In this region the frequency of the oscillation becomes smaller and the nonlinearity increases, so the nonresonant terms becomes also important. In this region the stochastical layer exists which we do not discuss for it is analagous to that near the separatrissa discussed in /11/.

What are the new features which appear in the quantum approach compared to the classical one /10/? Of course, in quasiclassical approximation many results, for example the

dependence of the oscillation amplitude on the field value, are identical. But the discreteness of the quasienergy levels is due to quantization, it leads to the emittance and absorption by the molecule in the field of new frequencies $\hbar \bar{\omega}_{nm} = \tilde{E}_n - \tilde{E}_m$ corresponding to transitions between different quasienergy values. As is shown in /12a/ this can be true up to addition of integer multiple $\hbar \Omega$. Note, that such new frequencies depend on the field intensity, so the phenomenon can be used for the creation of the fast modulation of the basic frequency.

The number of the quasienergy level is the adiabatic invariant in the changes of the frequency. So our description is very convenient in the discussion of the adiabatic frequency change proposed in /13/.

And finally, the found "tunneling" to the higher oscillation level is purely quantum phenomenon. Formally speaking this makes the molecule dissociation possible at any field intensity but exponentially small in probability. Still it is useful not to take $\varepsilon=0$ but its negative value. According to our estimates this may decrease the intensity of the field, needed for effective molecule dissociation, in several times, or even in order of magnitude.

3. Interaction between modes.

Classical treatment.

Let us remain in the framework of the small vibration approximation and write down the Hamiltonian as an expansion over small displacements of atoms from the equilibrium positions

$$H = \sum_i H_i^{(l)} + \varepsilon \cdot \sum_i c_i x_i + \sum_i H_i^{(n.l.)} + H^{(int.)} + H^{(e.n.l.)} \quad (8)$$

Here $H_i^{(l)} = (\dot{x}_i^2 + \omega_i^2 x_i^2)/2$, the diagonalized quadratic part, or the sum of the energies of the linear modes. The second

term is dipole interaction with the electric field, then the nonlinearities of the separate modes $H_i^{(n.e.)} = \alpha x_i^3 + \beta x_i^4 + \dots$ and finally the interaction between modes

$$H^{(int)} = \sum_i A_{i_1 i_2 i_3}^{(3)} x_{i_1} x_{i_2} x_{i_3} + \dots + \sum_i A_{i_1 \dots i_n}^{(n)} x_{i_1} \dots x_{i_n} + \dots \quad (9)$$

in which we are mainly interested, and the nonlinear corrections to the interactions with the field:

$$H^{(e.n.l.)} = \mathcal{E} \cdot \left[\sum_i d_{i_1 i_2}^{(2)} x_{i_1} x_{i_2} + \dots \right] \quad (10)$$

As far as x_i are small, the last three terms in (8) are also small and in many cases, say in Mandelshtam-Raman scattering, they can be considered as perturbations. But for rather long description of the motion the perturbation series are divergent because of the intermode resonances

$$\sum_{i=1}^N n_i \omega_i = 0 \quad (11)$$

(n_i are integer) which cause slow time dependence of the terms in Hamiltonian like $x_1^{n_1} \dots x_N^{n_N}$. Such terms although small lead to accumulating with time effects. Formally this reveals as "small denominators" in perturbation theory, see e.g. /14/. A. Poincare has called this problem "the main problem of the dynamics".

We are going to discuss this problem not for infinite time, but for time limited from above. In this case the effect of most resonances can be neglected. The initial stage of the decay of one initially excited linear mode which we are going to discuss, may in fact be made with the account of only several and more often with only one leading resonance. The opposite case, when many resonances determine the motion, will be discussed in chapter 5. This discussion, on the contrary, is limited in time from below.

Thus we assume some mode number 1 to be initially ex-

cited and there exist some closest resonance between its frequency ω_1 and the others. To generalize this case to arbitrary initial state is simple.

Our first example is the three frequency resonance $\omega_1 \approx \omega_2 + \omega_3$. For its account only one term in the Hamiltonian of the interaction, namely $A_{123}^{(3)} x_1 x_2 x_3$, is needed. One can see, that in this approximation the initial zero values of $x_2, x_3, \dot{x}_2, \dot{x}_3$ leads to their zero value for all times. But as we shall see, such solution may turn out to be unstable, that is the small initial conditions will then increase. Considering x_2, x_3 to be small we can neglect its nonlinearity and also their influence on x_1 , so that $x_1(t)$ is taken as a given external excitation.

The solution of this problem we shall find following the general scheme, from the action-angle variables $I_2, I_3, \theta_2, \theta_3$ of oscillators 2,3 we proceed to resonant phase $\alpha = \theta_2 + \theta_3 - \theta_1(t)$ and accompanying variables $\theta = \theta_2 - \theta_3$; $I_\alpha = (I_2 + I_3)/2$; $I_\theta = (I_2 - I_3)/2$; $\varepsilon = \omega_2 + \omega_3 - \omega_1$. We omit this simple calculation and present the resonance Hamiltonian for this problem: ($u = A_{123} \bar{x}_1 \bar{x}_2 \bar{x}_3 \sqrt{I_1} / \hbar^{3/2}$)

$$\hat{H}(I_\alpha, I_\theta, \alpha) = (\omega_2 - \omega_3) I_\theta + \varepsilon \cdot I_\alpha + u \sqrt{I_\alpha^2 - I_\theta^2} \cos \alpha; \quad (12)$$

Since in this approximation I_θ is conserved, it is just equal to its initial value, that is to zero. As the result, the problem is rather simple and the solution of the equations of motion can be explicitly found. The solution behaviour depends on the relation between ε and u . If the former is larger, solutions are some vibrations of limited amplitude. In the opposite case modes 2,3 increase and gain energy from the mode 1. The large time formula is

$$I_\alpha(t) = I_\alpha(0) \cdot \exp(\sqrt{u^2 - \varepsilon^2} \cdot t) \quad (13)$$

Of course, in reality for $t \rightarrow \infty$ our approximation is not valid and the amplitude growth of modes 2,3 will be limited either by the nonlinearity, or just by the amount of energy in the initial excitation of mode 1. Note, that the result (13) is sufficient for the explanation of some of the numerical experiments /6/ with the nonlinear chains. The observed "induction time" of the instability is just the time needed for exponent (13) to grow from the computer zero to the level of the order of unity.

Now let us proceed to discussion of the more general resonance with several frequencies: $\omega_1 = \omega_2 + \dots + \omega_m$. The corresponding resonant Hamiltonian is

$$\hat{H} = \varepsilon \cdot I_\alpha + V \cdot I_\alpha^{\frac{m-1}{2}} \cos \alpha; \quad V \in A_{1\dots m} \bar{x}_1 \dots \bar{x}_m I_1^{\frac{1}{2}} \hbar^{-\frac{m}{2}} \quad (14)$$

Its instability region is more complicated than for (12), and again the phase portrait (Fig.2) is useful. For $m > 3$ the large time solution is of the "explosion" type

$$I_\alpha(t) = I_\alpha(0) [1 - \alpha t]^{-\frac{2}{m-3}}; \quad \alpha = V \left(\frac{m-1}{2} \right) I_\alpha(0)^{\frac{2}{m-3}} \quad (15)$$

and turns to infinity in finite time.

It is important, that the net of resonances is dense at any point. But with increase in the order of the resonance its amplitude decreases rapidly and the instability time essentially increases. This situation leads to the result that the most effective decay of a given mode is caused as a rule by one resonance close enough in frequency and in the same time not too weak.

These conclusions can be easily generalized to the case when the mode 1 is under the influence of the external field. As is seen from Fig.1 it leads to periodic modulations of the phase α , so in its spectrum apart from harmonics of ω_1 also the harmonics of the frequencies of these modulations Ω_f . Important, that with the increase of

the field this frequency also increases as $\Omega_f \sim \varepsilon^{2/3}$. This means that the width of the spectrum of mode 1 increases and finally it gets into the instability region of some strong resonance. Therefore the dependence of the decay rate on the intensity of the field has a number of thresholds in which this quantity rapidly increases. In numerical experiments /6,7/ the analogous phenomena as a function of the coupling constant have been observed.

4. Interaction between modes.

quantum treatment.

The standard way to solve the problem of some state evolution in quantum mechanics is to find the stationary states of the system and expand over them the initial condition. Note, that this method has no time limits. But although this method is good in principle, for systems with several degrees of freedom it is not easy to find the stationary states. This can be seen already from the analogy with classical case, and the difficulty also is caused by resonances, which forbid to use perturbation theory even for small terms in Hamiltonian (9). Indeed, the condition $\sum n_i \omega_i = 0$ means that if one changes the quantum number of mode i to n_i , then the total energy changes very little. In other terms, resonances mean the degeneration of states and the part of the Hamiltonian, say $\chi_1^{n_1} \dots \chi_N^{n_N}$ in this case, which has matrix elements between such states, cause large mixing. The example of this kind is the famous Fermi resonance in CO_2 .

But if we are only interested in limited interval of time, then too small resonant terms are not important and only the most essential ones or even one resonance can be considered. Note, that from formal point of view this "cut off" Hamiltonian has rather interesting sense. Its eigenfunctions are not stationary and even not close to them, but are approximately conserved during the limited amount of time. Such quasi integrals of the motions are known in classical mechanics.

Begin with our first example, the three frequency resonance $\omega_1 \approx \omega_2 + \omega_3$. In the linear approximation considered in chapter 3 this case can be quantize easily for it turns out to be identical with the problem of the parametric resonance of the linear oscillator, studied in quantum case in works /15/. So we do not discuss it in details. Let us only say, that as usual in problems connected with linear oscillator, the quantum results do not differ much from the classical ones. In particular, the instability condition is the same and also the law (13) of the instability growth. The essential difference (also of general character) is the fact that instability can grow from the ground state as well. Let us present here as an example the probability of the transition from the ground state to $n_2 = n_3 = n$ /15/:

$$W_n = \frac{(2n)!}{2^{2n}(n!)^2} \sqrt{1-g} \cdot g^n; \quad g \equiv \frac{\varepsilon^2 \sin^2(\sqrt{\varepsilon^2 - u^2} \cdot t)}{\varepsilon^2 - u^2 + \varepsilon^2 \sin^2(\sqrt{\varepsilon^2 - u^2} \cdot t)} \quad (16)$$

which in the unstable region for large time becomes ($n \gg 1$):

$$W_n = \sqrt{\frac{2\hbar}{\pi n I(t)}} \exp\left(-\frac{n\hbar}{I(t)}\right); \quad I(t) = \frac{\hbar \varepsilon^2}{4(u^2 - \varepsilon^2)} \exp(\sqrt{u^2 - \varepsilon^2} \cdot t) \quad (17)$$

The comparison of (17) with the classical one (13) allow us to say that the instability begins due to zero quantum fluctuations. The simple quasiclassical treatment of such resonance can be found in /11/.

The quantisation of the M -frequency resonance can be made in quasiclassical approximation in the same way as in chapter 2. The resonant Hamiltonian is (14), and the phase portrait is shown in Fig.2. The new feature is the fact that in the instability region the quasienergy region is continuous. The following method can be used in this case. The small nonlinearity makes the spectrum discrete, but the results for initial period do not depend on the nonlinearity. This is equivalent to standard method of considering systems in large

box in discussing problems with continuous spectrum.

Another feature of quantum treatment is that even in quasiclassical approximation the amplitude of the mode 1 can not be considered as some definite function, but ensemble of such functions with properties representing the quantum state of mode 1. For example, the n -th stationary state corresponds to $I_1 = n\hbar$ and homogeneous phase distribution. Interesting, that for results (16,17) it is not important for they do not depend on phase. But for more general case(14) even the instability condition depend on phase. The ensemble averaging makes the procedure more complicated. The detailed calculation will probably needs the numerical methods and therefore is reasonable only in particular example. For our estimates to be given below our qualitative discussion is sufficient.

When the molecule is under the permanent influence of the external field the spectrum of exciting mode 1 contains frequencies $\hbar\omega_{mn} = \tilde{E}_m - \tilde{E}_n$, transitions between quasienergy levels. These frequencies are quantum analog of classical phase variations. They also make the spectrum of mode 1 wider and this lead to instability thresholds as a function of field intensity.

5. Stochasticity.

We have discussed above the initial stage of the decay of the mode, when only one resonance is essential. What happens later?

In principle, at low excitation energy, the excitation of other modes will be stopped and only more complicated periodic motion will take place and most of the modes will not be excited. But usually excitation of new modes leads to new resonances and so on. Note, the number of resonances increases also because those $\omega_1 = \sum n_i \omega_i$ with negative n_i become possible. Clear that the motion becomes more complicated and it is difficult to give its detailed description. But under certain condition this process goes so far that statistical

methods of its description becomes possible. This question has been studied with the number of models in /8/.

In the chapters 3,4 one important aspect of the interaction between modes has not yet been considered, that is the nonlinear frequency widening. For example, our resonance is $\omega_1 \approx \omega_2 + \omega_3$. We considered $\chi_1(t)$ as a given function neglecting the backward influence of χ_2, χ_3 to χ_1 . This results in some extra phase vibrations of mode 1, similar to the discussion in chapter 2 for the external force, and the width of ω_1 becomes:

$$\Delta\omega_1 \approx \left(\frac{\omega_1'}{\hbar}\right)^{1/3} (A_{123} \bar{\chi}_1 \bar{\chi}_2 \bar{\chi}_3 \bar{n}_{2,3})^{2/3} \quad (18)$$

where $\bar{n}_{2,3}$ is the average number of quanta in modes 2,3. With growth in excitation level \bar{n} quantity $\Delta\omega_1$ also increases and when they reach the distances between resonances in the system Δ_0 the whole spectrum becomes continuous. This is just the stochasticity criterion by Chirikov /8/ which gives the applicability condition of the statistical methods. It is shown in /8/ that this condition is the same for resonances of any order, so we may discuss only three frequency resonances. The distance between such resonances $\Delta_0 = \omega_0 / N_f$ where ω_0 is some characteristic frequency, and N_f is the number of such resonances with mode 1. Clear that $N_f \sim N_f^2$ where N_f is the number of frequencies in the system. Using these estimates we find the following condition of stochasticity of molecule vibrations:

$$\bar{n} \geq \left(\frac{\omega_0}{\hbar\omega_1'}\right)^{1/2} \frac{\hbar\omega_0}{|A_{123}| \bar{\chi}^3} \cdot \frac{1}{N_f^3} \sim \frac{10^2}{N_f^3} \quad (19)$$

The last expression corresponds to typical values $\hbar\omega_1'/\omega_0 \sim 10^{-2}$; $A_{123} \bar{\chi}^3 / \hbar\omega_0 \sim 10^{-1}$.

This estimate is rather crude approximation, but still some important conclusions can be made on its basis. For

example, at excitation energy of the order of several electron volts (energy of dissociation) molecules with number of atoms larger than 4 lies according to (19) in the stochasticity region. This gives the explanation of the observations, that statistical theory by Kassel et al /4/ gives reasonable description of monomolecular dissociation. If nonlinearity of molecules will be smaller, the result will be different. For three-atomic molecules (19) is not valid, and indeed in calculations /5/ it was found that the distribution over lifetimes is not simple exponential, but can be more complicated. It means that no true relaxation took place and the energy is distributed in molecule in some complicated way, but not complicated enough for the statistical description.

We do not discuss the kinetic stage of the intermolecule relaxation and proceed to more interesting case of the molecule in oscillating field. If the molecule is in the stochastic region, than due to interaction with other modes the phase of the excited mode 1 becomes random. The phase of the field is regular but only the phase difference determines whether energy is transferred from the field to molecule or vice versa. So the system behaves as the regular one in random field which is known to lead to average increase of energy. Such behaviour is known as the stochastic instability in various oscillatory systems.

This phenomenon can be described in the following way. The motion of any mode in the stochastic region is determined not by one leading resonance, but by many of them simultaneously, lying inside its nonlinear width $\Delta\omega_1$. So the Hamiltonian can be written as a sum over such resonant terms

$$H_1^{(int)} = I_1^{1/2} \cdot \sum_n F_n \cos(\theta_1 - \theta_n) \quad (20)$$

In the absence of this $H_1^{(int)}$ the quasienergy is conserved or \bar{E}_1 given by (1) remains unchanged. With the account of (20)

$$\frac{d\bar{E}_1}{dt} = I_1^{1/2} (\Omega - \omega_1(I_1)) \sum_n F_n \sin(\theta_1 - \theta_n) - \frac{e\bar{\chi}_1 \mathcal{E}}{2\hbar} \sum_n F_n \sin \theta_n \quad (21)$$

The first term in (21) describe the intermode relaxation, while the second the interaction with the field in which we are interested. Suppose θ_n are random, than the average change of \tilde{E} is zero. But its squared value increase linearly with time

$$\langle \Delta \tilde{E}^2 \rangle = \mathcal{D}(\tilde{E}) \cdot t \quad (22)$$

It means that energy growth is irregular process like ordinary diffusion. The quantity $\mathcal{D}(\tilde{E})$ in (22) which can be called the diffusion coefficient, can be found in a way similar to that in /8a/ which we do not describe here, with the result:

$$\mathcal{D}(\tilde{E}) = \frac{\pi}{4k} (e\chi, \varepsilon)^2 J(\Omega); \quad J(\Omega) = \frac{|F(\Omega)|^2}{\Delta_0} \quad (23)$$

The quantity $J(\Omega)$ which enter in (23) has rather simple physical sense: it is the spectral density of perturbation (20) acting on mode 1 from all others. The knowledge of the diffusion coefficient (23) allows to describe the quasienergy increase by Focker-Plank equation

$$\frac{\partial P(\tilde{E}, t)}{\partial t} = \frac{\partial}{\partial \tilde{E}} \mathcal{D}(\tilde{E}) \frac{\partial}{\partial \tilde{E}} P(\tilde{E}, t) \quad (24)$$

Finishing discussion of stochasticity in molecules let us note that since our consideration in this chapter is classical it is limited by obvious condition $\hbar \gg 1$. It is clear that at large enough number of modes similar phenomena may exist also at $\hbar \ll 1$ but this case is not yet studied. We also want to stress, that statistical methods, in particular well known in molecular physics equation (24), are used in essentially new situation: there is no collisions (heat bath) the external field is regular and not random. So the statistical element in the problem appears only due to complexity of the intermolecule motion.

6. Collisionless dissociation in resonant field.

This chapter contains applications of our discussion above to the phenomena of collisionless dissociation and to comparison with experimental data /1/.

The possibility of dissociation is determined by the fact whether the sufficient amount of energy can be given to molecule during the laser pulse. This, according to discussion of chapters 3,4, is first determined by the distribution of resonances near the frequency of the excited mode.

Let us first estimate what kind of resonances we need in experimental conditions. Amplitude of some term in interaction Hamiltonian (9) $A^{(m)} \bar{x}^m$ let us estimate as $\hbar \omega_0 \cdot A^{m-2}$ where ω_0 is some characteristic value of frequency and A is some constant which lies in region $0.03 \div 0.1$. The pulse duration τ is of the order of 10^{-7} sec so one may conclude that resonances with $m > m_0 = 6 \div 7$ can not effectively work. and can be neglected, for $A^{m-2} \ll 1/(\omega_0 \tau)$.

The distributions of intermode resonances in molecules COS , BCl_3 , CCl_4 , OsO_4 , SF_6 , studied in experiments /1/, is presented in Fig.3. The frequency values are taken from book /16/ and unfortunately its precision is in many cases not sufficient for our goal. In figure also the index of resonance m is given, that is the number of frequencies in resonance condition. It easy to see, that with increase in number of atoms the density of resonances rapidly increases. This effect will be even more pronounced if less simmetric molecules be considered, for simmetry causes essential degeneration in frequency spectrum.

The threshold of the excitation of a given resonance corresponds to such intensity of the field at which the nonlinear widening of the mode frequency $\Delta\omega$ reach the instability region of this resonance. Taking $\Delta\omega = (\frac{\omega'}{\hbar})^{1/2} (e\chi\varepsilon)^{2/3}$ and distances between ω_1 and $\Sigma n_i \omega_i$ from figure 3 we find the following values for threshold field intensity: $\text{COS} - 10^{12}$; $\text{BCl}_3 - 10^8$; $\text{CCl}_4 - 10^{10}$; $\text{OsO}_4 - 10^9$; $\text{SF}_6 - 3 \cdot 10^8$

in unites wt/cm².

This estimate at least is able to explain why in experiments with maximal intensity of the order of 10⁹ wt/cm² the dissociation of BCl₃, OsO₄, SF₆ was observed and of COS, CCl₄ not. But the accuracy of the threshold value is in fact rather low. First it is just due to low accuracy of the used values of frequencies. Second, we do not take into account the existence of several branches of some modes, which are due to molecule symmetry. In some cases this may be important and essentially decrease the threshold. An example is SF₆ molecule, the exciting mode ν₃ has three branches and as it is noted in /1e/, the "triple" resonance with the field is possible, that is the compensation of anharmonism by the transition to other branch.

Our estimate of the threshold is based on "classically allowed" mechanism. But due to quantum "tunneling" to the stochastic region also some "tail" below threshold must be present. It can also be essential in decreasing the experimental threshold. It is interesting in this connection, that according to estimates in chapter 5, the stochastic region in such molecules as SF₆ lies very low, at excitation energy of several quanta. This coincides with estimates in /2/, but of course the coincidence is purely accidental.

So due to discussed effects, our estimate must be considered as estimate from above. And indeed, for SF₆ it was found to be 2.3 · 10⁷ wt/cm² for ν₃ /1e/, one order of magnitude smaller than the estimate. In order to make more accurate calculation a lot of spectroscopical information is needed which is not yet available, at least to the author.

Since the final stage of the molecule excitation to dissociation takes place in the stochastic region, formulae of chapter 5 can be used for estimate of the energy gain of the molecule per one laser pulse. It is given by formula (22) with diffusion coefficient (23). The amplitude of the frequency term $F \sim A^{(s)} \bar{x}^3$ and their separation Δ₀ is estimated as above. The result is

$$\langle E \rangle (ev) \sim 10^{-1} e\bar{x} (deb) \cdot \left[I \left(\frac{wt}{cm^2} \right) \cdot t (sec) \right]^{1/2} \quad (25)$$

The data /1g/ agrees with $\langle E \rangle \sim I^{1/2}$ and with coefficient mag-

nitude. Moreover, as noted in /1d/ the dissociation rate is found to be proportional not to dipole moment of the transition squared, as usual in the absorption spectra, but to its first power. This observation is also in agreement with (25).

In order to check the proposed explanation of the collisionless dissociation more experiments are needed. For example, the dependence of the average energy gain per pulse on the duration of the pulse is of interest. Note, that in (25) t is strictly speaking not the duration of the pulse, but the duration of the stochastic motion only. So we have assumed, that the transition to it is rather fast.

The very vast field of investigations is open for experiments with two synchronized lasers with different frequencies. If the first pulse makes excitation up to stochasticity region, than the second will continue to excite the molecule irrespective of its frequency, for spectrum becomes continuous. Another interesting possibility is to excite transitions between different quasienergy values, for example for two atomic molecules which do not dissociate up to rather high intensity. Such experiments will open new chapter in spectroscopy, but their importance is even larger because it will be one of the first experimental observation of transition from dynamical behaviour to statistical one in the isolated finite system.

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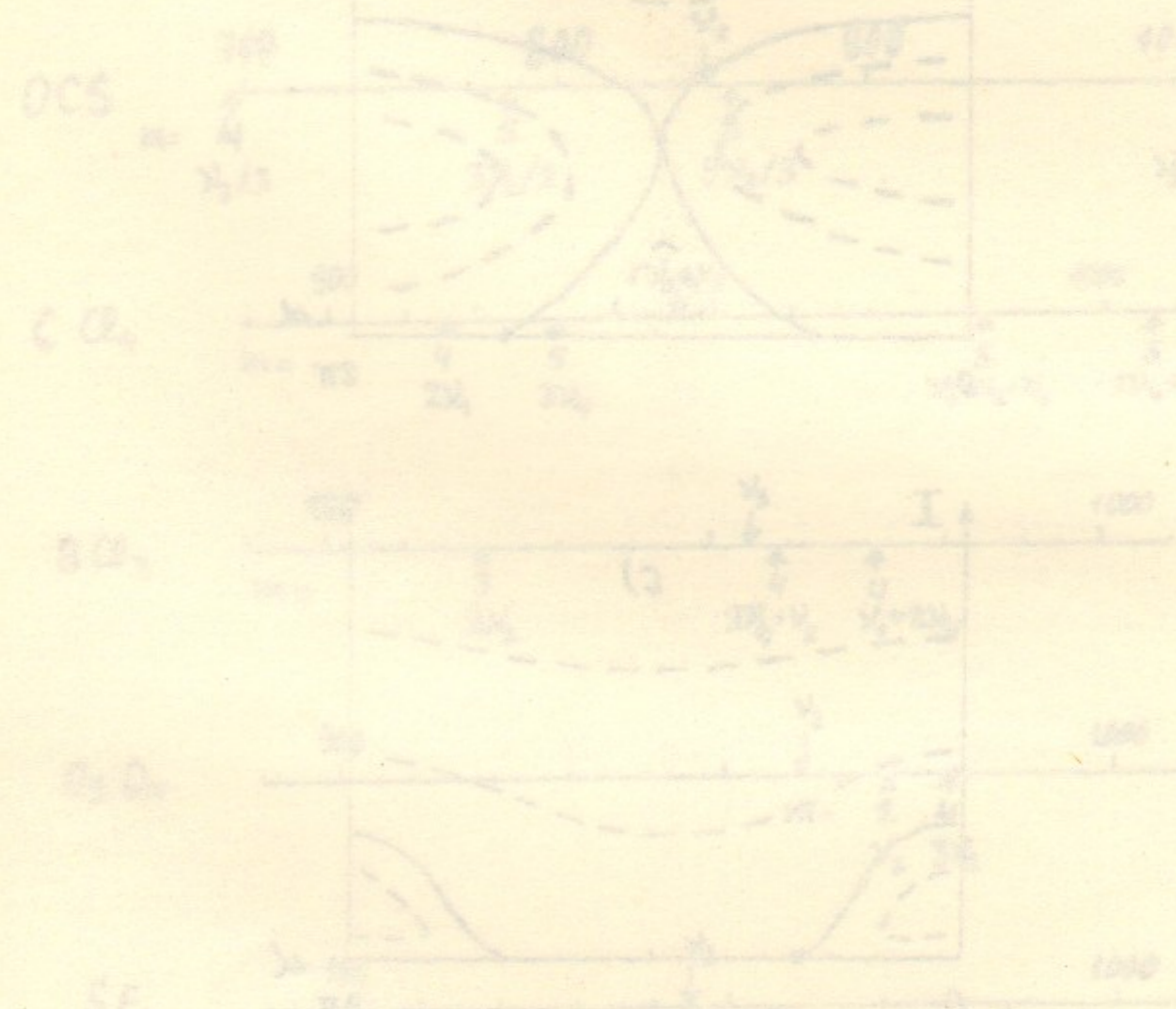
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Figure captions.

Fig. 1. Phase portraits of Hamiltonian (1,4) in three cases: a) $\varepsilon > \varepsilon_0 = -3/2 \cdot [\omega' \cdot f/2]^{1/3}$; b) $\varepsilon = \varepsilon_0$; c) $\varepsilon < 0; \omega' < 0$. The solid line is the trajectory with $\tilde{E} = 0$. In the case a) there are two of them: AB and CD. The dashed lines are other trajectories. The values of action I_1, I_2, I_3, I_4 shown in Fig. a) correspond to limits of phase vibration at some energy.

Fig. 2. The phase portrait of intermode Hamiltonian (14). The solid line is the stability boundary, the dashed ones are some trajectories in stable (A) and unstable (B), (C). The critical value of action is $I_0 = \left[\frac{2\varepsilon}{(m-1)V} \right]^{2/(m-3)}$.

Fig. 3. The intermode resonances in molecules $CO_2, BCl_3, CCl_4, OSO_4, SF_6$. The values of frequencies are taken from /16/. The index of resonance m is the number of frequencies in resonance condition.



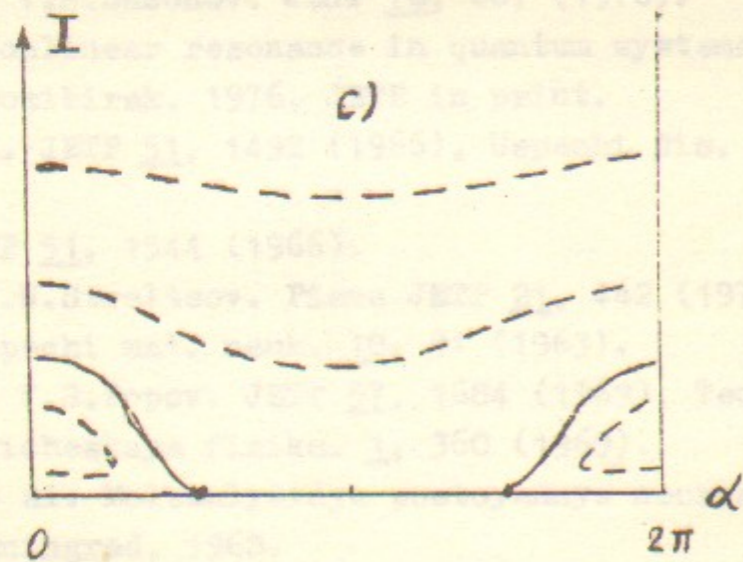
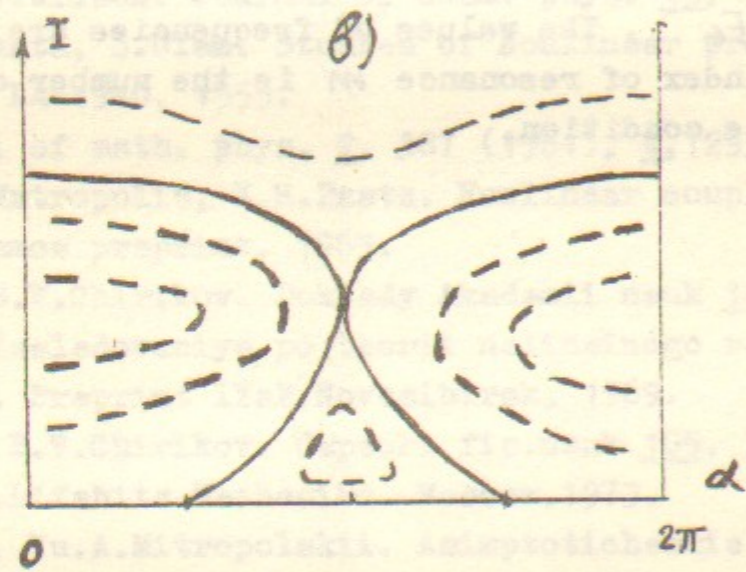
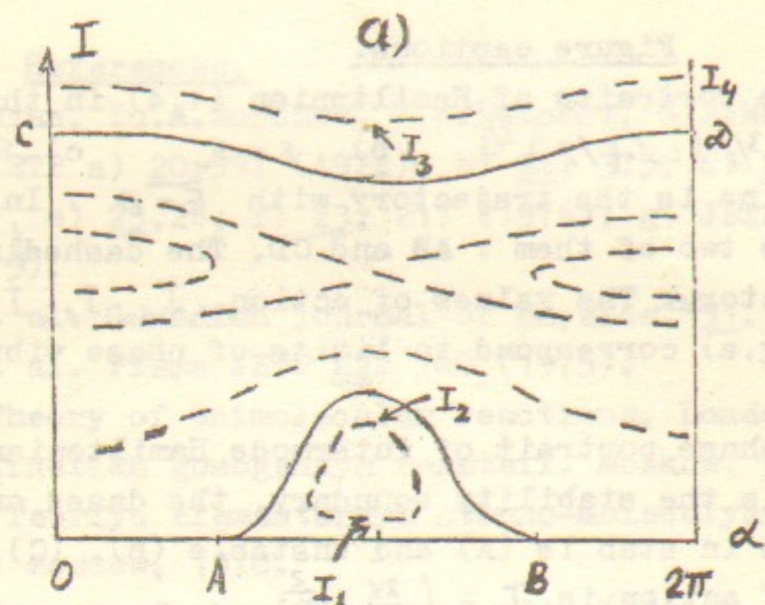


Fig. 1.

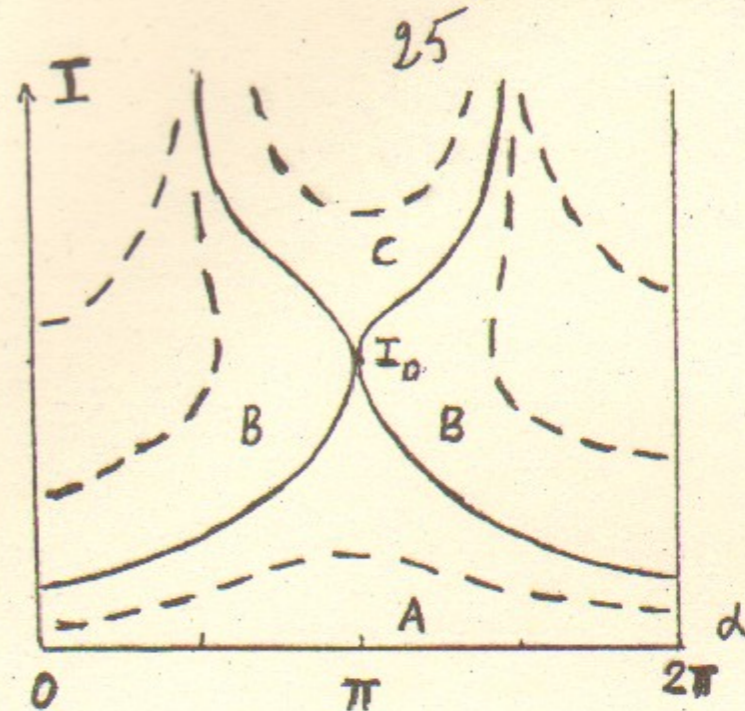


Fig. 2

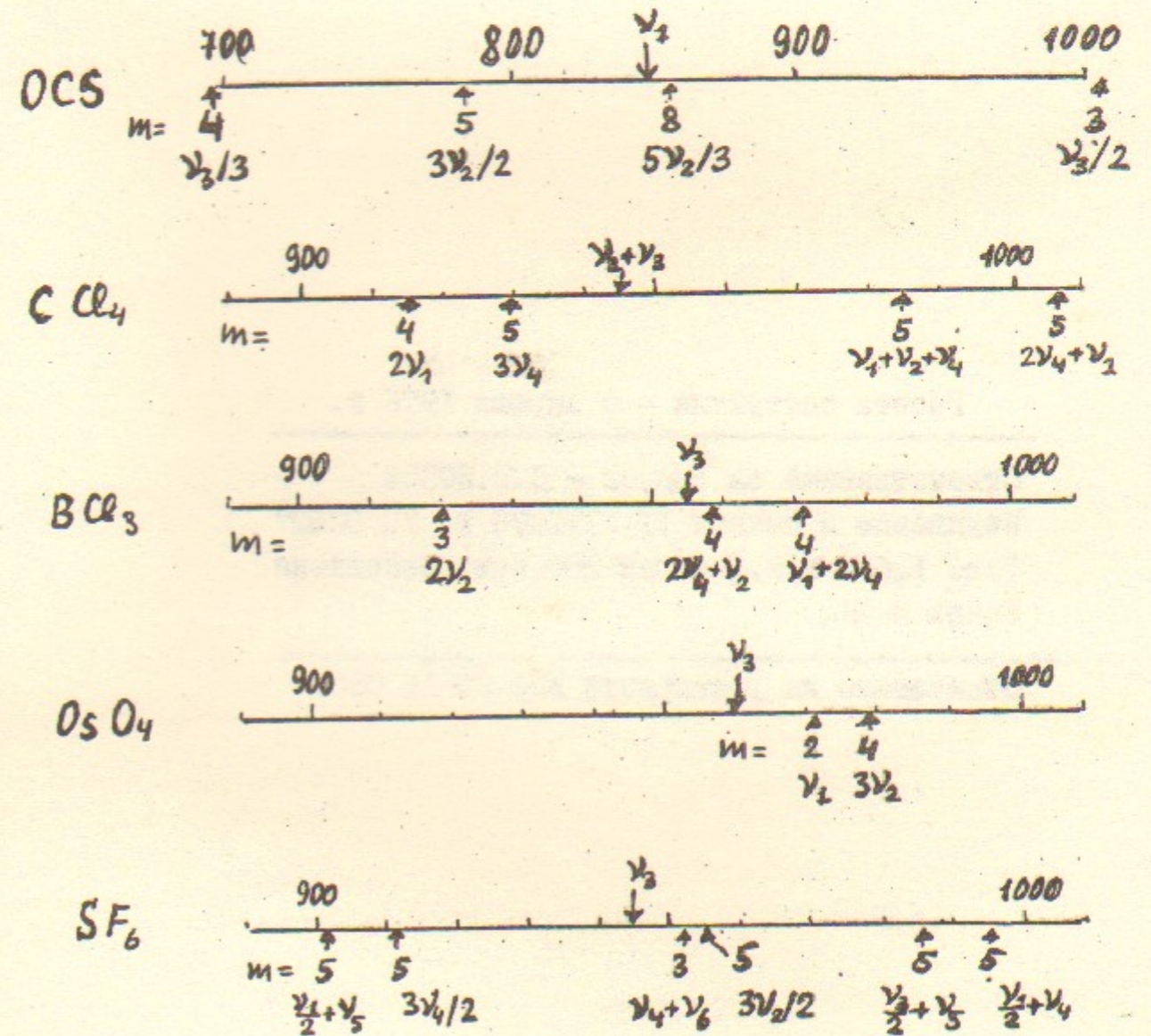


Fig. 3

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