

# Possibility of selected excitation of molecule vibrations in a field with time-varying frequency

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We discuss the possibility of selective excitation of a specified vibrational level of molecules of a low-pressure gas in an electromagnetic field in the infrared band with frequency that varies with time.

Recently, the problem of selective excitation of vibrational levels of molecules has attracted much attention (see, e.g.,<sup>1,2</sup>). In this article we call attention to the feasibility of selective excitation of a given vibrational level of gas molecules when they interact with an external electromagnetic field whose frequency varies adiabatically in time.

We consider the oscillations of gas molecules in an external linearly-polarized electromagnetic field  $E = \mathcal{E}_0 \cos(\omega_0 + \kappa(t))t$ . The frequencies  $\omega_{n, n+1}$  of the vibrational transitions of each of these molecules (for a chosen normal mode) decrease as a result of anharmonicity with increasing number of the vibrational level, and can be expressed in the form

$$\omega_{n, n+1} \approx \omega_e(1 - 2X_e n), \quad (1)$$

where  $\omega_e$  is the frequency of the transition between the ground and first excited vibrational levels. We have in mind the case of relatively low pressures, when a rotational structure is allowed in each vibrational level. In addition, we assume the following relations to be satisfied:

$$\left| \frac{d\kappa}{dt} \right| \ll \left( \frac{d_{12}^2 \mathcal{E}_0}{\hbar} \right)^2, \quad \frac{d\kappa}{dt} < 0, \quad (2a)$$

$$\left| \frac{d\kappa}{dt} \frac{\hbar}{d_{12} \mathcal{E}_0} \right| \ll \Delta\omega_{rot}, \quad 2\omega_e X_e, \quad (2b)$$

$$r_p \ll r_{rel}. \quad (2c)$$

Here  $d_{12}$  is the dipole moment of the vibrational transition.<sup>1)</sup> Condition (2a) signifies an adiabatic (see, e.g.,<sup>1,3</sup>) decrease of the frequency of the excited radiation; the condition (2b) means that during the time of inversion the change of the field frequency in the two-level system (see below) is much less than both the distance  $\Delta\omega_{rot}$  between neighboring rotational sublevels and the anharmonicity  $2X_e\omega_e$ ; the inequality (2c) determines the relation between the duration  $\tau_p$  of the exciting pulse and the relaxation time  $\tau_{rel}$  of the considered rotational sublevels. In accordance with (1), with decreasing frequency of the exciting radiation, successive resonances will be produced between the field of the incident beam and the rotational components of the neigh-

boring pairs of vibrational levels. When (2) is taken into account, the entire process of the interaction of the field with the considered multilevel system can be broken up into successive time intervals within which the evolution of the wave function of the molecule reduces to the dependence

$$\Psi(t) = \sum_{j, j', m, m'} a_{njm}(t) \Psi_{njm} + a_{n+1, j' m'} \Psi_{n+1, j' m'} \quad (2)$$

where  $\Psi_{njm}$  is the unperturbed wave function of the  $n$ th vibrational stationary state of this molecule with a total angular momentum  $j$  and with a projection of this angular momentum  $m$  on the direction of the field polarization vector.

The Schrödinger equation for  $\Psi(t)$ , with account taken of the selection rules for the dipole transitions and of the additional requirement  $\Delta j = +1$  brought about by the fact that the field frequency approaches the frequency of the given vibrational transition from above (and (2b) is simultaneously satisfied), reduces to a system of independent equations for the pairs of coefficients  $a_{njm}$  and  $a_{n+1, j+1, m'}$ , which describe the behavior of nondegenerate two-level systems in an adiabatic pumping field. Starting from the solution of the corresponding equations (see, e.g.,<sup>1,3</sup>), we obtain<sup>2)</sup>

$$|a_{n+1}|^2 - |a_n|^2 = - \frac{\kappa \hbar}{d_{12} \mathcal{E}_0} \frac{|a_n|^2}{\sqrt{1 + \frac{\kappa^2 \hbar^2}{d_{12}^2 \mathcal{E}_0^2}}}, \quad (3)$$

where  $|a_k|^2$  is the total population of the  $k$ th vibrational level. Formula (3) determines the evolution in time of the corresponding population difference between the  $n$ th and  $(n+1)$ -st vibrational levels in the considered time interval, under the condition that the population of the  $n$ th level, attained during the preceding time intervals, is equal to  $a_n^2$ . By the same token Eq. (3) yields a recurrence relation, from which we see that under the conditions (2), when the frequency of the external field changes from a value exceeding the frequency of the transition  $0 \rightarrow 1$  to the frequency of the transition  $N-1 \rightarrow N$ , there occur successive complete (in the approximations under consideration) transitions of the molecules from the preceding level to the neighboring higher level, so that at the end of the process practically all

the molecules are concentrated at specified levels with number  $N$ . It is obvious here that the distribution of the molecules of the rotational sublevels also deviates, generally speaking, from equilibrium.<sup>3)</sup>

Let us consider a numerical example. We assume  $d_{12} = 0.3D$ ,  $2X_e\omega_e \sim \Delta\omega_{\text{rot}} = 10^{12}$  rad/sec, a gas pressure  $P = 10^{-2}$  Torr (in which case we can assume  $\tau_{\text{rot}} \sim 10^{-6}$  sec<sup>(4)</sup>), and  $\tau_p = 0.3 \times 10^{-6}$  sec. For a selective excitation of the vibrational level with number  $N$  under the conditions (2) it suffices therefore to have an intensity  $\mathcal{E}_0^2 = 3N \times 10^2$  cgs esu at  $|d\kappa/dt| \sim 2X_e\omega_e N / \tau_{ip}$ . For example, at  $N = 10$  we obtain  $\mathcal{E}_0^2 = 3 \times 10^3$  cgs esu (i.e.,  $I_0 \approx 3 \times 10^5$  W/cm<sup>2</sup>) and  $|d\kappa/dt| \approx 3 \times 10^{19}$  rad/sec<sup>2</sup>.

We note in conclusion that when a sufficiently high vibrational level is excited, interest may attach also to the subsequent dissociation of the molecules under the influence of collisions with the remaining molecules or under the influence of additional external action.

<sup>1)</sup>For simplicity we assume throughout that  $d_{12}$  is the same for all the rotational sublevels of the vibrational transition  $n \rightarrow n+1$  and is independent of the number  $n$ .

<sup>2)</sup>It can also be shown that when account is taken of the constant dipole moment that can appear in the stationary states of the molecules, an expression of similar type remains valid also in the case of the combination resonance  $\omega_0 + \kappa(t) \approx (1/2)\omega_{n,n+1}$ .

<sup>3)</sup>We note that the requirement  $\Delta j = +1$  is generally justified only under the additional condition  $\Delta\omega_{\text{rot}} > 2X_e\omega_e$ . Under another condition,  $\Delta\omega_{\text{rot}} \leq (2/3)X_e\omega_e$ , the resultant rotational sublevel can be easily seen to correspond to the requirement  $\Delta j = 0$ . The evolution of the populations of the vibrational levels are then described by a system such as (3), so that the described results remain in force in this case, except that under these conditions the distribution of the molecules in a given vibrational level deviates from equilibrium only with respect to the values of the magnetic quantum number.

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