Effect of the fine structure of vibrational-rotational states on the dynamics of the excitation of multiphoton resonances in molecules of the spherical top type

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We investigate the dynamics of the excitation of multiphoton resonances in molecules of the spherical top type, whose spectrum has a fine structure due to the lifting of the K degeneracy of the vibrational-rotational states. It is shown that the excitation of these molecules resembles an irreversible process. The effect of the width of a laser radiation spectrum on the efficiency of the process is discussed. It is shown that study of the absorption of laser radiation by gases at finite temperatures may reveal anomalous dependences of the accumulated energy on the laser field intensity which do not correspond to the degree of photonicity of the resonance.

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Processes of selective laser action on the vibrational degrees of freedom of molecules have been under study[1,2] since 1964. At present the collisionless dissociation of polyatomic molecules in an intense infrared field is the most widely studied process.[3] This effect is made use of in experiments on the laser separation of isotopes.[4,5] It is customary to divide this phenomenon into three stages[6,7]: resonant multiphoton absorption of quanta in lower vibrational-rotational levels, the subsequent accumulation of energy in the region where the density of vibrational states is high, i.e., the quasicontinuum, and the decay of the molecule due to predissociation. The first stage of the process practically completely ensures the selectivity of the effect as a whole and is therefore of particular interest from the viewpoint of the laser separation of isotopes. Resonance processes in the lower levels of symmetric polyatomic molecules have been investigated in a number of studies,[8-11] where the spectral dependences of the laser quantum absorption probability have been obtained. In addition, the dependence of the lower-level populations on the time and on the parameters of the laser pulse are not unimportant characteristics of the processes.

In Ref. 9 the dynamics of the excitation of the lower levels were analyzed taking into account the specific features of the spectrum of polyatomic molecules; in addition, the effect of the excitation of molecules irrespective of the dependence on the rotational quantum number J, due to the existence of two- and three-photon resonances, was explained. In a rigorous analysis of the dynamics of the excitation of multiphoton resonances it is necessary to keep in mind the effect of the nonmonochromatic laser field[12] and the presence of the fine structure of excited vibrational-rotational states.[13-15] The present study is mainly devoted to the role of the fine splitting and also touches on the question of the effect of the nonmonochromaticity of the laser pulse.

Molecules of the spherical top type have a unique vibrational-rotational spectrum. The essence of the situation is as follows. In the rigid top approximation each vibrational-rotational level is degenerate in the projections M of the angular momentum on the axis of the lab frame and in the projection K of this angular momentum on the axis of the molecule. In the ground vibrational state this approximation is completely justified. However, the vibrationally excited molecule partially loses its rigidity—when it rotates, Coriolis forces can stir up modes which were not excited earlier. There are two consequences of this: 1) the projection of the angular momentum on the axis of the molecule is no longer conserved, that is, the quantum numbers K cease to correspond to states of definite energy, and 2) the degeneracy is partially lifted and a band of levels is produced, whose width Γ is considerably less than the distance to the adjacent vibrational-rotational level. We shall number the levels in these bands by the index m. In a circularly polarized field the degeneracy in the quantum number M is not important.

It should be noted that the lifting of the K degeneracy and the appearance of the fine structure can occur in different ways in different molecules. A situation is possible where the main effect is due to the violation of the spherical-top symmetry because of vibrational excitation of the molecule. If as a result of vibrational excitation the molecule becomes a symmetric top, then states of definite energy are close to states of definite K and approximate selection rules hold for transitions between fine structure states.[15b] In the more general case when the effect of rotational symmetry violation in the molecules is of the order of the effect of the loss of rigidity, states of definite energy differ considerably from states with definite K.[15c] In this case all the transitions allowed by symmetry have matrix elements of the same order of magnitude. It is just such molecules that we consider in the present study.

In fields of moderate intensity the excited-level splitting due to the polarizability (the quadratic Stark effect) of molecules is less than the fine splitting, and the ground vibrational state is not split because of its symmetry. This means that an external field E induces little more than multiphoton transitions between resonance levels. The matrix element of such a transition is determined by the degree n of photonicity of the resonance, by the values of the matrix elements d_l^{l+1} of the dipole moment operator, by the values Δ_l of the detunings of the intermediate levels, and by the values K and m of

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the quantum numbers in the ground and in the excited state:

$$V_K{}^m=\left(\frac{E\bar{d}}{\bar{\Delta}}\right)^n E d_{n-1}^n r_K{}^m; \tag{1}$$

here $\bar{d}$ and $\bar{\Delta}$ are the geometric means of the dipole moment of the vibrational transition and of the detuning of the intermediate levels from the resonances, and r_K^m is a factor that determines the role of the initial and final states.

At large laser field intensities, when the characteristic Rabi frequency $\tilde{V}$, which according to the sum rule is equal to the value of the root mean square matrix element of the transition multiplied by the square root of the number of levels $\tilde{N}$ in the first band, $\tilde{V}=\langle V^2\rangle^{1/2}\tilde{N}^{1/2}$, exceeds the width of the band Γ, the fine splitting of the level is not important and the dynamics of the excitation of the resonance can be described using a simple two-level model. On the other hand, for weak fields when the width of the multiphoton resonances $\langle V^2\rangle^{1/2}$ is less than the characteristic spacing between levels, only that fine structure component for which the resonance condition is satisfied can be excited in a band.

In this study we consider intermediate intensities, when the Rabi frequency is less than the band width and the width of the multiphoton resonance is larger than the characteristic spacing between levels in the bands:

$$\Gamma/\tilde{N}^{1/2}\gg\langle V^2\rangle^{1/2}\gg\Gamma/\tilde{N}$$

(for example, for the SF_6 molecule this inequality holds for radiation intensities in the range 10^5–10^7 W/cm). In fields of such intensity not all the fine structure components are excited from the lower, degenerate, state, but only a relatively small part of the band which, however, contains a large number of levels.[1)] Consequently, the behavior of the system is determined by a large number of constants—the detunings and the matrix elements V_K^m. Present-day methods of high-resolution laser spectroscopy make it possible in principle to find the values of the detunings and dipole-moment matrix elements for the fine structure components of a number of polyatomic molecules. However, it is obvious from physical considerations that the total population of the upper and lower vibrational-rotational levels in a given range of laser field intensities is determined by certain averaged characteristics of the spectrum and of the operator for the interaction with the field.

It seems advisable therefore to describe the excitation of a molecule not by exact numerical solution of the Schrödinger equation for this multilevel system, but rather by using a model approach which permits an analytic solution of the problem. For this approach it is necessary to choose the form of the distribution function for the values of the matrix elements of the transition operator $\hat{V}$. It was noted earlier[16] that for the matrix elements of transitions between states produced as a result of a complex interaction like the fine splitting of the levels in a molecule, it is most natural to choose the Wigner distribution function

$$g(\hat{V})=\prod_{m,K} g(V_K{}^m)=\pi^{-\tilde{N}^2/2}\exp\Big\{-\sum_{m,K}(V_K{}^m)^2\tilde{N}\tilde{V}^{-2}\Big\}, \tag{2}$$

where $\tilde{V}^2$ is the square of the Rabi frequency or, in other words, the sum of the squares of the matrix elements of the operator for the transition from the state K to all the fine structure components, $\tilde{N}$ is the number of such components, and $\tilde{V}^2\tilde{N}^{-1}\equiv\langle V^2\rangle$. The use of the Wigner distribution function reflects the fact that the matrix elements of transitions between different pairs of fine structure components can differ considerably both in value and in sign. This constitutes the fundamental difference between our problem and the problem of the coherent excitation of the preionization states of an atom,[17] where the matrix elements vary smoothly.

The next stop in solving the problem of the behavior of a molecule in an external field is to write down and solve the Schrödinger equation. For almost-resonant systems it is traditional to use the quasi-energy representation of the resonance approximation. The system of equations for the ψ functions is of the form

$$i\dot{\psi}_K=\sum_m V_K{}^m\psi_m,\quad i\dot{\psi}_m=\sum_K V_m{}^K\psi_K+\Delta_m\psi_m; \tag{3}$$

we have set $\hbar\equiv1$. Here the index K refers to the components of the lower, degenerate, level and the index m refers to the fine structure components of the upper level. If at the initial instant of time only one of the components of the lower level is populated, for example, that with $K=0$, the population of the components with K and m at a time t is given by the expressions

$$\begin{aligned}\rho_{KK}&=\Big\langle K\Big|\int\limits_{-\infty-i0}^{\infty-i0}e^{i\varepsilon t}\frac{1}{\varepsilon-\hat{H}}d\varepsilon\Big|0\Big\rangle\Big\langle 0\Big|\int\limits_{-\infty+i0}^{\infty+i0}e^{-i\xi t}\frac{d\xi}{\xi-\hat{H}}\Big|K\Big\rangle,\\ \rho_{mm}&=\Big\langle m\Big|\int\limits_{-\infty-i0}^{\infty-i0}e^{i\varepsilon t}\frac{d\varepsilon}{\varepsilon-\hat{H}}\Big|0\Big\rangle\Big\langle 0\Big|\int\limits_{-\infty+i0}^{\infty+i0}e^{-i\xi t}\frac{d\xi}{\xi-\hat{H}}\Big|m\Big\rangle,\end{aligned} \tag{4}$$

where $\hat{H}$ is the matrix on the right-hand side of (3), that is, the effective Hamiltonian of the system. It is convenient to use the expansion

$$\begin{aligned}\langle K|(\varepsilon-\hat{H})^{-1}|0\rangle&=\delta_{K0}\varepsilon^{-1}+\sum_m\varepsilon^{-1}V_K{}^m(\varepsilon-\Delta_m)^{-1}V_0{}^m\varepsilon^{-1}\\&+\sum_{mm'K'}\varepsilon^{-1}V_K{}^m(\varepsilon-\Delta_m)^{-1}V_{K'}{}^m\varepsilon^{-1}V_{K'}{}^{m'}(\varepsilon-\Delta_{m'})^{-1}V_0{}^{m'}\varepsilon^{-1}+\ldots\end{aligned} \tag{5}$$

and a similar expansion for ξ. After substituting (5) in (4) and averaging by means of the function (2), the principal sequence of the series is summed[16] and, using the Fourier representation in the time, we obtain the following expressions for the populations of the levels:

$$\begin{aligned}\rho_{KK}&=X_K(\varepsilon)X_K(\xi)\Big[1-\langle V^2\rangle\sum_{K,m}X_K(\varepsilon)X_K(\xi)X_m(\varepsilon)X_m(\xi)\Big]^{-1},\\ \rho_{mm}&=\langle V^2\rangle X_m(\varepsilon)X_m(\xi)\sum_K\rho_{KK},\end{aligned} \tag{6}$$

where X_m and X_K are found from the relations

$$\begin{aligned}X_K(\varepsilon)&=\Big[\varepsilon-\langle V^2\rangle\sum_m X_m(\varepsilon)\Big]^{-1},\quad X_K(\xi)=\Big[\xi-\langle V^2\rangle\sum_m X_m(\xi)\Big]^{-1},\\ X_m(\varepsilon)&=\Big[\varepsilon-\Delta_m-\langle V^2\rangle\sum_K X_K(\varepsilon)\Big]^{-1},\quad X_m(\xi)=\Big[\xi-\Delta_m-\langle V^2\rangle\sum_K X_K(\xi)\Big]^{-1},\end{aligned} \tag{7}$$

where the solutions (7) must be chosen with account taken of the signs of the imaginary parts of the variables

ε and ξ. We shall be interested in the behavior of the system at $t \gg \Gamma^{-1}$, assuming that the characteristic Rabi frequency is small compared to Γ. Then we can let the width Γ of the band tend to infinity, having fixed the mean level density at $(2\pi\tilde{\delta})^{-1}$. In this case the solutions of Eqs. (7) take the form

$$X_K(\varepsilon)=[\varepsilon-i\langle V^2\rangle\tilde{\delta}^{-1}]^{-1},\quad X_m(\varepsilon)=[\varepsilon-\Delta_m-\langle V^2\rangle(\varepsilon-i\langle V^2\rangle\tilde{\delta}^{-1})^{-1}]^{-1},$$
$$X_K(\xi)=[\xi+i\langle V^2\rangle\tilde{\delta}^{-1}]^{-1},\quad X_m(\xi)=[\xi-\Delta_m-\langle V^2\rangle(\xi+i\langle V^2\rangle\tilde{\delta}^{-1})^{-1}]^{-1}.$$

Substituting the solutions (7) in (6) and taking the inverse of the Fourier transform (4), we find the following expressions for the total populations:

$$\begin{aligned}\sum_K \rho_{KK} &= 1-\frac{\langle V^2\rangle}{\delta}\int_0^t \exp\left(-\frac{\langle V^2\rangle}{\delta}t\right) J_0(t\sqrt{\langle V^2\rangle N})\,dt,\\ \sum_m \rho_{mm} &= \frac{\langle V^2\rangle}{\delta}\int_0^t \exp\left(-\frac{\langle V^2\rangle}{\delta}t\right) J_0(t\sqrt{\langle V^2\rangle N})\,dt,\end{aligned} \tag{8}$$

where N is the degree of degeneracy of the lower level and $\delta \equiv 2\pi\tilde{\delta}$ is the mean spacing between adjacent components of the upper band. In addition, it should be noted that only those fine structure levels in the upper band lying in the vicinity $(N\langle V^2\rangle + \langle V^2\rangle^2\tilde{\delta}^{-2})^{1/2}$ of the resonance are populated significantly.

We note that our result is not valid at all times. In fact, expressions (8) are irreversible in time, while the original equations (3) are reversible. The reason for this is the incomplete summation of the series for the populations in going from (4) and (5) to (6). However, significant differences between the exact expression for the population and expression (6) begin to show up only for very large times, which are clearly much larger than the relaxation times existing in a real situation.

If the upper and lower states have the same number of components and the system (3) permits diagonalization in the indices m and K, the solutions (8) can be obtained by yet another method. In this case the multilevel, two-band structure can be represented as a set of two-level systems. The problem of the excitation of this structure reduces to averaging the populations over the Rabi frequencies:

$$\begin{aligned}\rho_{22} \equiv \sum_m \rho_{mm} &= \frac{\langle V^2\rangle^{1/2}}{\delta N^{1/2}}\int_{-\infty}^{+\infty}\left(\frac{\Delta^2}{4}-\langle V^2\rangle N\right)^{-1}\sin^2\left[\left(\frac{\Delta^2}{4}+\langle V^2\rangle N\right)^{1/2} t\right] d\Delta\\ &= \frac{\langle V^2\rangle}{\delta}\int_0^t J_0(t\sqrt{\langle V^2\rangle N})\,dt,\quad t\gg\Gamma^{-1},\end{aligned}$$

which agrees with (8) up to quantities $\sim\langle V^2\rangle N/\Gamma^2 \ll 1$. Moreover, in contrast to the above expression, formula (8) is also valid in the case where the number of components in the upper and lower bands is not the same: $\delta N < \Gamma$ and the smallness of $\langle V^2\rangle N/\Gamma^2 \ll 1$ does not imply the smallness of $\langle V^2\rangle N\delta^2 \ll 1$. In this situation the exponential in (8) no longer gives a small contribution, which means that the dynamics of the excitation of the upper band has a different nature.

It is interesting to consider the asymptotic behavior of the populations at large times, since under experimental conditions the duration of the laser pulse significantly exceeds the characteristic times for resonance saturation. After integrating from zero to infinity in Eqs. (8), we find $(2\pi\tilde{\delta} = \delta)$

$$\begin{aligned}\rho_{11} &\equiv \sum_K \rho_{KK} = 1-\rho_{22},\\ \rho_{22} &\equiv \sum_m \rho_{mm} = (4\langle V^2\rangle N)^{1/2}(4\langle V^2\rangle N + N^2\delta^2/\pi^2)^{-1/2},\end{aligned} \tag{9}$$

Expressions (9) admit of a clear physical interpretation. Actually, if the matrix element of the transition between fine structure components is of order V, the total matrix element of the transition between the upper and lower bands, that is, the characteristic Rabi frequency, is $\tilde{V} = VN^{1/2}$ because of the sum rule. When $VN^{1/2} \gg V^2/\delta$, $g_{\text{eff}} \approx VN^{1/2}/\delta$ levels of the upper band land in the Stark capture width and are populated up to a value of the order of the mean populations N^{-1}. This means that the total population of the upper band is of order $N^{-1}g_{\text{eff}} \approx VN^{1/2}/N\delta$. As the intensity of the laser field increases the effective statistical weight of the upper band g_{eff} also grows, since an even larger number of its components begins to satisfy the resonance condition $\Delta_m \leqslant VN^{1/2}$. If the total number of levels in the upper band is $\Gamma/\delta = \tilde{N} \gg N$, then as $V \to \infty$ the population of the upper band tends toward unity. The asymptotic ratio of the populations of the upper and lower bands is therefore equal to the ratio of the effective statistical weight of the upper band to that of the lower.

Up to now the excitation dynamics have been studied for the case of a field of constant amplitude switched on at $t = 0$. It is, however, of interest to generalize the results to the case of a slowly varying laser field. In the case of a slowly increasing field the result is *a priori* clear: formula (9) with the instantaneous value of $\langle V^2\rangle$ is valid for the total population of the upper band components at the time t. In the case of a slowly decreasing field it is necessary to determine whether or not a complete return of the system to the ground state occurs when the matrix element $\langle V^2\rangle^{1/2}$ tends to zero. The answer to this question depends considerably on how possible it is to represent the system as a set of pairs of interrelated levels. If this representation is possible, then it is necessary to study the dynamics of the excitation of a two-level system with a detuning Δ_2 and a matrix element of the transition between states 1 and 2 $V_{12} \sim (\langle V^2\rangle N)^{1/2}$ in a slowly varying field and then average over Δ_2.

An analytic solution to this type of problem can be found for certain specially selected profiles of the dependence $V_{1,2}(t)$. In particular, for $V_{1,2}(t) = V_0\cosh^{-1}\alpha t$ the solution to the problem can be expressed in terms of a hypergeometric function:

$$\psi_1 = F\left(\frac{V_0}{\alpha};\ -\frac{V_0}{\alpha};\ \frac{1}{2}+i\frac{\Delta_2}{2\alpha};\ \frac{1}{e^{-2\alpha t}+1}\right), \tag{10}$$

from which it is possible to find the probability of exciting the two-level system by an adiabatic pulse:

$$\rho_{22} = 1-\left|\frac{\Gamma(1/2+i\Delta_2/2\alpha)\,\Gamma(1/2+i\Delta_2/2\alpha)}{\Gamma(1/2+i\Delta_2/2\alpha-V_0/\alpha)\,\Gamma(1/2+i\Delta_2/2\alpha+V_0/\alpha)}\right|, \tag{11}$$

which significantly differs from zero for only the detunings $\Delta_2 \lesssim \alpha$ and $V_0 \gtrsim \alpha$. In other words, such a system appears after the removal of the adiabatically slowly varying field in the ground state if only the spectral width of the laser pulse does not cover the resonance.

If the system cannot be represented as a set of pairs of levels, that is, if it is not possible to simultaneously diagonalize the submatrix of the transition amplitudes and the Hamiltonian of the upper band, the adiabaticity condition becomes much stronger. In fact, the values of the quasienergy ε_n of the system vary with V in such a way that there is no intersection of the levels, $\varepsilon_n(V) \neq \varepsilon_K(V)$. However, for an adiabatically slow but finite rate of variation of V, Landau-Zener transitions between the levels ε_n and ε_K, which move fairly close to each other, are possible. The probability w of such transitions is exponentially small, but their number p is large. Therefore, the system returns to the ground state only when the following condition is satisfied:

$$1-(1-w)^p \ll 1. \qquad (12)$$

If the characteristic value of the nondiagonal matrix element of the Hamiltonian of the upper band is $g \sim (\Gamma\delta/3)^{1/2}$, the probability w can be estimated using the familiar formula[18]

$$w=\exp\left\{-g^2\left[\left|\frac{d\Omega_n}{dV}-\frac{d\Omega_K}{dV}\right|\frac{dV}{dt}\right]^{-1}\right\}\sim\exp\left(\frac{g^2\tau}{VN^{1/2}}\right),$$
$$\Omega_i\sim\bar{V}, \qquad (13)$$

where τ is the duration of the smooth pulse $V(t)$ and Ω_i is the Rabi frequency. The number of transitions can be estimated from the ratio $VN^{1/2}/\delta$. The adiabaticity condition is written in the form

$$\frac{VN^{1/2}}{\delta}\exp\left\{-\frac{\Gamma\delta\tau}{3VN^{1/2}}\right\}\ll 1. \qquad (14)$$

The spectral width of an adiabatic pulse must therefore be $(\Gamma/VN^{1/2})\ln(VN^{1/2}/\delta)$ times narrower than the distance δ between adjacent levels.

The different behavior, in a varying field, of systems which can and cannot be represented as a set of two-level systems is due to the difference of the population oscillation frequencies in their spectra. Whereas in the first case there is a finite minimum oscillation frequency $\Omega_{\min}\sim\tilde{V}=VN^{1/2}$, in the second case, because of the complex nature of the interaction, there are many oscillations with differential and therefore small frequencies $\Omega\ll\tilde{V}$. As a result, the adiabaticity requirement, that is, that the variation be slow compared to the characteristic frequencies of the system, is considerably more stringent in the second case.

We note that a similar estimate can be made for a slowly varying laser frequency. In this case it is necessary to replace in (14) the characteristic Rabi frequency by the characteristic value of the detuning change.

Therefore, if a multilevel two-band system can be represented as a set of two-level systems, then under the action of a laser pulse of spectral width $\Delta\omega_L$ such that

$$\Gamma\gg\Delta\omega_L\gg\frac{VN^{1/2}}{\Gamma}\delta\ln^{-1}\frac{VN^{1/2}}{\delta},$$

the upper band of the system is populated to values $\rho_{22}\sim\Delta\omega_L/\delta N$. In the opposite case the population of the upper band will be considerably larger: $\rho_{22}=(\langle V^2\rangle N)^{1/2}(\langle V^2\rangle N+\Gamma^2(2\pi)^{-2})^{-1/2}$.

Until now we have considered the behavior of a two-band system acted on by a resonant field. This system imitates the resonant multiphoton absorption of laser radiation by a molecule with fixed quantum numbers J and M. To obtain the dependences characteristic of the gas as a whole, the answer must be averaged over the rotational Boltzmann distribution. We shall restrict ourselves to the case where the Q branches of the two-photon transitions are excited and shall neglect the influence of absorption from excited states. In addition, we shall consider the case when of a transition from the ground vibrational state to the fine structure components of a degenerate vibrational state.

Let us use formula (9), in which the quantities $V\equiv\langle V^2\rangle^{1/2}$ and N depend on the quantum number J. It is obvious that $N=2J+1$ and the value of $VN^{1/2}$ for transitions in the Q branches is given by the expression

$$VN^{1/2}=\frac{E^2d_{0,J}^{1,J}d_{1,J}^{2J}}{\Delta}+\frac{E^2d_{0,J}^{1,J+1}d_{1,J+1}^{2J}}{\Delta+BJ}+\frac{E^2d_{0,J}^{1\,J-1}d_{1,J-1}^{2,J}}{\Delta-BJ}, \qquad (15)$$

where B is a rotational constant and Δ is the detuning of the Q branch of the ground state transition from the resonance. For $J\gg1$, (15) is approximately equal to

$$VN^{1/2}=(1-\cos^2\varphi)E^2d_0^1d_1^2J^2\Big/B\frac{\Delta}{B}\left[\left(\frac{\Delta}{B}\right)^2-J^2\right], \qquad (16)$$

where $\cos\varphi=M/J$. We shall neglect the dependence of $VN^{1/2}$ on the direction cosines and average (9) over the distribution of J:

$$\bar{\rho}_{22}=Z^{-1}\int\limits_0^\infty\left[J^2-\left(\frac{\delta B}{\pi E^2d^2}\right)^2\left(\frac{\Delta}{B}\right)^2\left(\frac{\Delta^2}{B^2}-J^2\right)^2\right]^{-1/2}$$
$$\times 4J^3\exp\left\{-\frac{BJ^2}{2kT}\right\}dJ; \qquad (17)$$

here T is the temperature of the gas, $d\equiv(d_0^1d_1^2)^{1/2}$, and Z is the rotational partition function. The mean population therefore depends on the following three dimensionless parameters:

$$r=\left(\frac{2kT}{B}\right)^{1/2},\quad s=\pi\frac{(Ed)^2}{\Delta\delta},\quad a=\frac{\Delta}{B},$$

the physical meaning of which is the following: r is the characteristic number of rotational states participating in the process, s is the number of fine structure components landing in the Stark capture region, and a is the number J for which there is rotational cancellation of the intermediate detuning. The dependence of $\bar{\rho}_{22}$ on s actually determines the dependence of the energy E_a absorbed in the gas on the laser field intensity. This dependence is different for different relations between the parameters:

1) for $a\ll r^2$ and $s^2\gg a$

$$\bar{\rho}_{22}\sim s^3e^{s/2r^2}\left[K_0\left(\frac{s^2}{2r^2}\right)-K_1\left(\frac{s^2}{2r^2}\right)\right]\sim\begin{cases}s^3, & a\ll s^2\ll r^2\\ \text{const}, & s^2\gg r^2\end{cases} \qquad (18a)$$

(K_ν is the MacDonald function);

2) for $s^2\ll a$

$$\bar{\rho}_{22}\sim s; \qquad (18b)$$

3) for $a\gg r^2$

$$\rho_{22}\sim\begin{cases} s & \text{for} \quad s^2\ll r^2 \\ \text{const} & \text{for} \quad s^2\gg r^2 \end{cases}. \tag{18c}$$

From (18) we see that the accumulated energy as a function of the laser field intensity $I\sim s$ has a region with a cubic dependence $E_a\propto I^3$ in addition to regions of linear growth and saturation. The existence of this region is due to the rapid increase of the number of saturated transitions with J lying in the region where the Boltzmann distribution function grows quadratically. In fact, in the case $a\ll r^2$, that is, $\Delta/B\ll(kT/B)^{1/2}$ there is a range of J

$$\Delta/B\ll J\ll(kT/B)^{1/2}$$

in which, on the one hand, the total transition probability amplitude $VN^{1/2}$ does not depend on J, while, on the other hand, the distribution function increases like J^2. The maximum value $J=J_{\max}$ for which there is saturation is determined by the condition $\delta(2J+1)\approx VN^{1/2}$, that is, $J_{\max}\sim VN^{1/2}$. The total number of saturated transitions is proportional to the integral of the distribution function from zero to $J_{\max}$, that is, $\propto J^3_{\max}$. Consequently, for an n-photon transition, when $VN^{1/2}\propto I^{n/2}$ there is a relation for the accumulated energy:

$$E_n\propto\rho_{22}\propto I^{3n/2}. \tag{19}$$

The dependences given here were obtained by us for molecules with fixed orientation. It is obvious, however, that averaging over the orientations does not significantly change these dependences outside the transition regions.

Therefore, the presence of a fine structure in the energy spectrum of molecules of the spherical top type significantly changes the nature of the coherent excitation of single-photon and multiphoton resonances in a laser field. The behavior of the molecule acquires the features of an irreversible process and the value of the accumulated energy reaches a stationary value proportional to the effective statistical weight of the excited state. The physical meaning of the effective statistical weight is the number of fine structure components which land in the Stark width of the multiphoton resonance. If the system is not a collection of pairs of levels, then radiation with a spectral width exceeding the product of the characteristic spacing between fine structure components and the ratio of the effective statistical weight to the actual weight leads to resonance excitation. Radiation with a smaller spectral width excites practically no multiphoton resonance. Its saturation occurs at a laser field intensity such that the effective statistical weight of the excited state reaches the same order of magnitude as the statistical weight of the ground state. For molecules with different J this intensity, generally speaking, is different. Therefore, in the excitation of a gas of molecules in thermodynamic equilibrium the dependence of the accumulated energy on the value of the statistical weight g_{eff} may no longer be linear. Thus, in particular, for a two-photon resonance when $g_{\text{eff}}\propto I$ there can be a cubic dependence of the absorbed energy on the laser pulse intensity. It should be noted that numerous experimental data indicate that the degree of excitation of the lower levels of multiatomic molecules is determined by the value of the transmitted energy $\int I dt$. Our calculation does not give such a dependence. Consequently, under experimental conditions processes occur which distort the picture of coherent multiphoton excitation of vibrational-rotational levels possessing a fine structure. Among such processes are the collisional redistribution of the populations among the fine structure components and the radiative decay of levels due to the removal of molecules to higher states of the vibrational quasicontinuum.

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[1] Here the field intensity determines the number of components that are at resonance with the radiation. Such problems were studied in Ref. 16.

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