Spectral-kinetic manifestations of nonadiabatic coupling of molecular states under conditions of fast vibrational relaxation

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Manifestations of nonadiabatic coupling of molecular states are investigated theoretically and experimentally under conditions when the vibrational relaxation is faster than the radiative damping of the excited levels. The possibility is demonstrated of substantial population of the metastable triplet state of the molecules by intense optical excitation of the singlet level, which is nonadiabatically coupled to the triplet level via spin-orbit interaction. The rate of population and deactivation of the triplet state and its spectral manifestations are investigated. It is shown that when a vapor is excited for a sufficiently long time by resonant radiation, a shift of the thermodynamic equilibrium between the atomic and molecular components of the vapor in favor of the latter is possible. Possible applications of the observed phenomena are discussed.

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Nonadiabatic processes in molecular systems are of considerable interest both from the spectroscopic point of view and when it comes to practical applications. In diatomic molecules this is the only channel of mutual energy exchange between the electron subsystem and the vibrational and translational subsystems. In an isolated molecule, the nonadiabatic coupling between its terms manifests itself either in predissociation and in the associated broadening of the molecular transitions, or in a perturbation of the vibrational-rotational structure of the molecular spectra.[1]

Under conditions of rapid collision-induced vibrational relaxation of molecular states, the nonadiabatic coupling leads to a substantial redistribution of the populations among the interacting states and to an associated large-scale change of the spectrum and of the kinetics of the molecular emission.

The present communication is devoted to the investigation of such process in the simplest system, that of diatomic molecules of rare-earth metals placed in the atmosphere of a buffer gas. The role of the latter reduces in first-order approximation only to establishment of a Boltzmann distribution over the vibrational sublevels. The simplicity of the chosen system and the availability of the information on its terms make it possible to investigate in detail not only the efficiency of the process of the nonadiabatic transition, but also its kinetics.

1. We consider optical excitation of a diatomic molecule from the electronic ground state $|0\rangle$ into two excited states: $|1\rangle$ and $|2\rangle$, between which a nonadiabatic coupling exists. The presence of this coupling leads to a "repulsion" of the diabatic terms by an amount $2V$, where V is the energy of interaction between them. The probability P per vibration of a nonadiabatic transition between terms is determined by the Landau-Zener equation[2]

$$P=2e^{-\delta}(1-e^{-\delta}),$$

where $\delta=2\pi V^2/\hbar v\Delta F$, while v and ΔF are the relative velocity of the nuclei and the difference between the slopes of the terms at the point of their quasicrossing.

If the Landau-Zener parameter $\delta\ll 1$, the structure of the vibrational levels of the coupled electronic states is close to the structure of the vibrational levels of the initial terms, and at $\delta\gg 1$ the vibrational levels should be related to the adiabatic terms in which the interaction V is taken into account.

In both cases, the wave functions corresponding to a definite nuclear vibration energy describe states belonging generally speaking to both electronic terms. If the vibrational sublevels of the adiabatic terms do not coincide in energy, the degree of mixing of these states is determined by P; in the resonance situation it is close to unity. A fraction of these resonant levels is $\sim(P\Omega_1/\Omega_2)^{1/2}$, where Ω_1 and Ω_2 are the values of the vibrational quanta of the first and second terms.[2]

Upon optical excitation of one of these bound electronic states $|1\rangle$ (we assume that the second state is metastable and the transition to it is forbidden by the selection rules or by the Franck-Condon principle), an entire set of vibrational sublevels is populated in the molecule is populated if $\hbar\Omega\ll kT$, as is the case for alkali-metal molecules. The population of the second state $|2\rangle$, which is not coupled with the ground state by an optical transition, is a small fraction $\sim P^{1/2}$ of the population of the first. For an isolated molecule (in the absence of collisions) this fact hardly manifests

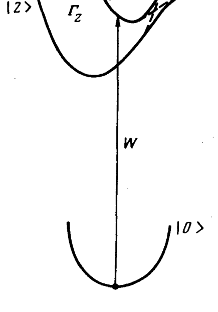

FIG. 1. Scheme of excitation of two interacting molecular terms.

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itself either in the spectrum or in the kinetics of the molecular emission (specially if the coupling between the terms is weak). Rapid collisional relaxation alters the situation substantially and ensures complete mixing of the populations of the interacting states. Indeed, assuming that a Boltzmann equilibrium of the populations with respect to the vibrational levels of each of the states is established within the radiative lifetimes γ_1^{-1} and γ_2^{-1} of the excited states, the process of populating such a system can be described by the following kinetic equations (Fig. 1):

$$\dot{n}_1=Wn_0-(\gamma_1+W+\Gamma_1)n_1+\Gamma_2 n_2,$$
$$\dot{n}_2=\Gamma_1 n_1-(\gamma_2+\Gamma_2)n_2,\quad n_1+n_2+n_0=N. \tag{1}$$

Here n_i is the population of the corresponding state, W is the rate of optical excitation, N is the total number of molecules in the system, and $\Gamma_{1,2}$ are the rates of the direct and inverse nonadiabatic transition between the states under the collision conditions.

The values of $\Gamma_{1,2}$ can be estimated on the basis of the following considerations. The nonadiabatic coupling is significant only for those vibrational levels which lie above the term-crossing point, so that not the entire populations of the interacting states participate in the transitions, but only the fractions $n_1\exp(-D_1/kT)$ and $n_2\exp(-D_2/kT)$, where D_1 and D_2 are the potential-well depths measured from the crossing point.

The transition from the first electronic state to the second can be regarded as the population, during the course of the vibrational relaxation, of resonant sublevels corresponding to approximately equal probability of the stay of the molecules in both electronic terms, and next, as the population of the sublevels of the second state as a result of the vibrational relaxation (it is assumed that the vibrational relaxation in each of the electronic states takes place independently of the presence and magnitude of the coupling between them). Since the fraction of the resonant states is of the order of $P^{1/2}$, we obtain for $\Gamma_{1,2}$

$$\Gamma_{1,2}=P^{1/2}f\exp(-D_{1,2}/kT),$$

where f is the collision frequency.[1] The ratio of these rates is $\Gamma_2/\Gamma_1=\exp(-\Delta E/kT)$, where ΔE is the difference between the depths of the interacting terms. The stationary solution of Eqs. (1) at $\Gamma_1\gg\Gamma_2\gg\gamma_2$ and $\gamma_1\gg\gamma_2$ is of the form

$$n_0=Ne^{-\Delta E/kT}\left[\frac{W+\gamma_1+\gamma_2 e^{\Delta E/kT}}{W+\gamma_1 e^{-\Delta E/kT}+\gamma_2}\right],$$
$$n_1=Ne^{-\Delta E/kT}\frac{W}{W+\gamma_1 e^{-\Delta E/kT}+\gamma_2},\quad n_2=n_1 e^{\Delta E/kT}. \tag{2}$$

It is easily seen that the greater part of the excited molecules are in the state $|2\rangle$, although it is not coupled with the ground state by a direct optical transition. It is seen that this result does not depend on the rates of the nonadiabatic transition between the terms (they enter only in the form of a ratio). We recall that in the absence of collisions the fraction of the population of this state amounts to $\sim P^{1/2}$ of the population of the state $|1\rangle$.

Obviously, the kinetics of the decay of the populations of the excited states after turning on the pump is determined by the processes of vibrational relaxation over the sublevels of the state $|2\rangle$ to the point of the term crossing, by a nonadiabatic transition into the state $|1\rangle$, and by spontaneous decay in the channel $|1\rangle-|0\rangle$ (Fig. 1). Indeed, analysis of Eqs. (1) shows that this kinetics is determined by two characteristic times, $\tau_1=\Gamma_1^{-1}$ and $\tau_2=(\gamma_1\Gamma_2/\Gamma_1+\gamma_2)^{-1}$; we note that $\tau_2\gg\tau_1$ (we assume as before that $\Gamma_1\gg\Gamma_2\gg\gamma_2$). The first and second of these times correspond respectively to the decays of the states $|1\rangle$ and $|2\rangle$. Observation of this kinetics enables us not only to determine uniquely the presence of a metastable state, but also to estimate a number of its parameters.

2. The processes considered above were experimentally investigated in a system of alkali-metal molecules (Na_2, Rb_2, Cs_2) in an atmosphere of a buffer gas (Xe, $p=100-1200$ Torr). The calculated term scheme of these molecules[3] is shown in Fig. 2 (the general character of the arrangement of the terms is the same for all the investigated molecules). Attention is called to the crossing of the two very lowest excited states $^1\Sigma_u^+$ and $^3\Pi_u$, the coupling between which is ensured by the spin-orbit interaction. The magnitude of this coupling (the Landau-Zener parameter δ) varies, as shown by estimates, in the Na_2–Cs_2 sequence from 10^{-2} to ~ 7. An optical transition into the triplet state $^3\Pi_u$ is spin-forbidden, so that its manifestation in the absorption spectrum of molecular vapors can be observed only for Cs_2 molecules,[4] where this hindrance is least rigorous. This is precisely why molecular-cesium vapor for which the crossing of the singlet and triplet terms was most reliably established[3-5] was chosen to be the main experiment object. The crossing manifests itself, in particular, in the abrupt structure of the long-wave edge of the absorption spectrum of the vapor[6] (Ref. 3). The dip in the absorption spectrum in the region $\lambda=1.16$ μm can be naturally attributed to the quasicrossing of the terms $^1\Sigma_u^+$ and $^3\Pi_u$, since its width is close in magnitude to the spin-orbit splitting by $\Delta\nu=554$ cm^{-1} of the atomic doublet of cesium.[2]

Thus, we identify the molecular terms $|0\rangle$, $|1\rangle$ and $|2\rangle$ of the model considered above with the terms $^1\Sigma_g^+$, $^1\Sigma_u^+$, and $^3\Pi_u$ of the Cs_2 molecule. The cesium vapor was excited with a neodymium laser whose wavelength

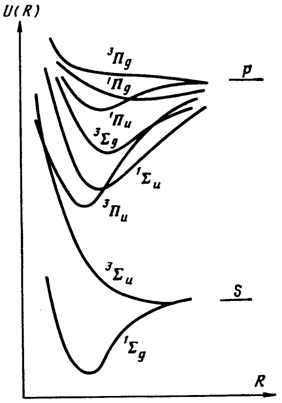

FIG. 2. Term scheme of alkali-metal molecules (Na_2).

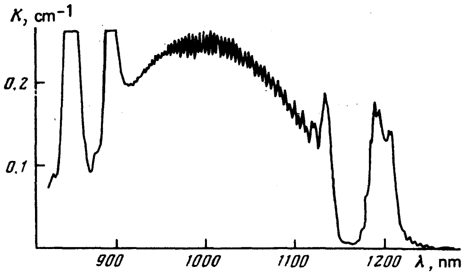

FIG. 3. Absorption spectrum of the cesium vapor, K—absorption coefficient at T = 650 K.

($\lambda = 1.06$ μm) lies in the region of the molecular $^1\Sigma_g^+ - {}^1\Sigma_u^+$ transition, the luminescence at the wavelengths of the single-singlet ($\lambda = 1.13$ μm) and triplet-singlet ($\lambda = 1.195$ μm) transitions was observed at right angle to the exciting radiation through an MDR-2 monochromator. The emission was registered with an FÉU-83 photomultiplier.

The kinetics of the Cs_2 vapor emission at $\lambda = 1.13$ μm in a xenon atmosphere ($p = 0.8$ atm) upon excitation by a single pulse from a neodymium laser[$\Delta t = (2-3)\cdot 10^{-8}$ sec] is shown in Fig. 4. It can be easily seen that it agrees with the notion that the metastable triplet state is substantially populated.$^{3)}$

The duration of the short component of the vapor emission was determined by the time resolution of the apparatus (3×10^{-8} sec), which exceeded somewhat the spontaneous lifetime of the $A^1\Sigma_u^+$ state, which is 2.5 $\times 10^{-8}$ sec according to the data of Ref. 5. It was verified that the ratio of the amplitudes of the short and long components of the emission is inversely proportional to the buffer-gas pressure (in the range 100–600 Torr) and that there is no short emission component when the luminescence is observed at the wavelength $\lambda = 1.195$ μm. This makes it possible to relate the absorption peak at this wavelength to the triplet-singlet transition. It was observed that the duration of the vapor emission depends on the gas temperature: with increasing temperature from 500 to 670 K it decreased from 0.25 to 0.1–0.15 μsec.

The presence of so long-lived a component of the Cs_2 vapor emission in the buffer gas is in our opinion the most direct spectroscopic manifestation of the metastable triplet state in this system.

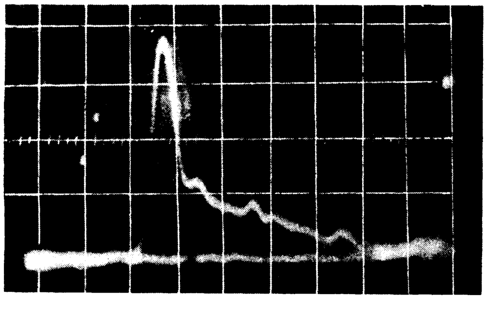

FIG. 4. Oscillogram of emission kinetics of Cs_2 vapor in a xenon atmosphere. Sweep 0.1 μsec/div.

At the same time, the data obtained are insufficient to establish an unequivocal connection between the observed kinetics of the vapor emission and the decay of metastable state via the indicated channels. The point is that in a number of the cited references it was postulated also that the bound term $^3\Pi_u$ crosses the repulsion term $^3\Sigma_u^+$ (see Fig. 2), and nonadiabatic transitions between them (which are due to spin-orbit and Coriolis interaction) can influence to a considerable degree the lifetime of the $^3\Pi_u$ state. The most convincing experimental proof of the presence of such a crossing was obtained in Ref. 7 in an investigation of the excitation of the emission of potassium D lines in atomic collisions, and in Ref. 8, where cascade predissociation of the molecules Rb_2 and Cs_2 was observed. Unfortunately, the energy position of the point of intersection of the terms $^3\Pi_u$ and $^3\Sigma_u$ could be determined in the cited papers only with a large error.

To clarify the role of the possible transitions from the $^3\Pi_u$ to the $^3\Sigma_u^+$ state, we have plotted the intensity of the molecular luminescence as a function of the gas temperature at constant excitation intensity. The decrease of this intensity with increasing T can be naturally connected either with the decrease of the molecule density in the vapor or with the quenching of the luminescence because of the increased rate of predissociation from the triplet $^3\Pi_u$ state. The solid line in Fig. 5 shows the theoretically calculated plot of the change of the number of molecules with increasing T at constant density of the atomic component of the vapor.^{4} The circles in the same figure mark the measured intensities of the molecular luminescence. It is easily seen that the luminescence quantum yield is constant, as is evidenced by the absence of quenching from the system. This, as well as that the vapor emission time is independent of the buffer-gas pressure in the range 100–600 Torr, allows us to conclude that the crossing point of the triplet terms lies not less than 3500 cm^{-1} above the minimum of the $^3\Pi_u$ potential, and that the predissociation of the molecules is neglibible under our conditions.

We can thus connect the observed kinetics of the molecular emission with the previously discussed processes—the short component of the emission in the region $\lambda = 1.13$ μm is due to direct decay of the singlet state, while the long component is due to the decay of the triplet state via the singlet. A detailed analysis of this kinetics, as well as the use of the published data on the rate of the vibrational rotational relaxation of the molecules^9 and on the parameters of the singlet

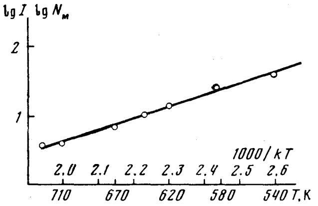

FIG. 5. Dependence of the cesium-molecule emission intensity on the gas temperature, N_M—theoretically calculated molecule density (solid line).

terms of the cesium molecule[4,5] allow us to determine the depth of the triplet state ($D = 6800$ cm^{-1}), the spontaneous lifetime[4] ($\tau = 0.5 \times 10^{-6}$ sec), and the magnitude of the coupling with the triplet term ($P \sim 10^{-3}$).

At the same time, the superposition of the absorption and emission spectra of the molecules in triplet-singlet and singlet-singlet transitions does not permit it at present to regard the problem of determining the parameters and form of the interacting terms as completely solved. This calls for further research.

An independent confirmation of the population of the state $^3\Pi_u$ by molecule collision was obtained in an investigation of the emission spectrum of vapors in the region of atomic lines. It was observed that an increase in the buffer-gas pressure produces, besides the emission corresponding to the molecular transitions, also atomic fluorescence whose intensity depends quadratically on the intensity of the exciting radiation. The natural channel for the production of excited atoms is photodissociation of the molecules from the populated state $^3\Pi_u$ and the repulsion state $^3\Pi_g$ (Fig. 2). An unambiguous connection between the formation of excited atoms and the population of the intermediate triplet state is confirmed not only by the almost complete absence of atomic emission in pure vapor (without the buffer gas), but also by the fact that the saturation of the molecular emission and the transition from a quadratic growth of the atomic fluorescence to a linear growth take place at one and the same excitation power (Fig. 6). It is hoped that further investigation of this induced triplet-triplet absorption will make it possible to determine the parameters of the triplet term $^3\Pi_g$.

3. The possibility of substantially populating the metastable triplet state for a specific investigated system makes it possible to realize also another interesting effect, namely a shift of the thermodynamic equilibrium between the atomic and molecular components upon optical excitation.

In fact, the stationary solution (2) of the kinetic equations that describe the excitation of the system, are transformed if the pumping rate $W \gg \gamma_2 + \gamma_1 \exp(-\Delta E/kT)$ into

$$n_0 = Ne^{-\Delta E/kT}\left(1 + \frac{\gamma_1 + \gamma_2 e^{\Delta E/kT}}{W}\right),$$
$$n_1 = Ne^{-\Delta E/kT}, \quad n_2 = N\left(1 - 2e^{-\Delta E/kT}\left(1 + \frac{\gamma_1 + \gamma_2 e^{\Delta E/kT}}{2W}\right)\right) \qquad (3)$$

which corresponds to a transition of the majority of the molecules present in the system into the triplet state. For a two-component system (pairs of atoms and molecules) such a situation is nonstationary. The recombination flux of the atoms will tend to restore the equilibrium density of the molecules in the ground state, whereas the intense optical radiation will maintain the ratio, described by Eqs. (3), of the populations of the molecular states. As a result, the total number of molecules can substantially exceed the thermodynamic equilibrium value, and the greater part of the molecules will be in the triplet state. The cause of this shift of the equilibrium between the atomic and molecular components under intense optical excitation lies in the prolonged stay of the molecules in the triplet state, the dissociation rate from which is much lower than from the ground state $^1\Sigma_g^+$.

As shown by an analysis of corresponding kinetic equations similar to the system (1), but with account taken of the coupling of the molecular and atomic reservoirs, the maximum attainable molecule density under these conditions is $\Gamma_1 N_0/(\Gamma_2 + \gamma_2)$ (N_0 is the thermodynamic-equilibrium density), and the rate of establishment of the new equilibrium state is $k_d \Gamma_2/\Gamma_1$ (k_d is the rate of dissociation of molecules from the ground state).

This effect is observed experimentally when cesium vapor is excited by a quasicontinuous pulse of radiation from a neodymium laser ($\Delta t \sim 10^{-3}$ sec, $I \sim 3 \cdot 10^5$ W/cm^2). To sharpen the leading front of the pulse, an exploding metallic film was used in some versions of the experiment.[10] Under these conditions, a noticeable flareup of the luminescence of the molecular vapor in the triplet-singlet transition ($\lambda = 1.195$ μm) was observed, see Fig. 7. The duration of this flareup ($\sim 10^{-5}$ sec) exceeds substantially all the observed radiation times in the system, so that the observed growth of the intensity of the molecular emission of the vapor can be associated with the increase of the number of molecules, compared with thermodynamic equilibrium, when the atoms recombine. The increase of the molecule den-

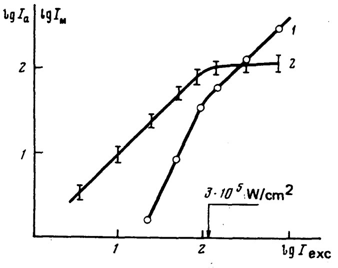

FIG. 6. Dependence of the intensity of the atomic (1) and molecular (2) emission on the excitation power.

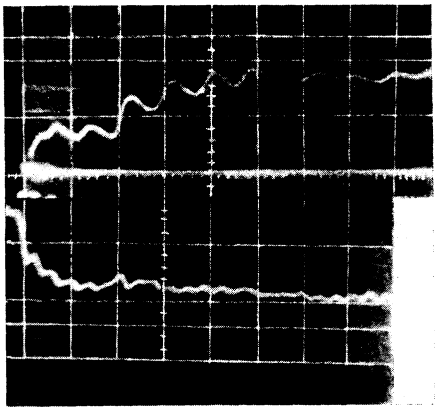

FIG. 7. Oscillogram of emission of molecular cesium vapor excited by a quasicontinuous radiation pulse. Lower trace—exciting pulse of negative polarity, upper trace—emission pulse. Sweep 5 μsec/div.

sity under the conditions of our experiment is expected to amount to 5–10 times. The molecule dissociation rate determined from these experiments, $k_d = 3 \cdot 10^6$ sec^{-1}, is in satisfactory agreement with the known published data.[11]

4. Thus, an investigation of a number of spectral-kinetic manifestations of the nonadiabatic coupling of the molecular states under conditions of rapid vibrational relaxation has shown that this relaxation leads to a transition of the molecules, if optically excited, to the deepest of the interacting states. Such processes serve as an illustrative example of how a rather weak action on the system (the collisions of the molecules with one another or with a buffer gas) alters radically its parameters (the two-level system becomes, in particular, essentially three-level). An investigation of the nonadiabatic transition has revealed a number of spectroscopic-manifestations of the metastable triplet state of alkalimetal molecules, and made it possible also to determine a number of its characteristics. It has been shown that the population of such a state by prolonged optical excitation of the system makes it possible to shift substantially the thermodynamic equilibrium between the atomic and molecular components of the vapor in favor of the latter.

The investigated phenomena can be significant not only for the development of the spectroscopy of triplet states of molecules, but can find also a number of practical applications. Inversion of the population of metastable state of alkali-metal molecules relative to the ground state can be used to design tunable lasers based on triplet-singlet transitions or a two-photon amplifier operating on the $^3\Pi_u - {}^3\Sigma_u^+$ transition (Fig. 2), as well as to convert the emission frequencies of available lasers by using anti-Stokes Raman scattering on electronic molecular transitions.

The possibility of substantially populating metastable molecular states at moderate rates of excitation of the singlet state that interacts with them (transition from which to the ground state is allowed) can be especially useful for lasing in the ultraviolet, where the requirements on the pumping rate in ordinary systems are particularly stringent, and there are no high-power radiation sources. An appreciable part of the population of the metastable state can be transferred to a closely lying working level by powerful pulsed long-wave radiation, which ensures saturation of the forbidden triplet-singlet transition, thereby greatly facilitating the lasing.

In conclusion, we wish to thank N. N. Kostin and S. G. Przhibel'skii for stimulating discussions during all stages of the work.

[1) In systems for which the vibrational quantum $\hbar\Omega \gtrsim kT$, the nonadiabatic-transition rates are described by the expression

$$\Gamma_{1,2} = Pf \exp(-D_{1,2}/kT).$$

[2) A more detailed discussion of the absorption and emission spectra of molecular cesium, and also of the forms of the potentials of the ground $^1\Sigma_g^+$ and excited $^1\Sigma_u^+$ states, is given in Refs. 4 and 5.

[3) Similar emission kinetics was observed by us in preliminary experiments on molecular sodium and rubidium, thus attesting to the presence of nonadiabatic transitions in these systems under impact relaxation.

[4) Owing to the strong dependence of the dipole matrix element of the triplet-singlet transition on the internuclear distance, the state $^3\Pi_u$ cannot be characterized by a single lifetime parameter. We cite here its averaged value (the decrease to the level $1/e$) at $T = 500$ K.

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