Cascade predissociation of the molecules CS^*_2 and Rb^*_2

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Nonradiative and collisionless decay of the molecules Cs^*_2 and Rb^*_2 that are optically excited in states with energy lower than the dissociation energy is established. The decay is attributed to a sequence of nonadiabatic intramolecular transitions.

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Observation of a change in the optical density in the transmission bands of Rb_2 molecules under the influence of ruby-laser radiation was reported earlier.[1] It was subsequently shown[2,3] that when alkali-metal vapors are excited in the region of the molecular-absorption bands, an effective photo-dissociation of the Me_2 molecules takes place. In this paper we investigate the mechanism of the photodecay process.

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In the experiment, saturated two-component vapors (Me + Me_2) of alkali metals were excited with a single pulse from a laser in the region of the $^1\Sigma_g - {}^1\Pi_u$ absorption band (see Fig. 1). The percentage of the decaying molecules was determined by mea-

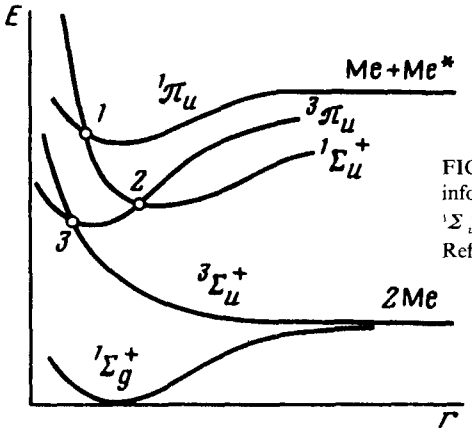

FIG. 1. Diabatic-term scheme of heavy alkali metals. The information on the crossing of the terms $^1\Sigma_u^+$ with $^1\Pi_u$(1), $^1\Sigma_u^+$ with $^3\Pi_u$ (2), and $^3\Pi_u$ with $^3\Sigma_u^+$ (3) were taken from Refs. 4, 5, and 6, respectively.

suring the relative change $\Delta\kappa/\kappa_0$ of the optical density in the $^1\Sigma_g - {}^1\Sigma_u$ band. The width of the laser emission spectrum was 1–0.1 cm^{-1}, and the duration of the monopulse 2×10^{-8} sec was close to the duration of the fluorescent decay of the $^1\Pi_u$ state. The main results of the experiment reduce to the following.

1) The monopulse produced homogeneous (simultaneous) bleaching in the entire $^1\Sigma_g - {}^1\Sigma_u$ band within a time not exceeding 10^{-7} sec—the resolution time of the recording apparatus—under conditions when the frequency of the gas kinetic collisions was $\lesssim 3\times10^6$ sec^{-1}. Independence of $\Delta\kappa/\kappa_0$ of the Cs vapor pressure was established for an atom concentration variation by a factor of 7 and a molecule concentration variation by a factor 25 ($T = 270-370$ °C).

2) The $\Delta\kappa/\kappa_0$ bleaching signal had a sublinear dependence on the excitation intensity I. Saturation of the dependence at $I = 10^7$ W/cm^2 corresponded to an appreciable ($\approx$50%) decay of the molecules (Fig. 2).

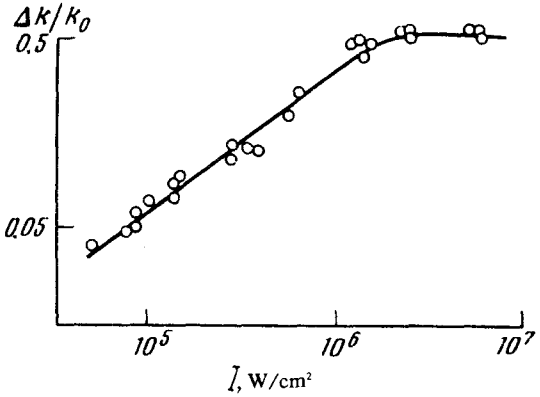

FIG. 2.

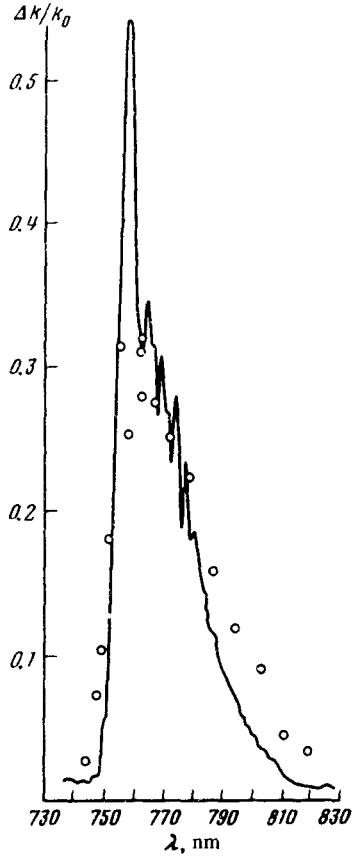

FIG. 3.

3) The dependence of the change of the optical density $\Delta\kappa/\kappa_0$ of the Cs_2 molecules on the wavelength λ of the exciting radiation, obtained at $I = 4\times 10^5$ W/cm^2, is shown in Fig. 3 (points). The solid curve in Fig. 3 shows the absorption spectrum in the $^1\Sigma_g - {}^1\Pi_u$ band of Cs_2. The similarity of these spectra is obvious.

The foregoing facts attest to a collisionless mechanism of the decay of the Me_2^* molecules excited in the state $^1\Pi_u$. That the photodecay is nonradiative is indicated by the observed shift of the thermodynamic equilibrium in the Me + Me_2 system: after the application of the laser pulse, the initial (equilibrium) optical density was restored, depending on the vapor pressure, within a time 10^{-2}–10^{-3} sec, which corresponds to the time required to remove the heat from the excitation volume. An estimate shows that heating of the subsystem of the atoms as a result of the nonradiative decay of the molecules produces the observed change of the equilibrium constant in the vapor.

The observed decay of the molecules can be attributed to predissociation from the $^1\Pi_u$ state. The effective decay channel can be the successive chain of transitions $^1\Pi_u \to {}^1\Sigma_u \to {}^3\Pi_u \to {}^3\Sigma_u$ (cascade dissociation). The choice of this channel and its effectiveness are governed by the presence of crossing points for the indicated terms (see Fig. 1). This chain of transitions is caused in succession by Coriolis, spin–orbit, and Coriolis perturbations. The frequency Γ of the decay of the molecules by this method

can be determined by quasiclassical predissociation theory,[10] but in view of the fact that the Coriolis coupling of the terms is weak while the spin–orbit coupling is of intermediate strength, a sufficient estimate of Γ is obtained by perturbation theory:

$$\Gamma = \nu_{\Pi} p_1 p_2 p_3, \tag{1}$$

where ν_{Π} is the frequency of the classic oscillations in the well of the $^1\Pi_u$ state and

$$p_i = 4\pi a_i^2 / v_i \hbar \Delta F_i \qquad (i = 1,2,3) \tag{2}$$

is the Landau—Zener nonadiabatic-transition probability in the standard notation.[7] The subscript i labels the values corresponding to the crossing points 1, 2, and 3 of Fig. 1, respectively. The contribution of the rapidly oscillating terms of interference origin in expressions (1) and (2) is negligible. For a numerical estimate of Γ we chose the following plausible values: $\nu_{\Pi} = 10^{12}$ sec^{-1}, $\Delta F_i = 5\times 10^{-5}$ dyn, $v_i = 5\times 10^4$ cm/sec, and $a_{1,3}/\hbar \approx \hbar l/\mu R_{1,3}^2 = 10^{12}$ sec^{-1}, since the characteristic orbital numbers are $l \approx (\kappa_B T/B\hbar)^{1/2} \approx 100$, while $R_{1,3} = 2.5\times 10^{-8}$ cm and the mass is $\mu = 10^{-22}$ g. The rotational constant is $B = 10^9$ sec^{-1}. The quantity p_2 must be assumed to be of the order of unity, since the matrix element a_2 is close in magnitude[7] to the atomic spin—orbit constant, which in this case is larger (the doublet splitting is 238 and 554 cm^{-1} for Rb and Cs, respectively). Thus, within the framework of the assumed model we have $\Gamma \approx 10^8$ sec^{-1}, which is close in magnitude to the frequency of the radiative relaxation of the excited molecule and the reciprocal of the excitation-pulse duration. An estimate points to a possibility of nonradiative decay of the molecules Me_2^* from the excitated $^1\Pi_u$ state within the radiative lifetime via cascade predissociation, and does not contradict the data on the fluorescent decay of the $^1\Pi_u$ state.[8]

A considerable percentage of the molecule decay at high excitation intensities can be explained on the basis of the concept of the molecular band as an inhomogeneously broadened ensemble of two-level systems.[8] Within the framework of the model of the uniform distribution of the transition frequencies, the population n of the state $^1\Pi_u$ under the action of radiation that is quasiresonant with the transitions is given by

$$n = (\Delta\omega)^2 \operatorname{arc\,tg}\left(\Delta\omega / \sqrt{(\Delta\omega)^2 + \gamma_2^2}\right) / 2\Delta_{\Pi}\sqrt{(\Delta\omega)^2 + \gamma_2^2}, \tag{3}$$

where $\Delta\omega$ is the spectral width of the dip produced in the inhomogeneously broadened band by saturation[9] of the $^1\Sigma_g - {}^1\Pi_u$ transitions ($\Delta\omega \sim (1)^{1/2}$) under saturation conditions), γ_2 is the frequency of the phase relaxation of these transitions, and Δ_{Π} is the maximum deviation from resonance of the optical excitation in the inhomogeneously broadened band (half the frequency of the vibrational quantum of the $^1\Pi_u$ state, $\Delta_{\Pi} = 6\times 10^{11}$ sec^{-1}). According to the data of Ref. 9 $\Delta\omega = 4.5\times 10^{10}$ sec$^{-1} \gg \gamma_2$ at $I = 10^6$ W/cm^2. Thus, according to (3), at $I = 10^7$ W/cm^2 we should expect a $\approx 20\%$ decay within the time of action of the laser monopulse. This is less than the registered value. It is possible that the discrepancy between the estimate and the measurements is due to the assumed approximation, namely, equipartition of the transition-frequency density in the inhomogeneously broadened band.

Cascade predissociation is of interest from several points of view (spectroscopy, physical chemistry, etc.) and should be of rather general character, since the crossing of the diabatic terms of the excited molecules is frequently realized, especially in

polyatomic systems. Photolysis of molecules at high excitation intensity, in addition to the traditional one, can reveal the predissociation channel in those cases when the frequency of the decay via this channel is small compared with that of radiative decay. The dependence of the photoreaction yield can become in this case a nonlinear function of the intensity and is determined by the character, particularly the width, of the excitation spectrum.

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