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Nonlinear Absorption of Ruby Laser Emission by Molecular Rubidium Vapor

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Resonance molecular fluorescence of saturated Rb_2 vapor excited by Q-switched ruby laser is studied. The usual linear dependence of fluorescence intensity on excitation intensity changes into a linear dependence on electric field intensity when the exciting power density exceeds 10^3 W/cm^2. The concentration dependence of fluorescence intensity is found to be different for weak and strong excitation. The linear dependence of fluorescence on emission field intensity is shown to be due to nonresonance excitation of molecules with inhomogeneously broadened absorption band. The different measured concentration dependencies are interpreted as a manifestation of the dependence of transverse molecular relaxation on vapor concentration.

1. INTRODUCTION

We reported previously[1] on the observed phenomenon of nonlinear population of the excited states of K_2 molecules by a Q-switched ruby laser emission. The degree of population of the excited states was determined from the change in molecular fluorescence intensity observed at a right angle to the direction of the exciting emission. We discovered that the fluorescence intensity is proportional to the square root of I_0 when the excitation intensity is $I_0 = 10^3 - 10^6$ w/cm^2. This dependence was interpreted as a manifestation of nonresonance excitation of K_2 molecules considered as an ensemble of two-level systems with different natural transition frequencies. The theoretical interpretation implies that the change from the usual linear dependence of fluorescence intensity on I_0 to a linear dependence on $\sqrt{I_0}$ (henceforth called root dependence) is determined by the constants of the longitudinal and transverse molecular relaxation. At the same time the linear and root regions have different dependence of fluorescence intensity on the longitudinal and transverse relaxation constants[2].

To verify the proposed theoretical interpretation we performed a more detailed investigation of the phenomenon using saturated vapor of molecular rubidium Rb_2 as the object. Compared to K_2, Rb_2 vapor has an order-of-magnitude greater density and absorption cross section at the ruby laser wavelength at the same temperatures. This permitted us to expand significantly the useful range of the resonance fluorescence signal, which is bounded below by the photomultiplier shot noise and above by the parasitic signal of the ruby laser light scattering. Furthermore, as we show below, the longer fluorescence decay time of Rb_2 (25 nsec) provides a relatively better justification of the theoretical model represented by the two-level absorption and emission systems under pulse excitation conditions.

2. THE EXPERIMENT

Figure 1 shows the spectral dependence of the molecular rubidium absorption cross section in the red band $^1\Sigma_g \to {}^1\Pi_u$ measured under standard conditions at T = 290°C (spectral resolution ~30 Å; the molecule concentration corresponding to the measurement temperature is taken from Nesmeyanov's book[3]). As seen from the figure, the molecular vapor absorption cross section near the ruby emission wavelength ($\lambda_0 = 6943$ Å) amounts to $(2 - 3) \times 10^{-16}$ cm^2. Direct measurement of the ruby emission absorption by Rb_2 vapor as a function of laser pulse power revealed bleaching of the molecular vapor.

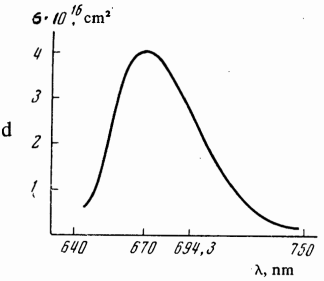

FIG. 1. Absorption cross section of molecular rubidium in the red band $^1\Sigma_g \to {}^1\Pi_u$.

To identify the ground-state vibrational level responsible for absorption of ruby laser emission we photographed the spectrum of resonance fluorescence of Rb_2. The cell (Wood's horn) with rubidium vapor saturated at 320°C was exposed to the emission of ruby laser operating in a spiking mode. The pulse energy was 0.5 J. Figure 2 shows a spectrogram of the anti-Stokes wing of resonance fluorescence accumulated from 100 pulses of spiking emission with a 5 Å spectral slit width of an STÉ-1 recording spectrograph. The set of equidistant lines in the spectrogram corresponds to transitions from the excited vibration level of the $^1\Pi_u$ state to the vibrational levels of ground state.

Analysis of the resonance fluorescence spectrum and data on the frequencies of the electron-vibrational transitions of Rb_2[6] showed that transitions occur from 6–10 vibrational levels of the ground $^1\Sigma_g$ state to 2–6 levels of the excited state, depending on the ruby laser frequency (in this experiment the width of free-running emission spectrum was ~1 cm^{-1}). The presence of discrete bands in the Rb_2 fluorescence spectrum indicates that no molecular relaxation from the vibrational states of the excited term takes place during fluorescence decay of the excited state.

Figure 3 shows the resonance intensity S of molecu-

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[1] The bleaching of molecular Rb_2 vapor by ruby laser emission was used by us for simultaneous passive Q-switching and stabilization of the ruby laser frequency[4]. Q-switching and frequency stabilization of a neodymium glass laser were achieved in a similar manner using Cs_2 vapor[5].

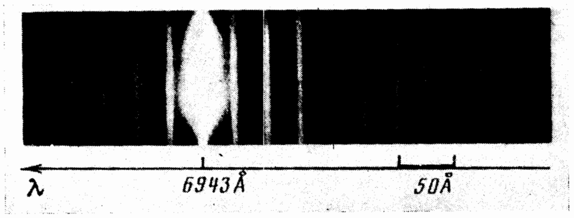

FIG. 2. Spectrum of anti-Stokes wing of Rb_2 vapor resonance fluorescence excited by ruby laser emission.

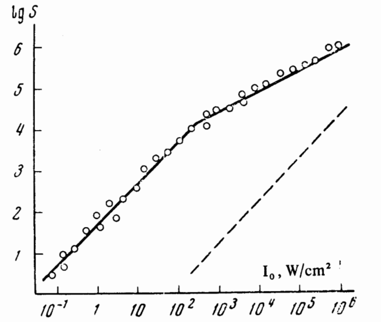

FIG. 3. Resonance fluorescence intensity S of Rb_2 vapor as a function of single pulse intensity I_0 of ruby laser.

lar rubidium as a function of the intensity I_0 of a single ruby pulse measured in the experimental setup shown in Fig. 4.

A molybdenum-glass cell (Wood's horn) with rubidium vapor saturated at 360°C was exposed to a ruby laser operating in the giant pulse mode. The laser was Q-switched by a solution of gallium chloride phthalocyanin in nitrobenzene. The frequency dispersion of a single laser pulse did not exceed 0.1 cm^{-1} from flash to flash, owing to the use of a double refraction crystal in the laser system as a frequency stabilizer, as was done by Circovic et al.[7] The length of the laser pulse (at half amplitude) was 20 nsec, and the resonance fluorescence was recorded in a direction perpendicular to laser emission. Fluorescence intensity was measured with an FEU-28 photomultiplier connected to an S1-11 pulsed oscilloscope. The laser emission intensity was attenuated in steps with calibrated neutral density filters, and the power of a single pulse was determined photoelectrically with a graduated FÉK-09 coaxial photocell and an Si-7 oscilloscope. Platinum neutral density filters were used to attenuate the light in the fluorescence recording channel.

The observed fluorescence signal was integrated over the spectrum within the range 720–900 nm. The maximum power density in the horn was ~ 2 MW/cm^2. An FS-7 optical filter effectively cut off the scattered emission of the ruby laser. Preliminary experiments revealed that a parasitic scattered signal is present along with the molecular vapor fluorescence signal in the spectral range. The parasitic signal is constant over the spectrum, does not depend on the temperature of the rubidium vapor horn, and increases linearly with laser pulse power. The magnitude of the parasitic scattering signal observed under our conditions (the fluorescence signal was observed in the region 2 cm away from the horn window to eliminate the effect of linear absorption of the exciting radiation within the range of Rb_2 pressures used) is shown by the dashed line in Fig. 3.

According to Fig. 3 the fluorescence intensity is proportional to laser intensity I_0 up to a certain limit (~1 kW/cm^2 for a rubidium vapor temperature of 360°C) beyond which the fluorescence intensity is proportional to $\sqrt{I_0}$ (in the logarithmic scale, the linear and root regions correspond to respective slopes equal to 1 and ½). The concentration dependence of the fluorescence signal was measured in the linear (weak excitation) and root (strong excitation) regions.

Figure 5 shows the relative magnitude of the resonance fluorescence signal as a function of the saturated molecular vapor pressure for weak (line 1) and strong (line 2) excitation. In the experiment we measured the temperature of the rubidium vapor horn, while the vapor pressure was obtained from data in Nesmeyanov's book[3]. Line 2 was plotted under the same conditions as those in plotting fluorescence intensity as a function of laser pulse power. To increase the range of fluorescence signal in the weak excitation region, line 1 of the concentration dependence was plotted by recording the total fluorescence spectrum in the region 640–900 nm. The FS-7 filter was removed from the photomultiplier, thus increasing the fluorescence signal by a factor of 70, so that the recording range of the fluorescence signal was now limited below by the scattered emission of the ruby laser. The ratio of fluorescence signals received from the entire band (640–900 nm) to those from the Stokes region (720–900 nm) was found to remain constant within the entire power range of the laser pulse.

The setup shown in Fig. 4 was used also to measure the fluorescence decay time of the excited $^1\Pi_u$ state of rubidium molecules. Fluorescence was excited by a 5–7 nsec ruby laser pulse. The fluorescence was recorded with fast FÉU-77 and FÉU-36 photomultipliers connected to the S1-11 pulsed oscilloscope. The resolution time of the recording system did not exceed

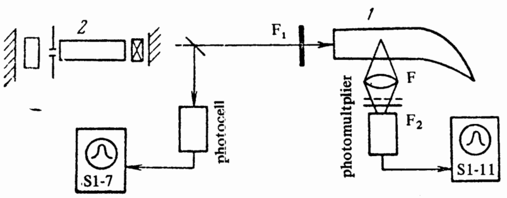

FIG. 4. Experimental setup. 1—Wood's horn with saturated rubidium vapor; 2—Q-switched ruby laser; F_1—calibrated neutral density filters; F_2—neutral density platinum filters; F—FS-7 optical filter.

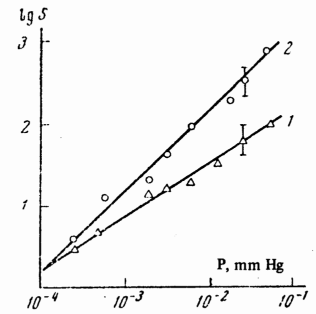

FIG. 5. Relative resonance fluorescence signal S as a function of molecular rubidium vapor pressure P: 1—weak excitation; 2—strong excitation.

4 nsec. The measurements showed that the fluorescence decay time τ_1 does not depend on the concentration of molecules within the entire range of temperatures used (~up to 400°C) and amounts to (25 ± 5) nsec. The measurement of τ_1 yielded the same result whether the fluorescence spectrum was recorded over the entire band or in the Stokes region, as well as for weak and strong excitation. Figure 6 shows oscillograms of the exciting pulse of the ruby laser and the fluorescence pulse. The measured value of τ_1 is in satisfactory agreement with the computation of τ_1 from the integral cross section of the absorption band (~40 nsec).

3. THEORY

The present theory, just as that of Burshteĭn[8], is based on a model of two-level systems with different natural transition frequencies ω_0 characterized by their distribution function $\rho(\omega_0)$ (inhomogeneous broadening of the absorption band). The fluorescence intensity is proportional to the total number of excited molecules $F(t)$. To compute it we must find the population of the upper level $f_{11}(\omega_0)$ for each species of molecules and then to average $f_{11}(\omega_0)$ over frequencies ω_0 with the aid of the distribution function $\rho(\omega_0)$.

The population $f_{11}(\omega_0)$ can be found from the following system of equations for the molecular density matrix in a monochromatic radiation field $E = \mathscr{E}\cos\omega t$:

$$\begin{aligned} \dot{f}_{11} &= \frac{1}{i\hbar}(V_{10}f_{01} - f_{10}V_{01}) - \gamma_1 f_{11}, \\ \dot{f}_{10} &= \frac{1}{i\hbar}(1 - 2f_{11})V_{10} - i\omega_0 f_{10} - \gamma_2 f_{10}. \end{aligned} \tag{1}$$

Here $\tau_1 = 1/\gamma_1$ is the time constant of excited state population relaxation, $\tau_2 = 1/\gamma_2$ is the time constant of transverse relaxation, and $V_{10} = V_{01}^* = d\mathscr{E}$, where d is a matrix element of dipole moment projected on the direction **E**.

The methods and nature of the solution of system (1) are known in sufficient detail (see[8,9] for example). We now merely consider some typical solutions necessary for the interpretation of the obtained experimental results.

1. Stationary excitation regime. In this case the solution of system (1) for a quasi-resonance excitation $\omega - \omega_0 \ll \omega_0$ leads to the following stationary value of $f_{11}(\omega_0)$:

$$f_{\text{stat}}(\omega_0) = \frac{1}{2}\frac{\Omega^2\gamma_2/\gamma_1}{\gamma_2^2 + \Omega^2\gamma_2/\gamma_1 + (\omega - \omega_0)^2} \tag{2}$$

Here and below $\Omega = d\mathscr{E}/\hbar$. To obtain the total number F_{stat} of excited molecules we integrate $f_{\text{stat}}(\omega_0)$ over the entire ensemble of molecules:

$$F_{\text{stat}} = \int_{-\infty}^{+\infty} d\omega_0 f_{\text{stat}}(\omega_0)\rho(\omega_0) \tag{3}$$

Under our experimental conditions the distribution function $\rho(\omega_0)$ is smooth in comparison to the function $f_{\text{stat}}(\omega_0)$; its effective width is of the order of the absorption bandwidth (~10^{14} sec^{-1}), whereas the width of the function $f_{\text{stat}}(\omega_0)$ for the maximum intensities used does not exceed 10^{12} sec^{-1}. Therefore

$$\begin{aligned} F_{\text{stat}} &= \frac{\rho(\omega)}{2}\frac{\gamma_2}{\gamma_1}\Omega^2\int_{-\infty}^{+\infty}\frac{d\omega_0}{(\omega - \omega_0)^2 + \gamma_2^2 + \Omega^2\gamma_2/\gamma_1} \\ &= \frac{\pi}{2}\rho(\omega)\sqrt{\frac{\gamma_2}{\gamma_1}}\frac{\Omega^2}{(\Omega^2 + \gamma_1\gamma_2)^{1/2}}. \end{aligned} \tag{4}$$

It follows from (4) that for low intensities of the exciting emission, when $\Omega^2 \ll \gamma_2\gamma_1$, the magnitude of F_{stat} and consequently the fluorescence intensity are proportional to the intensity of the exciting emission:

$$F_{\text{stat}}^{\text{weak}} = \frac{\pi}{2}\rho(\omega)\frac{\Omega^2}{\gamma_1}. \tag{5}$$

In the other limiting case of large intensities, when $\Omega^2 \gg \gamma_2\gamma_1$, the magnitude of F_{stat} is proportional to the square root of the intensity of the exciting emission:

$$F_{\text{stat}}^{\text{strong}} = \frac{\pi}{2}\rho(\omega)\sqrt{\frac{\gamma_2}{\gamma_1}}\Omega. \tag{6}$$

The change from linear to root dependence occurs with exciting emission intensities for which Ω^2 is of the order of $\gamma_2\gamma_1$. Hence it follows that the analysis of fluorescence intensity as a function of the intensity of exciting light represents a new method of measuring the time constants of the longitudinal τ_1 and transverse τ_2 relaxations with inhomogeneously broadened absorption band of the molecules.

The physical interpretation of the change from linear to root dependence is based on the fact that for $\Omega^2 \gg \gamma_2\gamma_1$ the excited state involves all molecules whose absorption frequency ω_0 falls within the interval $\omega \pm \Omega\sqrt{\gamma_2/\gamma_1}$ (see (2)) in proportion to the square root of the exciting emission intensity. On the other hand, in the case of $\Omega^2 \ll \gamma_2\gamma_1$ only those molecules whose ω_0 lies within the interval $\omega \pm \gamma_2$, independent of excitation intensity, can be effectively excited.

2. Nonstationary excitation regime for $\gamma_2 = \gamma_1 = \gamma$. In this case system (1) with the initial condition $f_{11} = f_{10} = 0$ at $t = 0$ has a solution for $f_{11}(\omega_0, t)$:

$$\begin{aligned} f_{11}(\omega_0, t) &= \frac{1}{2}\frac{\Omega^2}{Z}(1 - e^{-\gamma t}\cos Rt); \\ Z = \Omega^2 + \gamma^2 + (\omega - \omega_0)^2, &\quad R = \sqrt{(\omega - \omega_0)^2 + \Omega^2}. \end{aligned} \tag{7}$$

Exact integration of $f_{11}(\omega_0, t)$ over the ensemble of molecules

$$F = \frac{\rho(\omega)}{2}\Omega^2\int_{-\infty}^{+\infty} d\omega_0\frac{1 - e^{-\gamma t}\cos Rt}{Z} \tag{8}$$

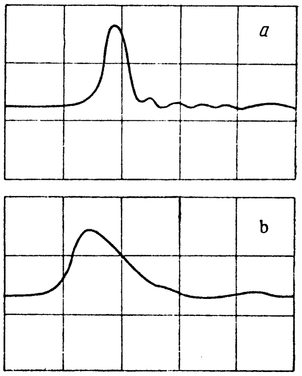

FIG. 6. Oscillograms of the exciting ruby laser pulse (a) and fluorescence pulse (b). Scale 20 nsec/division.

is difficult in this case. However, in the case of short excitation pulses $\Delta t \ll 1/\gamma$ (8) can be integrated approximately in the limiting cases of weak and strong excitation.

In the case of weak excitation intensities, when $\Omega \ll \gamma$, we have $\cos Rt \approx 1$ in the region of sharp variation of the function Z^{-1} and

$$F^{\text{weak}}(\Delta t) \approx \frac{\pi}{2} \rho(\omega) \Omega^2 \Delta t. \tag{9}$$

In the other limiting case of large excitation intensities, when $\Omega \gg \Delta t^{-1}$, the function $\cos Rt$ oscillates rapidly in the region $(\omega - \omega_0) \sim \Omega$ of the main contribution of the function Z^{-1} and

$$F^{\text{strong}}(\Delta t) \approx \frac{\pi}{2} \rho(\omega) \Omega. \tag{10}$$

Comparison of (9) and (10) with (5) and (6) shows that in the limiting case of strong excitation the fluorescence intensity for short excitation $\Delta t \ll 1/\gamma$ coincides with its stationary value for $\gamma_2 = \gamma_1 = \gamma$ and is proportional to the square root of the excitation intensity. On the other hand, in the case of low excitation intensities the fluorescence intensity is proportional to that of the exciting radiation and differs from the stationary value merely in that $\tau_1 = 1/\gamma_1$ is replaced by Δt. The change from linear to root dependence in the case of short-time excitation occurs at excitation intensities for which $\gamma < \Omega < t^{-1}$.

3. Nonstationary excitation regime for $\gamma_2 \gg \gamma_1$. In this case the approximate value of $f_{11}(\omega_0, t)$ can be obtained in the frequency region $(\omega - \omega_0) \geq \gamma_2$ and has the form

$$f_{11}(\omega_0, t) \approx \frac{1}{2} \frac{\Omega^2 \gamma_2/\gamma_1}{\gamma_2^2 + \Omega^2 \gamma_2/\gamma_1 + (\omega - \omega_0)^2} \times \left\{ 1 - \exp\left[-t \frac{\gamma_1 (\omega - \omega_0)^2 + \gamma_2 [\Omega^2 + \gamma_1 \gamma_2]}{\Omega^2 + \gamma_2^2 + (\omega - \omega_0)^2} \right] \right\}. \tag{11}$$

As in the preceding case, an approximate computation of the total number of excited molecules is possible

$$F \approx \rho(\omega) \int_{-\infty}^{+\infty} f_{11}(\omega_0, \Delta t)\, d\omega_0$$

for short-period excitation $\gamma_2^{-1} \ll \Delta t \ll \gamma_1^{-1}$ by strong and weak emission pulses. For weak emission excitation $\Omega^2 \ll \gamma_2 \Delta t^{-1}$

$$F^{\text{weak}}(\Delta t) \approx \rho(\omega) \frac{\pi}{2} \Omega^2 \Delta t. \tag{12}$$

In the converse case of strong pulse excitation $\Omega^2 \gg \gamma_2 \Delta t^{-1}$

$$F^{\text{strong}}(\Delta t) \approx \rho(\omega) \frac{\pi}{2} \Omega \sqrt{\gamma_2 \Delta t}. \tag{13}$$

Consequently for $\gamma_2 \gg \gamma_1$ the change from linear to root dependence occurs at excitation intensities for which Ω^2 becomes of the order of $\gamma_2 \Delta t^{-1}$ and depends on the pulse length Δt. In contrast to the case $\gamma_2 = \gamma_1$ the constant of proportionality in the root region is proportional to $\sqrt{\Delta t}$, i.e., it depends on the pulse length.

4. DISCUSSION OF RESULTS

Owing to the possible transition of a molecule from the excited electron-vibrational state to any vibrational sublevel of the electron ground state, the molecular rubidium vapor under investigation represents an inhomogeneously broadened multilevel system. The applicability of the model developed for the ensemble of two-level systems in this case is determined by the relation between the exciting laser pulse length Δt and time τ_1 of the fluorescent decay of the excited state of the molecule.

For $\Delta t \lesssim \tau_1$ the two-level model; is approximately valid and the fluorescence intensity for weak and strong excitation is described by (12) and (13).

For $\Delta t \gg \tau_1$ in a strong laser field rapid radiative decay of the excited state and depletion of the ground state electron-vibrational terms responsible for absorption result in complex kinetics of the fluorescence pulse. Nevertheless the results of the two-level model can be used in this case provided the rise time of the leading edge of the pulse is much smaller than τ_1.

For $\Delta t = \tau_1$ (as noted above under our experimental conditions, $\Delta t = 20$ nsec and $\tau_1 = 25$ nsec) Eq. (4) is approximately valid for the stationary regime. This equation determines the dependence of fluorescence intensity on excitation intensity and relaxation constants γ_1 and γ_2. The observed dependence of fluorescence intensity on excitation intensity (Fig. 3) is qualitatively in good agreement with the dependence predicted by (4).

As noted above we discovered that the lifetime of excited state of rubidium molecules is independent of vapor concentration in the investigated temperature interval (absence of concentration quenching of fluorescence). The difference in the concentration dependence of fluorescence intensity for weak and strong excitation we attribute to the dependence of transverse relaxation time $\tau_2 = 1/\gamma_2$ on the vapor concentration N. The concentration dependence of γ_2 can be obtained from (5) and and (6):

$$\frac{F_{\text{stat}}^{\text{strong}}}{F_{\text{stat}}^{\text{weak}}}(N) = A\sqrt{\gamma_2(N)}, \quad A = \frac{\sqrt{\gamma_1}\hbar\mathcal{E}_{\text{strong}}}{d\mathcal{E}_{\text{weak}}^2},$$

where A does not depend on concentration.

According to the plot in Fig. 5 γ_2 changes in the investigated range of temperatures of saturated rubidium vapor by a factor of 40. From Nesmeyanov's data[3] such is also the change in vapor concentration of atomic rubidium. The concentration of molecular vapor within this range changes by a factor of ~250. The concentration of Rb exceeds 100—150 times that of Rb_2. These data indicate that the quantity γ_2 is most probably determined by collisions of molecules with rubidium atoms. However the concentration dependence of fluorescence intensity for weak excitation (Fig. 5) differs considerably from linear. We assume that this difference is due to inexact determination of saturated Rb_2 vapor pressure P as a function of temperature T given in Nesmeyanov's book[3]. An analogous deviation of the P(T) function from[3] was also revealed by us in an independent experiment performed to measure the absorption cross section of Rb_2. A greater precision of the function P(T) will permit us to make a definitive conclusion about the mechanism of transverse relaxation in a rubidium molecule. Determination of γ_2 requires absolute measurement of molecular concentration and fluorescence intensity for weak and strong excitation.

5. CONCLUSION

We assume that the obtained experimental data allow us to validate the theoretical interpretation of the observed nonlinear phenomena based on the model of nonlinear absorption of intense emission by an ensemble of two-level systems with various natural transition frequencies (i.e., molecules with inhomogeneously broadened absorption bands).

The above method of studying nonlinear absorption of powerful monochromatic radiation by inhomogeneously broadened molecular systems can serve as a new technique of measuring the homogeneous broadening of individual molecular transitions masked by inhomogeneously broadened band and also of mechanisms causing such broadening. Of considerable interest is the study of nonlinear absorption of nonmonochromatic intense radiation by molecules with inhomogeneously broadened absorption bands.

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