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MOLECULAR SPECTROSCOPY

Structure of Spectra of Stimulated Raman Scattering in High-pressure Hydrogen

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Abstract—Spectral and time characteristics of stimulated Raman scattering (SRS) excited in high-pressure hydrogen with 400-fs pulses of the second harmonic (390 nm) of a sapphire : Ti laser are studied. Spectra of components of vibrational, rotational, and vibrational–rotational SRS in the wavelength range of 289–577 nm are measured. The efficiency of power conversion to the first Stokes component reached approximately 40%, and its pulses were compressed in duration by a factor of about three with respect to the pump pulses. In experiments on excitation of SRS with circularly polarized light, the intensity of vibrational–rotational components exceeded the intensity of purely vibrational components.

INTRODUCTION

Vibrational and rotational SRS in high-pressure gases is extensively used for controling the radiation frequency of high-power lasers and obtaining high-intensity coherent light beams at several frequencies at a time in the UV, visible, and IR spectral regions [1]. Spectral and space–time characteristics of scattered light are of most interest for solving these problems. In [2–4], these characteristics were studied in the quasi-stationary, transient, and nonstationary regimes of SRS excitation in high-pressure hydrogen with bandwidth-limited nanosecond pump pulses. High-pressure hydrogen is one of the readily available Raman-active media providing a high conversion efficiency. It is characterized by an extremely narrow spectral line of spontaneous Raman scattering, high thresholds of competitive nonlinear processes (SBS, optical breakdown, and self-focusing), high transparency, and low dispersion. These properties made it possible, for the first time in [5], to obtain highly coherent Stokes radiation with a high conversion efficiency (up to 50% for power conversion) and determine the condition for obtaining bandwidth-limited (without phase modulation) Stokes pulses. Such pulses are of fundamental importance for spectroscopy; holography; and coherent, nonlinear, and quantum optics. They provided the best spectral resolution for the given duration and, moreover, the highest efficiency of hologram recording and optical-signal detection.

The rapid development of pico- and femtosecond lasers in recent years has drawn attention to SRS as a method for converting their radiation frequency [6, 7], but the structure of SRS spectra excited with pulses of this duration has remained almost unstudied. Meanwhile, the excitation of SRS with femtosecond pulses is of considerable importance from the viewpoint of studying spectral properties of converted radiation.

The excitation with femtosecond pulses has the following distinctive properties:

(1) strong nonstationarity of the SRS process, associated with the fact that the pulse duration (~100 fs) is smaller by a factor of two to three than the transverse relaxation time T_2;

(2) a wide spectrum of exciting radiation (~150 cm^{-1}), caused by a small pulse duration, is responsible for the fact that the density of pump photons corresponding to the frequencies at which spectral lines of vibrational and rotational Raman components are excited in a medium exceeds the density of spontaneously emitted photons, which can substantially change initial conditions and the character of SRS generation [8];

(3) the dispersion of a medium considerably increases in importance, because the time delay of a pump pulse with respect to the Stokes pulse, which is of the order of 5–50 fs/cm in the region of normal dispersion, may have a substantial effect on the character of interaction in a path along a Raman-active medium [9];

(4) reverse energy exchange between the Stokes waves and the pump wave in a strongly nonstationary regime causes deep amplitude and phase modulation of pump radiation passing through a medium and, consequently, considerably broadens its spectrum [3];

(5) the effect of competitive nonlinear processes, namely, time and spatial phase self-modulation, generation of the spectral continuum, multiphoton processes, and optical breakdown caused by a sharp increase in the threshold power required for SRS excitation, become of greater importance; and

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(6) a strong increase in light field intensity (for both pumping and SRS) may affect the construction of electronic shells of molecules and cause changes in frequencies and transition probabilities of corresponding optical transitions [10].

In view of the fact that theoretical concepts describing the totality of processes taking place in the case of SRS excitation with pulses of such duration have not been developed up until now, experimental studies in this field are of crucial importance. The aim of our work is to study the spectral and time structures of vibrational, rotational, and vibrational–rotational components of SRS excited in high-pressure hydrogen with femtosecond light pulses and optimize conditions of excitation of various components in order to obtain pulses with the desired spectral, time, and energy properties.

EXPERIMENTAL

The schematic diagram of an optical set-up used for excitation of SRS and measurement of its parameters is presented in Fig. 1. It used a laser operating on sapphire crystals activated with titanium ions (Clark-MXR SPA-1 model). The laser operated at a pulse repetition rate of 1 kHz and produced pulses with a duration of $\Delta t = 200$ fs at the wavelength $\lambda = 780$ nm. Single pulses had an energy of up to 0.6 mJ. The frequency of output laser radiation was doubled in a KDP crystal 2.5 mm thick, and the conversion efficiency reached 30%. The second-harmonic pulses were found to have a duration of $\Delta t = 400$ fs [11]. The diameter and the angular divergence of the output laser beam at $\lambda = 390$ nm were equal to 5 mm and 0.001 rad, respectively. The laser radiation had nearly the same spectral widths at half-maximum (FWHM) at the fundamental and double frequencies. It ranged from 70 to 80 cm^{-1} ($\Delta f = 2.1$–2.4 THz). As for the fundamental frequency, this spectral width corresponds to nearly bandwidth-limited pulses, provided their envelope has the form $\mathrm{sech}^2(\Delta f \Delta t = 0.4)$. From this, it follows that the second-harmonic pulses are phase-modulated, because they are not bandwidth-limited ($\Delta f \Delta t = 0.8$).

A filter F placed behind the KDP crystal rejected radiation at the fundamental frequency. Quarter-wave plates were used to change the polarization of radiation from the linear to the circular one for both the fundamental wave and the wave of the second harmonic. A lens L_1 focused a pump beam to the center of a cell filled with hydrogen at a pressure from 10 to 70 atm. The cell had a length of 30 or 100 cm, and the focal length f of the lens L_1 ranged from 25 to 200 cm. A lens L_2 collimated the beam emerging from the cell. The output beam was split, and a portion of radiation was directed to units measuring the power, spectrum, and pulse duration.

RESULTS AND DISCUSSION

In our experiments, the SRS threshold was almost independent of the focusing conditions and the state of

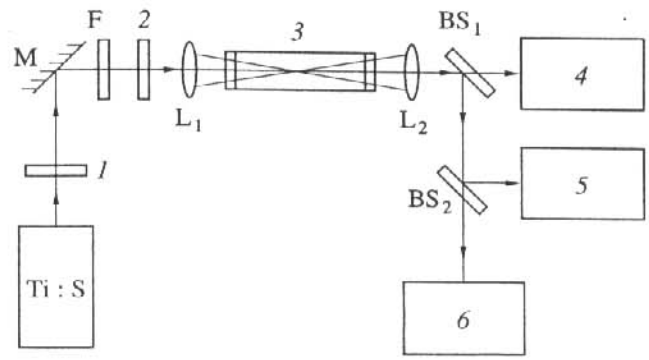

Fig. 1. Schematic diagram of the experimental set-up: (Ti : S) femtosecond laser system on the basis of the sapphire : Ti laser, (*1*) frequency doubler, (M) turning mirror, (F) filter separating the second-harmonic radiation, (*2*) quarter-wave plate, (L_1) focusing lens, (*3*) cell filled with high-pressure hydrogen, (L_2) collimating lens, (BS_1) and (BS_2) beam splitters, (*4*) system for measuring correlation functions of optical pulses, (*5*) power meter, and (*6*) spectrograph.

pump polarization and was about 20 μJ. The maximum efficiency of energy conversion to the first vibrational Stokes component at a wavelength of 465 nm reached 15% and was obtained in experiments with a 100-cm lens L_1, a hydrogen pressure of 40 atm, and excitation with second-harmonic pulses with an energy of 100–150 μJ. Under the same conditions, the efficiency of conversion to the second Stokes component (577 nm) was equal to 10%, and the main portion of SRS energy was concentrated in cone-shaped radiation. As the gas pressure was increased to 70 atm, the energy of axial radiation for the second Stokes component became equal to the energy of cone-shaped radiation, and the total conversion efficiency for this component reached 15%. Under these conditions, the efficiency of conversion to the first and second anti-Stokes components did not exceed 3%.

It should be noted that, in addition to the SRS components, one can see in the spectrum a weak extended background associated with the generation of the spectral continuum. According to the data [12], the generation of the spectral continuum is accompanied by a substantial spectral broadening of pump radiation at the output of the medium (Rayleigh component). In our experiments with linearly polarized pump radiation and a change in excitation geometry, which was provided by a change from focusing with a lens of 100 cm into a cell 100 cm long to focusing with a lens of 25 cm into a cell 30 cm long, the SRS threshold being exceeded by a factor of two to three, we observed an increase in Rayleigh component width as well, from 100 to 250 cm^{-1}. Figure 2a presents the initial spectrum of pump radiation and the spectrum of the Rayleigh component in the case of SRS excitation with linearly polarized radiation

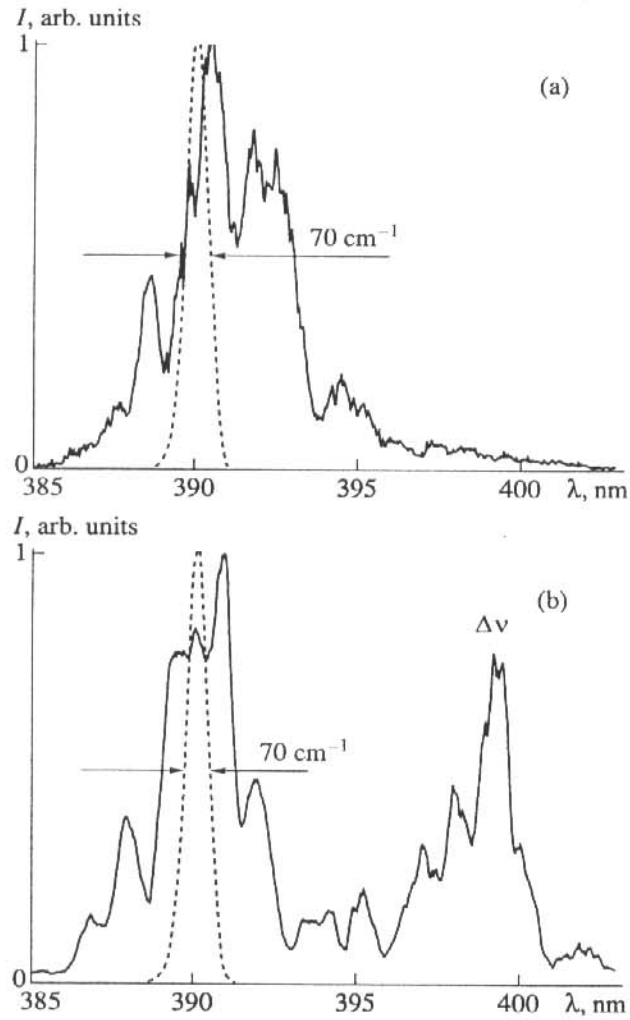

Fig. 2. Spectra of pump radiation at the output of the cell with high-pressure hydrogen for the SRS excitation with (a, solid line) linearly polarized radiation and (b, solid line) circularly polarized radiation; (a and b, dashed lines) initial spectrum of pump radiation.

of the second harmonic focused into a cell 30 cm long with a lens of 25 cm.

A change to a circularly polarized pump beam produced a strong rotational Stokes component shifted by $\Delta\nu = 590$ cm^{-1} and corresponding to the transition between the rotational sublevels with $J = 1$ and $J = 3$ ($\Delta\nu = 587$ cm^{-1}). The corresponding spectrum is illustrated in Fig. 2b. The peak spectral intensity of this component reached 70% of the maximum spectral intensity of the Rayleigh component, and its spectral half-width was equal to 100–150 cm^{-1}, independent of the focusing conditions.

The spectral half-width of the first Stokes vibrational component (Fig. 3a) changed with the focal length f as well and reached 200 cm^{-1} for the lens with $f = 25$ cm. In the case of soft focusing with a lens of 100 cm, the spectral half-width of the line was close to the spectral half-width of the input pump radiation. A change of pump radiation to circularly polarized radiation caused a sharp increase in the spectral intensity of the vibrational–rotational component shifted by the frequency $\Delta\nu$. Its intensity reached 70% of the spectral intensity of the vibrational component. In this case, the spectral half-width $\Delta\nu$ of the vibrational–rotational component ranged from 100 to 150 cm^{-1} and was virtually independent of focusing.

In experiments where the polarization of pump radiation was changed to the circular one, high-intensity Stokes and anti-Stokes vibrational–rotational components emerged close to the wavelength of the second vibrational Stokes component ($\lambda = 577$ nm, Fig. 3b). They were shifted by $\Delta\nu$ with respect to the frequency of the second vibrational Stokes component, and their spectral intensity was virtually equal to the intensity of the purely vibrational component (Fig. 3b). The Stokes and anti-Stokes vibrational–rotational components had a spectral width of 100–130 cm^{-1} that was independent of the focusing conditions.

A stronger increase in the intensity of vibrational–rotational components $\Delta\nu$ was observed for the first two vibrational anti-Stokes components ($\lambda_1 = 336$ nm and $\lambda_2 = 294$ nm) shown in Figs. 4a and 4b. One can see that in the case of a change to SRS excitation with circularly polarized radiation, the spectral intensity of Stokes vibrational–rotational components shifted by $\Delta\nu$ considerably exceeds the intensity of purely vibrational components, which was not previously observed in experiments with nano- and picosecond pump pulses [13, 14].

In addition to the study of the spectrum and intensity, we measured the duration of radiation pulses for a number of SRS components excited in the cell filled with hydrogen at a pressure of 40 atm for $f = 100$ cm. The autocorrelation function for radiation pulses of the first and second Stokes vibrational components was measured using noncollinear second-harmonic generation in a BBO crystal of 1-mm thickness (phase synchronism of type I). Figure 5a illustrates an example of the autocorrelation function for one of the shortest radiation pulses of the first vibrational Stokes components observed in the experiments. This pulse had a duration of 130 fs, i.e., it was approximately three times shorter than the pump pulse. The pulse durations of other SRS components (both rotational and vibrational components) were comparable to the pump pulse duration and ranged from 300 to 400 fs. In particular, Fig. 5b presents the autocorrelation function for radiation pulses of the second vibrational Stokes component. It corresponds to a pulse duration of 300 fs.

It was a surprise that in our experiments we did not manage to obtain efficient excitation of SRS with pump radiation at the fundamental frequency (780 nm). In these experiments, we used pump pulses with an energy of up to 400 μJ, focusing with $f = 25$–100 cm, and hydrogen pressures of up to 70 atm. In this domain of parameters, the efficiency of conversion to the first

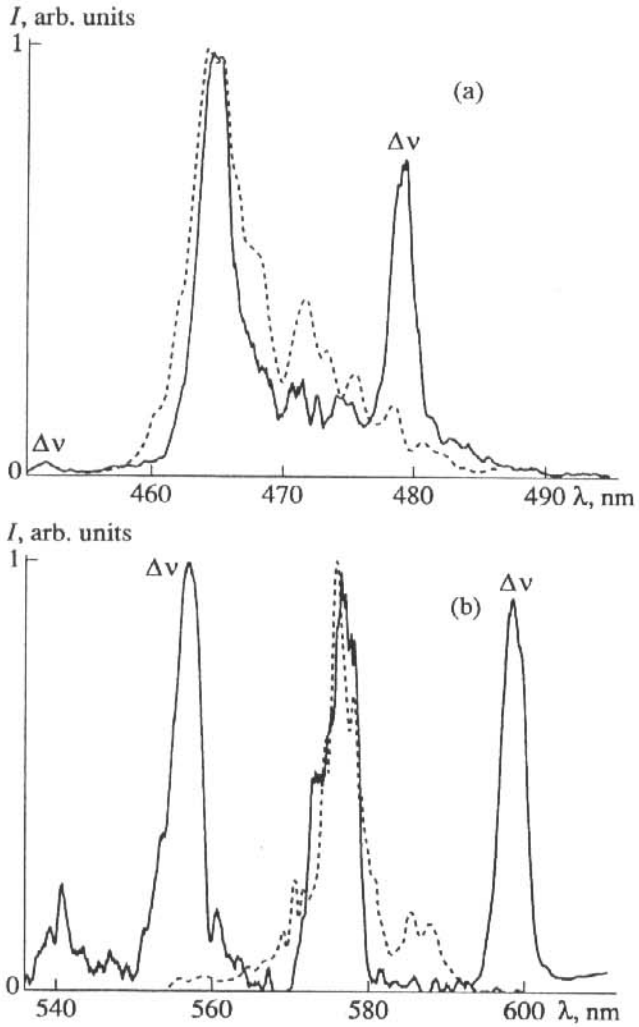

Fig. 3. Spectra of (a) the first and (b) second Stokes components of SRS excited in high-pressure hydrogen with femtosecond pulses of (dashed lines) linearly polarized and (solid lines) circularly polarized radiation.

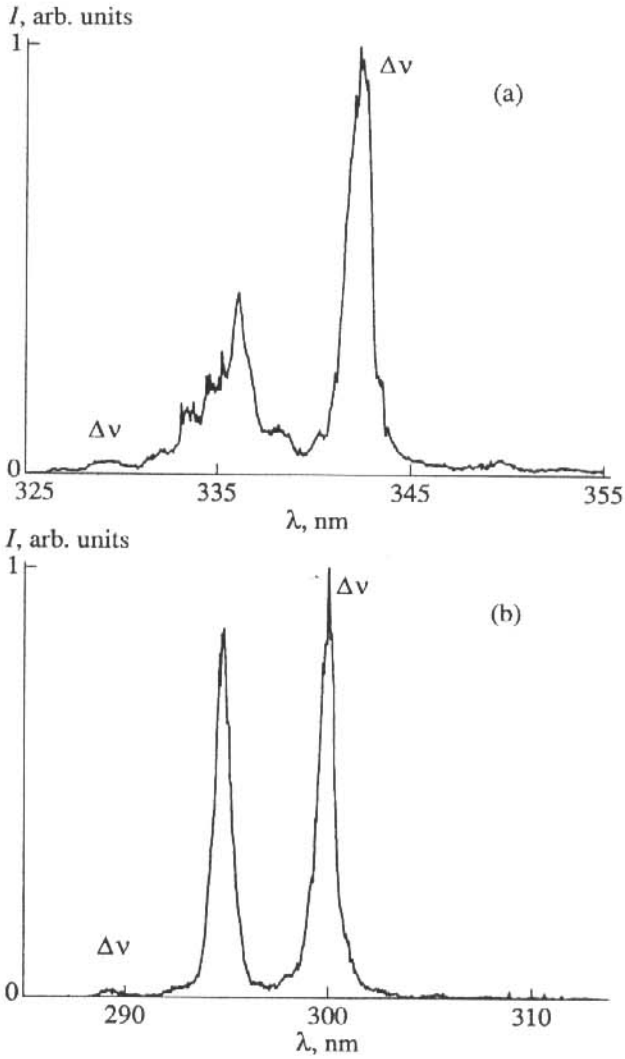

Fig. 4. Spectra of (a) the first and (b) second anti-Stokes components of SRS excited in high-pressure hydrogen with femtosecond pulses of circularly polarized radiation.

Stokes component ($\lambda = 1.154$ μm) did not exceed 1.5%. Because of the insufficiently high sensitivity of our spectral instruments in the IR spectral region, spectral measurements were performed only for the Rayleigh and anti-Stokes components for a hydrogen pressure of 40 atm and focusing with a lens of 10 cm. Spectral broadening observed in this case for the vibrational anti-Stokes component was considerable (up to 200 cm^{-1}) with respect to spectral broadening of the output pump radiation. However, these results do not give a clear understanding of the reasons responsible for such a low SRS efficiency in the case of pumping with IR radiation. It is likely that one of the possible reasons is the effect of competitive processes because of a substantial increase in SRS threshold. The main possibility is the generation of the spectral continuum, whose excitatio threshold is close to the SRS threshold.

The complexity of processes taking place in th medium and the absence of a consistent theory describ ing spectra of a strongly nonstationary SRS and takin into account competitive nonlinear phenomena ham pers a detailed analysis of the spectral structur observed in the experiments. Because of this, we giv only a brief discussion of those features of the SR spectra that were not observed previously in experi ments with pump pulses of larger duration. Amon these are the following features:

(i) multifold broadening of the spectrum of the out put pump radiation,

(ii) the spectral continuum generated in addition t SRS, and

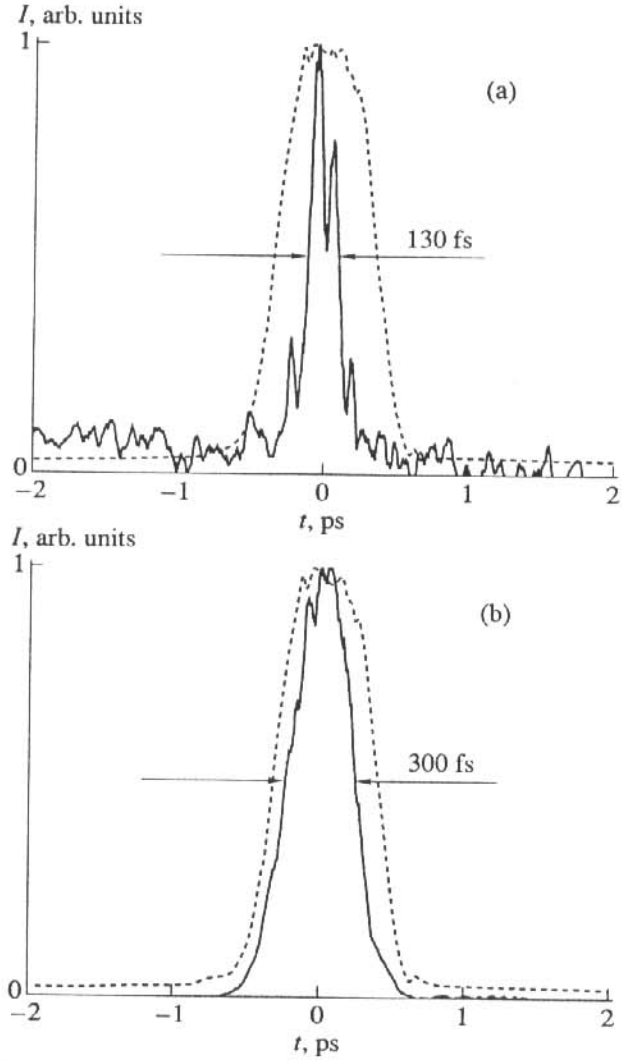

Fig. 5. (Solid lines) Autocorrelation functions of radiation pulses for (a) the first and (b) second vibrational components of SRS in high-pressure hydrogen; (a and b, dashed lines) cross-correlation function for pump pulses.

(iii) a considerable increase in intensity of rotational and vibrational–rotational components with respect to purely vibrational components.

Strong broadening of the spectrum of the output pump radiation (up to 250 cm^{-1}) may be attributed to the combined action of several processes, including the generation of spectral continuum [12]; the nonstationary reverse energy transfer from the Stokes wave to the pump wave producing a deep phase and amplitude modulation of the latter [3]; and the self-phase modulation of the pump beam, caused by the effect of the electronic component of the nonlinear refractive index [7].

The aforementioned excess of the intensity of vibrational–rotational components over the intensity of purely vibrational components (especially for vibrational anti-Stokes components), which was not observed previously for pumping with nano- and picosecond pulses [13, 14], may be attributed to the fact that these components are excited through four-wave mixing. In this case, their gain increment is independent of the excitation spectrum width, whereas the increment of purely rotational components is inversely proportional to the spectral width of pump radiation. This gives a qualitative description of the latter components in experiments with femtosecond pump pulses [15].

It seems impossible to make a consistent and detailed analysis of the totality of experimental data on the basis of the currently available theoretical works. This is caused by the fact that they do not take into consideration the group velocity dispersion, the parametric generation of axial and cone-shaped radiation for nonstationary SRS, the self-phase modulation, and other processes responsible for the excitation of spectral continuum. A further development of the theory, taking into account these and maybe other nonlinear phenomena, will form the basis for a consistent statement of experiments and the choice of experimental conditions.

CONCLUSIONS

The results of our study of the structure of SRS spectra excited in H_2 with linearly and circularly polarized femtosecond pulses of the second harmonic of a sapphire : Ti laser show a number of new phenomena and features, including the excitation of vibrational–rotational components, whose intensities exceed the intensities of simultaneously excited purely vibrational components, nonlinear broadening of components, and the generation of spectral continuum. The efficiency of power conversion to the first Stokes component reached 40%, and its pulses were compressed in duration by a factor of about three with respect to the pump pulses.

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