Investigation of stimulated electron Raman scattering of light by magnetic sublevels of potassium atoms

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Stimulated electron Raman scattering (SERS) is investigated experimentally in atomic potassium vapor in an external constant magnetic field. Investigations carried out for circularly polarized exciting radiation have shown that the SERS radiation polarization is reversed in sign relative to the polarization of the exciting radiation. For left-hand circular polarization of the pump radiation, in the presence of an external constant magnetic field H a linear attenuation of the SERS radiation intensity was observed with increasing field intensity H. For right-hand circular polarization of the exciting radiation, the attenuation was accompanied by a strong enhancement of the SERS radiation at definite values of the magnetic field H_1 and $H_2 = 2H_1$. In either case there was no SERS emission line at all in the spectrum in fields $H \gtrsim 35$ kOe at an atom density $N = 2\times 10^{15}$ cm^{-3}. The obtained amplification of the SERS radiation can be used to determine the Stark shift of the sublevels.

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INTRODUCTION

The investigation of multiphoton processes in nonlinear gaseous media has been the subject of a number of papers[1–11] dealing with the polarization characteristics and with the Stark shift of stimulated electron Raman scattering (SERS) of light, with two- and three-photon processes,[4–9] and with measurements of the hyperfine structure of spectra of atoms by using two-photon absorption without Doppler broadening.[10,11]

For a more detailed study of multiphoton processes and for an analysis of polarization effects it is of interest to investigate these processes in a constant magnetic field, when the degeneracy of the atomic levels in the magnetic quantum number is lifted.[12,13] The presence of the magnetic field can lead also to such interesting effects as the lifting of the forbiddenness of dipole-forbidden transitions on account of mixing of various states[14] or imposition of a hindrance on multiphonon processes under certain conditions. We have previously reported[15] observation of the absence of SERS radiation in atomic-potassium vapor in strong magnetic fields. It was indicated that the influence of the magnetic field on the SERS process would be different for different signs of circular polarization of the exciting radiation, depending on whether the Stark and Zeeman shifts of the sublevels have the same or opposite directions.

We present and discuss in this paper the results of an experimental investigation of the SERS process in an external constant magnetic field for the case of circular polarization of the exciting radiation.

EXPERIMENTAL SETUP

The investigations were made with the setup illustrated schematically in Fig. 1. The emission of ruby laser *1*, which was Q-switched with a passive shutter, excited SRS in nitrobenzene *2*, with a first Stokes component frequency $\omega' = 13\,055$ cm^{-1} close to the frequency $\omega' = 13\,043$ cm^{-1} of the atomic transition $4S_{1/2}-4P_{3/2}$ of potassium vapor, with a detuning from resonance $\epsilon = \omega' - \omega_0 = 12$ cm^{-1}. The radiation energy of the SRS Stokes components was measured with calorimeter *4* (the FS-7 filter *3* cut off the ruby-laser radiation). The SRS power density in the unfocused beam reached ~10 MW/cm^2. After passing through polarizer *5* and quarter-wave plate *6*, the circularly polarized resonant radiation was focused into cell *7* with potassium vapor, 20 cm long, placed in a longitudinal magnetic field. The magnet operating in a pulsed mode (pulse duration ~10^{-3} sec) produced a magnetic field up to ~50 kOe intensity. The light was next passed through an analyzer consisting of a quarter-wave plate *8* and an felspar crystal *9*, which separated two mutually perpendicular light-polarization components. The direction of one of the crystal polarization coincided with the direction of the polarization separated by the polarizer *6*. The spectrum of the emission of these two polarization components was registered simultaneously by STÉ-1 spectrograph 10 with dispersion 20.5 cm^{-1}/mm in the investigated region. The potassium-vapor temperature was varied from 250 to 350°C, corresponding to an atom density $N = 10^{15} - 10^{16}$ cm^{-3}. The synchronization of the pulses of the transimitted radiation and of the magnetic field, as well as the generation of the giant ruby-laser pulse, were monitored with an oscilloscope.

RESULTS AND DISCUSSION

For the case of circular polarization of the exciting radiation, we obtained the following results:

1. The experiments have shown that the polarization

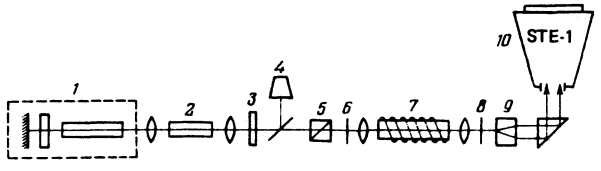

FIG. 1. Experimental setup: *1*—ruby laser, *2*—cell with nitrobenzene, *3*—FS-7 filter, *4*—calorimeter, *5*—polarizer, *6*, *8*—quarter-wave plates, *7*—cell filled with potassium vapor and placed in a magnetic field, *9*—felspar crystal, *10*—STÉ-1 spectrograph.

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of the SERS radiation connected with the $4P_{3/2}-4P_{1/2}$ transition has a sign opposite that of the exciting-radiation polarization.[15]

2. The investigation of the SERS process in the presence of an external constant magnetic field yielded different results for left- and right-hand circular polarizations of the exciting radiation.

For left-circular polarization of the pump, we observed a nonlinear attenuation of the SERS radiation intensity with increasing magnetic field intensity (Fig. 2a).

For right-circular polarization, the attenuation is excited by a sharp increase of the SERS radiation at definite values of the magnetic field (Fig. 2b). In this figure the gain corresponds to fields $H_1 \approx 8$ kOe and $H_2 \approx 16$ kOe. The intensity peak corresponding to the stronger field H_2 is approximately 2.5 times larger than the peak for the field H_1. With increasing (decreasing) intensity of the exciting radiation the intensity peaks were observed respectively at larger (smaller) values of the magnetic fields. The relation $H_2 = 2H_1$ was maintained constant, however.

At either sign of the circular polarization of the exciting pulse, there was no SERS radiation at all in the recorded spectrum at magnetic fields $H \sim 35$ kOe (the Zeeman spacing between the magnetic sublevels of the $4P_{3/2}$ level is $\delta\omega_z \approx 2.5$ cm^{-1}) at an atom density $N = 2 \times 10^{15}$ cm^{-2}.

It must be pointed out that in a magnetic field the SERS radiation frequency is shifted by the Zeeman splitting. The maximum measured Zeeman shift of the SERS radiation for left- and right-hand circular polarization of the exciting radiation was ≈ 2 cm^{-1} at $H \approx 30$ kOe, towards higher and lower frequencies, respectively.

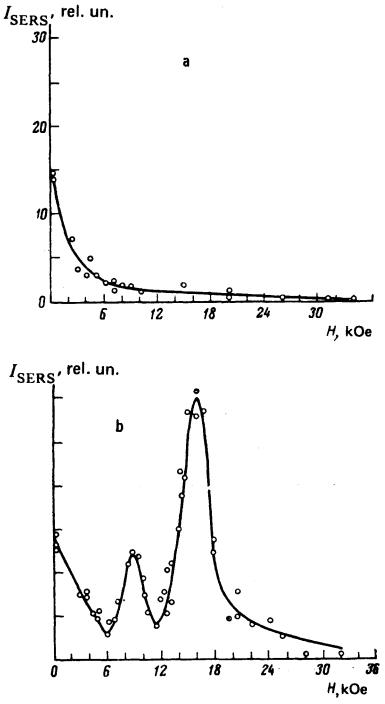

FIG. 2. Intensity of SERS radiation intensity vs. magnetic field intensity H at atom densities $N = 2 \times 10^{15}$ cm^{-3} and at a constant intensity of the input radiation: (a) left-hand circular polarization of the exciting radiation, (b) right-hand circular polarization of exciting radiation.

3. The investigation of the dependence of the SERS radiation intensity on the density N of the atoms (Fig. 3) shows that initially the SERS intensity increases quadratically with N, reaches a maximum, and then decreases at intensities $N > 10^{16}$ cm^{-3}. The curves were plotted for the case of left-hand circular polarization of the exciting radiation in the absence of a magnetic field ($H = 0$) and in a field $H \approx 15$ kOe. The intensity peak at $H \approx 15$ kOe is shifted relative to the peak at $H = 0$ towards larger N.

The results can be explained by taking into consideration the processes of population transfer between the magnetic sublevels of the atom and the influence exerted on them by the external constant magnetic field.

When intense resonant radiation interacts with potassium vapor, the $4P_{3/2}$ level can be substantially populated both via the three-photon process[8] and via one-photon absorption, provided that the line of the exciting radiation is broad enough.[3] The repopulation of the $4P_{3/2}$ level relative to $4P_{1/2}$ leads to SERS with frequency $\omega' + \Delta$, where $\Delta = \hbar^{-1}[E(4P_{3/2}) - E(4P_{1/2})]$. We consider the possible schemes of the SERS process for cases of right- and left-hand circular polarization of the exciting radiation (Fig. 4).

If the exciting radiation has right circular polarization, then the sublevels $m = +1/2$ and $m = +3/2$ of the $4P_{3/2}$ level are populated. Since the detuning from resonance $\epsilon = \omega' - \omega_0$ is positive, the bound levels come closer together as a result of the high-frequency Stark effect.[16,17] According to the selection rule with respect to the magnetic quantum number m, the SERS process can proceed from the levels $m = +1/2$ and $m = -3/2$ (Fig. 4a). The relative probabilities of these processes are 1 and 3, respectively[18], with the SERS from the sublevels $m = +1/2$ and $m = -3/2$ having right-hand and left-hand circular polarization, respectively. As already indicated, the SERS emission line registered in the experiment has a polarization that is the reverse of the polarization of the exciting radiation. It follows therefore that the SERS radiation goes from the $m = -3/2$ level, which is not directly populated by the exciting radiation. It can be assumed that the population of this sublevel is due to relaxations from the populated sublevels $m = +1/2$ and $m = +3/2$, relaxations due to the resonant collisions of the potassium atoms. These relaxa-

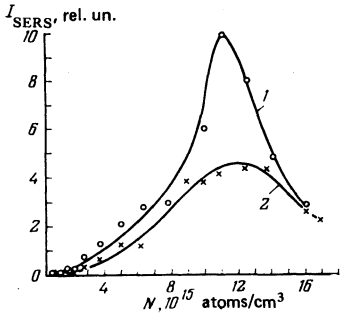

FIG. 3. Dependence of the SERS radiation intensity on the atom density N for left-hand circular polarization of the exciting radiation: curve 1—for $H = 0$, curve 2—for $H = 15$ kOe.

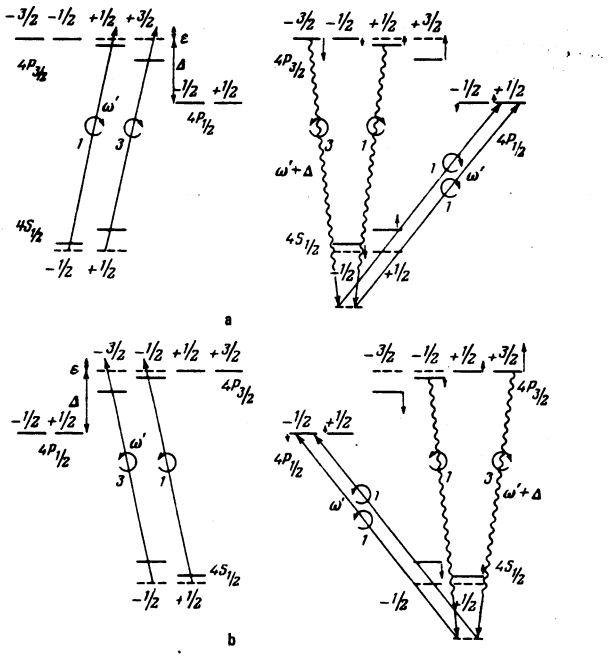

FIG. 4. Schemes of the SERS process for exciting radiation with right (a) and left (b) circular polarization. The vertical arrows indicate the directions of the sublevel shift when the magnetic field is turned on. The diagrams show also the polarizations and the relative probabilities of the transitions.

tions are described by a dipole-dipole interaction with transfer of excitation from atom to atom, wherein one of the interacting atoms is excited and the other is in the ground state. It appears that the population takes place effectively at the start and at the end of the exciting pulse, when the Stark shift is small and the magnetic sublevels are close in energy. Calculations show[19] that the time of these relaxations is $\tau \sim 10^{-9}$ sec at an atom density $N \approx 2 \times 10^{15}$ cm^{-3}. When the external constant magnetic field is turned on, the energy levels are split by the Zeeman effect. In the general case, the condition for effective population transfer between the magnetic sublevels is violated, and this should attenuate the SERS radiation. At the considered case of right-hand circular polarization of the pump, however, and at the sign of the detuning from resonance, the joint action of the Stark and Zeeman shifts can lead to realization of the resonance conditions in the collisions between the atoms and to effective population transfer between the sublevels $m = +1/2 \rightarrow m = -3/2$ and $m = +3/2 \rightarrow m = -3/2$ if the relations $\delta\omega^{st}_{m=3/2} = 2/3\mu_B H_2$ and $2\delta\omega^{st}_{m=3/2} - \delta\omega^{st}_{m=1/2} = 2\mu_B H_1$ are satisfied.[19] At these values of the magnetic field, amplification of the SERS radiation is observed. Since the probabilities of the transitions with $\Delta m = 0$ and $\Delta m = \pm 1$ between the levels $4S_{1/2}$ and $4S_{3/2}$ are different, the heights of the peaks on the plot (Fig. 2b) should be different. The difference observed in the experiment is by a factor 2.5. We note that since $\delta\omega^{st}_{m=3/2} = 3\delta\omega^{st}_{m=1/2}$ it follows that $H_2 \approx 2H_1$. It is also clear from the foregoing reasoning that when the pump intensity is increased (decreased), and with it also the size of the Stark shift, the conditions for effective population transfer and enhancement of the SERS radiation will be satisfied at larger (smaller) values of the magnetic field, in accord with the experimental results. In sufficiently strong magnetic fields, when there is practically no population transfer between magnetic sublevels, there will likewise be no SERS radiation.

We can consider in similar fashion the case of left-hand circular polarization of the pump radiation (Fig. 4b). But since the joint action of the Stark and Zeeman effects does not lead to resonance in this case, turning on the magnetic field leads only to a decrease of the population transfer between the sublevels and to attenuation of the SERS for all values of the field H (Fig. 2a).

The plots of the SERS radiation against the atom density N, shown in Fig. 3, demonstrate that competing processes participate in the mechanism that causes the SERS. The increase of the SERS intensity, which is quadratic in N, corresponds to a collision mechanism of population transfer between the magnetic sublevels of the given level. The decrease of the SERS radiation intensity with increasing density N is apparently connected with the enhancement of the competing processes, namely the collisions that do not lead to the initial-sublevel population needed for the SERS.

It follows from the resonance conditions cited above that from the position of the gain peaks on the plot of Fig. 2b and from a knowledge of the fields H_1 and H_2 we can determine the Stark shift of the sublevels. Since the positions of the gain peaks are determined with accuracy $\Delta H = 500$ Oe, the accuracy with which the Stark shift is determined is 0.05 cm^{-1}. Measurements made by the described method yielded, for the conditions of the present experiment, the following results: the Stark shift for the sublevels $m = +1/2$ and $m = +3/2$ of the $4P_{3/2}$ levels amount to $\delta\omega^{st}_{m=1/2} = 0.2 \pm 0.05$ cm^{-1} and $\delta\omega^{st}_{m=3/2} = 0.6 \pm 0.05$ cm^{-1}. The corresponding density of the radiation power inside the cell with the potassium vapor is of the order of 30 MW/cm^2.

The method employed in the present experiment is a convenient one for the study of the high-frequency Stark effect in similar experiments. This method does not call for the use of high-resolution spectral instruments. Moreover, since the accuracy ΔH with which the positions of the gain peaks are obtained can be improved, the resolution of this method can also be appreciably improved.

We point out in conclusion that an analogous effect, the absence of SERS in the spectrum in a longitudinal magnetic field, was observed also for the case of linear polarization of the exciting radiation. In this case the investigation of the effect is made somewhat more difficult by the presence also of Faraday rotation at the SERS radiation frequency.

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Theory of x-ray absorption spectra of central atoms in high-symmetry molecules and complexes

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On the basis of the reflection-matrix concept introduced by the authors earlier, the formation of near-threshold singularities in x-ray absorption spectra are investigated. The conditions for the onset of resonances in a many-center potential are determined. Formulas are derived for the energies and intensities of the lines of the Rydberg-series when a molecular state is superimposed on the latter. A criterion for the separation of molecular and Rydberg levels is proposed. For the SF_6 molecule, the matrix of reflection from the fluorine octahedron and the x-ray absorption spectra of sulfur are calculated. The results are compared with experiment.

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INTRODUCTION

X-ray absorption spectra (XAS), as is well known, make it possible to obtain important information on the structure of matter. The far fine structure of the spectra makes it possible to determine the coordination number, the distances to the nearest atoms, and the amplitudes of the thermal vibrations.[1,2] From the characteristics of the Rydberg series observed before the threshold of the continuous absorption it is possible to establish the charges of the ions and the symmetry of the nearest surrounding.[3] These effects in the XAS are caused mainly by the scattering of the photoelectron in the final state by potentials localized in the region of space adjacent to the absorbing atom. The scattering of an electron wave by surrounding atoms, which is sometimes described by specifying modified boundary conditions for the wave function on the surface of the investigated atom or group of atoms,[4] plays at any rate a very important role in the formation of the local electron density (LED) in matter. Without a detailed investigation of the singularities of this scattering and without revealing the role of the bearest and remote surroundings it is impossible to make serious progress in the understanding of the electron structure of defects in crystals, amorphous bodies, or liquids.

A number of authors have shown[5-8] that calculations of the XAS intensities by the method of multiple scattering in the $\chi-\alpha$ approximation[9] gives results that are in satisfactory agreement with experiment. There is no doubt now that this method makes it possible to describe quantitatively both the far and the near fine structure of the XAS. The calculations, however, do not explain qualitatively the causes of the singularities in the spectra and cannot separate the role of the potentials of the nearest surroundings and of the atom to which the x-ray transition takes place.

In this paper, using a new procedure recently proposed by us[10,11] to describe the influence of the surrounding potentials on the LED and on the XAS intensity, we carry out a systematic analysis of the role of the nearest surrounding in the formation of the local electron structure. We investigate the XAS and LED of central atoms of high-symmetry close-packed molecules, complexes, and clusters, and pay principal attention to the formation of the fine structure at the absorption edge. We consider the laws governing the onset of resonances in a many-center potential and of the theory of the Rydberg series in the presence of

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