# PROPAGATION OF BIMHARMONIC LASER RADIATION RESONANT TO SPIN FREQUENCIES TROUGH THE ATMOSPHERIC AND INERT GASES. PART. 1

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*This paper presents a description of experiments on scattering of a resonant biharmonic radiation by atmospheric and inert gases. Experimentally recorded angular–frequency spectrum of Raman light scattering by magnon polaritons is presented in the paper. This spectrogram enabled the determination of frequencies and wave vectors of the magnon polaritons involved in the light scattering process. It is shown in the experiments that signals do not change under variation of pressure inside the measurement cell from* $10^{-4}$ to 760 mm *of mercury column. Some results on the role of oxygen in the process under study are also presented in the paper.*

## 1. INTRODUCTION

As known[1] use of techniques of active Raman spectroscopy (ARS) in gas analysis enables an essential increase in signals compared to the schemes based on spontaneous Raman light scattering. However, use of ARS methods in remote sensing of the atmosphere is limited by atmospheric paths only tens of meters long, because of impossibility of maintaining phase synchronism between biharmonic components of sounding radiation propagating collinearly on longer paths. Since the length of coherent interaction is determined by the ratio $l_{coh} = \pi/\Delta\kappa$, where $\Delta\kappa$ is the phase mismatch between the components of a biharmonic radiation, one should decrease the value of $\Delta\kappa$, i.e. the frequency difference of the biharmonic, in order to increase $l_{coh}$. This paper describes a possibility of doing this with a biharmonic radiation whose difference frequency is resonant to spin frequencies of paramagnetic atmospheric gases, being, in the experiments described, about 500 MHz what is three orders of magnitude lower than those used earlier in atmospheric experiments using ARS methods.

## 2. EXPERIMENT

Our experiments have been carried out on a specially designed setup, which uses difference technique of measurement enabling one to achieve 1 per cent measurement accuracy.[2] The spectrum of biharmonic radiation scattering on elementary excitations of a medium connected with the motion of nuclei and electrons is first photographed on a highly sensitive film and then it is handled with a photoelectric technique. The difference scheme of measurements is arranged as follows. A beam of biharmonic radiation from a laser is split with a beam divider into two beams. One of these beams enters working chamber, passes through it, and then after passing through a modulator it is directed with an objective onto the entrance slit of a spectral device. The other beam, which is used as a reference one, passes a known path in air and after all reflections on semitransparent mirrors and beam folding mirrors it is also directed with an objective onto the entrance slit of this same spectral device where it is mixed with the beam coming from the working chamber. The modulator rotates at a fixed angular speed and alternatively directs laser beams either from the working chamber or from the reference arm of the optical setup to the entrance slit of the spectral device. Optical signals passed through the mirror objective, a disperse element, and an output mirror of the spectral device enter optical fibber waveguides through which they come to PMTs. Electric signals from the PMTs are then processed in the block of recording electronics, where they are stored and their amplitudes are compared. The difference signal is amplified and recorded with an oscilloscope.

The amplitude of the difference signal varies with variations in density and chemical composition of a gas mixture in the working chamber. The results of data processing enables obtaining information on the dependence of the scattering process cross section on the parameters of a gas medium inside the chamber.

Illumination of the entrance slit of a spectral device is performed in the same way for both photographic and photoelectric recording. In so doing, the entrance slit of a spectrometer is accurately placed in the focal plane of a receiving objective whose optical axis coincides with the optical axis of a laser beam. In such an optical arrangement the radiation scattered exactly forward is collected at the center of the entrance slit,[3] while the radiation scattered at certain angles with respect to the forward direction is collected with the receiving objective at the portions of the entrance slit below and above its center. For the source of biharmonic radiation we use a He–Ne laser with a 30 cm long cavity. To suppress transverse modes of higher orders we use diaphragms installed both inside and outside the laser cavity. The working chamber in our experiments is a 170 cm long quartz tube 5 cm in diameter. Normally, it is filled with air at room temperature. The pressure inside the chamber can be varied from 760 down to $10^{-4}$ mm of mercury column. The spectrum of output laser radiation is analyzed with a Fabry and Perot etalon IT–51. The spacing ring of 3 cm height used in the etalon provides for spectral resolution $\Delta\lambda = 0.002$ Å, which is quite sufficient to separate the laser emission lines used in the experiments. Special measures have been undertaken during the experiments to provide temperature stability better than 0.25°C necessary for a proper operation of the interferometer.

To measure pressure inside the working chamber we used a vacuum gauge of the precision class 1 (for pressure range from 760 down to 1 mm of mercury column), and an ionization thermocouple vacuum gauge VIT–2 with a manometric thermocouple converter PMI–2 (for pressure range from 1 to $10^{-2}$ mm of mercury column) and an

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ionization converter PMI–2 (for pressure range from $10^{-2}$ to $10^{-5}$ mm of mercury column). In our experiments we have use optical waveguides 3 mm in diameter what enables us to reliably intercept central zone of the spectrum under study, which involves five spectral lines. The measurements have been done both in the Stokes and anti–Stokes portions of the spectrum of scattered radiation, at the distance about 7 cm from the position of the laser emission spectral line, what makes about 500 Å on the wavelength scale. Spectral width of a spectrum portion recorded is 10 Å. In order to suppress background noise from extraneous light in the spectrometer we use special light traps. In our experiments we have recorded electric signals at the output of a measuring circuit as a function of gas density and gas composition inside the working chamber. The signals have been recorded with a microammeter M–1400 which measured the electric current at the output of a differentiator amplifier. The microammeter scale has ±50 divisions. This microammeter has a magnetoelectric sensitive element with the damping time constant of 4 seconds. Use of this device as an integrating element enables smoothing of high–frequency noise fluctuations of the signal and thus enhancing the measurement accuracy. Since experiments required long measurement time for making multiple measurements we have carefully checked the drift in zero position of the M–1400 microammeter pointer. Normally the drift didn't exceed, in our experiments, one division of a scale during several hours of continuous work. One scale division corresponds to 50 mV voltage at the input load of the microammeter. After correction for the off–duty factor of a signal and for amplification factors this makes only 15 mV variation in the input signal. The signals coming from the reference and working arms of the optical arrangement have been additionally recorded with an oscilloscope S1–91. This signals were 320 and 640 mV from the reference and working arms, respectively. At the input of the differentiator amplifier these signals were equalized both electrically using potentiometers and optically using filters.

The experimentally recorded spectrograms are then processed using a microscope MMI–2, which provides accuracy of linear and angular measurements better than ±3 μm and ±1 min. of an arc, respectively.

### 3. EXPERIMENTAL RESULTS

1. Within the wavelength range from 200 to 850 nm we have observed a spectrum of radiation scattered by atmospheric gases due to the interaction with a laser biharmonic radiation that is resonant with the spin frequencies of gas molecules. A typical spectrogram illustrating this result is shown in Fig. 1. One can see nine distinct horizontal lines symmetrical with respect to the central line, being the brightest among them.


*FIG. 1. Frequency–angular spectrum of light scattered by magnon polaritons in the atmosphere due to Raman scattering process.*

Positions of these lines with respect to each other and to the optical axis of the instrument are characterized by the following linear and angular dimensions. The lower and the upper lines with the numbers ±4 are 3.2 mm far from the central line (numbered by 0) in the spectrogram. Taking into account the absence of magnification in this optical arrangement (magnification factor equals one) and the focal length of the collimator of 1 m one readily obtains the value $3.2 \cdot 10^{-3}$ rad for the angle at which these lines are observed from the center of the entrance slit relative to the direction of exciting radiation propagation. The lines with numbers ±1 are spaced from the central line by 0.35 mm what yields the observation angle of $3.5 \cdot 10^{-4}$ rad. Corresponding values from lines with numbers ±2 and ±3 are ±0.7 and ±1.8 mm for linear spacing from the central one and $\pm 0.7 \cdot 10^{-3}$ rad and $\pm 1.8 \cdot 10^{-3}$ rad for angles at which they are observed from the entrance slit center. Corresponding wave numbers and resonance frequencies calculated from these values of observation angles for the lines recorded on spectrograms are ±1, ±35, ±70, ±180, ±320 (for wave numbers, $\kappa_{res}$, in $cm^{-1}$) and 0.016, 5.6, 11.1, 28.7, and 50.95 (for frequencies $\nu = \kappa_{res}/2\pi$, in $cm^{-1}$). The central, most bright line, is 0.05 mm thick, what coincides accurate to 5 μm with the size of focal spot on the entrance slit. Thicknesses of other lines are from 0.1 to 0.25 mm, as measured on the spectrogram. Taking into account the above discussion one can assume that such values of the observed lines thicknesses are the result of unresolved fine structures of the lines. The difference in observation angles for the unresolved

lines is about $10^{-6}$ rad. The angular size of all the spectral lines observed varies from $10^{-6}$ to $3.2 \cdot 10^{-3}$ rad.

As to the brightness of the lines we would like to note the following circumstances. The line–to–line variation of the brightness is insignificant, with the central line being the brightest one. The brightness of the rest eight lines is practically the same.

2. We have found in our experiments the threshold strength of the electric field of light at focus of the receiving objective at which the spectrum could still be recorded on a film. Its value is about 0.1 V/cm what corresponds to photon flux density of $10^{19}$ cm$^{-2}$ s$^{-1}$.

3. When studying the dependence of scattered light intensity on density and chemical composition of a gas mixture inside the working chamber we have observed that the amplitude of the electric signal recorded from the working arm of the optical setup keeps constant within the possible zero drift of the measuring device under the variation of pressure inside the chamber from 760 to $10^{-4}$ mm of mercury column. In other words the amplitude of the initial electric signal of 640 mV has not changed during the whole measurement cycle.

4. In the case when working chamber has been filled with oxygen the pointer of M–1400 microammeter deviates to the right from zero position by one division of the scale. This corresponds to a 15 mV decrease of the signal in the working arm of the optical setup, i.e. from the initial value of 640 mV to 625 mV. After pumping out the oxygen out from the chamber and filling it with air the microammeter pointer takes its initial position at zero division of the scale.

## 4. DISCUSSION

The spectrum shown in Fig. 1 has been recorded using a photographic technique that is normally used in studies of Raman light scattering by polaritons in crystals.[3] Let us consider in more detail the conditions necessary for observing Raman light scattering by polaritons. It should be emphasized first of all that in the medium under study there must exist dipole and Raman active phonons simultaneously (to provide the appearance of polaritons) in order the above process to occur. As known, optical phonons in crystals without a symmetry[3] center have such a property to be both dipole and Raman active. In our case the phonons occurring due to oscillations of the nuclear and electron spin in nitrogen and oxygen molecules can have such a property. As known, the spin values are equal to two for nitrogen molecule and to unity for the electron shell of oxygen molecule. Second, the observations of light scattering by polaritons are only possible at small angles between the direction of scattered light propagation and the direction of the incident beam propagation. The following considerations explain the choice of such a geometry of observations. As known, polaritons appear in crystals as a result of mixing of the transverse oscillations of a crystal lattice with the electromagnetic oscillations, that means that in this case optical phonons interact with photons. Based on the laws of energy and momentum conservation we can write the following expressions for the frequency and angular spectra of the light inelastically scattered by polaritons due to Raman scattering process

$$\omega_l = \omega_s + \omega \; ; \qquad \boldsymbol{\kappa}_l = \boldsymbol{\kappa}_s + \boldsymbol{\kappa} \; , \qquad (1)$$

where $\boldsymbol{\kappa}_l$, $\boldsymbol{\kappa}_s$, $\boldsymbol{\kappa}$, $\omega_l$, $\omega_s$, and $\omega$ are the wave vectors and frequencies of the exciting, *l*, and scattered, *s*, radiation and of a polariton, respectively. From Eq. (1) and Fig. 2 it follows that if we observe scattering at an angle of 90° with respect to the direction of incident radiation, the wave vector of a polariton is on the order of magnitude of the wave vector of the exciting photon, $\boldsymbol{\kappa} \sim \sqrt{2}\boldsymbol{\kappa}_l \cdot 10^5$ cm$^{-1}$. Usually, the frequency of optical phonons observed in ARS, $\omega$, is approximately equal to $10^{13}$ s$^{-1}$, what corresponds to $\kappa_{res} = \omega / c \sqrt{e_\infty}$ of $10^3$ cm$^{-1}$. This value of the wave number is about two orders of magnitude lower than that of scattered radiation observed at 90° scattering angle. It is natural, therefore, that at such large values of the wave vector, $\boldsymbol{\kappa}$, the frequency of a polariton only weakly depends on its magnitude. That means that actually light scattering occurs by phonons, or in other words, the polariton nature of the excitation dispersion is inessential in this region of scattering angles. As a result, one should make observations of scattering at small scattering angles in order to detect light scattering by polaritons that are the excitations of a medium with $\kappa_{res} \sim 10^3$ cm$^{-1}$. The value of scattering angle, $\varphi$ ($\varphi \sim \kappa / \kappa_l$, see in Fig. 2), should be on the order of $10^{-2}$ rad and smaller. In our experiments the scattering angles or angles of observations of light scattering were from $10^{-6}$ to $3.2 \cdot 10^{-3}$, what is well within the range of scattering angles required for observing light scattering by polaritons. In order to interpret the frequency values measured let us consider the mechanism of interaction between the laser biharmonic radiation and the electron shell of nitrogen and oxygen molecules.

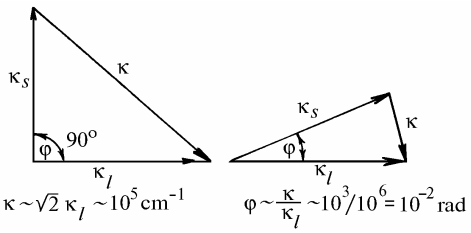


*FIG. 2. The scheme of scattering process illustrating the momentum conservation law in application to selection of the experimental geometry for observations of light scattering by polaritons.*

As was shown in Refs. 4 and 5, the joint action of two laser waves (biharmonic) on a linear medium could appear to be quite efficient if there is an elementary excitation whose frequency coincides with a combined (normally low) frequency of the two waves. The idea of making a biharmonic pump to work as an amplifier is quite simple. The matter is that a field of an optical wave, when interacting with fast electrons of a system, induces a dipole moment, which, in its turn, interacts with the field itself thus causing the appearance of the second–order susceptibility of the medium. Since the incident field is biharmonic there appears the difference frequency in the medium which, if it is in resonance with a natural oscillation of the system it is incident on, can play the role of an amplifier.

Thus, in order to describe interaction of a biharmonic light with a gaseous medium one should know spectra of elementary excitations of a gas and their contributions to the formation of the frequency dependences of the dielectric constant and magnetic permeability. In our experiments the difference frequency of biharmonic is 500 MHz, or 0.016 cm$^{-1}$ ($0.2 \cdot 10^{-5}$ eV) in wave numbers. As a result, the wave vector of the radiation at difference frequency is $\kappa = 2\pi\nu = 0.1$ cm$^{-1}$. The frequencies recorded in the experiments are within the energy range from $2 \cdot 10^{-5}$ to $6.2 \cdot 10^{-3}$ eV, which is characteristic of the interaction between the optical electron

and a nucleus and of the molecular rotations. It is known that such a hyperfine interactions lead to mixing of optical and microwave transitions which results in a fine structure of spectral lines in the optical range.[7,8] Hyperfine interaction makes it possible to orient nuclei[6] when exciting the optical electron of a molecular system with a circularly polarized light (optical pumping). Special emphases should be placed on the circumstance that all the above discussed effects occur because of the interaction of a laser radiation with the electron shell of an atom or a molecule and only the interaction between the electron shell and nuclei makes it possible to influence the processes the nuclei are involved in and/or to obtain information about nuclei characteristics from light scattered by atomic and molecular systems due to various interaction processes, including nonlinear ones. For example, one can polarize (orient) atomic nuclei with a circularly polarized light so that a monochromatic polarized radiation be absorbed exactly by a single component of a hyperfine structure of a transition. Such an interaction between the electron momentum and a nuclear spin results in a distribution of the momentum of a photon absorbed between the electron and the nucleus thus causing the appearance of preferred orientation of nuclei in the ensemble.[6]

Energy of a component of the hyperfine structure with the total angular momentum $F = I + J$, being caused by the interaction between the electron shell and a nucleus, is written as follows[7]

$$W_F = \frac{1}{2} K A + \frac{(3/4) K (K + 1) - I (I + 1) J (J + 1)}{2 I (2 I - 1) J (2 J - 1)} B, \quad (2)$$

where $K = F (F + 1) - I (I + 1) - J (J + 1)$.

As is seen from Eq. (2), this energy depends on the nuclear spin $I$, constant of a magnetic dipole interaction

$$A = \mu_I H_e(0) (J I)^{-1}, \quad (3)$$

and the constant

$$B = e Q_s \frac{\partial^2 \nu(0)}{\partial z^2} = e Q_s \varphi_{IJ}(0) . \quad (4)$$

of the electric quadrupole interaction.

The nuclear constants $\mu_I$ and $Q_s$ can be obtained from measurements of the hyperfine structure of spectral lines since information on $A$ and $B$ values can be obtained from them, or they can be calculated using either empirical or theoretical values of the hyperfine magnetic field $H_e(0)$ and of the electric field gradient, $\varphi_{JI}(0)$, on a nucleus.

Molecular rotation energy is as follows

$$E = B_e J (J + 1), \quad (5)$$

where $B_e$ is the molecular rotational constant (1.989 $cm^{-1}$ for nitrogen and 1.438 $cm^{-1}$ for oxygen).

According to the quantum selection rules for rotational transitions in the Raman scattering process $\Delta J = 0, \pm 2$, we obtain from Eq. (5) the following formula for the transition frequencies:

$$\nu = 4 B_e (J + 3/2), \quad (6)$$

where $J$ is the rotational quantum number of the initial state of the transition.

The frequencies of the Raman rotational transitions $0 \to 2$ ($\nu = 11.9$ $cm^{-1}$), $2 \to 4$ ($\nu = 27.8$ $cm^{-1}$) in molecular nitrogen and the transition $7 \to 9$ ($\nu = 48.9$ $cm^{-1}$) in oxygen, as calculated by formula (6), are most close to the frequencies observed in our experiments.

The differences between these frequencies are about 1 $cm^{-1}$, and the explanation of this fact needs for additional studies.

## CONCLUSION

The results of this study, namely, the high value of the cross section and low threshold of the process of scattering of biharmonic radiation in the medium where it is in resonance with the spin frequencies show good prospects of using ARS techniques for sensing the atmosphere. Of course, only further theoretical and experimental studies would allow a more detailed description of the dynamics of the scattering process to be done.

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