Nutation effect in the molecular gases BCl_3 and SF_6

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The nutation effect was observed in the gases BCl_3 and SF_6 on the absorbing transitions that are at resonance with the $P20$, $P18$, $P16$, and $P12$ emission lines of a CO_2 laser. A new method of observing nutations is developed, and a theoretical analysis of the nutation effect is presented. The dipole moments and the absorption cross sections of these transitions are determined, as is the relative number of particles that take part in the absorption. The influence of degeneracy on the effect is established and conclusions are drawn concerning the types of absorbing transitions.

1. At present there are three known basic effects of coherent interaction of monochromatic radiation with resonantly-absorbing media. They are self-induced transparency, photon echo, and optical nutation. Coherence of an interaction means that the time τ_{int} of the interaction of the field with the medium is much shorter than the relaxation time T_2 of the field-induced polarization of the medium:

$$\tau_{int} \ll T_2. \qquad (1)$$

In the case of self-induced transparency, the interaction time is the duration of the radiation pulse propagating in the resonantly absorbing medium, and in the case of the photon-echo effect it is the time interval between the first exciting pulse and the photon-echo pulse. The characteristic interaction time for the nutation effect is the period of the nutation.

Coherent-interaction effects are of interest because they serve as a convenient tool for the investigation of the characteristics of resonant media. Thus, an investigation of the photon-echo effect makes it possible to measure the homogeneous width of absorbing lines, and also to identify the type of the transitions [1-3]. Self-induced transparency yields an estimate of the transition dipole-moment matrix element and of the homogeneous line width [4-6]. The nutation effect makes it possible to measure the matrix element of the dipole moment of a resonant transition.

The present paper is devoted to the nutation effect in BCl_3 and SF_6 gases on several CO_2-laser emission lines that are at resonance with vibrational-rotational transitions of these gases.

2. The nutation effect was investigated and described as early as in NMR [7]. The name of the effect stems from the classical analogy, widely used in NMR, between the ensemble of spins in the constant magnetic field at resonant action of the alternating magnetic field on the one hand and, on the other, a rotating top whose axis precesses under the influence of a constant perturbation (the analog of the transition frequency) and rotates slowly (nutates) under the influence of a harmonic perturbation that is at resonance with the precession frequency.

The possibility of observing the optical analog of the nutation effect was predicted by Tang and Statz [8], who discussed the possibility of observing the effect in an amplifying CO_2 medium in which a pulse of CO_2-laser radiation propagates and calculated the nutations for this case.

The optical nutation effect consists in modulation of the amplitude of an optical field passing through a resonant medium. The modulation frequency, called the nutation frequency, is proportional to the field amplitude and to the dipole moment of the resonant transition. The perturbing field must be turned on within a time shorter than the nutation period, and furthermore it is necessary to satisfy the principal condition of interaction coherence, i.e., it is necessary that the nutation period be much shorter than the relaxation time T_2 of the medium.

The optimal type of perturbation for observation of the effect is a perturbation in the form of a small step of the electric field of the optical wave, the production of which entails purely experimental difficulties. Hocker and Tang [9] used as the perturbation a radiation pulse from a CO_2 laser, of 300 nsec duration and rise time 100 nsec. Although they succeeded in observing the effect, measurement of the dipole moment of the resonant transition was made difficult by the inconstancy of the field of the pulse in time, by the absorption of the pulse by the medium, and furthermore by the fact that the pulse rise time was comparable with the nutation period.

We observed nutations against the background of a constant CO_2-laser power level after exposing the medium to a short radiation pulse of higher intensity but of the same frequency resonant with the transition frequency (Fig. 1). The pulse served as a short front for the constant perturbation, and the procedure for observing the nutations was closer to the optimal one in which the perturbation is a step of the electric field of the light wave.

3. In theoretical description of the coherent-interaction effects it is customary to use a semiclassical approximation, in which the ensemble of particles is described quantum-mechanically with the aid of the density-matrix formalism, the field-induced polarization of the medium is calculated, and the reaction of the polarization on the perturbing field is described classically with the aid of the wave equation. The most

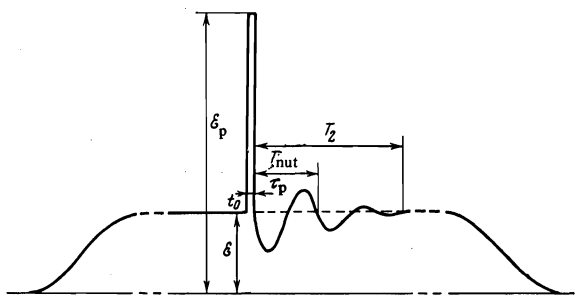

FIG. 1. Nutation effect at a constant-power level following exposure of the medium to a short radiation pulse.

exhaustive simultaneous solution of the Maxwell and Schrödinger equations was obtained by McCall and Hahn[4] for the self-induced transparency effect. The results of this solution can easily be generalized to include the case of the nutation effect.

The equations for the density matrix reduce to the form

$$\frac{dU}{dt}=V\Delta-\frac{U}{T_2},\qquad \frac{dV}{dt}=U\Delta-\frac{2\mu^2}{\hbar^2\omega}\mathscr{E}W-\frac{V}{T_2},$$
$$\frac{dW}{dt}=\frac{V\mathscr{E}\omega}{2}-\frac{W-W_0}{T_1}, \tag{2}$$

where U and V are respectively the dispersion and absorption components of the electric-polarization vector of the medium

$$\mathbf{P}=\mathbf{x}[U(z,t)\cos(\omega t-kz)+V(z,t)\sin(\omega t-kz)]$$

and are determined by the off-diagonal elements of the density matrix. The function W describes the population difference of a two-level system and is determined by the diagonal elements of the density matrix. For a system in the ground state, the value of the function W is determined by the expression

$$W_0=-N\hbar\omega/2.$$

In addition, $\mathscr{E}$ in (2) denotes the envelope of the perturbing electric field of the wave $\mathbf{E}=\mathbf{x}\,\mathscr{E}(z,t)\cos(\omega t-kz)$, Δ is the difference between the transition frequency and the field frequency, T_2 and T_1 are respectively the relaxation times of the polarization and of the population difference of the system N, and μ is the matrix element of the transition dipole moment

In the case of exact resonance ($\Delta=0$) and neglecting the secondary action of the polarization-induced field on the polarization, i.e., in the given-field approximation

$$\mathscr{E}=\begin{cases}\mathscr{E}_0, & t\geqslant 0\\ 0, & t<0\end{cases}$$

Eqs. (2) reduce to an equation for the absorption component of the polarization V, which is responsible for the appearance of the nutations,

$$\frac{d^2V}{dt^2}+\left(\frac{1}{T_1}+\frac{1}{T_2}\right)\frac{dV}{dt}+\left(\frac{\mu^2\mathscr{E}^2}{\hbar^2}+\frac{1}{T_1T_2}\right)V=0, \tag{3}$$

the solution of which takes the form

$$V=N\mu\sin\Omega t\exp\left\{-\frac{1}{2}\left(\frac{1}{T_1}+\frac{1}{T_2}\right)t\right\},$$
$$\Omega=\left[\frac{\mu^2\mathscr{E}_0^2}{\hbar^2}-\frac{1}{4}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)^2\right]^{1/2}. \tag{4}$$

Consequently, the polarization of the medium varies with time harmonically at a frequency Ω determined principally by the value of the electric field and by the dipole moment of the transition, while the amplitude of the oscillations attenuates exponentially with a characteristic time $T_2'=2T_1T_2/(T_1+T_2)$.

The dependence of the frequency Ω on the relaxation time becomes appreciable when the nutation period is comparable with T_2, and under the usual assumption we have $T_2\ll T_1$. However, as shown by our measurements [10], in the molecular gases SF_6 and BCl_3 the time T_1 differs little from the time T_2, thus evidencing a low probability of elastic collisions, i.e., collisions that randomize the phases of the radiating molecules without changing their energy. This allows us to assume that the polarization and the population difference have the same relaxation time T_2':

$$V=N\mu\sin\frac{\mu\mathscr{E}_0}{\hbar}t\exp(-t/T_2'). \tag{5}$$

Inasmuch as the polarization is connected with the field by the wave equation

$$\frac{\partial^2E}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2E}{\partial t^2}=\frac{4\pi}{c^2}\frac{\partial^2P}{\partial t^2} \tag{6}$$

which can be rewritten for slowly varying amplitudes in the form

$$\frac{\partial\mathscr{E}}{\partial z}+\frac{1}{c}\frac{\partial\mathscr{E}}{\partial t}=-\frac{2\pi\omega}{c}V, \tag{7}$$

the field passing through the medium is modulated at a frequency Ω:

$$\mathscr{E}=\mathscr{E}_0\left[1-\frac{\alpha z}{2T_2'\Omega}\sin\Omega t\exp(-t/T_2')\right], \tag{8}$$

where $\alpha=4\pi N\omega T_2'\mu^2/\hbar c$ is the linear absorption coefficient.

The solutions (5) and (8) are valid for a nondegenerate two-level system with homogeneous broadening. Real systems – molecular gases – are, as a rule, strongly degenerate with respect to the projection m of the angular momentum J on a preferred direction, and in addition are inhomogeneously broadened as a result of the Doppler effect.

To take into account the influence of the degeneracy on the nutation effect, it is necessary to sum the contributions made to the polarization by different degenerate states. The dependence of the dipole moment for transitions between degenerate states under the influence of linearly polarized light on J and m for molecules of the symmetrical-top type is determined by the following expressions: $\mu_m=\mu_0 m/J$ for transitions of the Q branch ($\Delta J=0$) and $\mu_m=\mu_0(J^2-m^2)^{1/2}/J$ for transitions of the P and R branches ($\Delta J=\pm1$), where μ_0 is the maximum matrix element and m runs through the values from J to –J.

The polarization of the degenerate medium per unit volume is determined by the expression

$$V=\sum_{m=-J}^{J}\frac{N}{2J+1}\mu_m\sin\frac{\mathscr{E}_0\mu_m}{\hbar}t.$$

For large values of the angular momentum J we can use the quasiclassical description, assuming the dipole-moment distribution over the different degenerate states to be continuous, i.e., assuming $\mu=\mu_0\cos\psi$ for the Q branch and $\mu=\mu_0\sin\psi$ for the P and R branches, where $\cos\psi=m/J$, $\sin\psi=(J^2-m^2)^{1/2}/J$. In this case, changing from summation to integration, we obtain the expressions

$$V_Q=N\mu_0\left(\frac{\sin\Omega t}{\Omega^2t^2}-\frac{\cos\Omega t}{\Omega t}\right)$$

$$V_{P,R}=N\frac{\mu_0}{2}\int_0^{\pi}\sin^2\psi\sin(\Omega t\sin\psi)\,d\psi.$$

Figure 2 shows plots of the polarization per unit volume of gas against the time for a nondegenerate system with dipole moment μ_0 and for a degenerate system of Q and P, R branches with maximum dipole moment μ_0.

It is important that the nutations in a degenerate system attenuate even in the absence of relaxation, and that the damping of the nutations on a Q-branch transition is

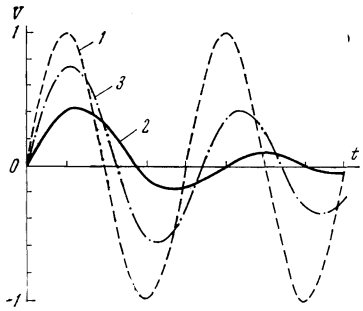

FIG. 2. Dependence of the absorption component V of the polarization of the medium on the time: 1–for a nondegenerate system with dipole moment μ_0; for a degenerate system with maximum dipole moment μ_0; 2–Q-branch transition, 3–P, R branch transition, t is in units of $\pi\hbar/2\mu_0\mathcal{E}$, and V is in relative units.

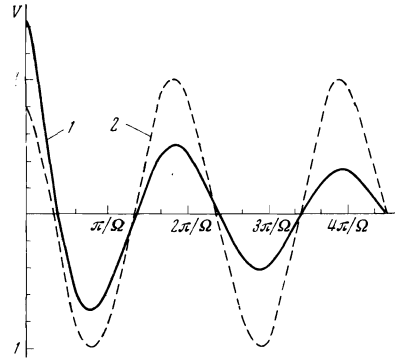

FIG. 3. Dependence of the absorption component V of the polarization of a medium on the time: 1–for an inhomogeneously broadened transition with $\Delta\omega_{Dop} \gg \Omega$, 2–4 transition that is homogeneously broadened with $\Delta\omega_{ham} \ll \Omega$.

much larger than on a P, R branch transition. This can be used to identify the type of transition responsible for the nutation.

It is also seen from the plots in Fig. 2 that the presence of degeneracy leads to a change in the nutation frequency. The degenerate system can always be set in correspondence with a nondegenerate system with damping, having a certain effective dipole moment μ_{eff}, which is connected to μ_0 by the relations

$$\mu_{eff}^{Q}=\mu_0/1{,}41, \qquad \mu_{eff}^{P,R}=\mu_0/1{,}14.$$

It is precisely this effective dipole moment which is measured in experiment and which determines the absorption cross section.

We shall take the inhomogeneity of the transition broadening as a result of the Doppler effect into account for the case when the nutation frequency is much smaller than the inhomogeneous line width, inasmuch as this is precisely the case realized in our method.

Recognizing that the nutation is observed against a background of constant radiation power propagating in the medium following a short radiation pulse of much higher intensity but of the same frequency, it is necessary to solve Eqs. (2) with respect to the absorption component V of the polarization as a function of the detuning Δ and of the time, with initial conditions at the instant $t_0+\tau_p$ (see Fig. 1). The polarization of the medium at the instant of time t_0 is determined by the stationary solutions of (2):

$$V(\Delta)=\frac{N\mu}{T_2\Omega}\frac{\Omega^2}{\Omega^2+\Delta^2}.$$

the polarization at the instant $t_0+\tau_p$, i.e., after the action of a pulse of duration τ_p and amplitude $\mathcal{E}_p$, is determined by the expression $Vt_{0+\tau}=Vt_0\cos\theta$, where $\theta=\mathcal{E}_p\tau_p\mu/\hbar$, and we use here the condition $\mathcal{E}_p \gg \mathcal{E}_0$. As a result we get

$$V(t+t_0+\tau_p,\ \Delta)=V(t_0+\tau_p)\cos\sqrt{\Omega^2+\Delta^2}t.$$

To find the total polarization it is necessary to integrate the polarization $V(t+t_0+\tau_p, \Delta)$ with respect to Δ:

$$V\sim\int_{-\infty}^{\infty}\frac{\Omega^2}{\Omega^2+\Delta^2}\cos\sqrt{\Omega^2+\Delta^2}t\,d\Delta.$$

The result of the integration is shown in Fig. 3. Consequently, the presence of inhomogeneous broadening also leads to damping of the nutation.

Thus, experimental investigation of the nutation effects enables us, knowing the nutation frequency and the electric field intensity of the light wave, to measure the effective dipole moment of the absorbing transition. In addition, the type of the absorbing transition can be determined from the difference between the character of

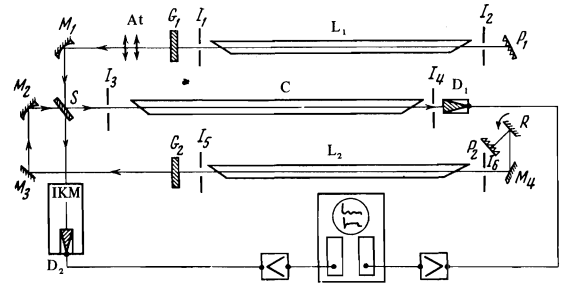

FIG. 4. Experimental setup for observation of the nutation effect in the gases SF_6 and BCl_3: L_1, L_2–laser tubes, C–cell with investigated gas, G_1, G_2, exit mirrors of the resonators, P_1, P_2–diffraction gratings, R–rotating mirror, M_1–M_4–tiltable mirrors, I_1–I_6–iris diaphragms, S–beam splitter, IKM–monochromator, At–attenuator, D_1, D_2–radiation detectors.

the nutation damping for the Q and R or P branches. It must be borne in mind here that the nutation damping can have three causes: relaxation, degeneracy, and inhomogeneous broadening.

4. The experimental setup is shown in Fig. 4. The setup consists of two CO_2 lasers, L_1 and L_2. The laser L_1 operates in a quasicontinuous regime, i.e., with modulation of the laser-type supply. This generates a pulse of 1 msec duration with an intensity of several W/cm^2, with a repetition frequency 25 Hz. The laser resonator comprises a plane-parallel dielectric-coated germanium plate G_1, which serves as the exit mirror for the resonator and has a reflection coefficient of 70%, and a diffraction grating of 100 lines per millimeter (P_1). The use of modulation of the laser-tube current greatly increases the gain of the active medium [11], ensures high stability of the output-radiation amplitude, and makes it possible to operate with a low-Q resonator. Such a laser does not require water cooling and operates practically without flow of the working medium. The second laser L_2, besides having its power supply modulated, is also Q-switched by a rotating mirror R. The resonator of this laser is made up of a semitransparent germanium mirror G_2, the rotating mirror R, and a diffraction grating P_2, and it generates radiation pulses of 200 nsec duration and 100 W/cm^2 intensity. The use of diffraction gratings makes it possible to tune the laser generation frequencies relative to the emission lines in a wide range. The frequency is monitored by an IKM-21 monochromator equipped with a diffraction grating to increase the resolution.

The emission of the laser is directed, with the aid of tilting spherical mirrors M_1, M_2, and M_3 and beam splitter S to a cell C, 3 m long, filled with the investigated gas. The use of spherical mirrors makes it pos-

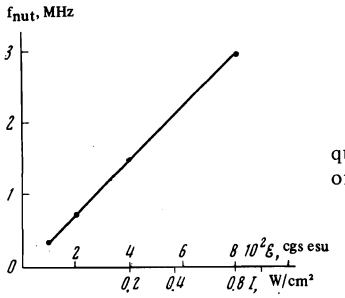

FIG. 5. Plot of the nutation frequency against the field (intensity) of the cw laser.

sible to compensate for the diffraction divergence of the beams. The radiation is registered with a Cd-Hg-Te receiver D_1 with a reception bandwidth 30 MHz. Particular attention was paid to calibration of the receiver. Two calibration methods were used: ordinary calorimetry of the millisecond pulses with a measuring cone, and in addition, the use of a CO_2 laser in the cw regime, the power of which was determined by measuring the evaporation of liquid nitrogen as a result of absorption of the radiation. The fact that the sensitivities obtained by both methods were the same indicates that the results are reliable.

With the aid of this setup we observed the nutation effect in SF_6 gas at the frequencies 947.73, 945.94, and 944.15 cm^{-1}, corresponding to the CO_2 laser emission lines P16, P18, and P20. In the BCl_3 gas, the nutation effect was observed at the frequency 951.16 cm^{-1} (the P12 line). We measured the period of the nutation and the field intensity of the quasicontinuous laser. The gas pressure in the cell ranged from 5 to 50 mTorr and was set at a value such that this field saturated the transition and propagated in the medium without absorption, inasmuch as the absorption-induced variation of the field along the sample introduces an uncertainty into the obtained value of the dipole moment. In addition, simultaneous controllable variation of the field intensity and of the gas pressure makes it possible to preserve the satisfaction of the inequality $\Omega > 1/T_2$. Thus, the nutation frequency decreases with decreasing radiation intensity, and to saturate the transition it is necessary to decrease the pressure of the absorbing gas, and this leads to a lengthening of the relaxation time.

Figure 5 shows a plot of the nutation frequency against the field. It is the linearity of this plot which enables us to use the relation $\Omega = 2\pi f_{nut} = \mu_{eff}\mathcal{E}_0/\hbar$ to determine the dipole moment. It should be noted that with further increase of the perturbation field, the linearity is disturbed and the effect vanishes, since the nutation period approaches the duration τ_p of the pulse that serves as a front for the constant perturbation.

The dipole moments μ_{eff} of the investigated transitions, determined by the procedure described above, turned out to be 2.8×10^{-19}, 2.8×10^{-19}, and 2.5×10^{-19} cgs esu in the SF_6 gas for transitions that resonate with the P16, P18, and P20 emission lines of the CO_2 laser, respectively, and 2×10^{-19} cgs esu for the absorbing transition, in the BCl_3 gas, which resonates with the P12 emission line. The accuracy of the obtained values is determined principally by the accuracy of the calibration of the radiation receiver and is at best 10%, with the relative accuracy determined only by the accuracy with which the period of the observed nutations is measured, and therefore much higher.

We also measured the linear absorption coefficients

Gas, frequency in cm^{-1}	α, cm^{-1}, Torr^{-1}	10^{19} μ_{eff}, cgs esu	10^{19} σ, cm^2. Torr	10^4 q, Torr^{-1}	10^4 q_0	10^4 q_T^{max}
BCl_3; 951.16 (P12)	0.43	2.0	0.8	0.5	0.8	1.5
SF_6; 944.15 (P20)	0.38	2.5	1.0	1.1	1.6	2
SF_6; 945.94 (P18)	0.55	2.8	1.3	1.2	1.8	2
SF_6; 947.73 (P16)	1.05	2.8	1.3	2.4	3.6	2

α of the gases SF_6 and BCl_3 at the foregoing frequencies. The absorption coefficients, referred to the gas pressure, are listed in the table. Knowledge of the dipole moments, the linear-absorption coefficients, and the homogeneous widths of the transitions, which we measured with the aid of the photon-echo phenomenon [3], makes it possible to determine the absorption cross sections $\sigma = \alpha/qN = 4\pi\omega T_2\mu_{eff}^2/\hbar c$ and the relative number of particles q_0 in one and possibly several overlapping vibrational-rotational transitions. The maximum value of this quantity q_T^{max} can also be estimated theoretically, assuming a Boltzmann distribution of the particles with respect to the rotational sublevels of the vibrational ground state, if the configurations of the molecules and the value of the rotational constant are known. Estimates of this quantity are also listed in the table. In estimating q_T^{max} for the SF_6 molecule it was assumed that the degeneracy with respect to K (K is the projection of the angular momentum J on the molecule's symmetry axis), which is a feature of spherical-top type molecules, is lifted. The fact that q_T^{max} and q_0 agree in order of magnitude confirms this assumption experimentally.

In applications, it is frequently necessary to know the relative number q of the particles that take part in the absorption. In the case of the molecular gases BCl_3 and SF_6, which have exceedingly frequent rotational spectra, this quantity increases linearly with pressure in a wide range, from several mTorr to dozens of torrs. At low pressures, when the homogeneous line width is smaller than the inhomogeneous width, the mechanism that increases q is the inhomogeneity of the broadening, and with further increase of pressure the absorption begins to take in neighboring rotational sublevels. The values of q divided by the pressure are also given in the table.

It should be borne in mind that the quantities listed in the tables were measured at low pressures (5–50 mTorr) for particular absorbing transitions. Extrapolation of these values into the region of high pressures is, generally speaking, arbitrary, since it requires that the dipole moments of the transitions newly included in the absorption remain of the same order as the dipole moments of the investigated transitions with increasing pressure. Nonetheless, the values obtained serve as perfectly satisfactory estimates of the quantities up to pressures on the order of several dozen Torr. This is indicated, for example, by the constancy of the absorption coefficient α relative to the pressure in this pressure range.

In the theoretical analysis of the nutation effect it was noted that the type of transition can be deduced from the difference in the character of the damping of the nutations. Figure 6 shows oscillograms of the effect in SF_6 at the frequencies 947.73 (P16) (Fig. 6a) and 944.15 cm^{-1} (P20) (Fig. 6b). The time T_2 and the inhomogeneity of the broadening were assumed to be the same in both cases. The faster damping of the nutation at 947.73 cm^{-1} (P16) seems to indicate that the absorp-

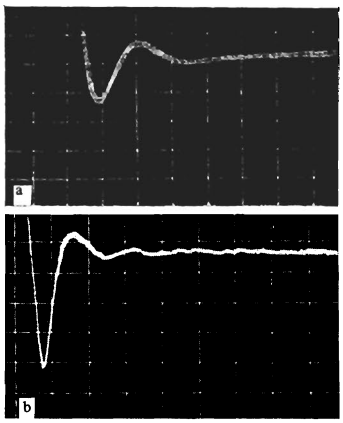

FIG. 6. Oscillograms of the nutation effect in SF_6: a–at 947.73 cm^{-1} (P16), time scale 250 nsec/div; b–at 944.15 cm^{-1} (P20), 500 nsec/div. In both cases $T_2 = 1.5$ μsec.

tion of this frequency by SF_6 gas is due to the Q-branch transition, while the absorption of the frequencies 944.15 cm^2 (P20) and 945.94 cm^{-1} in SF_6 and of 951.16 (P12) in BCl_3 are due to the transitions of the P or R branches (the character of the damping of the nutations at the frequencies P18 in SF_6 gas and P12 in BCl_3 gas is similar to the damping at the P20 frequency). A similar conclusion with respect to the type of transition that resonates with the P16 line in SF_6 gas was drawn by us in an investigation of the photon-echo effect in this gas [3].

Thus, an experimental investigation of the nutation effect in the molecular gases BCl_3 and SF_6 has made it possible to determine such characteristics of these gases as the dipole moment, the absorption cross section, and the relative number of particles that take part in the absorption. In addition, it was possible to establish that degeneracy exerts a significant influence on the effect and to draw conclusions concerning the types of transitions responsible for the nutations in these gases.

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