

*THE STUDY OF ROTATION AND VIBRATION-ROTATION SPECTRA OF GASES BY THE
METHOD OF COMBINATION (RAMAN) SCATTERING OF LIGHT**

P. A. BAZHULIN

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THE main direction of work on molecular spectroscopy in the optical laboratory directed by G. S. Landsberg was the study of vibrational spectra, i.e., the infrared absorption spectra and combination (Raman) scattering spectra.

Over a number of years the laboratory carried on work on the spectra of individual molecules. Photographic and photoelectric methods were developed for determining the main parameters of combination-scattering lines, namely the intensity at the maximum of a line, the integrated intensity, the line width, and so on. We should particularly mention the papers on studies of the widths of lines—a quantity which had remained almost without study before our work.^[1]

At the same time this question is of both theoretical and practical interest. The study of the shapes and widths of combination-scattering lines could throw light on the nature of the processes causing the damping of the characteristic oscillations of molecules. The change of shape of the lines when there is a change of the state of aggregation could serve as a more delicate method for observing intermolecular interactions of the van-der-Waals type. Over a number of years much of the laboratory's time was devoted to the study of this important property of lines. It was shown by M. M. Sushchinskii that a knowledge of the line width is of fundamental importance in the determination of the true intensities of lines, and in particular in making quantitative molecular analyses from combination-scattering spectra. Kh. E. Sterin^[2] developed an interferometric method for studying line widths and line shapes in combination scattering. He made more detailed studies of the benzol line $\Delta\nu = 992 \text{ cm}^{-1}$ and the cyclohexane line $\Delta\nu = 802 \text{ cm}^{-1}$. These are the brightest lines and belong to completely symmetrical vibrations of the molecule. These same lines were also studied in vapors.

The main experimental results of the research are as follows: 1) The lines studied have the dispersion shape; 2) the line width is about 2 cm^{-1} ; 3) there is practically no change of the line width on going from liquid to vapor.

The last fact indicates that there is only a weak dependence of these lines on intermolecular processes, in particular on collisions. Therefore the effect of

collisions, as well as of other possible causes of broadening, deserved detailed study.

Sterin's analysis of the causes of broadening of combination lines shows that the Lorentz collision broadening $\delta\nu_C$ is 0.6 cm^{-1} for benzene and 0.5 cm^{-1} for cyclohexane. The Doppler-effect broadening is $\delta\nu_D = 3.6 \times 10^{-2} \text{ cm}^{-1}$ for benzene and $\delta\nu_D = 3.5 \times 10^{-2} \text{ cm}^{-1}$ for cyclohexane, that is, 2 percent. The effect of anharmonicity is also small.

Kh. E. Sterin also examined the effect of rotational broadening on the line shapes. A careful analysis showed that the shape and width of these lines are mainly characteristic of the isotropic part of the scattering, which corresponds to completely symmetrical vibrations of the benzene and cyclohexane molecules; in these cases rotational broadening plays only a small part.

Thus none of the causes considered can explain the widths of these lines. It might be supposed that this width characterizes the mean lifetime of the infrared vibration, which is of the order of 10^{-11} sec . This assumption agrees with the dispersion shape of the line and with the lack of change of width on going from liquid to gas, but on the other hand this estimate leads to serious difficulties. First, the ordinary radiative losses would have to give a much larger lifetime for the infrared vibrations, especially if one takes into account the complete symmetry of the vibrations for these lines. It is also hard to connect such a small lifetime (10^{-11} sec) with the effect of energy exchange between vibrations and other degrees of freedom, for which the lifetime is 10^{-5} – 10^{-7} sec .

I. I. Sobel'man^[3] called attention to the following fact: the general laws of line broadening are the same for combination scattering as for emission lines (natural damping; radiative and collision damping, frequency shifts owing to effects of external fields, and Doppler effect are all the same). The specific features are the complexity of the molecular spectrum and the special characteristics associated with the rotation of the molecule.

From this point of view the most convenient objects of study, which can give information about the width of an individual component, are the Q branches of the fundamental completely symmetrical vibrations of symmetrical tops, which are without any rotational structure, and also the Q branches of symmetrical diatomic molecules. In both cases, however, the individual components of the Q branch coincide only in

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first approximation. The splitting of the Q branch caused by the interaction between vibration and rotation leads to a broadening of the line which as a rule is much larger than the effect of intermolecular interactions at pressures 1 to 2 atm.

Knowing the vibration-rotation interaction coefficient, one could estimate the broadening for benzene and cyclohexane. Unfortunately, there are no data on this coefficient, and only a rough estimate is possible. Such an estimate has been made and gave satisfactory results. It can explain in order of magnitude the broadening observed by Sterin, but this made necessary a much deeper approach to the problem, and in particular a more detailed study of the behavior of the rotational and vibrational spectra with changes of pressure.

Therefore there is much interest in studies of simple nonpolar molecules with well known structures and accurately measured molecular constants. From this point of view it is reasonable to begin the investigation with gases at moderate pressures; the kinetics of the motions in gases is known, and this facilitates the interpretation of the results. In this case the effect of intermolecular interactions is small, and, as is well known, the line shape is most sensitive to it. When a theory of the collision broadening is available a study of line shapes allows us to find the effective optical collision cross sections which determine the broadening of the combination-scattering line.

Our information about the widths of the rotational components consists of data on absorption spectra in the infrared and microwave regions and on spectra of the combination scattering of light. The most detailed and systematic studies have been those on broadening in microwave spectra. Owing to its high resolving power and the small amount of instrumental distortion the radiospectroscopy method has been very effective and fruitful. Its possibilities are limited, however: with few exceptions (the only exceptions are molecules of the type of oxygen, which have a magnetic absorption) it applies only to polar molecules and takes in only the lowest frequencies. In this respect optical methods, which do not have these limitations, offer much wider possibilities. Very little is known about broadening in the spectra of nonpolar molecules. It is still not clear what interactions cause the broadening, or to what degree multipole moments, for example quadrupole moments, affect the widths of rotational lines.

There is no doubt that such studies are of great scientific interest. The combination-scattering method is a very effective one for the solution of these problems. An important point is that this method applies equally well to both polar and nonpolar molecules. These possibilities for spectroscopy of the gas phase are far from having been fully utilized. It is true that there are considerable experimental difficulties in the registration of combination-scattering spectra of gases, which have extremely low intensities. These difficul-

ties have now been overcome, however, and a possibility is opening up for registration of the spectra by means of ordinary photoelectric radiation detectors.

Both photographic and photoelectric methods have been used in these researches. For a number of gases studies have been made over the range from 1 atm to 120 atm.

The studies in gases from 1 to 10 atm were made by Yu. A. Lazarev^[4] with a photoelectric method. He devised an apparatus which permitted photoelectric registration of spectra and measurements of the intensities, widths, and shapes of rotational and vibrational combination-scattering lines of vapors in this range of pressures and the temperature range 30–250°C.

The main components of the apparatus are: 1) a DFS-4 spectrometer with a plane reflecting grating with 1200 lines per mm, linear dispersion 6.4 Å/mm, and relative aperture 1:10; 2) a multiple-reflection mirror gas cell of length 600 mm and diameter 40 mm, and two focusing condensers; 3) two cooled-discharge low-pressure mercury lamps, of length 600 mm; 4) a screening jacket lined inside with MgO. The mirrors of the cell were of the dielectric type, with reflection coefficient not below 95 percent in the region 4000–5000 Å. Aluminized mirrors were used in some experiments. The operating current through the lamps did not exceed 25 A. The radiation detector was a FÉU-17 photomultiplier, specially chosen for optimal signal-to-noise ratio.

The rotational spectra of the gases were recorded with equivalent slit widths of the order of 0.5–0.6 cm⁻¹, the vibrational (Q-branch) spectra with widths 0.3–1.5 cm⁻¹, and the rotation-vibration (O, P, R, and S branches) spectra with widths 2–3 cm⁻¹. The entrance and exit slits were identical. The half-width of the apparatus function, measured with slits 0.1 cm⁻¹, together with that of the excitation, is 0.5–0.7 cm⁻¹, (depending on the wavelength). The slit height is 15 mm. The scanning rate is 3.5 cm⁻¹/min. The processing of the contours and determination of true widths for isolated lines were done in the usual way by the use of Voigt functions. A special method was used for overlapping lines.

The studies in the pressure range from 10 to 200 atm were made by G. V. Mikhailov^[5] with a photographic method. He constructed a special illuminator (Fig. 1). Three PRK-2 lamps, surrounded by a cooling filter with running water, are placed parallel to the scattering volume and illuminate it through transparent-plastic cylindrical lenses. The lenses, set in "hot" fittings, also serve as the seals of the illumination windows. A multiple-reflection system is located inside the scattering volume. A two-lens condenser was used; the front slit of the mirror system was imaged on the spectrograph slit, and the back mirrors were imaged on the collimator. Combination-scattering spectra were excited by the mercury lines 4047 Å and 4358 Å and were registered with a NIET

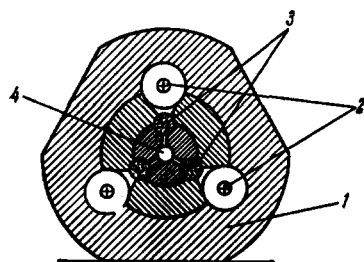


FIG. 1. Scheme of the high-pressure illuminator. 1 - casing; 2 - illuminating lamps with water filters; 3 - cylindrical lenses; 4 - scattering volume.



FIG. 2. Combination-scattering rotational spectrum of gaseous oxygen at pressure 3 atm. Grating "ghosts" are marked with arrows.

V-III spectrograph which had linear dispersion $22.7 \text{ cm}^{-1}/\text{mm}$ in the 4047 \AA region and $36.2 \text{ cm}^{-1}/\text{mm}$ in the 4358 \AA region. The exposure times used were from 3 h to 40 h. The spectrograph temperature was thermostatically controlled. The sum of the widths of the exciting line, the slit, the instrument function of the spectrograph, and the photographic layer (1.5 cm^{-1}), was eliminated from the results by adjustment of the data. Figure 2 shows the rotational spectrum of gaseous oxygen at pressure 3 atm, as registered by the photoelectric method.

The objects studied were simple nonpolar molecules: H_2 , O_2 , N_2 , CO_2 , C_2H_2 , and CH_4 , and also the weakly polar molecule CO , both pure and in mixtures with inert gases (Ar , He , CH_4). All of the gases were carefully purified.

ROTATIONAL SPECTRA

The substance we studied most completely was oxygen. The pressure dependence of the widths in the rotational spectra was studied over the range from 1 atm to 125 atm, at $T = 300^\circ\text{K}$.

Oxygen has the simplest rotational spectrum. The rotational bands correspond to $\Delta v = 0$, $\Delta J = \pm 2$. The distance between lines is 11.5 cm^{-1} . The spectrum of O_2 consists of the O and S branches of the rotational band, located on either side of the exciting line. The lines of the rotation band are observed as far as components corresponding to transitions with $J = 25$ in the O branch and with $J = 35$ in the S branch. The intensity distribution in the band is the typical thermal distribution. At pressures above 75 atm the lines merge into a solid band with weak maxima.

The main regularities observed are as follows:

a) frequency agrees to accuracy $\pm 0.2 \text{ cm}^{-1}$ with calculations based on the rigid-rotator model; b) the lines have the dispersion shape

$$I(\omega) = \frac{\gamma/2}{(\omega - \omega_0)^2 + (\gamma/2)^2},$$

and their width γ has a linear pressure dependence from 1 to 125 atm; c) γ is independent of J over the entire range of pressures; d) at a given pressure the broadening is the same for all values of J .

Figure 3 shows the pressure dependence of the width of the rotational lines. The main cause of the observed broadening is the broadening through molecular collisions. This is indicated by the absence of a residual width on extrapolation to zero pressure. The dispersion shape and the linear pressure dependence allow us to apply the theory of collision broadening.

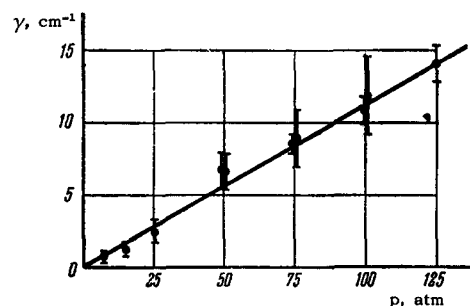


FIG. 3. Pressure dependence of the width of rotational-spectrum lines of oxygen.

According to this theory^[6] the width is given by the relation

$$\gamma = 0.5 \frac{pd^2}{\sqrt{\mu T}},$$

where p is the gas pressure (in atm), d is the effective optical collision diameter (in \AA), μ is the molecular weight, and T is the temperature (γ is expressed in cm^{-1}). By using the ratio γ/p , we can easily get from the graph the value of the effective optical collision diameter. Table I shows values of the optical diameter for O_2 obtained by various authors. It can be seen from the table that our values are in good agreement with the data obtained from absorption in the microwave region at pressures 1–8 mm Hg.^[7]

Table II shows values of the optical diameter obtained from the rotational spectra of a number of other gases at low pressures; the table also shows some data for mixtures. As can be seen from these data, the largest differences between optical and gas-kinetic diameters are found for CO_2 and H_2 . The probability of energy transfer from a translational to a rotational degree of freedom is extremely small in hydrogen.^[8] As has already been pointed out, at present it is still

Table I. Experimental data on optical diameters of O_2

Measured by	G. V. Mikhaïlov	Yu. A. Lazarev	Anderson et al.
Method	Combination scattering		Microwave absorption
Pressure range	7–125 atm	1–10 atm	1–8 mm
d (in \AA)	4.43 \AA	4.2 \AA	4.35 \AA
	Gas-kinetic diameter 3.6 \AA		

Table II
a) Optical diameters (in Å) obtained from rotational spectra, $T = 300^\circ\text{K}$

	O ₂	O ₂ +Ar	O ₂ +He	N ₂	N ₂ +Ar	CO ₂	CO ₂ +Ar	H ₂	CO	C ₂ H ₂
Our data	4.2	3.9	2.2	4.1	3.8	7.1	6	<1	4.7	8.1
Anderson et al.	4.35	3.57	—	—	—	—	—	—	—	—

b) Gas-kinetic collision diameters (in Å)

O ₂	H ₂	N ₂	CO ₂	Ar	He	CH ₄	C ₂ H ₂	CO
3.6	2.7	3.7	4.5	3.6	2.1	4.1	4.8	3.7

far from clear for nonpolar molecules and weakly polar molecules just what interactions are responsible for the broadening of the rotational lines, and to what extent multipole moments, in particular the quadrupole moment, affect the widths.

Starting from the relations of Anderson's theory,^[9] Yu. A. Lazarev has made calculations of the optical diameters for these molecules. From a comparison of the experimental and theoretical values one can draw a conclusion about the interactions which cause the broadening of the rotational lines. For example, for oxygen the broadening effect of quadrupole forces is small compared with that of dispersion forces, for the N₂ and CO molecules dispersion and quadrupole forces are of the same order of magnitude, and for CO₂ and C₂H₂ quadrupole forces predominate. Table III shows a comparison of the calculated and experimental optical diameters for various interacting pairs of molecules.

THE ROTATIONAL WINGS OF VIBRATION-ROTATION BANDS

Since the intensities of the rotational components of vibration-rotation bands are about two orders of magnitude smaller than those of the lines of the pure rotation spectrum, it is quite difficult to register these lines, and even more difficult to measure their widths. Never-

theless we succeeded in obtaining traces of the vibration-rotation spectra of oxygen and methane at pressure 10 atm and making estimates of the half-widths of the vibration-rotation components (Fig. 4). Table IV shows values of the half-widths of the rotational components found as averages from 4 or 5 spectra and corresponding to transitions from the most strongly populated levels.

For O₂ a comparison with the pure rotation spectrum taken at pressure 10 atm shows that the width of

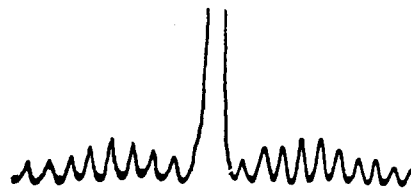


FIG. 4. Rotational wings of the vibration-rotation spectrum of oxygen at pressure 10 atm.

Table IV
Half-widths (in cm⁻¹) of rotational components of vibration-rotation lines

O ₂	$\nu_3\text{CH}_4$	$\nu_2\text{CH}_4$
3 ± 1	≤ 1.5	≤ 2
$p = 10 \text{ atm}$		

Table III

Interacting pair of molecules	Calculated optical diameter (in Å)			Experimental value of optical diameter (in Å)
	dispersion	quadrupole	total	
O ₂ -O ₂	4.2	2.5	4.2	4.2
O ₂ -He	2.3	—	2.3	2.2
N ₂ -N ₂	4.2	4.0	4.4	4.1
N ₂ -Ar	3.8	—	3.8	3.8
CO-CO	4.2	4.3	4.7	4.7
CO-Ar	3.8	—	3.8	3.5
CO ₂ -CO ₂	5.5	6.3	6.6	7.1
CO ₂ -Ar	4.6	—	4.6	5.0
C ₂ H ₂ -C ₂ H ₂	5.5	7.6	7.7	8.1
C ₂ H ₂ -He	2.7	—	2.7	2.7

the rotational components of vibration-rotation lines is larger by a factor three than that of the lines of the pure rotation spectrum; clearly this is due to a larger optical cross section in the excited rotational state.

VIBRATIONAL BANDS OF THE COMBINATION-SCATTERING SPECTRUM

Oxygen. In the vibration band of O_2 ($\Delta\nu = 1$) one sharp line is observed with frequency $\Delta\nu = 1555 \text{ cm}^{-1}$. The corresponding Q branch ($\Delta J = 0$), O branch, and S branch were observed by the photoelectric method. The band of O_2 is asymmetrical with a wing on the violet side. The width of the line does not vary with the pressure.

The lack of pressure dependence of the width of the Q branch shows that its collision broadening is small. The Q branch consists of transitions $\Delta J = 0$ without change of the rotational state, and therefore it is very probable that its width is affected only by the perturbation of the vibration by collisions (this perturbation must be smaller than for the rotation), and that the perturbation of the rotation has no effect.

Analysis shows that the observed width and shape of the Q branch is completely explained by its rotational structure, i.e., by the interaction between the vibration and rotation of the molecule. The change of the moment of inertia of the molecule during its vibration changes the distance between the rotational levels of the upper vibrational state, so that the rotational components of the Q branch do not coincide, but are somewhat split apart.^[3] As is well known, the frequencies of the components of the rotational structure are described by the formula

$$\omega = \omega_0 - 2x_0\omega_0 - \alpha J(J+1),$$

$\omega_0 - 2x_0\omega_0$ is the frequency of the undisplaced component, and $B_0 - B_1 = \alpha$ is the coefficient for the interaction between vibration and rotation.

From the transition probability (sic) $W = C(2J+1) \exp[-BJ(J+1)/kT]$ we can determine the intensity distribution of the J-components,

$$I_J = I_0 \sqrt{1 + 4 \frac{\omega}{\alpha}} e^{-\frac{B}{kT} \frac{\omega}{\alpha}}.$$

Figure 5, a shows the rotational structure of the Q branch for oxygen as found from these calculations. This structure, which is not resolved by the apparatus, leads to the finite width of the Q branch.

From this structure the shape of the Q branch to be observed for $T = 300^\circ\text{K}$ was calculated, with each component broadened by an apparatus function of Gaussian form. The results so obtained show that in first approximation the width and shape of the Q branch are completely explained by the broadening of the components of its rotational structure by apparatus effects alone, in the absence of any natural width. In Fig. 5, a the observed structure is shown by a solid curve, and calculated values by points.

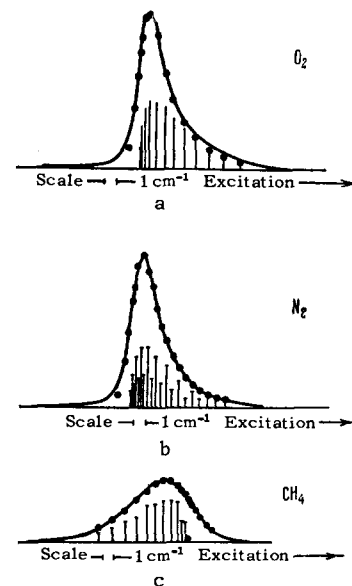


FIG. 5. Shapes of rotation-vibration bands of oxygen (a), nitrogen (b), and methane (c). Solid curves are observed contours at pressure 10 atm; points are calculated values.

We have also studied the Q branches of the rotation-vibration bands in H_2 , N_2 , CO_2 (ν_1 and $2\nu_2$), CH_4 (ν_1) in the pressure range 1–10 atm.

These studies showed that all of the lines are asymmetrical with shadings both to the violet and to the red sides, and that within experimental error the shape and width of the strongly polarized lines are independent of the pressure. By varying the widths of the individual components and comparing calculated and observed shapes one can get an estimate of the true widths of the components. As can be seen from Fig. 5, the observed shapes agree well with the calculated contours.

For H_2 the components of the Q branch were completely resolved (Fig. 6), so that their half-widths could be measured directly. Estimates of the true half-widths of the components of the Q branch, obtained at gas pressure 10 atm, are shown in Table V. It must be pointed out in particular that for the vibrations of frequencies ν_1 and $2\nu_2$ of the CO_2 molecule it was impossible over the whole pressure range (1–10 atm) to determine the halfwidth, not only for the individual components, but also for the entire Q branch, because of insufficient experimental accuracy; this can be directly ascribed to the fact that for these frequencies the coefficients for the interaction between vibration and rotation are extraordinarily small.^[10] The estimates of the half-widths of these lines given in^[11] are evidently much too high.

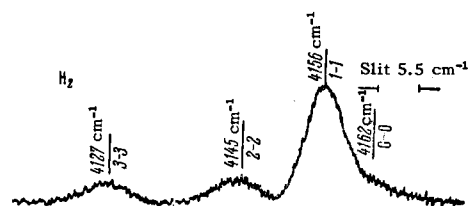


FIG. 6. Trace of the rotation vibration band of hydrogen.

Table V. Half-widths of the lines of various gases (in cm^{-1}) and degrees of depolarization

	H ₂	O ₂	N ₂	CO ₂		CH ₄	
	4160	1580	2330	1389 ν_1	1285 $2\nu_2$	2915 ν_1	1535 ν_2
Degree of depolarization	0.05	0.11	0.1	0.05	0.08	0.00	Depol.
Halfwidth of observed Q branch	—	3	2.7	—	—	1.3	6.3
Calculated γ of individual component of Q branch	<0.2	<0.3	<0.3	<0.2	<0.2	—	1.5–0.7

$p = 10 \text{ atm}$

For the vibrations ν_2 of CH₄ the moment of inertia is smaller in the excited state than in the normal state, [12] and therefore the Q branch (unlike those of O₂ and N₂) is shaded on the high-frequency side. The Q branch of the frequency ν_3 of CH₄ (corresponding to threefold degenerate vibrations of the molecule) undergoes an additional splitting through the removal of the degeneracy owing to the Coriolis interaction of the vibrations, [13] so that the corresponding maximum is double (Fig. 7).

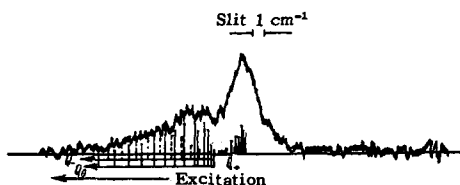


FIG. 7. Trace of the vibration-rotation line of methane ($\nu_3 = 3018 \text{ cm}^{-1}$) at pressure 10 atm.

As the result of the processing and analysis of the experimental data we can come to the conclusion that for linear molecules and molecules of the spherical-top type there are the following regularities: a) the asymmetry and width of the Q branch are completely explained by the splitting of the Q branch owing to the interaction between vibration and rotation and to the Coriolis interaction of the vibrations; b) in this pressure range the true half-width of an individual component of a Q band of strongly polarized lines is a small quantity (smaller than 0.3 cm^{-1}), and cannot be determined within the limits of accuracy of our experiments; c) the individual components of the Q branch of the depolarized line $\nu_2\text{CH}_4$, measured at pressure 10 atm, are broadened (1.5 cm^{-1}) just as the rotational components of the vibration-rotation wing are. The results of work on the infrared spectra by V. I. Malyshev [14] are evidently very similar.

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