Rayleigh scattering

Questions of terminology are resolved during a historical excursion through the physics of light-scattering by gas molecules

Andrew T. Young

We all know that blue skies and red sunsets are due to the "Rayleigh scattering" of sunlight. But beyond that, Rayleigh scattering means different things to different scientists.

The "Rayleigh line" of Raman spectroscopists, who study the rotational and vibrational behavior of molecules by analyzing frequency shifts that occur when monochromatic light is scattered, is not the same as the "Rayleigh line" of Brillouin spectroscopists, who analyze light scattered by acoustic phonons, or density fluctuations. Their "Rayleigh line" is only the unshifted central component of the Raman spectroscopists' line, and contains less than 30% of the scattered energy; if we restricted "Rayleigh scattering" to it, we would have to say the blue sky is due chiefly to Brillouin scattering.

For many, Rayleigh scattering implies coherence or elastic scattering, or it brings to mind functions such as λ^{-4} and $(1 + \cos^2\theta)$. Yet the scattering of sunlight by air molecules or density fluctuations in the atmosphere is not strictly proportional either to λ^{-4} or to $(1 + \cos^2\theta)$. And if we exclude inelastic scattering of light by rotating molecules, which accounts for about 3% of the sky light, only the remaining 96.6% of molecular scattering is without frequency shift. Furthermore, only 98.8% of *this* light is coherent in the forward direction.

The conflicting uses of Rayleigh's name, and the confusion about details of the phenomenon that bears his name, are not "just" matters of nomenclature. These problems recently caused an error in physics to be published in a reputable journal, to be amplified by other authors and cited approvingly by still others before being corrected[1]—in spite of having been forseen and cautioned against[2] nearly fifty years ago! Also, a question of the accurate reflection of history is involved, as the conflicting uses of the term "Rayleigh line" illogically refer to phenomena discovered long after Lord Rayleigh's death.

Why do we honor Rayleigh with eponymy in molecular scattering? What phenomena did he actually explain? Is unchanged frequency a central feature of his work or not?

To see what use of Rayleigh's name is most appropriate, we will look at what he did. Other, more suitable names will turn up to replace the conflicting and inappropriate uses of Rayleigh's.

The blue sky

To appreciate Rayleigh's contributions one must understand how the blue sky was explained in the mid-19th century. A number of observers, from Leonardo da Vinci to Johann Wolfgang von Goethe, had noticed the sky-blue color in smoke. Isaac Newton attributed the blue sky to first-order interference in "Vapors when they begin to condense and coalesce into small Parcels." Rudolf Clausius pointed out that refraction within macroscopic droplets would cause problems, which could be avoided if the droplets were hollow, so he argued for minute bubbles of water suspended in the air.

Ernst Wilhelm von Brücke objected that first-order interference blue is too unsaturated, and demonstrated the sky-blue color in hydrosols. In 1809, Dominique-François-Jean Arago discovered the strong polarization of the sky 90 degrees from the Sun (see figure 1), a finding inconsistent with Clausius's bubbles.

The color and polarization of sky light remained unexplained for another six decades. In 1869, John Tyndall[3] stated that "these questions constitute, in the opinion of our most eminent authorities, the two great standing enigmas of meteorology."

The authority most eminent in Tyndall's opinion was Sir John Herschel, who had stated the polarization problem in these terms:

> The cause of the polarization is evidently a reflection of the sun's light upon *something*. The ques-

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Photographs taken with and without a polarizing filter demonstrate the polarization of light from the sky. With the filter (right), clouds appear more distinct. The increased contrast occurs when polarized light from the sky is attenuated to a larger extent than is the largely unpolarized light from the clouds. Smaller wavelengths in sunlight are scattered preferentially by air molecules or density fluctuations in the atmosphere, giving the sky its blue color. The photographs were taken by Alistair B. Fraser (department of meteorology, Pennsylvania State University) near Kootenay Lake, British Columbia, Canada. Shift in scene is due to motion of airplane between photos. Figure 1

> tion is, On what? Were the angle of maximum polarization 76°, we should look to water or ice as the reflecting body, however inconceivable the existence in a cloudless atmosphere on a hot summer's day of unevaporated molecules (particles?) of water. But though we were once of this opinion, careful observation has satisfied us that 90°, or thereabouts, is a correct angle, and that therefore, whatever be the body on which the light has been reflected, *if polarized by a single reflection*, the polarizing angle must be 45°, and the index of refraction, which is the tangent of that angle, unity; in other words, the reflection would require to be made *in* air *upon* air!

George Stokes had argued, in his 1852 paper *On the Change of Refrangibility of Light*, that the transverse vibrations of light waves implied that particles smaller than the wavelength should not "diffract" in the direction of vibration any intensity from a polarized beam, and confirmed this experimentally with hydrosols. In 1868, Tyndall[4] noticed the sky-blue color in a beam of light that he was using to make photochemical smog. In his notebook, he wrote, "connect this blue with the colour of the sky," and he soon

> took a pleasure . . . in determining whether in all its bearings and phenomena the blue light was not identical with the light of the sky. This to the most minute detail appears to be the case. The incipient actinic clouds are to all intents and purposes pieces of artificial sky, and they furnish an experimental demonstration of the constitution of the real one.

He believed these clouds contained particles "whose diameters constitute but a very small fraction of the length of a wave of violet light."

Tyndall was puzzled that not only natural background aerosols but also those he made from "substances of widely different refractive indices, and therefore of very different polarizing-angles as ordinarily defined" by Brewster's law, all gave the same results, "*absolutely independent of the polarizing-angle*. The law of Brewster does not apply to matter in this condition; and it rests with the undulatory theory to explain why."

Rayleigh answered this challenge. In only his eighth published paper,[5] he pointed out that "the difficulty is imaginary, and is caused mainly by misuse of the word reflection," which has "no application unless the surface of the disturbing body is larger than many square wave-lengths . . . ."

By repeating Stokes's argument more clearly, he shows that the polarizing phenomena follow from the transverse-wave nature of light, adding, "I cannot see any room for doubt as to the result." He then uses dimensional analysis to show that

> *the ratio of the amplitudes of the vibrations of the scattered and incident light varies inversely as the square of the wave-length, and the intensity of the lights themselves as the inverse fourth power.*

His own measurements of the ratio of skylight to sunlight as a function of wavelength agree well with this "important law" and disagree with the λ^{-2} dependence of the first-order interference blue. Thus blue light of 450 nm wavelength, for example, is scattered more intensely than red light of 670 nm wavelength by a ratio of $(670/450)^4$ or about 5 to 1.

Furthermore, Rayleigh's detailed analysis produces the $(1 + \cos^2\theta)$ phase function; he suggests that the imperfect polarization of light from the sky is due to multiple scattering, "but it must be remembered that an insufficient fineness of some of the particles of foreign matter would have a like result"; and he shows, as Brücke had demonstrated with hydrosols, that the transmitted light is reddened by the "rapid diversion of the rays of short wave-length."

These substantial results are based entirely on the elastic-solid theory of the luminiferous ether. Ten years later,[6] he rederived them using Maxwell's electromagnetic theory. Here he also considered higher-order effects for spheres of finite size, for infinite cylinders and other possibilities.

Aerosol, or air itself?

Rayleigh's 1871 paper[5] begins,

> It is now, I believe, generally ad-

> mitted that the light which we receive from the clear sky is due in one way or another to small suspended particles which divert the light from its regular course. On this point the experiments of Tyndall with precipitated clouds seem quite decisive.

(The photograph in figure 2 was taken around the time Rayleigh wrote this.) Rayleigh accepts Tyndall's repeated assertions that clean gases are "optically empty" and incapable of scattering light. But he rejects the general assumption "that the foreign matter in the atmosphere is water or ice," as the "blue haze evidently akin to the azure of the sky . . . on a hot day, cannot possibly be attributed to aqueous particles." He suggests that "a strong case might be made out for common salt."

James Clerk Maxwell wrote to Rayleigh two years later, posing the question:

> Suppose that there are N spheres of density ρ and diameter s in unit of volume of the medium. Find the index of refraction of the compound medium and the coefficient of extinction of light passing through it.
>
> The object of the enquiry is, of course, to obtain data about the size of the molecules of air.

In 1899, Rayleigh succeeded in relating the molecular extinction to the refractive index of a gas and was able to show[7] that "even in the absence of foreign particles we should still have a blue sky." This relation also provided the first accurate method of estimating Avogadro's number. The replacement of aerosols by air molecules as the scatterers was itself as revolutionary as Rayleigh's earlier replacement of "reflection" by "scattering".

"To facilitate comparison with former papers," Rayleigh again develops the theory from the elastic-solid picture. "By considering the resultant of the primary vibration and of the secondary vibrations which travel in the same direction," he shows "that the phases are no more distributed at random." This *coherence* in the forward direction retards the phase of the resultant wave; the phase delay is related to the refractive index μ of the gas. If the energy of the incident beam falls with distance x, as $\exp(-hx)$, the extinction coefficient is

$$h = 32\pi^3(\mu - 1)^2/(3n\lambda^4) \qquad (1)$$

where n is the number of molecules per unit volume. Consequently, the "observed fact" that the index of refraction increases with decreasing wavelength means that "the falling off of transparency at the blue end of the spectrum will be even more marked than according to the inverse fourth power of the wave-length." (For air, the effective power is about -4.08 in visible light.)

Lord Rayleigh (John William Strutt), 1842–1919, in a photograph he took himself around 1870. (Photograph courtesy of John Arthur Strutt.) Figure 2

> Let us now inquire what degree of transparency of air is admitted by its molecular constitution, *i.e.*, in the absence of all foreign matter. . . . The calculation requires the value of n. Unfortunately this number—according to Avogadro's law the same for all gases—can hardly be regarded as known.

Rayleigh shows that Maxwell's crude estimate of 1.9×10^9 molecules per cubic centimeter agrees fairly well with values from Pierre Bouguer's stellar measures of atmospheric extinction.

> If n be regarded as altogether unknown, we may reverse our argument, and we then arrive at . . . a lower limit for n, say 7×10^{18} per cubic centimetre. . . . When we take into account the known presence of foreign matter, we shall probably see no ground for any reduction of Maxwell's number.

(The modern value is about 2.7×10^{19} per cm^3.)

It is remarkable that the relation between refractivity and extinction had been found in the 1880's by Ludwig Lorenz, during his development of the theory of refraction. Lorenz even used it to estimate the number density in air, and found 1.63×10^{19} molecules per cubic centimeter. But Lorenz published it in Danish, in a long paper on another topic, so like Stokes's explanation of the polarization, it was ignored. Rayleigh's papers brought these matters to everyone's attention.

Subsequently, Sir Arthur Schuster showed that the best atmospheric extinction measurements closely agreed with improved laboratory values of n, a result that Rayleigh saw as "apparently justifying to the full the inference that the normal blue of the sky is due to molecular scattering."[8] A few years later, Charles Fabry's student Jean Cabannes measured molecular scattering in the laboratory,[9] thus finally refuting Tyndall's wrong notion.

Raleigh also pointed out that molecules in dense media cannot overlap, which "detracts from the random character of the distribution. And when, as in liquids and solids, there is some approach to a regular spacing, the scattered light must be much less. . . ." We should note here that in our tenuous atmosphere, summing the scattering from individual molecules gives the same result as a calculation of scattering from density fluctuations in the gas. Thus these two ways of analyzing the scattering of sunlight in the atmosphere are equivalent.

Molecular anisotropy

So far, all is straightforward: Rayleigh has explained the blue sky with molecular scattering. But real molecules are not isotropic little spheres. Already in 1871, Rayleigh noted[10] that higher-order terms in the scattering would depend on "the *shape* of the disturbing particles." In 1881 he says,[6] "We must remember that our recent results are limited to particles of a spherical form," and adds, with a restraint rare among theoreticians a century later, "In the case of an ellipsoidal particle the problem is soluble; but it is perhaps premature to enter upon it, until experiment has indicated the existence of phenomena likely to be explained thereby."

In his great 1899 paper,[7] he observes that

> In the electric theory, to be preferred on every ground except that of easy intelligibility, the results are more complicated in that . . . the scattered ray depends upon the shape and not merely upon the volume of the small obstacle. . . .
>
> If we abandon the restriction as to sphricity, . . . the theoretical conclusion that the light diffracted in a direction perpendicular to the primary rays should be *completely* polarized may well be seriously disturbed. If the view, suggested in the present paper, that a large part of the light from the sky is diffracted from the molecules themselves, be correct, the observed incomplete polarization at 90° from the Sun may be partly due to the

Table 1: Depolarization ratios (diatomic and linear molecules at 90°)

Spectral region	Unpolarized incident light	Vertically polarized incident light
Cabannes line	$\rho_o{}^c = \dfrac{6\epsilon}{180 + 7\epsilon}$	$\rho_v{}^c = \dfrac{3\epsilon}{180 + 4\epsilon}$
rotational wings	$\rho_o{}^w = 6/7$	$\rho_v{}^w = 3/4$
total scattering	$\rho_o{}^t = \dfrac{6\epsilon}{45 + 7\epsilon}$	$\rho_v{}^t = \dfrac{3\epsilon}{45 + 4\epsilon}$

A small depolarization ratio indicates a large degree of polarization in the scattered light. For air, ϵ has an effective value of approximately 0.22. The extinction relations given in the text require $\rho_o{}^t$, which was the depolarization usually measured before lasers were used. Now authors usually report $\rho_v{}^t$, and sometimes $\rho_v{}^c$, because they use laser light, which is polarized.

molecules behaving rather as elongated bodies with indifferent orientation than as spheres of homogeneous material.

In 1910, he again warns[8] that "If the shape be elongated, there would be incomplete polarization," and that "a molecule, especially a diatomic molecule, can hardly be supposed to behave as if it were the dielectric sphere of theory. Questions are here suggested for whose decision the time is perhaps not yet ripe."

Finally, in a 1918 paper[11] (his 430th publication) *On the Scattering of Light by a Cloud of Similar Small Particles of any Shape and Oriented at Random*, Rayleigh says, "My son's recent experiments upon light scattered by carefully filtered gases reveal a decided deficiency of polarization in the light emitted perpendicularly, and seem to call for a calculation of what is to be expected from particles of arbitrary shape."

He considers first an axially symmetric molecule, and then a general triaxial one, whose electric polarizabilities along its axes are A, B, and C. After averaging over all orientations, he calculates "the *ratio* of intensities of the two polarized components in the light scattered at right angles." This ratio, which had been measured by his son, Robert John Strutt,[12] was soon denoted by ρ in Cabannes's thesis,[13] and then was named the *depolarization* by Louis Vessot King.[14] We should note that a small depolarization ratio signifies a large degree of polarization in the scattered light.

Rayleigh treats two kinds of depolarizations. The first, which I shall call $\rho_v{}^t$ (where t and v denote total scattering and vertical polarization, respectively), occurs "when the primary light, propagated parallel to X, is completely polarized with vibrations parallel to Z, the direction of the secondary ray [the observed ray] being along OY," as shown in figure 3. The second, $\rho_o{}^t$ (which is almost twice as great), arises "if the primary light travelling in direction OX is unpolarized." Rayleigh finds that polarized light scatters into light that has a depolarization ratio of

$$\rho_v{}^t = \frac{A^2 + B^2 + C^2 - AB - BC - CA}{3(A^2 + B^2 + C^2) + 2(AB + BC + CA)} \qquad (2)$$

and that for unpolarized incident light, the scattered light has a depolarization ratio of

$$\rho_o{}^t = \frac{2(A^2 + B^2 + C^2 - AB - BC - CA)}{4(A^2 + B^2 + C^2) + AB + BC + CA} \qquad (3)$$

It is important not to confuse $\rho_o{}^t$ with $\rho_v{}^t$ as some recent authors have done.[1] The relation between the two depolarizations (given implicitly in table 1) is sometimes attributed to Kariamanikkam Krishnan or Cabannes, but was first published by King.[14]

The younger Strutt had problems with impurities (and probably stray light) in his first experiments,[12] and found spurious depolarizations of 3.2% for argon and 42% for helium. He later reported[15] much lower values, explaining that "the argon formerly used, which was, I believe, of French origin, had been put away in bottles. . . . A very definite smell of hydrogen sulphide was noticed in emptying the old bottles. The presence of a trace of this gas would quite account for a fog giving misleading results." As Cabannes[13] had obtained negligible depolarization from *his* argon, and had correctly concluded that the proper value to adopt was zero, while Rayleigh *fils* (figure 4) continued to claim a small residual depolarization for the monatomic gases, which "I do not think . . . can be explained away," the reader may judge on which side of the Channel something was rotten.

A more convenient parameter

Cabannes[13] noticed that only two functions of Rayleigh's A, B, and C appear in equations 2 and 3, $(A^2 + B^2 + C^2)$ and $(AB + BC + CA)$, which he denoted by ΣA^2 and ΣBC for short. These two independent quantities can also be expressed in many other ways.

> For example, Rayleigh[11] inquired whether a want of equality among the coefficients A, B, C interferes with the relation between attenuation and refractive index, explained in my paper of 1899. The answer appears to be in the affirmative, since the attenuation depends upon $A^2 + B^2 + C^2$, while the refractive index depends upon $A + B + C$. . . .

This distinction between the mean-square polarizability and the square of the mean is fundamental. It is readily expressed in Cabannes's notation, as $\Sigma BC = [(\Sigma A)^2 - \Sigma A^2]/2$.

Cabannes[13] preferred to use the depolarization $\rho_o{}^t$ and the refractive index μ as the two independent parameters. In these terms, he found the intensity scattered at right angles to be larger by a factor

$$F_c = (6 + 6\rho_o{}^t)/(6 - 7\rho_o{}^t)$$

than for a gas of isotropic molecules with the same refractive index. He erroneously assumed that the extinction would increase by the same factor.

However, King[14] showed that because the molecular anisotropy makes the scattering more nearly isotropic, the extinction increases by the factor

$$F_k = (6 + 3\rho_o{}^t)/(6 - 7\rho_o{}^t)$$

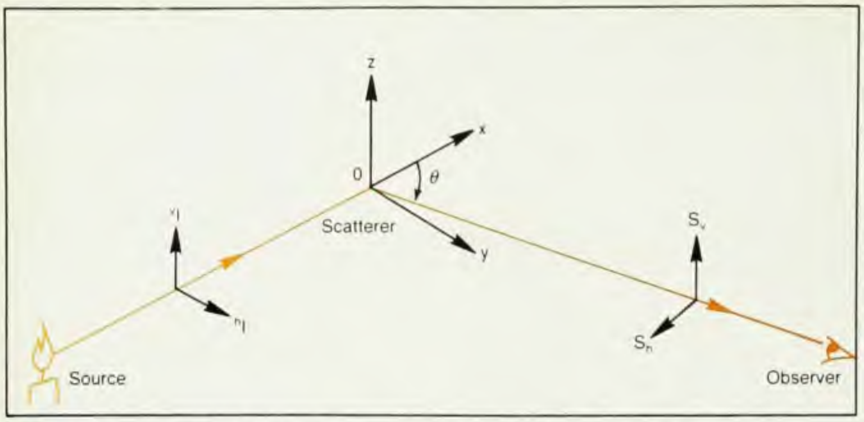
instead. Thus, while the fraction of the incident unpolarized illumination that is scattered by a unit volume of gas into a unit solid angle at θ, is

$$\frac{\pi^2(\mu^2 - 1)^2}{2n\lambda^4} \times \frac{6 + 6\rho_o{}^t}{6 - 7\rho_o{}^t}\left[1 + \frac{(1 - \rho_o{}^t)}{(1 + \rho_o{}^t)} \cdot \cos^2\theta\right]$$

which contains F_c, the extinction coefficient, found by integrating this expression over the sphere, contains F_k. (It is F_k times the extinction coefficient given in equation 1.)

Unfortunately, F_k is widely but mistakenly called "the Cabannes anisotropy factor." In fact, Cabannes[16] calls only F_c "*le facteur d'anisotropie*;" F_k does not appear explicitly in his work.

Later, George Placzek chose as parameters the trace α and the anisotropic part γ of the polarizability tensor, and these two invariants are widely used today. The refractivity is proportional to α, and the depolarizations, given in table 1, are more compactly expressed[17] by writing $\epsilon = (\gamma/\alpha)^2 = (\Sigma A^2 - \Sigma BC)/(\Sigma A/3)^2$. The parameter ϵ is a measure of the anisotropy in a molecule's polarizability. In this notation, the ratio of the mean-square polarizability to the square of the mean, α, is just $F_k = 1 + (2\epsilon/9)$. For air, ϵ has an effective value of about 0.22.



Scattering geometry and notation. Incident light (*I*) is scattered by a molecule at the origin (*O*) through an angle θ. The scattered light *S* is resolved into vertical and horizontal components S_v and S_h with electric vectors perpendicular and parallel to the scattering plane xy. Superscripts are used to denote the polarization of incident radiation; subscripts, the polarization of scattered radiation. Figure 3

Moving molecules

The real confusion began with Chandrasekhara Raman's 1928 announcement of his observation of "a new radiation," due to *vibrational* combination scattering. Cabannes[18] recognized the new frequencies as the "optical beats" between the molecules' internal frequencies and that of the monochromatic illumination, an effect he had sought since 1924. He gave a classical analysis, showing that the changing polarizability presented by a rotating molecule also causes the scattered wave to be amplitude-modulated. The spectrum of scattered light then contains the incident "carrier" frequency and two side-bands shifted by twice the rotation frequency. Cabannes and Yves Rocard[18] gave the relative intensities of the shifted and unshifted parts in both polarization states and showed that they add up to Rayleigh's result for stationary molecules (see table 2).

Charles Manneback[19] treated the problem quantum-mechanically, and found that "in the limit $J \to \infty$ . . . one gets full agreement with the results of Cabannes." At temperatures high enough to populate states with large rotational quantum number *J*, Cabannes's results are valid, "if one thinks of the Rayleigh line as split into just three parts," with all the rotationally-displaced lines on each side of the carrier frequency lumped together.

> We will for brevity call the radiation displaced by vibrational fundamentals and overtones Raman radiation or lines, whereby we also think of the attendant fine structure as included. The undisplaced scattering, including its fine structure, we will call Rayleigh radiation or lines

says Manneback. Placzek and Edward Teller[20] likewise speak of the "rotational fine structure of the Rayleigh line." Cabannes[21] said explicitly,

> Let us suppose that there are no intramolecular vibrations and that the atomic nuclei remain fixed at their stable equilibrium positions; the coefficients *A*, *B*, *C* are constants. . . . One gets nothing in the scattered light but the exciting radiation (or, more exactly, the slightly-dispersed ensemble of the exciting line and the rotational lines.) This ensemble constitutes the radiation of Lord Rayleigh.

These papers are among the first to use the terms "Rayleigh scattering" and "Rayleigh radiation" for scattering by anisotropic molecules. Their usage is perfectly justified historically, as the younger Rayleigh discovered depolarization by anisotropic molecules and his father developed the basic theory. How, then, did the conflicting uses of the term "Rayleigh line" arise?

First, careless readers of Manneback's abstract[19] got the wrong idea, as he mentions "radiation scattered without change of frequency (Rayleigh lines) and with change of frequency (Raman lines)," and implies that only vibrational changes are meant, by referring to "rotational fine structure." Franco Rasetti had already called the rotational parts of Manneback's "Rayleigh" line "rotational Raman" lines. From here it was an easy step for S. Bhagavantam[22] to reproduce Cabannes's expression[18] for the middle of Manneback's "three parts" ($^{v}C_{v}$ and $^{v}C_{h}$ in table 2), and to call this the "intensity of the true Rayleigh scattering," as opposed to the "pure rotational Raman lines" on either side of this "Rayleigh line." He finds that "the true *depolarisation* of the Rayleigh scattering . . . should be only a *fraction* (about 1/4th) of the depolarization of *unresolved* scattering." (Compare ρ^{c} with ρ^{t} in table 1.)

Herbert Stuart[2] was aware of the dangers of this terminology,

> . . . the broadening of the Rayleigh line, and thus the intensity of the unresolved fine structure, increases with the anisotropy of the scattering molecule and . . . the edges, unlike the line center, are unpolarized. The intensity of all the rotational lines can thus make a marked contribution to the total radiation of strongly anisotropic molecules, and thereby appreciably influence the observed depolarization. Hence, one might at first fear that all previous depolarization measurements were counterfeit and worthless. But theoretical investigation immediately shows . . . that the previously derived connection between the optical anisotropy and the usually observed depolarization remains true even when molecular rotation is taken into account.

In spite of this warning, the error he had foreseen has recently been committed,[1] as a direct result of restricting Rayleigh's name to the central line.

Because Cabannes[18] first predicted the intensity and polarization of this central line, I think it is appropriate to call it "the Cabannes line." Cabannes also deserves recognition for having first observed molecular scattering in the laboratory. Finally, as Cabannes correctly found no significant depolarization in the light scattered by argon —light that consists entirely of the central line—while the younger Rayleigh was claiming large spurious anisotropic effects, Cabannes deserves eponymy for his good experimental work on the line, but Rayleigh does not.

Thus, Rayleigh scattering is the sum of the Cabannes line and the rotational lines (see figure 5b).

Structure of Cabannes line

After the elder Rayleigh's death, but before the rotational structure of Rayleigh scattering had been thought of, Marcel Louis Brillouin and Leonid Isaakovich Mandel'shtam predicted a splitting of molecular scattering in dense media. Their doublet, due to the Doppler shifts caused by sound waves that create a Bragg reflection condition for light, can be thought of as the *translational* "Raman" spectrum. (Doppler broadening due to thermal motions had been explicitly excluded from consideration by Cabannes and Rocard.[18])

Soon after the discovery of the Raman effect, Evgenii Feodorovich Gross,[23] in Leningrad, "attempted to find out whether in light scattered in various organic liquids the Raman lines, due to frequencies in the rotation spectrum, are present." He found, instead, a triplet structure "due to acoustic oscillations like those used by P.

Debye . . . for explaining the variation of the specific heat of solids," which he verified by checking the angular dependence of the splitting. "Such an experiment was necessary because the presence of undisplaced and multiple components seemed to contradict the above interpretation." He called the components of the triplet "modified" and "unmodified."

Gross's "unmodified" line was finally explained by Lev Landau and Placzek[24] in a note, *Structure of the undisplaced scattering-line*. They say

> If we consider the scattered light connected with the density fluctuations . . . for fluids and gases that are not too dilute, the undisplaced line splits into a triplet. The two outer components of this form the familiar Brillouin–Mandelstam doublet with angle-dependent splitting $\Delta\nu = \pm\nu(v/c)\,2\sin\theta/2$ (v the sound speed); but besides this there is still an undisplaced component, and the ratio of the two outer components to the intensity of the triplet is given to a good approximation by the ratio of specific heats c_v/c_p. . . .
>
> The widths of the 3 components can be given quantitatively; they are determined by viscosity and heat conductivity.
>
> For gases, these results are valid so long as $l \ll \lambda/(2\sin\theta/2)$ (l the mean free path). For greater mean free paths the 3 components flow into one another and the structure of the line ultimately attains the Gaussian form, with angle-dependent width, as required by the Doppler effect.

(Notice that this width collapses to zero in the forward direction, as is necessary for this to be coherent.)

The central component of the Cabannes line, due to scattering from density fluctuations that do not propagate, could be called the "Gross line" after its discoverer. As Rayleigh had nothing to do with it, his name should clearly *not* be used. Likewise, the common term "Rayleigh–Brillouin scattering" is unsuitable for the resolved Cabannes line; "Landau–Placzek scattering" would be appropriate. Although Placzek contributed heavily to both the quantum-mechanical theory of the Cabannes line and the thermodynamical theory of its triplet fine structure, it seems historically inadequate to attach just one or two names to this triplet. Perhaps a descriptive term like "fluctuation scattering" is the most suitable way to refer to the triplet structure of the undisplaced central line.

Coherence

Even in low-density gases, at angles far enough from forward scattering that this Landau–Placzek triplet structure does not appear, the Cabannes line can be divided another way: into coherent and incoherent parts.

The incoherent part is the Q branch[19,20] of the rotational Raman band. (See figure 5.) It is due to transitions between degenerate states with different magnetic quantum numbers, but the same rotational and vibrational quantum numbers. This incoherent part, associated with the molecular anisotropy, has the same depolarization as the ordinary S-branch rotational lines that form the rotational "wings" (see table 2). In diatomic and linear molecules, such as oxygen, nitrogen and carbon dioxide, one-fourth of the rotational band intensity is in the Q branch, so the depolarization of the Cabannes line is about one-fourth that of the whole Rayleigh scattering, as Bhagavantam[22] found.

The coherent part (Placzek's "trace scattering") is associated with the mean polarizability and the refractive index. It corresponds to isotropic scatterers. It is spectrally superimposed on the rotational Q branch of the anisotropic scattering, which does not contribute to the refractive index because it is incoherent. The sum of the coherent or "trace" scattering and the incoherent rotational Q branch is the Cabannes line (see figure 5).

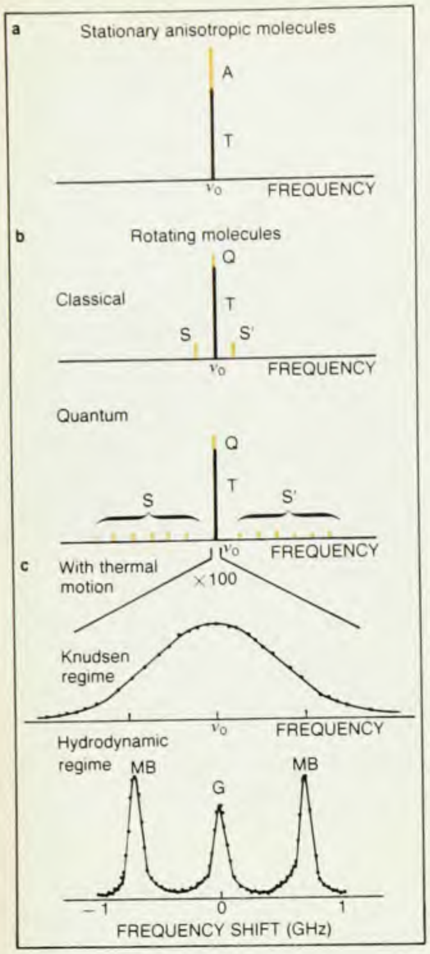
Robert John Strutt, 1875–1947, son of John William. Sketch by Augustus John. (Courtesy of John Arthur Strutt.) Figure 4

While the frequency displacement of the rotational S branches depends on molecular rotation, the incoherence of the rotational band (both Q and S branches) does not. The incoherence is due to the random orientations of the

Table 2: Relative intensities of scattered light

	Vertically-polarized-light input	Horizontally-polarized-light input	Natural-light input (the sum)
Cabannes line (no frequency shift)	${}^{v}C_{v} = 180 + 4\epsilon$ ${}^{v}C_{h} = 3\epsilon$ ${}^{v}C_{o} = 180 + 7\epsilon$	${}^{h}C_{v} = 3\epsilon$ ${}^{h}C_{h} = 3\epsilon + (180 + \epsilon)\cos^2\theta$ ${}^{h}C_{o} = 6\epsilon + (180 + \epsilon)\cos^2\theta$	${}^{o}C_{v} = 180 + 7\epsilon$ ${}^{o}C_{h} = 6\epsilon + (180 + \epsilon)\cos^2\theta$ ${}^{o}C_{o} = (180 + 13\epsilon) + (180 + \epsilon)\cos^2\theta$ $= 12\epsilon + (180 + \epsilon)(1 + \cos^2\theta)$
Rotational Raman wing (frequency shifted)	${}^{v}W_{v} = 12\epsilon$ ${}^{v}W_{h} = 9\epsilon$ ${}^{v}W_{o} = 21\epsilon$	${}^{h}W_{v} = 9\epsilon$ ${}^{h}W_{h} = 9\epsilon + 3\epsilon\cos^2\theta$ ${}^{h}W_{o} = 18\epsilon + 3\epsilon\cos^2\theta$	${}^{o}W_{v} = 21\epsilon$ ${}^{o}W_{h} = 18\epsilon + 3\epsilon\cos^2\theta$ ${}^{o}W_{o} = 39\epsilon + 3\epsilon\cos^2\theta$ $= 36\epsilon + 3\epsilon(1 + \cos^2\theta)$
Rayleigh scattering (total)	${}^{v}T_{v} = 180 + 16\epsilon$ ${}^{v}T_{h} = 12\epsilon$ ${}^{v}T_{o} = 180 + 28\epsilon$	${}^{h}T_{v} = 12\epsilon$ ${}^{h}T_{h} = 12\epsilon + (180 + 4\epsilon)\cos^2\theta$ ${}^{h}T_{o} = 24\epsilon + (180 + 4\epsilon)\cos^2\theta$	${}^{o}T_{v} = 180 + 28\epsilon$ ${}^{o}T_{h} = 24\epsilon + (180 + 4\epsilon)\cos^2\theta$ ${}^{o}T_{o} = (180 + 52\epsilon) + (180 + 4\epsilon)\cos^2\theta$ $= 48\epsilon + (180 + 4\epsilon)(1 + \cos^2\theta)$

Superscripts give polarization of incident radiation; subscripts give polarization of scattered radiation; v, h, and o denote vertical, horizontal and natural (unpolarized), respectively. Placzek's coherent "trace scattering" is scaled to 180 here, to avoid fractions. Intensities are for linear and diatomic molecules.



Spectral distribution of scattered monochromatic light. **a** The effect of molecular anisotropy alone gives two components in the scattered light: A depolarized incoherent anisotropy radiation (A), and a coherent part (T) due to the isotropic part of the polarizability. Both have the same frequency (ν_0) as the incident radiation. **b** Effects of molecular rotation. A splits classically into equal Stokes (S) and anti-Stokes (S') components, and an unshifted part, Q. All three components have the same depolarization ρ^w, given in table 1. $S + S' = W$, the rotational Raman wing, and $Q + T = C$, the Cabannes line listed in table 2. Quantum mechanically, S and S' are unequal and split into rotational lines, forming the S branches of the rotational Raman band. The Q branch coincides with T, Placzek's "trace scattering" (scaled to 180 in table 2). **c** Effects of thermal motion become apparent when the frequency resolution is increased, here by a factor of 100. The profile of the Cabannes line depends on the density. At low densities molecules scatter independently, producing a Gaussian line-profile. At high densities the central Gross line (G, due to scattering from stationary density fluctuations) bisects the Mandel'shtam–Brillouin doublet (MB, due to scattering from moving density fluctuations, sound waves). In either case, the halfwidth of the whole pattern is proportional to $2\nu_0(v/c) \times \sin(\theta/2)$. Bottom curve is actual data for nitrogen, from Q. H. Lao, P. E. Schoen, B. Chu, J. Chem. Phys. **64**, 3547 (1976). Figure 5

molecules. Hence, the anisotropy radiation remains undiminished in liquids, where the coherent radiation, due to density fluctuations, is much reduced.

If we observe for a time short compared to the period of molecular rotation, our frequency resolution is so poor that we cannot separate the S-branch lines from the Cabannes line. Then we can regard the molecules as stationary, but randomly oriented. This is just the case Lord Rayleigh treated in his 1918 paper[11] (see figure 5a). The total Rayleigh scattering depends on the mean-square polarizability, while the refractive index and coherent scattering depend on the square of the mean.

Terminology

The whole of molecular scattering, the Cabannes line, and the Gross line have all been called "the Rayleigh line" by different workers. The latter two phenomena, unknown during Lord Rayleigh's lifetime, are clearly inappropriate uses of his name. The confusing term "Rayleigh line" should be avoided.

Although the Cabannes line is not monochromatic, and contains a mixture of coherent and incoherent scattering, one sometimes wants a single term to describe its cause. "Elastic scattering" may be appropriate, as the *internal* molecular energy remains unchanged. Brillouin spectroscopists, however, might want to restrict this term to Gross's "unmodified" line. The whole triplet structure might logically be attributed to "Landau–Placzek scattering" or "fluctuation scattering," composed of the Brillouin doublet and the Gross line. But this is inappropriate at low densities, where the Cabannes line has a Gaussian profile. Some consistent terminology is required to distinguish the Raman spectroscopists' "undisplaced line" from that of the Brillouin spectroscopists, to accommodate situations[17] that involve both Brillouin and rotational Raman scattering simultaneously.

Finally, what about the term "Tyndall scattering"? It is used for all particulate scattering by some authors, and applied to the Cabannes line by others. Scattering by turbid media (hydrosols) had been studied by Brücke and Stokes, among others, before Tyndall. The neutral points Tyndall found for large particles had been discovered earlier by Gilberto Govi. Historically, Tyndall's seminal contribution was to provoke Rayleigh's life-long interest in scattering, starting with *small spheres*. As large-sphere scattering is generally called "Mie scattering", it seems best to restrict "Tyndall scattering" to that by small spheres.

Molecular scattering should certainly be excluded, because of Tyndall's belief that clean gases were "optically empty." As Cabannes[16] says,

> it is in error that some authors apply "Tyndall phenomenon" to the molecular scattering of light, to which should remain attached the name of Lord Rayleigh.

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