Colors of the sky

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How can anyone have the audacity to write about colors of the sky in the year 1985? Surely by now everything that *can* be said *has* been said. Perhaps, but we can't help noting that all explanations we have read in textbooks or monographs are either incorrect in one or more particulars or incomplete. This is a strong statement, perhaps even an abrasive one. We shall do our best to support it.

Blueness of the sky

Up until about a century ago the origin of the sky's blueness was still a topic of keen scientific interest. It had attracted such giants as Newton, Clausius, and Tyndall. But it wasn't until 1871 that a satisfactory explanation began to emerge. In this year, Lord Rayleigh, then only 29 years old, published a paper entitled "On the light from the sky, its polarization and colour."[1] Rayleigh was drawn to the problem of the blue sky as an outgrowth of his interest in color vision. In his landmark paper he showed by simple dimensional analysis that particles with diameter much smaller than the wavelength of the light illuminating them scatter light according to the inverse fourth power of the wavelength. Rayleigh's arguments are so simple that they are worth repeating here, although in a modern form.

If a particle is very small compared with the wavelengths of the light illuminating it, then scattering by it is proportional to its volume V. That is, under the stimulus of an external field all the elementary oscillators into which the particle may be subdivided scatter waves that are in phase with one another because of the particle's small dimensions. Note that because of the assumed small size of the particle, the wave penetrates and affects all parts equally. The total scattered electric field E_s is therefore proportional to the particle's volume. But this scattered field arises because of excitation by the incident field with amplitude E_i, hence E_s is also proportional to E_i. The scattered field must diminish with distance from the particle in such a way that energy is conserved. If we imagine a sphere of radius r, hence surface area $4\pi r^2$, to be centered on the particle, then the total energy scattered across this spherical surface must be independent of r. This will be true if the irradiance or radiant flux density (J/m^2) decreases as $1/r^2$ (since the area increases as r^2). But the irradiance is proportional to $E_s{}^2$, so E_s must be proportional to $1/r$. Dimensional homogeneity therefore requires the scattered field to be inversely proportional to the square

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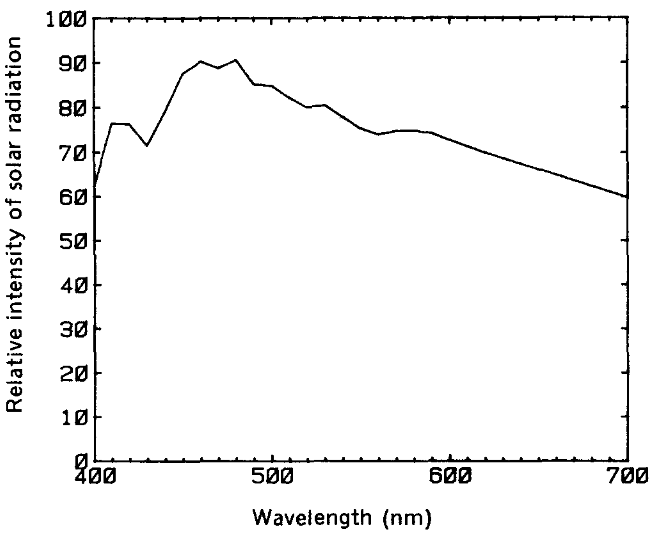

Fig. 1. The spectrum of sunlight outside the earth's atmosphere.[3]

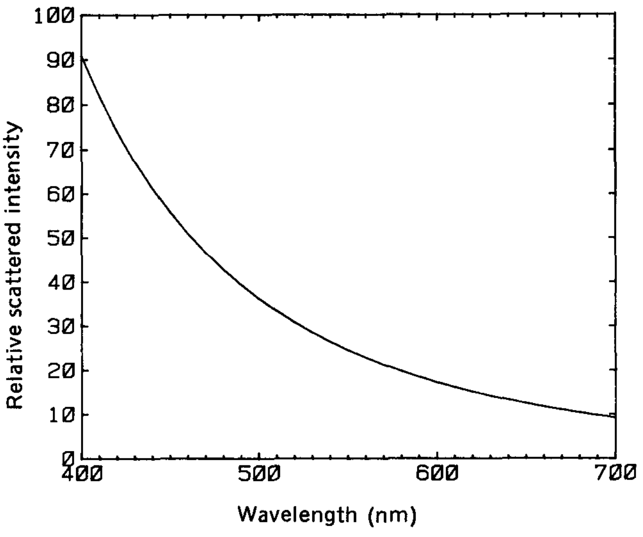

Fig. 2. Spectral dependence of scattering by atmospheric molecules. The wavelength dependence of the molecular scattering coefficient taken from Ref. 4 is to good approximation given by Eq. (2).

of the wavelength λ, the only remaining relevant quantity with dimensions of length (recall that V is the volume of the particle):

$$E_s = KE_i V/\lambda^2 r \qquad (1)$$

where K is a dimensionless constant. The scattered irradiance I_s is determined by squaring the preceding equation:

$$I_s = K^2 I_i V^2/\lambda^4 r^2 \qquad (2)$$

where I_i is the irradiance of the incident light. We have called K a dimensionless constant although this is not strictly correct. Dimensionless it certainly is, but it does depend on wavelength (specifically, on the refractive index of the material of which the particle is composed). But we can ignore this at wavelengths well longward of strong absorption bands. Equation (2) is often said to describe "Rayleigh scattering," although this term has many meanings, which has been pointed out in an incisive article by Young.[2]

It follows from Eq. (2) that if a small particle is illuminated by white light the shorter wavelength components (e.g., blue) are scattered more than the longer wavelength components (e.g., red). Indeed, this is the usual explanation that is glibly tossed out to students to explain the blue sky: particles suspended in the atmosphere scatter blue light more than red, hence the sky is blue. It is a rare event in our experience for a student to raise his hand upon hearing this explanation and snort indignantly, "That's rubbish. Violet is even shorter than blue. According to your argument the sky should be violet."

What is missing from this argument is that what one perceives when looking at the sky is determined by more than just the properties of the scatterers in the atmosphere. Three functions, the solar spectrum (Fig. 1), the wavelength dependence of the scattering (Fig. 2), and the spectral response of the eye (Fig. 3) combine to give a signal that is processed by the brain to yield the sensation we call blue. Although violet light is indeed scattered more than blue, the eye is less sensitive to violet light and, of less importance, the solar spectrum is somewhat depleted of the shorter wavelengths.

The sky is not blue in the sense that a blue laser is. *All* colors are present in skylight, although the *dominant* wavelength lies in the blue. A source of visible light gives the same visual sensation as one composed of a mixture of white light and light of a single wavelength,[6] which provides a convenient way to characterize any light source. The relative amount of light of this dominant wavelength is called the *purity* of the source. One of our graduate students, Ray Lee (a propitious name for someone interested in optics), wrote a program for determining the dominant wavelength and purity of any light source. With this program we calculated that the purity of skylight cannot exceed about 42%; the dominant wavelength is 475 nm, which is in the blue. This is an upper limit; the purity of real blue skies will be less than this, often much less. Thus, the blue sky is really not all that blue.

Lord Rayleigh was somewhat circumspect about the nature of the small particles in the atmosphere responsible for the blue sky. He did not believe that they were composed of water or ice, which his predecessors took for granted. "If it were at all probable that the particles are all of one kind," he wrote in 1871, "it seems to me that a strong case might be made out for common salt. Be this as it may the optical phenomena can give us no clue." That is, *all* sufficiently small particles, regardless of composition, scatter light according to the inverse fourth power of the wavelength in spectral regions far from strong absorption bands.

This loose end must have bothered Rayleigh because he returned to the problem of the blue sky 28 years later, at which time he wrote that "I think that even in the absence of foreign particles we should still have a blue sky."[7] That is, air molecules themselves are sufficient to make the sky blue. After all, they are certainly much smaller than the wavelengths of visible light; moreover, unlike particles, they can neither be blown away nor be washed out of the atmosphere by rain.

We'll go one step beyond Rayleigh and state that not only are foreign particles not necessary for the explanation, but they are undesirable. Before supporting this assertion, let us dispose of a few misconceptions, one of which is shockingly long lived, and criticize what is sometimes put forward as the real explanation of the blue sky.

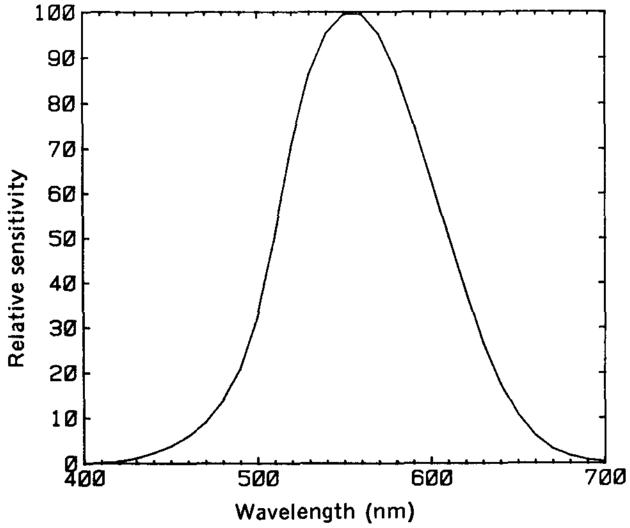

Fig. 3. Spectral sensitivity (luminous efficiency) of the human eye.[5]

The mystical properties of water vapor

We often hear it said or, worse, see it written, that water vapor is responsible for the blue sky. Water vapor, to some people, possesses mystical properties. At visible wavelengths scattering by water vapor is not vastly different, *molecule for molecule*, from scattering by the other molecular constituents of the atmosphere. Indeed, the water molecule scatters visible light somewhat less than either nitrogen or oxygen. "But water is a polar molecule," is likely to be the response to this statement. True enough. Unfortunately, water's permanent dipole moment does it precious little good at 10^{15} Hz. "But water is intrinsically blue," might be a further response by a proponent of water vapor as the cause of the sky's blueness. This is also true – but irrelevant. A beam of white light must be transmitted through many meters of liquid water to become colored because of selective absorption of red light, whereas if all the water vapor in the atmosphere were condensed it would, on average, be a few centimeters thick.

Water vapor is at a distinct disadvantage compared to nitrogen and oxygen because it is much less abundant. It would make as much sense to say that argon (one of its discoverers was Rayleigh, by the way) causes the blue sky as to say that water does because argon's abundance is about equal to that of water's. Argon and water vapor do contribute to skylight, but they are minor contributors. Without them in the atmosphere, the sky would still be blue; indeed, as we shall show, it would be bluer.

To paraphrase H. L. Mencken, one observation is worth a thousand syllogisms. We have yet to encounter in the writings of desert travelers any mention of the strange absence of blue skies. This by itself ought to dispel forever the notion that water vapor causes the blue sky – but it won't of course: people believe what they want to believe.

Ozone

Absorption of visible light by most of the molecular constituents of the atmosphere is negligible. One exception is ozone, which has weak absorption bands between 450 and 750 nm, the Chappuis bands[8] (absorption in the ultraviolet, particularly shortward of 300 nm, is much greater). Absorption by ozone tends to be greater toward the long wavelength end of the visible spectrum. Ozone is therefore a contributor to the blue sky, but it is a minor contributor. Only when the sun is very low, hence path lengths of sunlight through the atmosphere are greatest, does absorption by ozone appreciably modify the spectrum of skylight.[9] During most of the day the effect of ozone on the sky's blueness is negligible. Even near twilight, ozone intensifies the sky's blueness but is not its primary cause. Without ozone, therefore, we should still have a blue sky.

Fluctuation theory of scattering

We sometimes encounter people who assert that it isn't molecular scattering that causes the sky to be blue, it is "really" scattering by density fluctuations. This statement, without qualification, is tantamount to denying the existence of molecules, something which ceased to be respectable in about 1913. This was the year of publication of Jean Perrin's *Les Atomes,*[10] the culmination of many years of experimental investigations of Brownian motion. Perrin and others recognized that Brownian motion was the key to demonstrating molecular reality (for an excellent appraisal of Perrin's work, we heartily recommend Ref. 11). After years of painstaking work Perrin did not proudly proclaim that Brownian motion is really caused by fluctuations but rather that it is really caused by molecules. Indeed, Brownian motion provides a glimpse into a microscopic world that many eminent scientists of the last century, most notably Ostwald and Mach, refused to accept as anything other than an unverified – and unneeded – hypothesis.

If the blue sky is really caused by fluctuations then so also is Brownian motion, hence molecules don't exist. There are strong parallels between molecular scattering of light and Brownian motion. To say that small particles suspended in a liquid are kicked here and there by fluctuations is no more than shorthand for saying that at any instant the molecular collisions on one side of a particle are not exactly balanced by collisions on the opposite side, hence the chaotic trajectories of particles in Brownian motion. But it is the molecules that do the kicking; a fluctuation is neither capable of kicking nor of being kicked. Nor is it capable of scattering: only molecules do that. Just, as the correlations in molecular motions determine the amplitude of Brownian motion, so also do they determine the total light scattered by a collection of molecules.

There is something called the fluctuation theory of light scattering in optically dense media, that is, media in which there are many scatterers in a cube one wavelength on a side. By means of this theory, which is associated with the names of Einstein and Smoluchowski, one can circumvent the detailed structure of matter. One pretends that matter is continuous, but characterized by a refractive index that is a random function of position. The resulting expressions for scattering are more or less in agreement with experiments. Einstein stated that "it is remarkable that our theory does not make *direct* use of the assumption of a discrete distribution of matter."[12] Note the emphasis on the word "direct" here. Einstein circumvented a difficulty, but this hardly implies that one could not meet it head on. Indeed, the expression that Einstein derived without explicitly considering molecular scattering can be obtained from a molecular point of view. This was done by Zimm, for example, in 1945.[13]

There is no dispute, then, about what "really" causes the sky to be blue? It is really scattering by molecules. Or,

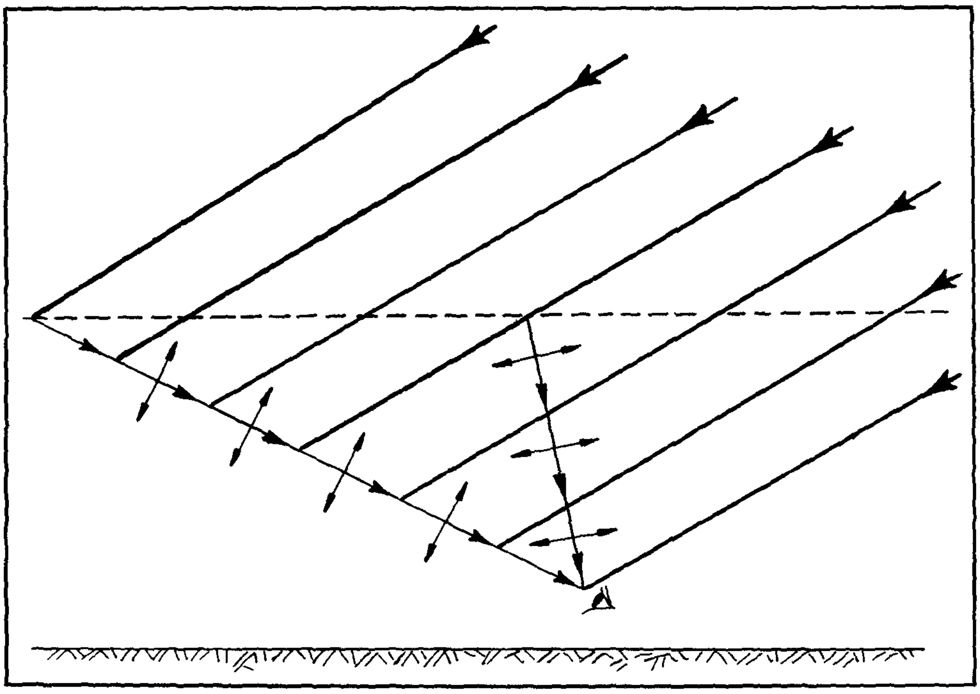

Fig. 4. Path lengths in the atmosphere. An observer receives light scattered by all the molecules and particles along his line of sight.

if you want to be more precise, scattering by electrons. Even more precise, scattering by *bound* electrons: free electrons would not give us a blue sky. The preposition "by" indicates an agent, and molecular scattering is the agent responsible for the sky's blueness. But what about its brightness, that is, how do N molecules scatter if scattering by one is known? Gas molecules (at NTP) are separated by distances that are small compared with the wavelengths of visible light, so it is by no means obvious that one can merely add intensities of the light scattered by individual molecules to obtain the total intensity of scattered light. Yet if the molecules are completely uncorrelated, as in an ideal gas, then scattering by N is N times scattering by one. This is the only sense in which the blue sky can be attributed to scattering by fluctuations. Stated another way, there is no such thing as perfectly homogeneous matter.

Variation of purity and brightness

It is not enough merely to say that the sky is blue. The sky is neither uniform in color nor in brightness. Students of architecture are told not to render the sky uniformly blue; they aren't told why, of course, they are just threatened with dire consequences. The best blues are found near the zenith. Toward the horizon it is whiter. Almost invariably, the whiteness of the sky near the horizon is attributed to pollution. In this instance, pollution serves the same function as friction does in the undergraduate physics laboratory. If you set some students the task of measuring a physical constant, they rarely obtain the accepted value. And why is this? Friction, of course, good old friction. If it didn't exist it would have to be invented, for by good fortune there is always just enough friction in apparatus to account for the discrepancy between what students measure and what they should have measured. So it is also with pollution: in atmospheric optics, it is the universal solvent for ignorance.

We have seen white horizons in extraordinarily clean environments, in particular, the southeast coast of Iceland, the most remote part. About a quarter of a million people live in Iceland, which is about the same size as Pennsylvania. There is almost no industry in Iceland, and it is about 600 miles upwind of the nearest industry. The capital city, Reykjavik, is heated geothermally. The visibility, on the rare days when it is not raining, is extraordinary. The air is deceptively clear; one is likely to greatly underestimate distances to faraway objects. And yet the horizon sky is white on clear days. It would seem from these observations that pollution cannot be necessary for a white horizon. Why, then, is it white?

In a given direction skylight is light scattered by all the molecules and particles along the path in that direction. Incident sunlight is composed of all wavelengths; the shorter ones are more likely to be scattered toward your eye, but the longer ones are more likely to make it to your eye without being scattered again. There are fewer scatterers along a path through the atmosphere toward the zenith than toward the horizon (Fig. 4). Hence, along a zenith path the scattered sunlight, which is enriched in shorter wavelengths, is likely to reach your eye without being scattered again. Near the horizon, path lengths are longer. Hence the horizon sky is brighter at the expense of purity of color. The conventional explanation of the sky's blueness invokes only *single* scattering. But without invoking multiple scattering it is not possible to explain the nonuniformity of the sky's color and brightness. Although single scattering giveth, multiple scattering taketh away. The purest blue would be obtained in an atmosphere consisting of a *single* molecule. Of course, the brightness wouldn't be very high.

Multiple scattering is hardly mentioned at all in textbooks on optics. Yet there are many observations that are inexplicable on the basis of single scattering. Aside from the nonuniformity of the sky's color and brightness, there is the rather prosaic example of a glass of milk. Milk is a suspension of fat globules smaller than the wavelengths of visible light. If you add a drop of milk to a beaker of clean water and illuminate the resulting suspension with an intense source of white light, the scattered light has a bluish

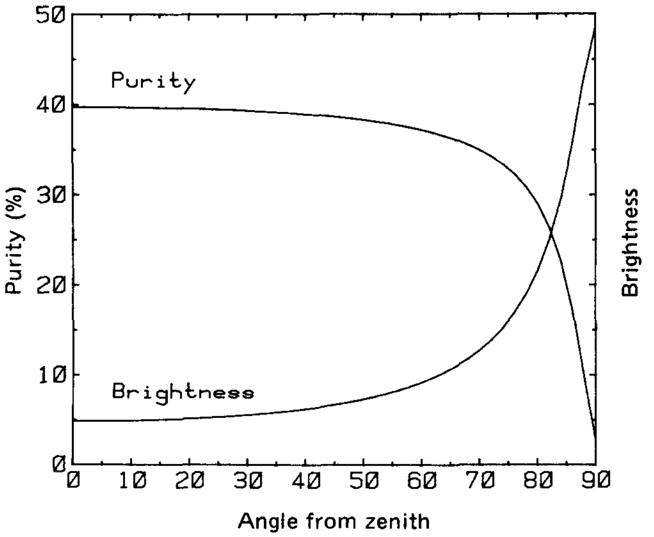

Fig. 5. Purity and brightness of the sky as functions of angle from the zenith (molecular atmosphere).

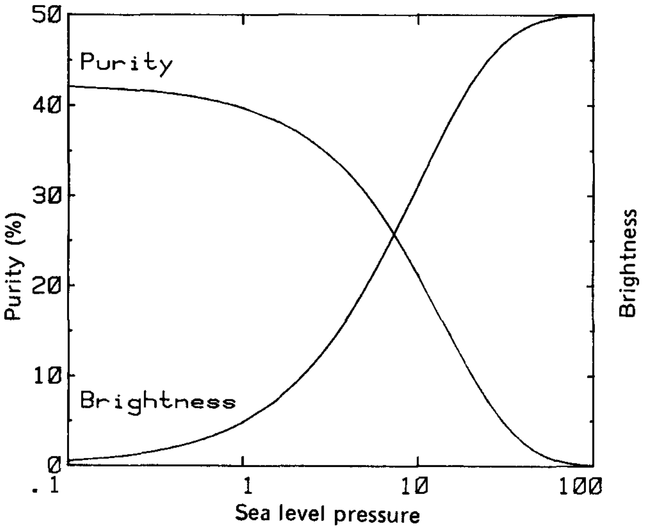

Fig. 6. Purity and brightness of the zenith sky (molecular atmosphere) as functions of sea level atmospheric pressure.

cast. And yet a glass of milk is white. If only single scattering prevailed, milk should be blue. Multiple scattering by milk and other common objects is discussed at an elementary level in Refs. 14 and 15.

We have done calculations of the purity and brightness of a molecular atmosphere, one completely free of particles (Fig. 5). Toward the zenith the purity is highest, the brightness lowest. Toward the horizon the brightness increases while the purity decreases. A white band extending to perhaps five degrees above the astronomical horizon is an intrinsic property of our atmosphere. Pollution only enhances what is inevitable. And while we are on the subject of pollution, we should mention in passing that some pollution of the atmosphere is not only inevitable, it is desirable. Even if our planet were uninhabited, its atmosphere would still be polluted in the sense that it would contain particles as well as molecules. The only way to ensure a completely unpolluted atmosphere would be to wrap our planet in a material with a low vapor pressure, aluminum foil for example, a heroic but senseless undertaking. Every cloud droplet begins its existence as a small particle composed of something other than water. Without such particles, clouds could still form, but the conditions under which they would do so would be vastly different from what we have come to expect as normal, as would be the global pattern of rainfall.

One of the implications of what we said in the previous paragraph is that if our atmosphere were much thicker the sky would be brighter but not as blue. We have done calculations to show this (Fig. 6). The brightness and purity of the overhead sky are shown as functions of sea level pressure, where the value 1 indicates the present atmosphere. It seems that we live at the bottom of the best of all possible atmospheres. If sea level pressure were, say, ten times its present value, the sky would be brighter but it would not be as pure a blue. If the atmosphere were thinner, the sky's purity would be slightly higher but it wouldn't be as bright.

We hope that it is now evident why we said that foreign particles in the atmosphere are not only unnecessary to give the sky its blue color, they are undesirable. Even particles much smaller than the wavelengths of visible light will make the sky brighter at the expense of its purity of color. More, in this instance, is not better.

We have now laid the groundwork for discussing when water vapor influences the sky's brightness and color: it is when it ceases to be water vapor. As we stated previously, the atmosphere contains particles, a great many of which are soluble in water (e.g., salt and ammonium sulfate particles). When the relative humidity exceeds about 75%, such solid particles are transformed into small solution droplets, called haze. These droplets are much smaller than typical cloud droplets, which require supersaturation for their formation (see, e.g., Ref. 16). Small though they may be, haze particles are much larger than molecules, hence they scatter light more strongly. According to Eq. (2), scattering increases as the square of the scatterer's volume (provided that it is small compared with the wavelength). When water vapor condenses, the total mass of water substance remains constant, but its state of aggregation changes. N independent water molecules scatter incoherently: scattering by N is N times scattering by one. But when these same water molecules condense into a small droplet, they scatter coherently in phase. The amplitude of a wave produced by coherent addition of N waves is proportional to N. The intensity is equal to the square of the amplitude and thus proportional to N^2. It is therefore no wonder that visibility tends to be poor on very humid days.

Water vapor does indeed affect the sky's color and brightness, but only when it ceases to be water vapor. Water vapor *per se* makes a negligible contribution to skylight. When it condenses onto soluble particles, the resulting solution droplets (haze) make the sky brighter at the expense of its purity of color. Water vapor is therefore not only not the reason why the sky is blue, it can be a reason why the sky may not be as blue as it would otherwise be.

Red sunsets and sunrises

It is sometimes stated that red sunsets and sunrises are merely inverses of the blue sky: if you understand the blue sky, the red sunset follows as a corollary. After all, if blue light is preferentially scattered out of direct sunlight, then that which is unscattered (i.e., transmitted) is

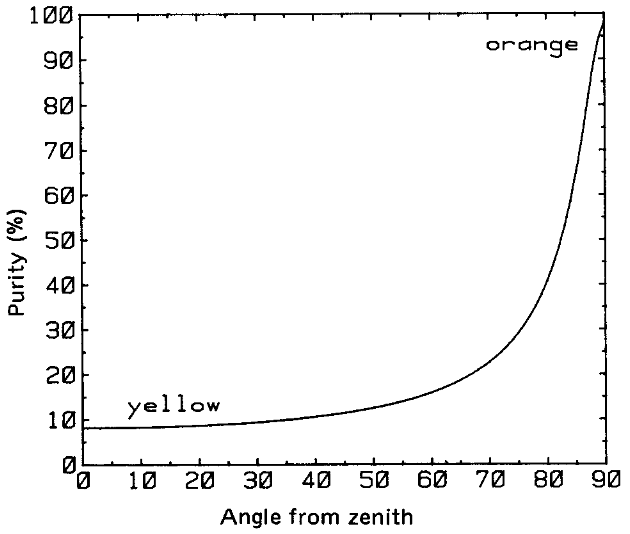

Fig. 7. Purity of color of the setting sun (molecular atmosphere).

enriched in red light. But this is only a half-truth. We think that it is fair to say that when people ask why sunrises and sunsets are red, they have in mind blood red displays like the ones that occurred following the eruption of El Chichon.

We have calculated the purity of sunlight transmitted by a molecular atmosphere, one free of all particles, as a function of solar zenith angle (Fig. 7). The purity of sunlight does indeed increase as the sun descends in the sky. At its purest, however, the dominant wavelength of this light is about 595 nm, which corresponds to orange,[17] not red. And even this orange is obtained only when the sun is within about a degree of the horizon. Otherwise, sunlight transmitted by a molecular atmosphere is yellow or yellowish-orange. This is the color one might observe in very clean environments. Even in heavily populated regions of North America yellowish-orange sunsets and sunrises are sometimes seen on cold days when clean air masses have swept down from the Arctic. Deep red sunsets and sunrises are also seen, of course. If molecular scattering is insufficient to cause them, then it must be the additional scattering by small particles in the atmosphere that shifts the hue of setting and rising suns toward the red.

Sunsets and sunrises are often more spectacular when they are accompanied by cloud layers, which may give the impression that the clouds are responsible for the colors. It is understandable why this connection might be made, but it is nonetheless false. Cloud droplets scatter visible light of all wavelengths about equally, hence they cannot color white light. They can, however, scatter sunlight that has been reddened because of scattering by small particles and by molecules. Clouds are spectrally nonselective (diffuse) mirrors, which when illuminated by white light are white and by red light are red.

Concluding remarks

Rayleigh's first paper on the sky discusses both its color and polarization. We have not discussed polarization of skylight, which requires a separate article in itself. Such an article, at an elementary level, is Ref. 18.

We end with a summarizing statement that might have sounded paradoxical had we made it at the beginning of this article. Foreign particles in the atmosphere are not necessary to give the sky its blue color, indeed, they detract from its blueness. Yet such particles are necessary to give setting and rising suns deep red colors.

Acknowledgments

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References

1. Lord Rayleigh (J. W. Strutt), "On the Light from the Sky, Its Polarization and Colour," Philos. Mag., 41, 107, 274 (1871) (reprinted in *Scientific Papers by Lord Rayleigh*, Vol. I, No. 8, Dover, New York, 1964).
2. A. T. Young, "Rayleigh Scattering," Phys. Today. **35** (1), 42 (1982).
3. M. P. Thekaekara and A. J. Drummond, "Standard Values for the Solar Constant and Its Spectral Components," Nature Phys. Sci. **229**, 6 (1971).
4. R. Penndorf, "Tables of the Refractive Index for Standard Air and the Rayleigh Scattering Coefficient for the Spectral Region between 0.2 and 20.0 μ and Their Application to Atmospheric Optics," J. Opt. Soc. Am., 47, 176 (1957).
5. M. Born and E. Wolf, *Principles of Optics*, 3rd ed. (Pergamon, Oxford, 1965), p. 185.
6. Committee on Colorimetry of the Optical Society of America, *The Science of Color* (Optical Society of America, Washington, D.C., 1963), p. 42.
7. Lord Rayleigh (J. W. Strutt), "On the Transmission of Light Through an Atmosphere Containing Small Particles in Suspension and on the Origin of the Blue of the Sky," Philos. Mag., 47, 375 (1899) (reprinted in *Scientific Papers by Lord Rayleigh*, Vol. IV, No. 247, Dover, New York, 1964).
8. R. M. Goody, *Atmospheric Radiation* (Oxford University Press, London, 1964), pp. 210-212.
9. J. V. Dave and Z. Sekera, "Effect of Ozone on the Total Sky and Global Radiation Received on a Horizontal Surface," J. Meteorol. 16, 211 (1959).
10. J. Perrin, *Atoms* (Constable, London, 1923) (English translation of *Les Atomes*).
11. M. J. Nye, *Molecular Reality* (American Elsevier, New York, 1972).
12. A. Einstein, "Theory of the Opalescence of Homogeneous Liquids and Mixtures of Liquids in the Vicinity of the Critical State," Ann. der Physik, **33**, 1275 (1910) (An English translation of this is in *Colloid Chemistry*, Vol. I, J. Alexander, ed., The Chemical Catalog Company, New York, 1926, p. 323. Following Einstein's paper is one by W. H. Martin, which gives an excellent overview of much of the early work on light scattering).
13. B. H. Zimm, "Molecular Theory of the Scattering of Light in Fluids," J. Chem. Phys. **13**, 141 (1945).
14. C. F. Bohren, "Multiple Scattering at the Breakfast Table," Weatherwise, 36 (3), 143 (1983).
15. C. F. Bohren, "Multiple Scattering at the Beach," Weatherwise, 36 (4), 197 (1983).
16. H. R. Byers, *Elements of Cloud Physics* (University of Chicago Press, Chicago, 1965), p. 35.
17. F. W. Billmeyer and M. Saltzman, *Principles of Color Technology*, 2nd ed. (Wiley-Interscience, New York, 1981), p. 50.
18. C. F. Bohren, "Polarization of Skylight," Weatherwise, 37 (5), 261 (1984).