

SHORT PAPER

RAYLEIGH SCATTERING BY AIR

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ABSTRACT

The Rayleigh scattering cross section for air is calculated from published experimental and theoretical results account being taken of the dispersion of the King correction factor. The spectral region $0.2\text{m}\mu \leq \lambda \leq 1.0\text{m}\mu$ is covered.

1. INTRODUCTION

In several instructive recent articles Young (1980, 1981a and b, 1982) has drawn attention to misconceptions regarding Rayleigh scattering, has discussed the terminology and has surveyed the history. As he pointed out (Young 1980) there is uncertainty in the Rayleigh scattering cross section for air Q_R (air) because the correction factor of King (1923) and in particular its dependence on the wavelength λ have not been properly taken into account. Accurate values of Q_R (air) are required in connection with, for example, the calculation of the rate of photo-dissociation of molecular oxygen by solar radiation in the Herzberg continuum. (See Nicolet et al 1982).

If $n(X)$ be the refractive index of constituent X at standard temperature and pressure (0°C , 760 torr) and $F_K(X)$ be the King correction factor then

$$Q_R(X) = (32\pi^3/3N^2\lambda^4) \{n(X) - 1\}^2 F_K(X) \quad (1)$$

where N is Loschmidt's number (cf Dalgarno & Williams 1962). The King correction factor may be expressed

$$F_K(X) = 1 + 2 \{\gamma(X)/3\bar{\alpha}(X)\}^2 \quad (2)$$

with

$$\gamma(X) = \alpha^{\parallel}(X) - \alpha^{\perp}(X) \quad (3)$$

and

$$\bar{\alpha}(X) = \{\alpha^{\parallel}(X) + 2\alpha^{\perp}(X)\}/3 \quad (4)$$

$\alpha^{\parallel}(X)$ and $\alpha^{\perp}(X)$ being the parallel and perpendicular components of the dynamic polarizability (cf Young 1980). Denoting the fractional volume abundance of X in dry air by $f(X)$ we have

$$Q_R(\text{air}) = \sum_X f(X) Q_R(X) \quad (5)$$

where the summation is over the main constituents (nitrogen, oxygen, argon and carbon dioxide). In order to compute Q_R (air) it is evident that accurate tabulations of both $\{n(X)-1\}$ and $F_K(X)$ against λ are needed.

2. REFRACTIVE INDICES

Peck and Khanna (1966) have made interferometric measurements on $\{n(N_2)-1\}$ at selected wavelengths in the range $2.06\text{m}\mu > \lambda > 0.468\text{m}\mu$ and have shown that their results may be represented closely by

$$10^8 \{n(N_2) - 1\} = 6855.200 + 3243157.0/(144-\sigma^2), \quad \lambda > 0.468\text{m}\mu \quad (6)$$

with

$$\sigma = 1/\lambda \text{ (in } \mu\text{m)} \quad (7)$$

Abjean et al (1970) have made similar measurements in the range $0.254\mu\text{m} > \lambda > 0.181\mu\text{m}$. A good representation of them is

$$10^8 \{n(N_2) - 1\} = 6998.749 + 3233582.0/(144 - \sigma^2), \quad \lambda < 0.254\mu\text{m} \quad (8)$$

To cover the intermediate spectral region data points near $0.468\mu\text{m}$ and $0.254\mu\text{m}$ were fitted by expressions of the same form as (6) and (8) giving

$$10^8 \{n(N_2) - 1\} = 5989.242 + 3363266.3/(144 - \sigma^2), \quad 0.468\mu\text{m} > \lambda > 0.254\mu\text{m} \quad (9)$$

A check on the precision is provided by the work of Dalgarno et al (1967) who constructed a model dipole spectrum of N_2 and used it to calculate various dipole properties. They give a table of $Q_K(N_2)/F_K(N_2)$, each entry a three digit number. For $\lambda > 0.18\mu\text{m}$ our corresponding values do not differ from these by more than 1 in the last digit. Although for $\lambda = 0.17\mu\text{m}$ the difference is 3 in the last digit this signifies that the values of $\{n(N_2) - 1\}$ here differ by only 0.2 per cent.

Accurate data on $\{n(O_2) - 1\}$ are available at 48 GHz (Newell and Baird 1965), at $0.546\mu\text{m}$ (Kerl 1982) and in the range $0.288\mu\text{m} > \lambda > 0.198\mu\text{m}$ (Smith et al 1976). They can be represented accurately by

$$10^8 \{n(O_2) - 1\} = A + B/(40.9 - \sigma^2) \quad (10)$$

with A and B as follows:

A = 21351.1	B = 218567.0	,	$\lambda > 0.546\mu\text{m}$	}	(11)
20564.8	248089.9	,	$0.546\mu\text{m} > \lambda > 0.288\mu\text{m}$		
22120.4	203187.6	,	$0.288\mu\text{m} > \lambda > 0.221\mu\text{m}$		
23796.7	168988.4	,	$0.221\mu\text{m} > \lambda$		

Dalgarno and Kingston (1960) and Bideau-Mehu et al (1973) have given expressions for $\{n(\text{Ar}) - 1\}$ and $\{n(\text{CO}_2) - 1\}$ respectively. Neither is actually needed with high precision.

As an overall test

$$\{n(\text{air}) - 1\} = \sum_X f(X) \{n(X) - 1\} \quad (12)$$

with X as in (5) and $f(X)$ as given by Stergis (1965) was computed for $\lambda = 0.175(0.005)$ 0.23 (0.1) 0.4 (0.5) $1.0\mu\text{m}$ and comparison was made with the corresponding values obtained from the most elaborate of the formulae of Peck and Reeder (1972) which gives an excellent fit to the accurate data of themselves and others (Rank et al 1958, Svensson 1960, Erickson 1962, Peck and Khanna 1962) in the range $1.69\mu\text{m} > \lambda > 0.23\mu\text{m}$ and also to the less accurate early data of Traub (1920) in the range $0.215\mu\text{m} > \lambda > 0.185\mu\text{m}$. The difference at $\lambda = 0.175, 0.180, 0.185$ and $0.190\mu\text{m}$ is 0.59, 0.38, 0.24 and 0.15 per cent; for $\lambda \geq 195\mu\text{m}$ the difference does not exceed 0.1 per cent. The lack of close agreement in the region $\lambda < 0.195\mu\text{m}$ (where molecular bands disturb the regularity of the dispersion) is not a matter for concern. The calculations on $Q_K(\text{air})$ to be reported are confined to the region $\lambda > 0.20\mu\text{m}$ in which Schumann-Runge absorption is unimportant. Table 1 gives $\{n(\text{air}) - 1\}$ as obtained from (12) for this region.

3. KING CORRECTION FACTORS AND RAYLEIGH SCATTERING CROSS SECTIONS

Laser measurements have been carried out which lead to the values of $F_K(N_2)$ at $0.6328\mu\text{m}$ (Bridge and Buckingham 1966) and at $0.5148\mu\text{m}$, $0.4880\mu\text{m}$ and $0.4579\mu\text{m}$ (Alms et al 1975). Using the second order polarization propagator approximation Oddershede and Svendsen (1982) have performed calculations in the region from the long wave length limit to $0.2\mu\text{m}$. The agreement between theory and experiment is to rather better than 1 per cent. The combination of the results may be represented by

$$F_K(N_2) = 1.034 + 3.17 \times 10^{-4} \sigma^2 \quad (13)$$

Laboratory work gives $F_K(O_2)$ at $0.6328\mu\text{m}$ (Bridge and Buckingham 1966) and at 0.4880

Table 1

Wave length λ (mu)	Refractive Index (n(Air)-1) $\times 10^4$	Rayleigh Scattering Cross Section(cm^2)	Effective King Correction Factor F'_K (Air)
0.200	3.421	3.619(-25)	1.080
0.205	3.384	3.198(-25)	1.077
0.210	3.352	2.842(-25)	1.074
0.215	3.323	2.537(-25)	1.072
0.220	3.298	2.275(-25)	1.070
0.225	3.274	2.046(-25)	1.068
0.230	3.252	1.846(-25)	1.066
0.240	3.215	1.518(-25)	1.064
0.250	3.183	1.262(-25)	1.062
0.260	3.156	1.059(-25)	1.060
0.270	3.133	8.956(-26)	1.059
0.280	3.113	7.635(-26)	1.057
0.290	3.095	6.553(-26)	1.056
0.300	3.078	5.656(-26)	1.055
0.310	3.064	4.910(-26)	1.055
0.320	3.051	4.285(-26)	1.054
0.330	3.039	3.758(-26)	1.053
0.340	3.029	3.311(-26)	1.053
0.350	3.019	2.929(-26)	1.052
0.360	3.011	2.601(-26)	1.052
0.370	3.003	2.318(-26)	1.052
0.380	2.996	2.073(-26)	1.051
0.390	2.989	1.860(-26)	1.051
0.400	2.983	1.673(-26)	1.051
0.450	2.959	1.027(-26)	1.050
0.500	2.944	6.663(-27)	1.049
0.550	2.932	4.513(-27)	1.049
0.600	2.924	3.167(-27)	1.048
0.650	2.917	2.288(-27)	1.048
0.700	2.912	1.695(-27)	1.048
0.750	2.908	1.282(-27)	1.048
0.800	2.904	9.882(-28)	1.047
0.850	2.902	7.739(-28)	1.047
0.900	2.899	6.147(-28)	1.047
0.950	2.897	4.944(-28)	1.047
1.000	2.896	4.022(-28)	1.047

Note: $3.619(-25) = 3.619 \times 10^{-25}$

(Rowell et al 1971). Albertson et al (1980) have calculated the O_2 frequency dependent polarizabilities by the multi configurational time dependent Hartree-Fock approximation. Later Yeager et al (1981) obtained more accurate vertical excitation energies and total oscillator strengths for the prime transitions: those from the $X^3\Sigma^-$ state to the $B^3\Sigma^-$ and $E^3\Sigma^-$ states and to the three lower $^3\Pi$ states. They also gave the original values of these entities so that the appropriate corrections may readily be made to the polarizabilities calculated by Albertson et al (1980). The $X^3\Sigma^- - B^3\Sigma^-$, that is Schumann-Runge, transition is of paramount importance. Instead of obtaining the contribution which this broad system makes to $\alpha^u(O_2)$ just from the vertical excitation energy and total oscillator strength it was judged best to use the measured cross section curve for the Schumann-Runge continuum (Ackermann et al 1970) and the individual Schumann-Runge band oscillator strengths (Yoshino et al 1983 for $v' < 12$. Allison et al 1971 for $v' > 12$). In fact however this does not change the derived anisotropies $\gamma(O_2)$ very much: thus at 0.2 μ where the change is greatest it increases $\gamma(O_2)$ by only 6 per cent (and hence increases $F_K(O_2)$ by only 2 per cent). The mean polarizabilities $\alpha(O_2)$ were obtained from $\{n(O_2) - 1\}_K$ and are virtually exact. The calculated values of $F_K(O_2)$ at 0.6328 μ and 0.4880 μ are 1.11₂ and 1.11₆ in close agreement with the laboratory values 1.10₅ and 1.10₄ respectively. Although the correction is of little consequence all were arbitrarily multiplied by the factor 0.992 as a gesture towards utilizing the information provided by experiment. This yields

$$F_K(O_2) = 1.096 + 1.385 \times 10^{-3} \sigma^2 + 1.448 \times 10^{-4} \sigma^4 \quad (14)$$

The difference between (13) and (14) stems mainly from oxygen being unlike nitrogen in having a strong parallel transition of rather low excitation energy. If the Schumann-Runge transition did not contribute to the anisotropy $F_K(O_2)$ would be 1.01 through the spectral region considered.

The amounts of argon and carbon dioxide in air are so low that the values of $F_K(\text{Ar})$ and $F_K(\text{CO}_2)$ scarcely matter. They were taken to be 1.00 and 1.15 (Alms et al 1975) respectively.

Table 1 gives the derived Rayleigh scattering cross sections for air $Q_R(\text{air})$ (probably accurate to about 1 per cent) and also the effective King correction factors for air $F'_K(\text{air})$ defined to be such that

$$(32\pi^3/3 N^2 \lambda^4) \{n(\text{air}) - 1\}^2 F'_K(\text{air}) = Q_R(\text{air}) \quad (15)$$

As may be seen the dispersion of $F'_K(\text{air})$ is appreciable. Note that a small contribution to $F'_K(\text{air})$ arises because

$$F'_K(\text{air}) \equiv \sum_X f(X) \{n(X) - 1\}^2 / \{n(\text{air}) - 1\}^2 \quad (16)$$

is not precisely unity. The value of $F'_K(\text{air})$ is 1.0015 through the infra-red and visible spectrum, falling to 1.0010 near 0.3 μ and to 1.0002 near 0.2 μ (where $n(N_2)$ and $n(O_2)$ have become almost equal).

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