Optical cavity resonances in water micro-droplets: Implications for shortwave cloud forcing

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[1]   The influence of narrow optical resonances, which result from trapping of light rays via total internal reflection in water droplets, on the absorption of shortwave (SW) solar radiation has been estimated through high resolution Mie scattering calculations. Our results indicate that these resonances engender an increase in absorption of solar radiation by cloud droplets that is several W/m^2 above the linear direct absorption process. Mie scattering calculations performed at the $\Delta x = 0.1$ ($x = 2\pi r/\lambda$) resolution typically implemented in cloudy sky radiative transfer models are shown to be insufficient for accurate determination of the attenuation of SW radiation when considered over relatively narrow wavelength ranges, consistent with the recent finding of *Nussenzveig* [2003]. However, for broadband calculations we find positive and negative errors in Mie calculations at $\Delta x = 0.1$ nearly cancel resulting in reasonable estimates of SW attenuation.   INDEX TERMS: 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0360 Atmospheric Composition and Structure: Transmission and scattering of radiation; 3359 Meteorology and Atmospheric Dynamics: Radiative processes. **Citation:** Cappa, C. D., K. R. Wilson, B. M. Messer, R. J. Saykally, and R. C. Cohen (2004), Optical cavity resonances in water micro-droplets: Implications for shortwave cloud forcing, *Geophys. Res. Lett.*, *31*, L10205, doi:10.1029/2004GL019593.

[2]   The role of clouds and aerosols on the radiative balance of the atmosphere remains incompletely understood. For example, while global circulation model parameterized radiation transfer models (RTMs) accurately predict clear sky shortwave (SW) absorbance of solar radiation, *Cess et al.* [1995] and *Ramanathan et al.* [1995] found that the cloudy sky atmosphere absorbs roughly 30 W/m^2 more SW radiation than is theoretically predicted, a considerable discrepancy, given an average clear sky absorption of $100-150$ W/m^2. More recently, comparison of SW radiation measurements by *Valero et al.* [2003] to theoretical predictions from five different RTMs of varying spectral resolution show that the models systematically predict cloudy sky absorbances that are 17 to 61 W/m^2 less than the observations. *Ackerman et al.* [2003], using the same data set and one of the same models, found no significant difference between the model and observations but concluded that a >10% uncertainty in the measurements limited the possibility for comparisons to test models of cloud effects. Thus, both studies leave room for climatically significant effects due to absorption by clouds. Some analyses have suggested interstitial aerosols and carbon particulates within cloud droplets as possible absorbers

that would cause a measurable cloud effect [*Chylek et al.*, 1984; *Chylek et al.*, 1996; *Jacobson*, 2000]. However, no significant correlation between pollution sources and cloud absorption has yet been identified [*Cess et al.*, 1995]. Similarly, considerations of enhanced photon pathlengths due to multiple scattering from cloud droplets has led to investigation of the possible influence of gaseous species like $(H_2O)_2$ and $(O_2)_2$ on absorption of incoming solar radiation, but these effects are minor [*Pfeilsticker et al.*, 1997; *Chylek et al.*, 1999; *Pfeilsticker et al.*, 2003]. Here, we assess the role of narrow optical resonances (cavity or Mie resonances) on the absorption properties of clouds through high resolution Mie scattering calculations. Our calculations show that cavity resonances contribute significantly to absorption of SW radiation by clouds, consistent with the recent findings of *Nussenzveig* [2003]. We find that current RTMs may sufficiently account for these resonances when considered over a broad wavelength range but that higher resolution calculations are required for narrow (<50 nm) wavelength ranges.

1.   Methodology

[3]   Rigorous theoretical calculations based on the Lorentz-Mie theory of light scattering from micron sized particles (e.g., liquid droplets) demonstrate the existence of a sharp and irregular spectral structure ("ripple structure") superimposed on a series of broad maxima and minima. This structure depends on the real part of the refractive index of the medium (m_R) and the size parameter (x), where $x = 2\pi r/\lambda$, with r the droplet radius and λ the wavelength. The fine-structure in the light scattering intensity arises from (nearly) total internal reflection of light within a droplet, effectively trapping light at the droplet surface for timescales of nanoseconds [*Zhang et al.*, 1988]. This process leads to an enhancement in scattering and spontaneous emission (fluorescence) intensities within droplets, as well as to very long effective photon pathlengths [*Eversole et al.*, 1992; *Lin et al.*, 1992]. Moreover, due to this photon pathlength increase, absorption is also enhanced and both the scattering and fluorescence enhancements are sharply attenuated by the presence of an absorbing species in the droplet [*Chylek et al.*, 1991]. The scattering properties of droplets can be accurately and easily calculated from Mie theory, given knowledge of the appropriate scattering and absorption cross-sections for the droplet. For the present work, all Mie scattering calculations were performed using a code based on that of *Bohren and Huffman* [1983]. The optical properties of water are taken from *Segelstein* [1981] and have been linearly interpolated to the desired wavelength.
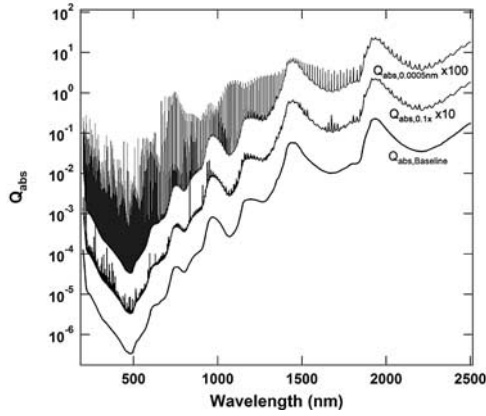
Figure 1. Q_{abs} calculated for a 10 μm radius water droplet at 0.0005 nm resolution (top) and $\Delta x = 0.1$ resolution (middle). The baseline (bottom) absorption is shown for comparison.

[4] In order to assess the specific contribution of cavity resonances to light absorption by clouds, we compare the optical absorption properties of water droplets determined from Mie scattering calculations performed at very high resolution ($\Delta \lambda = 0.0005$ nm) and at lower resolution ($\Delta x = 0.1$) to a "zero-resonance" condition. This zero-resonance baseline condition was calculated directly from the molecular absorption coefficient of liquid water, given as

$$E_m = \frac{4\pi\overline{\nu}kv_m}{1000 \ln 10}, \quad (1)$$

where k is the imaginary part of the refractive index, $\overline{\nu}$ is the energy in cm^{-1} and v_m is the molar volume [Bertie et al., 1994]. We determine the baseline droplet optical absorption efficiency from $Q_{abs,baseline} = D \cdot E_m$, where the coefficient D was found through direct comparison to the explicit high resolution Mie scattering calculations. D was found to be proportional to r (r is the droplet radius), with $D = 2.2286 \times 10^{-2}$ mol/$cm^3 \cdot r + 3.524 \times 10^{-3}$ mol/cm^2. Q_{abs} is given from conservation of energy by $Q_{abs} = Q_{ext} - Q_{scat}$, where Q_{ext} is the total extinction efficiency and Q_{scat} is the extinction efficiency due to scattering. Shown in Figure 1 are the calculated droplet absorption properties for the high resolution, low resolution and baseline cases for a 10 μm radius water droplet over the range 200–2500 nm. Some of the very sharp cavity resonances show increases in Q_{abs} two orders of magnitude above the baseline.

2. Cavity Resonance Contributions to Absorption by a Monodisperse Cloud

[5] For a homogenous distribution of cloud droplets, the optical depth through the cloud, neglecting all vapour absorption, is calculated according to [Liou, 1992]

$$\tau_{abs}(r, \lambda) = \pi r^2 Q_{abs}(r, \lambda)n(r)\Delta z, \quad (2)$$

where Δz is the cloud thickness in meters and n(r) is the droplet concentration in droplets/m^3. Although n(r) is typically expressed as a distribution of droplet sizes, here the model calculations have been performed using mono-

disperse clouds, with the monodisperse cloud droplet radii incremented from 1–10 μm in 1 μm steps for successive calculations. For each droplet size we have conserved the total droplet volume rather than droplet number, with a liquid water content (LWC) of 1 g/m^3. In this manner the total number of droplets in this cloud varies inversely with droplet radius with $N = 3 \cdot LWC/4\pi r^3\rho$, where ρ is the density of liquid water. The cloud thickness is taken as $\Delta z = 100$ m.

[6] For each droplet radius we have calculated the attenuation of SW radiation (approximated as a blackbody at 5800 K) from

$$F_{abs}(\lambda) = F_{BB}(\lambda) \cdot e^{-\tau_{abs}(\lambda)}, \quad (3)$$

and

$$F_{BB}(\lambda) = \frac{2\pi c^2 h \lambda^{-5}}{e^{hc/k\lambda T} - 1}, \quad (4)$$

where F_{BB} is the incident SW flux in W m^{-2} μm^{-1}, c is the speed of light, h is Plank's constant and k is the Boltzmann constant. The attenuation of SW radiation due to this monodisperse cloud is calculated as $F_{cloud}(\lambda) = F_{BB}(\lambda) - F_{abs}(\lambda)$ for the high resolution and baseline cases over the range 200–3950 nm (Figure 2a). The calculated values of
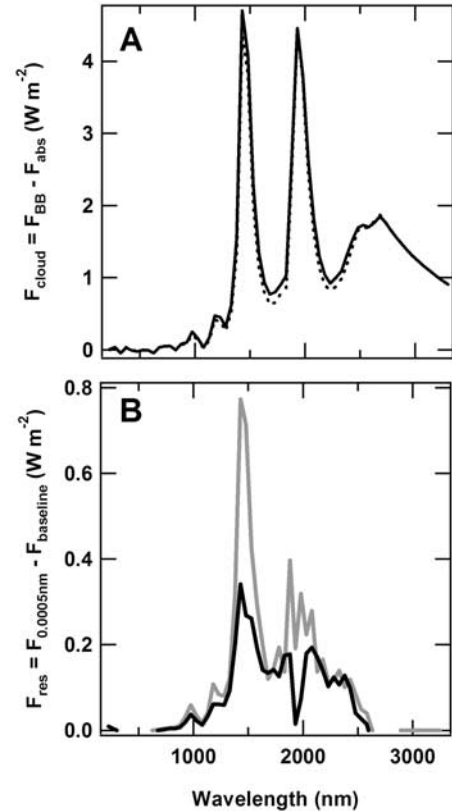

Figure 2. (a) Attenuation of SW radiation by absorption ($F_{cloud} = F_{BB} - F_{abs}$) for 10 μm radius water droplets with resonances (solid) and without (dashed) integrated in 50 nm bins. (b) The contribution of cavity resonances (F_{res}) to SW absorption for 10 μm droplets (black) and 5 μm droplets (gray).

F_{cloud} have been integrated into 50 nm bins. At wavelengths longer than ~2700 nm there is no difference observed between the high resolution calculations and the baseline case because at these long wavelengths the absorption of water is sufficiently strong for nearly all incident light to be absorbed. Also, as x gets small the cavity resonances become very broad. At wavelengths short of ~800 nm there is also no difference between the high resolution and baseline, despite the large density of cavity resonances at these wavelengths. This is due to the very weak water absorption at short wavelengths. However, for 800 nm < λ < 2700 nm, relatively large differences are observed between the high resolution and baseline cases, calculated as $F_{res} = F_{cloud,0.0005nm} - F_{cloud,baseline}$ (Figure 2b). This results from the efficient overlap of water absorption and cavity resonances.

[7] Although the total broadband (0.2–3.95 μm) absorption was determined to be relatively independent of droplet size with $F_{cloud} \sim 75$ W/m^2 for the conditions considered here (because of the specified constant volume condition), the broadband resonance contribution depends on droplet radius (Figure 3). This dependence arises primarily from the variation in cavity resonance density with droplet radius for a given wavelength interval (specifically, on size parameter). For very small droplets, the cavity resonances shift towards shorter wavelengths where water absorption is not as strong and thus the resonance contribution decreases. For larger droplets, the cavity resonances shift to longer wavelengths where water absorption is very strong and all incident SW radiation is already attenuated even in the absence of resonances. Thus, we find a maximum in the resonance contribution to the broadband integrated F_{cloud} for a monodisperse cloud with droplets having 4 μm ≤ r ≤ 7 μm. The maximum resonance contribution to SW attenuation for the conditions considered here is 6.5 W/m^2, or ~9% of the total SW absorption. Although the absolute contribution is dependent on the specific cloud parameters (such as LWC and Δz), the percent contribution provides a fairly robust estimate of the resonance contribution. Note that if a similar analysis is performed to determine the resonance contribution to Q_{abs} explicitly (Q_{res}), rather than to F_{abs}, it is found that resonances contribute a greater amount (~20%), consistent with the calculations of *Nussenzveig* [2003], who calculated the resonance contribution to Q_{abs} for a 10 micron droplet at λ > 1000 nm. The differing contribution of resonances to F_{abs} vs. Q_{abs} can be reconciled by recognizing that F_{res} depends on the overlap
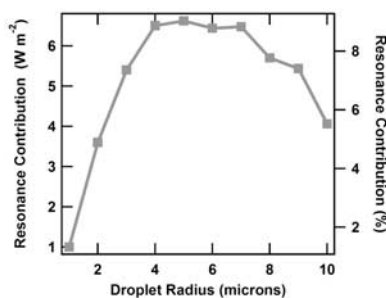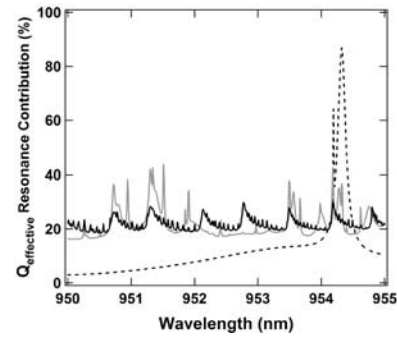

Figure 4. The resonance contribution to $Q_{effective}$ calculated for a polydisperse cloud (see text). Calculations are performed over the range 950–955 nm at 0.001 nm resolution using droplets with radii that range from 0.1–20 μm. The radius stepsize used is Δr = 0.01 μm (black) and Δr = 0.1 μm (gray). The resonance contribution for a 10 μm droplet is shown for comparison (dashed).

of Q_{abs} and F_{BB}, whereas Q_{res} is independent of the solar spectrum.

3. Effects of Cavity Resonances in a Polydisperse Cloud

[8] For a monodisperse cloud, resonance enhancement can only occur at wavelengths where a cavity resonance exists; i.e., cavity resonances are discrete with respect to size parameter. However, real clouds are composed of droplets with a continuous distribution of radii. Because the position of cavity resonances in wavelength space depends explicitly on droplet radius, it is possible for cavity resonances to contribute to absorption in a polydisperse cloud at all wavelengths, rather than at discrete wavelengths as in a monodisperse cloud (see Figure 4). Nonetheless, because Maxwell's equations (which govern Mie scattering) are linear, the maximum contribution of resonances to SW absorption is ascertained by consideration of a single radius droplet. We can, however, calculate an effective Q_{abs} from a weighted average of $Q_{abs}(r)$ over droplet radius, where the weight depends on the specific cloud properties (e.g., particle number distribution):

$$Q_{effective}(\lambda) = \frac{1}{A_0} \int \pi r^2 n(r) Q_{abs}(r, \lambda) dr, \quad (5)$$

where

$$A_0 = \int \pi r^2 n(r) dr \quad (6)$$

and n(r) is the droplet size distribution. Here we use for n(r) a modified gamma distribution with $r_{mean} = 4$ μm [*Liou*, 1992]. To characterize the effect of using a polydisperse rather than monodisperse cloud, we have calculated the percent resonance contribution to Q_{abs} over the wavelength range 950–955 nm. We have calculated $Q_{effective}$ at a resolution of 0.001 nm from equation (5) numerically, using a stepsize of Δr = 0.1 μm and Δr = 0.01 μm over the range 0.1–20 μm (Figure 4). Although it is evident that the contributions from individual cavity resonances become

Figure 3. The integrated broadband (0.2–3.95 μm) contribution of cavity resonances to absorption of solar radiation as a function of droplet radius.

washed out as $\Delta r \rightarrow 0$, the contribution from resonances to $Q_{effective}$ persists for a polydisperse cloud. Thus, the total resonance contribution to $Q_{effective}$ between 950 and 955 nm approaches 20% for a polydisperse cloud.

4. Effect of Resolution on SW Attenuation

[9] The typical resolution used to determine cloud optical properties in RTMs is $\Delta x = 0.1$; however, cavity resonances exist in water droplets with widths much smaller than $\Delta x = 0.1$ and may thus contribute significantly to absorption [*Nussenzveig*, 2003]. Therefore, Mie scattering calculations performed at $\Delta x = 0.1$ resolution will lead to errors in determination of the actual cloud optical properties. These errors may actually either underestimate or overestimate the contribution of cavity resonances to SW absorption. This is shown visually in Figure 5, where the high resolution calculations are compared to calculations performed at $\Delta x = 0.1$. Note that the maximum value of Δx used in the high resolution calculations is $8 \cdot 10^{-4}$, which is found for a 10 micron droplet at 200 nm. When the wavelength in a low resolution calculation happens to lie on top of a very sharp cavity resonance the total area under the curve may be greater than that of the high resolution calculation. Conversely, the low resolution calculations may completely miss features apparent in the high resolution case and underestimate the cloud absorption. Our calculations (using a 10 μm radius droplet) show that an error of as much as ~30% in the calculated wavelength distribution of F_{cloud} (in 50 nm bins) may be effected if the calculations are performed at low resolution (Figure 6). For smaller droplet sizes we have observed errors as large as 100%. However, if F_{cloud} is integrated over the entire solar spectrum (here, 0.2– 3.95 μm), it is found that these positive and negative errors tend to cancel and the overall difference between the calculated F_{cloud} at high and low resolution is <0.5% of the total absorption, which can be compared to the ~9% total resonance contribution calculated above. This result suggests that, for broadband calculations, current RTMs that use $\Delta x = 0.1$ to determine the cloud optical properties perform sufficiently well due to the substantial cancellation
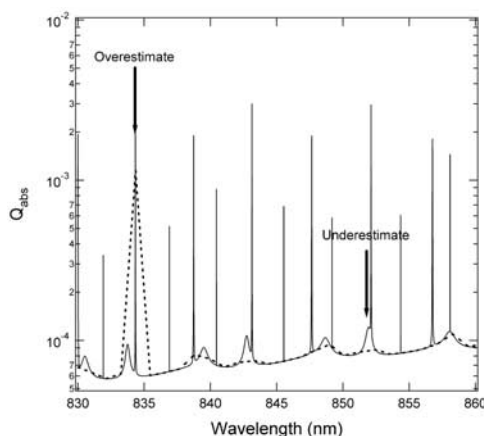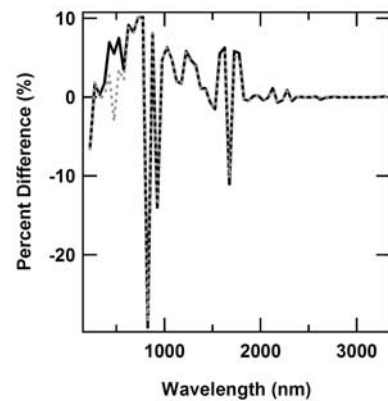

Figure 6. Percent difference between the 0.0005 nm and $\Delta x = 0.1$ resolution calculation of Q_{abs} (solid) and F_{cloud} (dashed) for a 10 μm cloud.

of errors. We have performed convergence tests demonstrating that the specified 0.0005 nm resolution is sufficient at $\lambda > 650$ nm, although higher resolution is necessary at shorter wavelengths. However, because the resonance contribution to cloud absorption is minimal at $\lambda < 800$ nm (see Figure 2), the above conclusions are still valid. Thus, improper consideration of cavity resonances is most likely not the source of the still unresolved debate over broadband anomalous cloud absorption properties. However, because the errors associated with resolution may be large over smaller wavelength intervals, it is important to perform Mie scattering calculations of cloud optical properties at high resolution when considering narrow wavelength ranges.

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Figure 5. Calculations of Q_{abs} at low ($\Delta x = 0.1$, dashed line) and high (0.0005 nm, solid line) resolution demonstrating that the $\Delta x = 0.1$ stepsize may either over or underestimate the integrated Q_{abs}.

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