Effect of line mixing on atmospheric brightness temperatures near 15 \( \mu m \)

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The effect of line mixing on the effective blackbody brightness temperature of the earth in the region of the 15-\( \mu m \) \( \nu_2 \) Q branch of CO\(_2\) is calculated. The procedures used to compute line mixing follow those used to successfully model mixing observed in laboratory spectra of two near-infrared CO\(_2\) Q branches. The atmospheric radiances are calculated between 664 and 670 cm\(^{-1}\), a spectral region that is of interest for sounding the upper troposphere and the stratosphere. Mixing was found to lower the observed brightness temperatures by as much as 3 K for some temperature profiles. Ignoring this effect would significantly impact the ability of advanced sounders to produce temperature retrievals which meet the projected accuracy requirement of 1 K/km.

I. Introduction

Rotational collisional narrowing, or line mixing, has recently been detected in the Q-branch spectra of two \( \pi - \Sigma \) bands of CO\(_2\) near 2000 cm\(^{-1}\) for both self-broadening and N\(_2\) broadening.\(^{1,2}\) The observed line mixing, which is caused by rotationally inelastic collisions that produce interference effects among overlapping lines during the absorption process,\(^{3-5}\) was found to alter absorption coefficients by as much as 65% in the wings of these Q branches. This paper considers the influence of Q-branch mixing on atmospheric radiative transfer near the strong \( \nu_2 \) Q branch of CO\(_2\) at 15 \( \mu m \).

Advanced satellite-borne infrared atmospheric temperature sounders have been proposed that will detect atmospheric emission in the region of the \( \nu_2 \) Q branch at 15 \( \mu m \) with much higher resolution than existing instruments such as the HIRS sounder on the NOAA-9 satellite. Increases in resolution to 0.5 cm\(^{-1}\) or better will dramatically increase the sensitivity of the soundings to the CO\(_2\) line shape. A candidate platform for a new high resolution infrared sounder is the proposed EOS (earth observing system) to be placed on the Space Platform.\(^6\) We present here calculations of line mixing in the \( \nu_2 \) Q branch using the same theoretical formulation that successfully predicted line mixing to an accuracy of better than 10% in the 2000-cm\(^{-1}\) CO\(_2\) Q-branch spectra. Our results are presented as brightness temperatures at the top of the earth's atmosphere. These brightness temperatures correspond to radiances averaged over a 0.5-cm\(^{-1}\) channel.

The effect of line mixing on the atmospheric spectrum of O\(_2\) in the microwave was examined some years ago by Rosenkranz.\(^7\) More recently, Braun\(^6\) and Armstrong\(^8\) performed theoretical calculations of line mixing in \( \nu_2 \) of CO\(_2\) that established the possible importance of this effect for atmospheric physics, although neither author applied his results to atmospheric spectra. The recent study of the R-branch head of \( \nu_2 \) of CO\(_2\) at 4.3 \( \mu m \) by Cousin \textit{et al.}\(^9\) has shown that mixing is partially responsible for some of the sub-Lorentz absorption in the region of the bandhead. In this work we examine the effects of line mixing very close to the centers of the Q-branch transitions. Consequently, uncertainties in far-wing Q-branch line shapes due to duration of collision effects that influence the 4.3-\( \mu m \) CO\(_2\) spectrum can be ignored.

II. Theory of Line Mixing

Q-branch line mixing occurs when the rotational line structure overlaps and collisions induce transitions between different rotational states that give rise to the Q-branch lines. These rotationally inelastic collisions are the predominant cause of pressure broadening for an isolated CO\(_2\) transition. However, when Q-branch lines overlap, rotationally inelastic collisions can transfer intensity from one line to another instead of quenching the absorption. The net result, in extreme cases, is an overall narrowing of the Q-branch profile.

The most widely used theories of overlapping lines
utilize a relaxation matrix formalism for the calculation of the absorption coefficient.\textsuperscript{10,3} The off-diagonal relaxation matrix elements describe the couplings between spectral lines that are caused by rotationally inelastic collisions. These matrix elements are formed from doubled state operators $| j\rangle$ that represent spectral lines that are caused by rotationally relaxed matrix elements describe the couplings between levels involved in the transitions.$^3$ Within the framework of the impact approximation the absorption coefficient at frequency $\nu$ for overlapping lines may be written as$^4$ 

\[ k(\nu) = \frac{N}{\pi IM} \left( \sum_{j,k} d_jd_k^* \langle (\nu - \nu_0) - i\nu W \rangle^{1/2} k \right), \]  

(1)

where $d_j$ and $d_k$ are the dipole moment matrix elements for the radiative transitions $| j\rangle$ and $| k\rangle$, $\rho_k$ are density matrix elements that give population differences between levels involved in the transitions $| k\rangle$, $\nu$ is a diagonal matrix with $\langle j|\nu| k\rangle = \nu_{jk}$, $\nu_0$ is the diagonal matrix $\langle j|\nu_0| k\rangle = \nu_{0jk}$ and $\nu_j$ is the frequency associated with the transition $| j\rangle$, $P$ is the total pressure, $N$ is the absorber number density, and $W$ is the relaxation matrix. If mixing is only allowed between the Q-branch lines, the diagonal elements of $W$ are the Q-branch pressure-broadening coefficients and $| j\rangle$, $| k\rangle$ represent Q-branch transitions.

The off-diagonal matrix elements of $W$ determine how effectively collisions transfer intensity from one line to another. If these matrix elements are sufficiently small or the lines are far enough apart, the spectrum becomes the sum of noninteracting Lorentzian lines. The rotational energy levels of CO$_2$ are separated by much less than thermal translational energies at atmospheric temperatures, so collisions are energetically able to allow the transfer of rotational and translational energy. The combination of closely spaced transitions (spacings of the order of the inverse of the time between collisions) and the high rate of rotationally inelastic collisions leads to significant line mixing. This mixing narrows the profile of the overlapping Q-branch lines compared with the profile of Lorentzian lines. The narrowed spectrum can be calculated if the off-diagonal elements of the $W$ matrix are known in addition to the standard isolated Lorentz line parameters.

The $W$ matrix elements are calculated here by way of a scaling law that parameterizes rotational energy transfer as a function of the energy gap between the rotational energy levels. The calculation of these matrix elements from first principles would be exceedingly complex, computationally expensive, and dependent on a good CO$_2$ intermolecular potential. The procedure used here to generate the $W$ matrix elements is almost identical to that described in Refs. 1 and 2. First it is assumed that elastic-reorientation collisions and vibrational relaxation do not contribute significantly to the widths. The pressure-broadened halfwidth for a single line can then be written as$^1$ 

\[ W_{jj} = \frac{1}{2} \left( \sum_{j' \neq j} 2K_{jj'} + \sum_{j' \neq j} K_{jj'} \right) \]  

(2)

where $W_{jj}$ is the pressure-broadening coefficient of Q($j$), and $K_{jj'}$ is the rate for collision-induced transitions from $j$ to $j'$ within a single vibrational state. The subscripts on the $K$ matrix elements each stand for a simple rotational energy level eigenstate. This convention will be used throughout the rest of this paper.

The odd rotational levels are missing in the ground state of CO$_2$ due to nuclear symmetry requirements so the sum over $j_{lower}$ in the lower vibrational level includes only states of even $j$. The sum over $j_{upper}$ in the upper level includes all $j$ values except for the missing $j_{upper} = 0$ level. The factor of 2 in the sum over the ground state relaxation rates reflects the fact that in the ground vibrational level the density of rotational states is one-half of that of the upper vibrational level and thus the collision rate to any individual rotational energy level in the lower state is approximately twice the rate between corresponding rotational levels in the upper vibrational state. Aside from this factor of 2, the rates are assumed to be independent of the vibrational state. Following Refs. 1 and 2 we also ignore any effects of I-type doubling on the collision rates.

For the energetically upward transitions the state-to-state rates for a single temperature are modeled with the scaling law 

\[ K_{jj'} = a_1 \left( \frac{\Delta E}{B_0} \right)^{a_2} \exp \left( -\frac{a_3 \Delta E}{T} \right), \]  

(3)

where $a_1$, $a_2$, and $a_3$ are the parameters to be determined. Detailed balance gives the rates for energetically downward transitions. The CO$_2$ rotation constant, $B_0 = 0.4$ cm$^{-1}$, is included in the power-law portion of Eq. (3) to give $a_1$ the unit of a rate. The $a_1$, $a_2$, and $a_3$ parameters are determined by a least-squares fit of Eq. (2) to the known pressure-broadened linewidths. The absorption coefficients are then calculated by letting $W_{jj'} = -K_{jj'}$, which follows from the assumption that the collision rate is independent of vibrational state. This model for rotational relaxation permits collisions to effect large $\Delta J$ changes in contrast to Rosenkranz’s$^7$ weak-coupling model for the W matrix which only allows neighboring lines to mix.

It is emphasized that this procedure predicted the observed room temperature line mixing in the 2000-cm$^{-1}$ Q branches to an accuracy of better than 10%. The calculated absorption coefficients were not derived in any way from least-squares fits to the spectra that exhibit significant line mixing. The line strengths, widths, and frequencies were derived from a combination of low-pressure Q-branch spectra and P- and R-branch data. CO$_2$ linewidths have little vibrational dependence, so this procedure should be accurate for mixing in the $v_2$ band as well. In addition, the line spacings in the $v_2$ Q branch are very close to the 2000-cm$^{-1}$ Q-branch line spacings.

Laboratory measurements of line mixing in CO$_2$
have thus far been limited to room temperature. For atmospheric calculations the temperature dependence of the linewidths and the line mixing must be taken into account. Numerous experiments have shown that the temperature dependence of CO$_2$ linewidths is adequately described by the power law $\gamma_0(T_0/T)^{0.75}$, where $\gamma_0$ is the pressure-broadening coefficient at the temperature $T_0 = 296$ K.$^{12}$ The deviation of this law from the $(T_0/T)^{0.5}$ dependence on temperature predicted by kinetic theory comes about primarily from the temperature or velocity dependence of the collision cross sections.

The most straightforward way to approximate the temperature dependence of the linewidths with the scaling law is to place the kinetic theory $(T_0/T)^{0.5}$ factor in front of Eq. (3), and to use the exponential term to model the temperature dependence of the cross sections. Equation (3) then becomes

$$K_{jj} = a_1(T_0/T)^{0.5} \left( \frac{\Delta \nu}{B_0} \right)^{a_2} \exp \left( -\frac{a_3 \Delta \nu}{T} \right).$$

(4)

There is no assurance that the resulting scaling law is physically reasonable beyond the required increase in the cross sections with temperature. The surprising ability of these energy gap scaling laws to predict the experimentally observed line mixing is partially due to the insensitivity of the mixing to the details of the W matrix. We expect Eq. (4) to give reasonable results if it can adequately model the $j$ dependence of the linewidths via Eq. (2). The least-squares determination of $a_1$, $a_2$, and $a_3$ was performed using widths for $j = 2$–50 at six temperatures between 200 and 250 K on the left-hand side of Eq. (2). The linewidths were calculated from the room temperature N$_2$-broadened widths reported by Gentry and Strow$^2$ for $j = 2$–8 and by Arie et al.$^{13}$ for $j = 10$–50. These widths were then multiplied by $(T_0 = 296K/T)^{0.75}$ to obtain the lower temperature widths.

This numerical method requires only one set of parameters to describe the W matrix at all temperatures. Considering the present lack of any laboratory measurements of the temperature dependence of line mixing, this simple approach seems reasonable since it produces line mixing which has a temperature dependence consistent with the temperature dependence of the linewidths. Another approach is to determine a separate scaling law at each temperature. When this approach was tried, it was found that the calculated absorption coefficients differed at most by 4% from those determined with a single scaling law. Differences of this order are negligible, and the single scaling law was chosen on the basis of computational simplicity. A more sophisticated treatment of the temperature dependence of line mixing must await the appearance of experimental data.

The least-squares determined values for $a_1$, $a_2$, and $a_3$ appropriate for a 200–250 K temperature range are $a_1 = 0.02597$ cm$^{-1}$/atm, $a_2 = 0.3307$, and $a_3 = 1.035$. This temperature range is large enough to cover all atmospheric levels contributing significantly to the outgoing atmospheric radiance at frequencies near the 15-μm Q branch. These scaling law parameters reproduce the linewidths to an accuracy of 4%. Errors of this order are not considered serious since the $(T_0/T)^{0.75}$ temperature dependence used to estimate the low temperature widths could also be in error by that amount, especially for the low-$J$ lines.

III. First-Order Theory of Line Mixing

Once the relaxation matrix elements are determined the spectrum can be calculated in a straightforward manner using Eq. (1). A matrix inversion for each frequency point can be avoided by following the procedures discussed by Koszykowski et al.$^{14}$ and Gordon and McGinnis$^{15}$ and outlined by Gentry and Strow$^2$ for the case of infrared spectra. For frequencies near the 15-μm CO$_2$ Q branch most of the radiance at the top of the atmosphere comes from pressures <200 Torr. In this case Rosenkranz’s$^7$ low-pressure approximation for Eq. (1) is sufficiently accurate. However, for frequencies near weaker atmospheric CO$_2$ Q branches where the radiances have a large component due to emission at higher pressures this approximation may not be valid. For the 15-μm Q branch Rosenkranz’s approximation is accurate to at least 13% at 760 Torr, 5.5% at 200 Torr, and 1.5% at 50 Torr. This approximation, which assumes that $PW_{j,k}(v_j - v_k)$ is small for all lines, should not be confused with Rosenkranz’s weak-coupling approximation for the calculation of the W-matrix elements mentioned earlier.

The low-pressure approximation for the absorption coefficient can be written following Rosenkranz as

$$k(v) = \frac{N}{\pi} \sum_j S_j \left( \frac{P_{Y_j} + (v - v_j)(P_{Y_j})^2}{(v - v_j)^2 + (P_{Y_j})^2} \right) = k_L + k_M.$$  

(5)

which introduces the first-order mixing coefficients

$$Y_j = 2 \sum_{k} d_{kj} W_{kj},$$  

(6)

where $\gamma_j = W_{jj}$ is the Lorentz halfwidth/atm for $Q(j)$ and $S_j = \rho d_{ji}^2$ is the line strength. This method for calculating the mixing is convenient once the $Y_j$ values are known and is easily incorporated into existing radiative transfer codes. If the pressure is low enough this expression for $k(v)$ must be convolved with a Doppler line shape. This is a simple task numerically because the convolution of the mixing term in Eq. (5) can be calculated from the same complex probability function that is used to generate the normal Voigt line profile.$^2$

Figure 1 illustrates the effect of line mixing on the Q-branch spectrum at 15 μm for $T = 220$ K and 50-Torr N$_2$-broadened pressure. This spectrum includes only Q-branch lines so that local absorption due to the P- and R-branch lines does not mask the mixing. This plot clearly shows that sufficiently far away from the Q-branch line centers the ratio of the mixing part of the absorption coefficient, $k_M$, to the Lorentz coefficient, $k_L$, has a constant value of about $-0.45$. This ratio does not depend on pressure and is only weakly dependent on temperature. The calculations shown in this figure were performed using the exact expression for $k(v)$, Eq. (1). We used the fact that this ratio is
recognizing that the first term in the numerator equals zero. This can be shown by substituting the series equation for $Y_j$ [Eq. (6)] into Eq. (11) to obtain

$$\sum_j S_j Y_j = 2 \sum_{j<k} \frac{\rho_j \rho_k d_k W_{kj}}{v_j - \nu_k},$$

using $S_j = \rho_j d_j^2$. Detailed balance requires that

$$\rho_j W_{kj} = \rho_k W_{jk},$$

so for every term in the sum

$$\rho_j d_k W_{kj},$$

there will be a corresponding negative term which cancels the first term. Thus, within the Rosenkranz approximation,

$$\sum_j S_j Y_j = 0.$$  

Equation (11) now becomes

$$\frac{k_L - k}{k_L} = \frac{\sum_j S_j Y_j \gamma_j}{\sum_j S_j \gamma_j},$$

which is independent of $\nu$. Both $Y_j$ and $\gamma_j$ are independent of pressure, consequently this ratio is also independent of pressure.

At first glance it would seem that Eq. (16) would only be valid quite far from the Q branch. However, it must be recalled that each term in the sums of Eq. (7) is multiplied by $S_j$, which is proportional to $\rho_j$. Therefore it is reasonable to expect that those terms corresponding to $j$ values far from the Boltzmann peak would not contribute much to either sum. Thus $\nu$ in Eq. (8) may be chosen to minimize the effects of terms in Eq. (11) with relatively large values of $\delta_j$. In light of this it is not surprising that our calculations indicate that a constant value for $k/k_L$ may be used at 666.5 cm$^{-1}$, which is within 1 cm$^{-1}$ of the Q-branch head.

A further application of detailed balance to the numerator of Eq. (16) allows this ratio to be written alternatively as

$$\frac{k_L - k}{k_L} = \frac{-2 \sum_j \rho_j d_k d_k W_{jk}}{\sum_j \rho_j d_j^2 W_{jk}}.$$  

Detailed balance has eliminated the $\delta_j$ terms, so this ratio is also independent of the Q-branch line spacings. Our formulation of line mixing has implicitly assumed that the off-diagonal elements of $W$ scale linearly with the diagonal elements. Therefore the ratio of the mixing and Lorentz absorption coefficients in the wing is also independent of the magnitude of the widths and only depends on the distribution of final states in rotationally inelastic collisions. These results permit
the use of simple methods for calculations of line mixing in the wings of all CO$_2$ Q branches when P- and R-branch mixing can be ignored. The results of this section were derived within the framework of Rosenkranz's low-pressure formulation of Eq. (1). However, these results also appear to be applicable to Q-branch wings at higher pressures even though Rosenkranz's approximation breaks down near the line centers. Our calculations show that values of $k/k_{L}$ calculated using Eq. (17) agree with those obtained directly from Eq. (1) to better than 0.1% at 666.5 cm$^{-1}$. In addition, this ratio only changes by ~5% between 200 and 250 K. This weak temperature dependence was ignored in our atmospheric calculations.

IV. Radiative Transfer and Atmospheric Model

Assuming a plane-parallel atmosphere in local thermodynamic equilibrium and negligible scattering, one can write the monochromatic radiance at nadir at the top of the atmosphere as

$$R_{\nu} = e_{s} B_{s}(T)r_{\nu}(P) + \int_{P_{r}}^{P} B_{r}(T(P)) \frac{d}{d \ln P} \int_{P}^{P} k_{L}(P')dP' d \ln P + R_{\nu}^{'},$$

where $e_{s}$ is the emissivity of the surface $s$, and $B_{s}(T)$ is the Planck function for emitted radiation of a blackbody at frequency $\nu$ and temperature $T$ given by

$$B_{s}(T) = 1.19 \times 10^{-4} \frac{\nu^{3}}{\exp[1.439v/T] - 1}.$$  \hspace{1cm} (19)

$r_{\nu}(P)$ is the atmospheric transmittance from pressure $P$ to the top of the atmosphere, given by

$$r_{\nu}(P) = \exp\left[-\int_{P}^{P_{r}} k_{L}(P') dP\right],$$

where $k_{L}(P)$ is the atmospheric absorption per unit pressure at frequency $\nu$ and pressure $P$, and $R_{\nu}^{'}$ represents the contribution of reflected radiation, which is negligible in our case. Due to the strength of $v_{2}$ of CO$_2$, most of the radiance originates from pressures <200 Torr so the surface term is also negligible.

Radiance calculations were performed for each of the climatologies shown in Fig. 2, one with line mixing and the second without line mixing. The radiances, calculated at a resolution of 0.01 cm$^{-1}$, were then averaged over a 0.5-cm$^{-1}$ square bandpass to simulate the response of a high resolution satellite radiometer before being converted to effective brightness temperatures. A sixty-six-layer atmosphere and line parameters from the AFGL line compilation$^{16}$ (except the $v_{2}$ Q-branch parameters) were used. Only the Q branch lines of the $v_{2}$ fundamental were allowed to mix. The H$_2$O continuum is included in the calculations but contributes very little to the radiance near the strong $v_{2}$ Q branch.

Numerous spectroscopic studies of the $v_{2}$ R-branch head of CO$_2$ at 4.3 $\mu$m have shown that the far-wing absorption coefficients are significantly sub-Lorentzian. Beyond the bandhead the sub-Lorentzian behavior has been attributed to the effects of collision duration which decrease the far-wing absorption of an isolated line. Most atmospheric calculations model this non-Lorentzian behavior by use of the empirical $\chi$-function that multiplies each Lorentz line shape by an appropriate factor. Recently, Cousin et al.$^{9}$ have shown that the sub-Lorentz absorption within the R branch can be partially attributed to line mixing among the R-branch lines. However, the R-branch mixing appears to become negligible beyond the bandhead where the sub-Lorentz characteristics of the isolated line shape start to dominate. We have not included an empirical $\chi$ function in the calculations presented here. It is possible that the experimentally determined $\chi$ function contains contributions from both far-wing line shapes and line mixing. In any case more experimental work is needed at 15 $\mu$m to separate out these effects in the spectrum. When empirically determined$^{17}$ far-wing line shape effects are included in our calculations, the results show even larger deviations from the Lorentz approximation in the Q-branch wing, i.e., the absorption coefficients become even more sub-Lorentzian. Therefore, the results presented here show approximate lower bounds for the combined effect of line mixing and far-wing line shapes. Our concern here is primarily with regions of the spectrum close to strong Q branches, where duration of collision effects due to the Q-branch lines themselves should be very small. Additional sub-Lorentzian behavior in these spectral regions may be due to the far wings of P- and R-branch lines, however, the theoretical calculation of these effects has proved very difficult and is beyond the scope of this study.

Fig. 2. Climatological temperature profiles used in the radiance calculations.

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V. Results

A high resolution spectrum of the effective brightness temperature at the top of the atmosphere for the April 40°N profile is shown in Fig. 3. The low-J Q-branch lines are clearly visible as well as the low-frequency Q-branch wing. Note that below the Q-branch head at 667.4 cm⁻¹ to ~666 cm⁻¹ the spectrum is relatively free of any local line absorption and is dominated by the Q-branch wing absorption/emission. Many of the strong lines in Fig. 3 have peak equivalent blackbody temperatures of 265 K. This common peak temperature for many lines is an artifact of the atmospheric model. The lowest pressure layer is at 1 mbar and has a temperature of 265 K. Consequently all the extremely strong CO₂ line centers are radiating at this temperature. This cutoff has no impact on the results presented here since line mixing is only important at the higher pressures found in the lower layers of the atmosphere.

The brightness temperatures calculated without mixing minus brightness temperatures calculated with mixing, averaged over a 0.5-cm⁻¹ square bandpass for the three different climatological temperature profiles, are shown in Fig. 4. As seen in this figure line mixing effects may alter the brightness temperatures by more than 3 K at 667 cm⁻¹ directly below the Q-branch head. These deviations are dependent on the profile, and for some profiles line mixing changes the calculated temperatures by much less.

The two profiles exhibiting the larger brightness temperature differences, April 40°N and January 20°N, have qualitatively different shapes from the third profile. In the region of the Q branch the atmospheric brightness temperatures for both of these two profiles, with or without line mixing, is dominated by emission above the tropopause where the temperature decreases rapidly with decreasing altitude. When line mixing is included in the calculation, the absorption coefficient in the wing of the Q branch is lowered and the dominant atmospheric emission originates near the tropopause where the temperature is lower. Therefore the temperature differences plotted in Fig. 4 are positive in the Q-branch wing. For the third profile the situation is somewhat different because the area above the tropopause is relatively isothermal and in fact the slope of the temperature profile changes sign. In this case \(dT/dP\) is negative at the highest altitudes shown in Fig. 2 and is slightly positive at lower altitudes. This results in the positive brightness temperature differences seen in Fig. 4 close to the Q branch head and negative differences further in the low frequency wing.

A weak dependence of the brightness temperature on line mixing is due in part to the fact that for some profiles the regions being sensed by the channels are in a relatively isothermal part of the atmosphere. However, 3 K effects may produce temperature retrieval errors significantly larger than projected requirements of 1 K/km for temperature profiles obtained from future infrared sounders. Several other weaker CO₂ Q branches are currently being investigated for use in temperature sounding. These weaker Q branches emit radiation from lower parts of the atmosphere that are not as isothermal and thus their brightness temperatures may be more sensitive to line mixing.

Clearly, line mixing can play a significant role in atmospheric radiative transfer for CO₂ and may affect the retrieval of atmospheric temperature profiles from future satellite radiometers operating in the 15-μm spectral region. Several of the proposed channels for future infrared temperature sounders which sense in the mid to upper stratosphere are centered in the spectral region shown in Fig. 4 where mixing affects the spectrum most severely. The effects of mixing, if ignored, introduce calibration errors in radiometer channels that are spectrally very close to each other. This defeats one advantage of using CO₂ Q branches for sounding, the ability to use sounding channels that are very close, and which are therefore affected similarly by calibration errors and atmospheric affects that vary slowly with frequency.

VI. Conclusions

Calculated equivalent brightness temperatures at the top of the earth’s atmosphere may be lowered by more than 3 K when the effects of line mixing are included. Thus atmospheric temperature retrieval
methods which are dependent on a model of atmospheric transmittance should include these effects if the retrieval products are to be accurate. Laboratory studies of room temperature line mixing in higher frequency CO$_2$ Q branches broadened by N$_2$ and by O$_2$ have shown that line mixing can be accurately calculated if the standard line parameters are known. This line mixing model should be sufficiently accurate for atmospheric radiance calculations in the 15-µm CO$_2$ Q branch, if temperature dependencies are ignored. The temperature dependence of line mixing has not yet been experimentally studied, thus our methods for including temperature effects are as yet untested.

A number of conclusions are drawn concerning the behavior of line mixing in a Q-branch wing, some of which greatly simplify the radiance calculations. Most importantly, we find that the ratio of the mixing to the Lorentz absorption coefficients is independent of frequency in the wing. In addition this ratio is shown to be independent of pressure, the Q-branch line spacing, and the magnitude of the pressure-broadened linewidths.

Other CO$_2$ Q branches are now being explored for use in atmospheric temperature sounding and it is expected that line mixing will also be important for some of these sounders. Line mixing has also recently been observed in two N$_2$O Q branches and therefore line mixing may also impact atmospheric spectroscopy of N$_2$O.

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References

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