LINE MIXING SUM RULES FOR THE ANALYSIS OF MULTIPLET SPECTRA

A. S. PINE
Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, U.S.A.

(Received 12 June 1996)

Abstract—In the impact approximation, the spectrum of transitions overlapped by collisional broadening is given by a sum over Lorentzian absorption and dispersion profiles about each transition. The dispersion components arise from the interference among lines coupled by the collisions, and their magnitudes and signs are given by the line mixing parameters. The line mixing parameters, as well as the transition intensities, widths and shifts, are obtained from inversion of the relaxation matrix and may be highly non-linear in pressure when the coupled lines are strongly overlapped. For any overlap, however, the line mixing parameters summed over all coupled lines is zero and the total integrated intensities, widths and shifts are conserved. These sum rules may be used as constraints in least-squares fitting of multiplet spectra to reduce the number of free parameters and their correlation. Also for the fitting of spectra at atmospheric pressures, a prescription is given for incorporating Doppler broadening and Dicke narrowing. Published by Elsevier Science Ltd

1. INTRODUCTION

When pressure-broadened spectral lines overlap, the resulting profile may deviate significantly from a linear superposition of Lorentzian line shapes if the lines are collisionally coupled. Various aspects of the phenomenological theory of overlapping lines within the impact approximation were developed by Baranger, Kolb and Griem, and Fano, describing the interference among the transitions in Liouville or “line” space coupled by a “relaxation” matrix. The interference between lines leads to a merging of the spectral components and a reduction of their effective widths and is variously known as rotational or collisional narrowing, coherence transfer and line mixing. Ben-Reuven and Gordon presented semiclassical scattering formulations for the relaxation matrix elements.

Gordon and McGinnis calculated line coupling scattering cross sections for a model CO/He potential for comparison to their measurements of the CO infrared fundamental at He pressures high enough to blend the P and R branch lines. Later, first- and higher-order approaches to line mixing theory were developed by Rosenkranz, Lam, and Smith for modeling the important atmospheric microwave spectrum of O2 which exhibits magnetic-dipole-allowed spin splittings in the ground \(^{13}\Sigma_u^+\) electronic state.

More recently, strong line mixing has been observed in the isotropic Raman Q branches of N\(_2\), CO, and CO\(_2\). In most of these Raman studies, scattering cross sections were not available, so the relaxation matrix was modeled empirically using energy gap or energy-corrected-sudden (ECS) scaling laws to fit the broadening coefficients measured at sufficiently low pressures to minimize overlap. The broadening coefficient of a line was assumed to be equal to the sum of all of the rotationally inelastic (\(\Delta J \neq 0\)) state-to-state collision rates from the \(J\) level of the transition. This sum rule is reasonably well justified for scalar Raman scattering, which does not depend on the orientation of the molecule, but shows minor deviations due to vibrational relaxation. The utility of the energy gap or ECS law is then judged on a comparison with, not a fit to, the higher pressure spectra. Very dramatic line mixing effects are exhibited by the 1388 cm\(^{-1}\) v1 Q branch of
CO$_2$, where the $\Delta B$ is so small that the lines are overlapped at the Doppler limit and subsequently broaden at a rate $\sim 30$ times less than a single isolated $P$ or $R$ branch line in the infrared.

The same energy gap or ECS law methodology has been applied to infrared $Q$ branches of linear molecules such as CO$_2$, N$_2$O, HCCH, and HCN. However, the sum rule equating the broadening of one line with the total inelastic coupling to other lines within the $Q$ branch is not valid in this case where reorientations and degenerate vibrational levels are present, so that an empirical coupling factor has been introduced to fit the pressure-blended spectra. Consideration of angular momentum coupling within the IOS or ECS framework has shown that the effective coupling is about 50%, which agrees well with the observations on CO$_2$, but not adequately with the greater and lesser decouplings seen in HCCH and HCN respectively.

For polyatomic molecules that are not linear, we have no simple models for the relaxation matrix elements, but even more fine structure splittings available, providing opportunity for line mixing at modest pressures. Consequently, it has proved difficult to fit blended spectra of some simple molecules at atmospheric pressures. In particular, we noted that additive Voigt or Rautian line shape fits to the CH$_4$ $v_3$ band $Q$ branch were unstable above $\sim 13$ kPa and that linear extrapolations from lower pressure yielded significant deviations from the measurements. Though the deviations were characteristic of line mixing, we were unable to gauge the contributions of quasielastic ($\Delta J = 0$) collisions among the various tetrahedral components relative to the inelastic ($\Delta J \neq 0$) collisions seen in linear molecules. However, the $J$ manifolds in the $P$ and $R$ branches of a spherical top are well separated so that quasielastic line coupling can be isolated at atmospheric pressures.

Benner et al. have recently reported simultaneous multispectrum fits to the CH$_4$ $v_3$ $P(J)$ and $R(J)$ manifolds, recorded with a Fourier transform interferometer, demonstrating the presence of line mixing using the Rosenkranz first-order approximation. In the accompanying paper, we present tunable laser measurements of these $P(J)$ and $R(J)$ manifolds with somewhat higher resolution, sensitivity and precision, indicating the presence of higher-order line mixing. We also impose symmetry-based collisional selection rules and zero sum rules on the mixing coefficients. The sum rules on the mixing coefficients, as well as on the integrated line intensities, the line shifts and widths, follow mathematically from the impact line mixing formulation as will be shown in this note. They are quite general, valid to all mixing orders, and are independent of the nature of the relaxation matrix, the transition or energy level quantum numbers or the tensor properties of the probe. Most importantly, they provide physical constraints on the non-linear least-squares fitting of real data, reducing the number of independent parameters, their mutual correlation and uncertainties.

We will also present some illustrative examples involving coupled doublets and simulated $J$ manifolds for methane as well as the modifications necessary to account for Doppler broadening and Dicke narrowing.

2. LINE MIXING SUM RULES

Within the impact approximation, the absorption coefficient for a spectrum of overlapping lines can be written,

$$\kappa(\omega) = (N_s/\pi) \text{Im} \left\{ \sum_{m,n} \mu_m \langle m | \omega \mathbf{1} - \omega_0 - iW^{-1} | n \rangle \mu_n \rho_n \right\}. \quad (1)$$

Here $N_s$ is the density of active molecules, the indices $m$ and $n$ represent transitions in Liouville or “line” space and imply all of the relevant quantum labels of the initial and final radiative states coupled by a transition moment $\mu$, $\rho_n$ is the fractional population in the lower level of transition $n$. The matrices between the double-bracketed state vectors are the unit matrix, $\mathbf{1}$, a diagonal matrix, $\omega_0$ such that $\langle m | \omega_0 | n \rangle = \omega_0^m \delta_{mn}$, where $\omega_0^m$ are the unperturbed transition frequencies in the absence of collisions, and $W$ is the “relaxation” or scattering rate matrix whose elements are given by collisional scattering cross sections. The real and imaginary parts of the diagonal elements of $W$ are the broadening, $\gamma_m^0$, and shift, $\delta_0^m$, respectively, of each transition in the absence of overlap. The off-diagonal elements of $W$ are minus the line coupling or coherence transfer rates.
The reverse rates are related by detailed balance, \( W_{mn} = W_{nm} \rho_m / \rho_n \). In principle, the double sum in Eq. (1) is over all transitions in the spectrum, but in practice can be restricted to isolated regions of overlapping lines.

One can avoid the matrix inversion at each frequency, \( \omega \), in Eq. (1) by diagonalizing the non-Hermitian matrix \( \omega + iW \) with the matrix \( A \) such that:\(^1,^2\)

\[
A^{-1}(\omega + iW)A = \Omega,
\]

where the diagonal matrix \( \Omega \) has complex eigenvalues \( \Omega_{mn} = (\omega_m + i\gamma_m) \delta_{mn} \) and the matrix \( A \) has columns made up of eigenvectors for the corresponding eigenvalues. If we consider the \( \mu_m \) as components of a vector and the \( \rho_m \) as diagonal elements of a diagonal matrix \( \rho \), then Eq. (1) can be written:\(^1,^2,^8,^9\)

\[
\kappa(\omega) = (N_s/\pi) \text{Im} \left\{ \sum_m (\mu \cdot A)_m (A^{-1} \cdot \rho \cdot \mu)_m / (\omega - \omega_m - i\gamma_m) \right\}.
\]

If we define the real and imaginary parts of the numerator in the sum as,

\[
\xi_m \equiv \text{Re}\{ (\mu \cdot A)_m (A^{-1} \cdot \rho \cdot \mu)_m \},
\]

\[
\eta_m \equiv \text{Im}\{ (\mu \cdot A)_m (A^{-1} \cdot \rho \cdot \mu)_m \},
\]

then Eq. (3) becomes a sum over Lorentzian and dispersion terms,

\[
\kappa(\omega) = (N_s/\pi) \sum_m \left[ \xi_m + (\omega - \omega_m) \eta_m \right] / (\omega - \omega_m + i\gamma_m^2).
\]

As shown previously,\(^1,^4\) no approximations have been used in deriving Eqs. (3–5) from Eq. (1), so they are valid for any overlap. These expressions are reviewed here simply to introduce the notation for what follows and to indicate the physical origin of the generalized line parameters, \( \xi_m \), \( \eta_m \), \( \omega_m \) and \( \gamma_m \), to be fit to an experimental spectrum. \( \xi_m \) may be considered the coupled line strength, \( \eta_m \) the line mixing parameter, and \( \omega_m \) and \( \gamma_m \) are the renormalized line frequency and half width, respectively. If the off-diagonal W-matrix elements were zero, then \( A \rightarrow 1 \), \( \omega_m \rightarrow \omega_m^0 \), \( \xi_m \rightarrow \xi_m^0 \), \( \eta_m \rightarrow \eta_m^0 \), \( \omega_m \rightarrow 0 \), and \( \kappa(\omega) \) would be the usual sum over Lorentzians with widths and shifts linear in pressure as are all the W-matrix elements. In general, however, the line parameters are complicated functions of the W-matrix elements and may be considerably non-linear with pressure under conditions of strong overlap. Rosenkranz\(^2\) and Smith\(^9\) have given linear and quadratic expansions for the parameters in the realm of weak overlap. Their line mixing coefficients are obtained by perturbation theory from the \( \eta_m \) above divided by \( \rho_m \) for Rosenkranz\(^2\) and \( \mu_m^2 \rho_m \) for Smith\(^9\), and their W-matrix elements are written explicitly linear in pressure.

We note that the dot products in Eqs. (3) and (4) are \( (\mu \cdot A)_m \equiv \sum_i \mu_i A_{im} \) and \( (A^{-1} \cdot \rho \cdot \mu)_m \equiv \sum_x A^{-1}_{xm} \rho_x \mu_x \) so the sum of their product over all lines in the spectrum gives

\[
\sum_m (\xi_m + i\eta_m) = \sum_{m,x} \mu_x A_{xm} A^{-1}_{xm} \rho_x \mu_x = \sum_x \mu_x^2 \rho_x.
\]

Here we have reversed the order of summation and noted that \( \sum_{m,x} A_{xm} A^{-1}_{xm} = \delta_m \) by orthonormality of the eigenvectors defining the inverse matrix.\(^4\) Thus the sum of all the line strengths and \( i \times \) the line mixing parameters is purely real and equal to the sum of the unperturbed line strengths. This is an expression of the sum rule that the total integrated intensities are conserved and the line mixing parameters sum to zero, independent of the overlap or the magnitude of the line coupling elements. Similarly, because the trace of a matrix is invariant to diagonalization, the sum of the line shifts, \( \delta_m = \omega_m - \omega_m^0 \), and widths are preserved; that is

\[
\sum_m (\delta_m + i\gamma_m) = \sum_n (\delta_n^* + i\gamma_n^*).
\]
As stated earlier, these sum rules are exact and may be used to reduce the number of independent parameters in a fit. Alternatively, they may be used to test the reliability of a fit when all parameters are unconstrained.

In some cases, usually for symmetry reasons, lines or groups of lines that overlap may not be coupled. For example, the $A$, $E$ and $F$ symmetry nuclear spin modifications in tetrahedral molecules or the singlet–triplet levels in HCCH or HOH will have essentially no collisional cross relaxation. This leads to block diagonalization of the $W$-matrix for which the sum rules, Eqs. (6) and (7), pertain to each symmetry group separately.

3. EXAMPLES

3.1. Doublets

To illustrate the sum rules, it is useful to discuss some realistic and representative cases. The coupled doublet is the simplest case where Eq. (1) can be inverted analytically as has been shown by Ben-Reuven and Henck and Lehmann for the inversion doublets in NH$_3$. The results can also be applied to line shapes of $l$-type doublets in polar linear molecules, $\Lambda$-doublets in open shell species, and many other systems where pairs of collisionally coupled lines overlap away from more remote spectral lines. The examples considered above involved balanced doublets with the two components equal in intensity ($p_1 = p_2$, $\rho_1 = \rho_2$) and width ($W_{11} = W_{22}$, $W_{12} = W_{21}$) and initially separated by $\Delta = \omega_0^1 - \omega_0^2$ with no intrinsic shifts, $\Re(W_{m}) = 0$. Their expressions and discussions can be summarized in Fig. 1(a), where we show the reduced line parameters of Eq. (5) as a linear function of pressure as measured by the overlap given by the average width, $y = (W_{11} + W_{22})/2$, divided by the initial separation, $\Delta$. The solid curves correspond to the parameters for line 1 and the dashed for line 2. The $\zeta_m$ and $\eta_m$ parameters are scaled to the average intensity, $y_0 = (y_1 y_2)/2$.

The balanced doublet parameters in Fig. 1(a) exhibit distinctive behavior in two regions separated by singularities in the intensity and mixing coefficients. At lower pressures, the widths and intensities do not vary from their average values, while the magnitude of the dispersion components start out linearly and then diverge, and the shifts begin quadratically until the lines coalesce exactly. After coalescence the shifts stop, the dispersion components vanish abruptly, and the two remaining Lorentizians develop different widths with the broader having a negative intensity. The symmetry of the plot about 1 for the $\gamma_m/y_0$ and about 0 for the others indicates the sum rules or Eqs. (6) and (7). The cancellations arising from the sum rules prevent any singularities in the spectrum where the $\zeta_m$ and $\eta_m$ parameters diverge.

The position of the singularities depends on the magnitude of the off-diagonal $W$-matrix elements and occurs for $W_{12} W_{21} = \Lambda^2/4$ as long as $W_{11} = W_{22}$ and is independent of the relative line intensities. In Fig. 1(a), we have arbitrarily chosen $|W_{12}|/W_{11} = 0.5$, but larger ratios just move the singularities to the left and smaller to the right. If, however, we unbalance the widths of the doublet, the singularities are rapidly suppressed as shown in Fig. 1(b) where we have chosen $W_{22}/W_{11} = 0.9$. In this case, all of the parameters vary non-linearly with pressure throughout, but the sum rules, indicated by the symmetry of the diagram, persist. We note that line mixing averages the positions of the doublet, but not the widths, contrary to our expectations in an earlier study of differential broadening of the $\Lambda$-doublets in NO.

3.2. Multiplets

We now address a case characteristic of a $J$ manifold in a spherical top molecule, pertinent to the accompanying study, where many fine structure components may overlap with restrictive collisional coupling selection rules. In Fig. 2, we show a low pressure experimental trace of the $R(6)$ manifold of methane in the triply-degenerate $v_3$ C–H stretching band along with a stimulated pressure-broadened spectrum at $P_0 = 13.33$ kPa (100 torr) in an Ar buffer gas. The low pressure trace has essentially Doppler-limited resolution with negligible instrumental distortion. The manifold consists of 6 allowed lines with different tetrahedral symmetry labels and nuclear spin weights as given in Table 1 along with initial frequencies and estimated $W$-matrix elements ignoring any intrinsic shifts. The frequency units in Table 1 are arbitrary grid points, not cm$^{-1}$, and the pressure units are scaled by $P_0$. Since the intermolecular potential is expanded in angular operators
Fig. 1. Reduced line parameters for a coupled doublet with (a) balanced widths, $W_2 = W_{11}$, and (b) unbalanced widths, $W_2 = 0.9W_{11}$. In both cases $\mu = \mu_1$, $\rho = \rho_1$, $|W_0| = 0.5W_{11}$, $\Delta = \omega_2 - \omega_1$, $\gamma_0 = (W_0 + W_{11})/2$, $\gamma = (\mu_1^2 + \mu_3^2)/2$. 

Balanced Doublet Mixing

$W_{12}/W_{11} = 0.50$
$\Delta = \omega_2 - \omega_1$

Unbalanced Doublet Mixing

$W_{12}/W_{11} = 0.90$
$\Delta = \omega_2 - \omega_1$
Fig. 2. Experimental Doppler-limited and simulated pressure-broadened spectra of the \( R(6) \) manifold of the \( v_1 \) band of methane. Doppler-limited trace recorded at \( P = 13 \) Pa and \( T = 295 \) K; simulation for Ar buffer at \( P = 13.33 \) kPa; relative absorbance scales are arbitrary. From left to right, the line symmetries are \( E, F, A, F, F, A \). Dotted trace is least-squares fit using \( \Sigma \eta_e = 0 \) sum rule constraint. Simulation-fit residuals are shown dotted, displaced below the spectra and multiplied by three for visibility. Residuals \((x3)\) also shown for sum-rule fit parameters, but with all \( \eta_e \) set to zero, and for refit parameters with all \( \eta_e \) constrained to zero.

of only \( A_1 \) or \( A_2 \) symmetry in the \( T_d \) group, there is zero coupling between lines of different \( A \), \( E \) or \( F \) symmetry,\(^n\) thus, the two \( A \) and three \( F \) lines mix only among themselves.

The simulated spectrum is calculated using Eqs. (1)–(5) yielding the line parameters of Eq. (5), also given in Table 1. The simulated spectrum includes a convolution with Dicke-narrowed Doppler...
Line mixing sum rules

Table 1. Line parameters for simulated CH$_4$ v$_1$ R(6) manifold in Ar buffer.†

<table>
<thead>
<tr>
<th>$\alpha_s^*$</th>
<th>1213.16</th>
<th>1241.45</th>
<th>1323.29</th>
<th>1597.59</th>
<th>1662.40</th>
<th>1719.51</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_{rN}$</td>
<td>13.21</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$W_{rF}$</td>
<td>14.01</td>
<td>0</td>
<td>0</td>
<td>0.27</td>
<td>0.81</td>
<td>0</td>
</tr>
<tr>
<td>$W_{rE}$</td>
<td>13.36</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.20</td>
</tr>
<tr>
<td>$W_{rA}$</td>
<td>15.01</td>
<td>0</td>
<td>0</td>
<td>2.31</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$W_{rI}$</td>
<td>14.49</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$W_{rW}$</td>
<td>13.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For $m = 1, 2, 3, 4, 5, 6$

Table 1 also compares the retrieved parameters for the fits with $\eta_m = 0$ with the original values. Here, the deviations are generally much larger than the least-squares 1σ standard errors from fit in terms of last digits because of systematic model errors. The non-linearities in the parameters due to higher-order mixing beyond the Rosenkranz approximation are indicated by the percent change in the coefficients at a pressure of 66.66 kPa indicating non-linearity. This parameter retrieval is done with line mixing parameters from fit with no sum rule constraint.

distribution, as discussed in the next section, since the Doppler width seen in the low pressure ($P = 13$ Pa) spectrum is comparable to the line broadening. We then fit the simulated spectrum with only the line mixing parameter sum rule constraint, $\sum_{m} \eta_m = 0$, for each $A, E$ or $F$ symmetry block. This fit reproduces the spectrum within the “noise” level given by round-off errors of $10^{-4}$ due to an intermediate storage of the spectrum with a 4 digit format. The retrieved parameters generally agree with the input parameters to within this round-off error as given in Table 1. The fitted trace is shown dotted, superimposed on the solid curve simulation in Fig. 2, and the residuals, multiplied by 3, are displaced below the trace for visibility. There are no deviations visible on the scale of this figure. In order to gauge the effect of line mixing, we then set $\eta_m = 0$ but use the other retrieved parameters from the line mixing fit. This results in the residuals, again $\times 3$, shown in the next lower trace. Finally we refit the trace with the $\eta_m$ constrained to zero, so that the other parameters can adjust to minimize the deviations. In this case, we also constrained the relative intensities to the spin weights $c_s$, to stabilize the fit (particularly at higher pressures). The residuals $\times 3$ from this case are shown on the bottom trace of Fig. 2. The large systematic residuals seen in the lower two traces are characteristic of our experimental results presented in the following paper when mixing is ignored, and indicate the necessity of including line mixing even at modest pressures encountered in the upper atmosphere.
measured.\textsuperscript{47} Since the intrinsic shifts were arbitrarily set to zero, the shifts due to line mixing are measured relative to the Doppler width (FWHM), and are a maximum of \( \sim 11\% \) for the two \( F \) lines 4 and 5 which attract each other. The non-linearities in the widths are very small, \( \leq 0.1\% \). The intensities are only \( \sim 1\% \) non-linear at worst, and the mixing parameters for the close \( F \) lines are non-linear by \( \sim 7\% \). The non-linearities in the shifts and mixing parameters are large enough to invalidate the use of the Rosenkranz approximation for pressures close to an atmosphere.

Finally, in the last line of Table 1, we give the mixing parameters from a totally unconstrained fit, and they change sensibly only for the first two lines of \( E \) and \( F \) symmetry which are partially blended even at the Doppler limit. Thus, correlation among the parameters and the finite noise level from round-off errors results in a slight departure from the line mixing sum rules, which fractionally is not very significant. The lone \( E \) transition does acquire a false mixing coefficient which affects its shift slightly. Real data, however, may have a worse signal-to-noise ratio, may contain systematic errors due to baseline uncertainties, non-linearities in the pressure measurements, in the frequency scale, and in the detector/amplifier/divider/analog-to-digital converter chain, may have weak extraneous (isotopic, hot band, forbidden, etc.) lines buried in the background, and in fact, real spectra may not even obey the physical model completely. Then the extra constraints afforded by the sum rules may help to stabilize the fits and provide better estimates for the model parameters.\textsuperscript{47}

4. DOPPLER BROADENING AND DICKE NARROWING

As seen in Fig. 2, Doppler broadening is a significant fraction of the total line widths at atmospheric pressures for infrared and Raman spectra and must be considered in the line shape analysis. This is accomplished by a convolution of the Doppler spectral distribution, \( D(\omega) \), with the line mixing spectrum, \( \kappa(\omega) \), given in Eq. (5), such that

\[
\alpha(\omega) = \int_{-\infty}^{+\infty} \kappa(\omega - \omega')D(\omega') d\omega',
\]

where the integral of \( D(\omega) \) is normalized to unity. For a thermal equilibrium velocity distribution, ignoring the velocity-changing collisions, the Doppler profile is Gaussian,

\[
D(\omega') = \left( \frac{1}{\sqrt{2\pi}\sigma} \right) \exp\left( -\frac{\omega'^2}{2\sigma^2} \right),
\]

where \( \sigma = \omega_0(2k_BT/Mc^2)^{1/2} \) is the Doppler half width at \( e^{-1} \) intensity, \( k_B \) is the Boltzmann constant and \( M \) is the mass of the active molecule. Then

\[
\alpha(\omega) = \frac{N_{\omega}}{\pi^{3/2}} \sum_{m} \int_{-\infty}^{+\infty} [\xi_m y + \eta_m (x - t) \exp(-t^2)] dt / [(x - t)^2 + y^2].
\]

Here we have defined some dimensionless variables scaled to the Doppler width,

\[
t \equiv \omega' / \sigma, \quad x \equiv (\omega - \omega_m) / \sigma, \quad y \equiv \gamma_m / \sigma,
\]

and taken the sum outside the integral since the Doppler width depends on the transition frequency. Equation (10) may be rewritten in terms of the real and imaginary parts of the complex probability function,\textsuperscript{52}

\[
w(x, y) \equiv (i/\pi) \int_{-\infty}^{+\infty} \exp(-t^2) dt / [x - t + iy];
\]
Line mixing sum rules

\[ x(\omega) = \left( N_s / \sqrt{\pi} \right) \sum_m [\xi_m \text{Re}\{w(x, y)\} + \eta_m \text{Im}\{w(x, y)\}] / \sigma. \] (13)

For an isolated line, this is just the usual Voigt profile, here it is generalized for line mixing at any overlap. A similar expression was given by Strou and Gentry in the first-order Rosenkranz limit. Despite this generalization, Eq. (13) is still restricted to low pressures where the Gaussian Doppler distribution is valid.

When the mean-free-path for velocity-changing collisions becomes comparable to or less than the probe wavelength, the Doppler distribution narrows analogously to the effects of line mixing on overlapped rotational fine structure. This Doppler constriction is known as Dicke narrowing, and useful expressions have been given by Galatry and Rautian and Sobelmann in the weak and strong collision limits, respectively. Dicke narrowing is by now a commonly observed feature in high-resolution spectra of isolated lines, with only minor operational distinctions between the two limits. In the strong collision regime, expected when the buffer gas is heavier than the active species, the Rautian function for the Doppler profile is

\[ D(\omega') = \left( 1 / \sqrt{\pi} \right) \text{Re}\{w(x', z) / [1 - \sqrt{\pi} z w(x', z)]\}, \] (14)

where again \( w(x', z) \) is the complex probability function, Eq. (12), with \( x' \equiv \omega' / \sigma \) and \( z \equiv \beta_n / \sigma \), and \( \beta_n \) is a velocity-changing collision rate which may depend in principle on the particular transition or energy levels. The convolution of the Rautian with Eq. (5), yields

\[ x(\omega) = \left( N_s / \sqrt{\pi} \right) \sum_m [\xi_m \text{Re}\{r(x, y + z)\} + \eta_m \text{Im}\{r(x, y + z)\}] / \sigma, \] (15)

where we have defined

\[ r(x, y + z) \equiv w(x, y + z) / [1 - \sqrt{\pi} z w(x, y + z)], \] (16)

and, again, all the dimensionless variables depend on the transition \( m \). Equation (15) follows from Eqs. (14), (8) and (5) using Cauchy's integral formula and the residues for the poles at \( \omega' = \omega - \omega_n + i \eta_n \) in the upper half of the complex frequency plane as discussed by Rautian and Sobelmann for the case of isolated lines. In the limit of no velocity-changing collisions, \( r(x, y + z) \rightarrow w(x, y) \), so Eq. (15) reduces to the Voigt line mixing profile, Eq. (13). Rautian and Sobelmann point out that the convolution procedure is only valid when the velocity- and phase-changing collisions are statistically independent and when the shifts and line widths are independent of the relative speed of the collision partners.

In the case of diffusional or weak velocity-changing collisions, the convolution of the Dicke-narrowed Galatry profile with \( \kappa(\omega) \), Eq. (5), using a similar contour integration, yields

\[ x(\omega) = \left( N_s / \sqrt{\pi} \right) \sum_m [\xi_m \text{Re}\{g(x, y, z)\} + \eta_m \text{Im}\{g(x, y, z)\}] / \sigma, \] (17)

where the complex Galatry function is

\[ g(x, y, z) = \left( 1 / \sqrt{\pi} \right) \int_0^\infty d\tau \exp\{i x \tau - y \tau + (1 - \tau^2 - e^{-\tau^2}) / 2z^2\}. \] (18)

and \( x, y \) and \( z \) have the same definitions as in Eqs. (11) and (14) above.

For the simulated spectrum of Fig. 2, we have performed a direct numerical convolution of the Dicke-narrowed Rautian distribution, Eq. (14), with the line mixing sum of Eq. (5). Then, we retrieved the parameters with a least-squares fit using Eq. (15). We employ the Humlicsek algorithm for computing the complex probability function. The negligible deviations in the sim-fit residuals verify both Eq. (15) and the non-linear least-squares fitting routine. For this test we used \( \beta_n = 8.0 \) points for all transitions (recall Doppler FWHM = 2 ln 2 \( \sigma \) = 18.97 points) and fixed \( \beta_n \) at this value in the fits shown in Fig. 2 and Table 1. If we then float the \( \beta_n \) in the fit, we find only
small variations in $\beta$, due to parameter correlation, with largest deviations of $\sim -0.9\%$ for line 5 and $\sim -0.6\%$ for line 1 and $\leq 0.01\%$ for the other line parameters.

We have also generated synthetic spectra for the Dicke-narrowed Galatry profile by direct numerical convolution of Eq. (5) with $\text{Re}\{g(x', 0, z)\}$ using the Herbert continued fraction algorithm. These spectra could then be fit with the complex Galatry expression, Eq. (17), with comparable precision to the Rautian fits described above; thus confirming Eq. (17) and the least-squares fitting procedure.

5. CONCLUSIONS

We have shown that the line mixing parameters for collisionally-coupled multiplets sum to zero and that the total integrated intensities, broadening and shift parameters are preserved, independent of the overlap. These line mixing sum rules have been illustrated for coupled doublets and spherical-top $J$ manifolds, the latter indicating a block diagonal structure among the different symmetry lines. The sum rules are useful for testing and stabilizing non-linear least-squares fitting routines, and can reduce the number of free parameters, their correlations and uncertainties in fitting realistic spectra. Since Doppler broadening and Dicke narrowing are encountered in atmospheric spectra, we incorporate models of these effects into the formalism for coupled transitions. An application to measurements of the $P$ and $R$ branches of the $v_3$ band of methane is given in the following paper.

Acknowledgements—The author is grateful to T. Gabard for the theoretical justification of the $A \neq E \neq F$ collisional selection rules in tetrahedral molecules to J. P. Looney for helpful comments on the extension of the Dicke-narrowing effects to the Galatry regime. This work was supported by the NASA Upper Atmosphere Research Program.

REFERENCES