

Line-mixing in the 106←000 overtone transition of HCN

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By using cavity ring-down spectroscopy (CRDS), we have obtained visible overtone absorption spectra of HCN which display a large collisional line-mixing effect in the proximity of the *R* branch band heads, for $J \sim 18$. We consider in detail the 106←000 (1=CN, 0=bend, 6=CH) parallel transition. The *R* branch profile was modeled using the modified-exponential-gap (MEG) and energy-corrected-sudden approximation (ECS) population transfer rate laws. We used the rates previously determined by Pine and Looney (PL) by fitting the self broadening coefficients measured for the *Q* branches of Π - Σ infrared perpendicular stretch-bend combination bands of HCN [J. Chem. Phys. **96**, 1704 (1992)]. Contrary to what is found by these authors, in the present case the MEG law reproduces the *R* branch line-mixing satisfactorily, while the ECS model fails. This reflects an increasing propensity at higher *J* for collisional transitions with smaller ΔJ . Using the MEG law, we found we need to include, as had PL in their fits to the infrared *Q* branches, an empirical dephasing scale factor $F \sim 0.6$ for the coherence transfer rates to obtain a satisfactory simulation of the *R* band head. PL suggested that dephasing in the *Q* branch spectra are due to cross relaxation across *l*-type doublet levels of the Π state, but no such mechanism would be available in the present case. However, we have found that by using a 50/50 linear combination of the ECS and MEG rate laws, it is possible to fit our data even with $F = 1$, which would imply no dephasing of coherence. We take this as a demonstration that the dephasing factor *F* cannot be reliably extracted from line-mixing studies alone but instead requires some independent source of information on the relative value for state to state inelastic collision rates. © 1996 American Institute of Physics. [S0021-9606(96)02025-9]

I. INTRODUCTION

Line-mixing consists of the non-additivity of absorption lines as pressure broadening blends them together. This effect is due to collisional transfer of coherence among the rovibrational transitions of overlapping lines. The effect is analogous to Dicke narrowing of Doppler broadened lines and the familiar NMR motional narrowing.¹ As we will show later, the mixing effect can be significant, even if a fit to the spectrum by a sum of independent line shapes appears to be quite satisfactory. Due to the flexibility of the predicted band shape when each line is given independent fit parameters (intensity, width and position), a fit of this kind can converge to non-physical effective parameter values that partially compensate for the line-mixing effect.

Since in many pressure-broadened spectra the size of line-mixing effects is far from negligible, a good description of this phenomenon is essential for the accurate spectral modeling in activities such as atmospheric monitoring or combustion diagnostics. Besides practical applications, there is a direct connection to the vast field of collisional energy transfer. Since it is a manifestation of collisional transfer of optical coherence among resonant transitions, line mixing gives information not available in population transfer cross-section measurements. Indeed, it is an unresolved question, directly related to the use of the empirical *F* dephasing factor

to be discussed below, whether one could calculate line mixing in practice even given the complete set of state-to-state rates.

By ‘‘coherence’’ it is meant a nonzero average value for an off-diagonal element of the single molecule reduced density matrix. In the present case, we are considering the optical coherence between two molecular states that participate in a transition in the observed spectrum. Coherence transfer occurs when collisions change both the upper and the lower molecular states of the optical transition. This process can be described by introducing a super-operator $\Gamma_{ij,kl}$ for the evolution of the density matrix in presence of molecular collisions: $d\rho/dt = (i\hbar)^{-1}[H_0, \rho] - \Gamma\rho$, where H_0 gives the evolution of the isolated molecule. The element $\Gamma_{ij,kl}$ corresponds to the transfer of coherence from the density matrix element ρ_{ij} to ρ_{kl} . This collisional coupling of the coherences of different transitions is responsible for the non-additivity of the associated absorption lines. The coherence transfer is observable only for transitions whose lines at least partially overlap, since otherwise there is destructive interference of the coherence transferred at different times during its decay. Since collisions in ammonia are predominantly across inversion doublets, its spectrum provides a clear and simple experimental example of coherence transfer in a four-level system.²

It is presently not possible to make accurate first principles calculations except in the simplest of systems at low temperatures. As a result, most experimental studies of collisional spectral profiles have relied on modeling and fitting the data using empirical laws for the transfer rates. The con-

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nection between the transfer rates and the spectral profiles is given by a binary collision “*W*-matrix” formalism developed by Baranger,³ Kolb and Griem,⁴ and later by Fano.⁵ In the modeling, the coherence transfer rates are estimated from state-to-state population transfer rates, which are calculated by using empirical rate laws. Even if these fitting laws have limited physical justification,^{6,7} they have been quite successful when applied to spectra of non-polar molecules, such as CO₂, N₂O, C₂H₂, etc. (see references in Ref. 6). Their main advantage is that only a few parameters are needed to fit the experimental data over a wide pressure range. These laws are usually variations of the power-exponential-gap (PEG) law,⁸ such as the modified-exponential-gap (MEG)⁹ and the rotational-energy-gap (REG)^{10,11} laws. Definitions of PEG and MEG will be given below in Eq. (7) and Eq. (5), respectively.

On the other hand, PEG and the related laws have generally not been found to work well in the case of strongly polar molecules, where long-range dipole–dipole or dipole–quadrupole interactions dominate the collisional processes. In their study of very high quality spectra of perpendicular infrared transitions in HCN, where line-mixing effects are especially important in the low-*J* region of the *Q* branch, Pine and Looney (PL) have shown that PEG and most of its modifications fail to quantitatively describe even the pressure broadening coefficients.⁶ Among these laws MEG is found to behave acceptably well excepted in the high pressure range (~1 atm), where even the binary collision model might be starting to break down.

The energy-corrected-sudden (ECS) inelastic rate scaling laws are also tested by these authors and found to give a good fit at any pressure. It should be noticed that ECS is one of the few descriptions based on well understood physical approximations.¹² The *J* dependence of the pressure broadening coefficients calculated by the fitted MEG and ECS models was found to be almost identical.

It is interesting to note that the rotational dependence of the pressure broadening coefficients of HCN has a maximum near the peak of the Boltzmann distribution and has a similar width. This suggests that rotationally resonant dipole collisions, where one molecule goes from *J* to *J*+1 and the other from *J*+1 to *J*, dominate the pressure broadening.¹³ The slight detuning of the upper state rotational spacings compared to the ground state qualitatively explained the difference in broadening between *R*(*J*) and *P*(*J*+1) lines.¹³ Both the MEG and ECS laws ignore the rotational levels of the collision partner which is effectively treated as a structureless system, i.e. an atom. PL attempted to fit a rate law based upon rotational resonance, but paradoxically found that it did not give a good fit of the pressure broadening rates. Likely this is because other processes are important far from the Boltzmann maximum, and thus a single rate law will not capture the much more complex interactions between two highly polar HCN molecules.

In their modeling PL also found that they needed to scale the coherence transfer rates by an empirical factor *F*~0.6 in order to reproduce the observed degree of line mixing. This *F* factor can be viewed as correcting for inelastic transitions

to levels not explicitly included in the model, for reorientation, and other sources of dephasing. The need for this correction had been already recognized for the line mixing in infrared spectra as opposed to the case of Raman spectra, where empirically it is found not to be needed.^{14–16} The rotational levels of the Π states reached in the PL experiment have nearly degenerate *e* and *f*, *l*-type doubling levels, and only the *f* levels contribute to absorption in the *Q* branch of a Π – Σ transition. PL suggested that the observed *F*~0.6 value reflected population transfer from *f* to *e* levels in ~40% of inelastic collisions.^{6,14,17} The *e* levels only radiate in the *P* and *R* branches of the band, which do not overlap with the *Q* branch in the pressure range studied by PL.

By using cavity ring-down spectroscopy (CRDS), we have been able to obtain overtone absorption spectra of HCN where collisionally induced line mixing is a large effect in the proximity of the *R* branch band head. Since in Σ – Σ transitions of the type that dominate the overtone absorption spectrum, all rotational states of both vibrational levels are of *e* symmetry, *e*–*f* collisional transfer is not expected to contribute significantly to dephasing the line-mixing effect. Thus comparison of the effective *F* value needed to fit these spectra to that found by PL may provide a test of the importance of such collisions.

We have modeled the *R* branch profiles by the MEG and ECS population transfer rate laws using the method described by PL.⁶ This was done so that results for parallel transitions could be directly compared with their work on perpendicular transitions. Contrary to what is found by these authors for HCN infrared combination bands, we find that the MEG rate law gives a much better description than the ECS law for the line mixing. This likely reflects the fact that the two experiments are sensitive to coherence transfer at very different values of *J*. In the *Q* branch lines overlap at low *J* (<10), while in the *R* band head they overlap at higher *J* (~15). Despite these differences, the overtone *R* band head is accurately reproduced by the MEG law using the same rate law parameters and the same *F*~0.6 value found by PL. There are also other experimental observations of coherence transfer in strongly polar molecules, where the efficiency of coherence transfer is close to 70%.^{2,18} However, we have also found that using a linear combination of the MEG and ECS rate laws, it is possible to obtain a good fit of our data with *F*=1, i.e. no dephasing at all. The conclusion is that there cannot be any rigorous meaning to be attached to the *F* factor unless one has a compelling physical reason to choose a specific rate law. A better theoretical understanding and direct measurements of the population transfer rates are needed.

It has been found in earlier work that pure dephasing from elastic collisions makes a small contribution to the self pressure broadening of strongly polar systems.¹⁹ Physically, this arises from the strong torques induced by the dipole–dipole interaction which lead to rotationally inelastic collisions even at long range. In HCN, the collisional radius derived from the pressure broadening is ~24 Å.⁶ However, we believe there is no reason to suppose that there will not be a significant dephasing for inelastic collisions, which likely

contribute over a large range of impact parameters (partial waves), and occur with collision partners in all thermally populated levels. In fact, the underlying physical basis for line mixing is inelastic collisions that transfer coherence from a given transition to another and then back again before the coherence is lost due to the different rate of precession (i.e. optical frequency). It is thus meaningful to consider the dephasing introduced by these inelastic processes. Clearly, theoretical calculations are needed to disentangle the various possible contributions to the line-mixing dephasing, which could be computed from a thermal average of the matrix elements of the collisional S matrix.²⁰

II. EXPERIMENT

Recently, we applied CRDS to the study very highly excited and weak vibrational overtones in HCN.²¹ Some of the spectra were obtained with an excellent signal-to-noise ratio (>100). In addition to the extreme sensitivity ($<10^{-9}/\text{cm}$), an attractive feature of CRDS is that the absolute sample absorbance is measured directly as a function of frequency. In our measurements the spectral resolution was limited by the pulsed dye laser (0.04 cm^{-1}), which is sufficient to resolve HCN pressure broadened lines above ~ 50 torr (1 torr = 133.322 Pa). We could therefore obtain pressure broadened rovibrational band profiles of high quality for accurate lineshape studies.

For the large vibrational excitation in the observed HCN transitions, the change of moment of inertia is such that the R branch progression folds onto itself much earlier than in typical infrared transitions. In HCN overtones with 7 vibrational quanta, the turning point occurs for values of the angular momentum $J \sim 20$, not far above the Boltzmann intensity maximum, $J \sim 10$. Therefore, these overtone transitions are ideal for studying line-mixing effects for large J values. Indeed, by choosing overtones with different degree of vibrational excitation, it would be possible to tune the range of J values where the mixing is most effective.

Since in this study we were primarily interested in comparing the line mixing in a $\Sigma-\Sigma$ transition to that observed earlier for $\Pi-\Sigma$ bands, we chose to focus on a single band. We measured several spectra of the R branch profile of the $106\leftarrow 000$ overtone at different pressures. Previous work has shown little variation in pressure broadening with vibrational band in HCN from the infrared through visible overtone bands.¹³ Line mixing has been shown to be remarkably independent of the vibrational character of the transition⁶ for $\Pi-\Sigma$ transitions as well. As a result, we anticipate only minor changes in the line mixing of other $\Sigma-\Sigma$ vibrational transitions.

Fig. 1 shows some spectra of the $106\leftarrow 000$ overtone transition R branch at different values of the sample pressure. For all these spectra, we verified that the integrated R branch intensity and the linewidths of the low- J lines (fitted to independent Voigt profiles), scale linearly with pressure. This is a good indication that these data are free of appreciable distortion or saturation effects. Line mixing produces only a redistribution of intensity, thus the integrated area

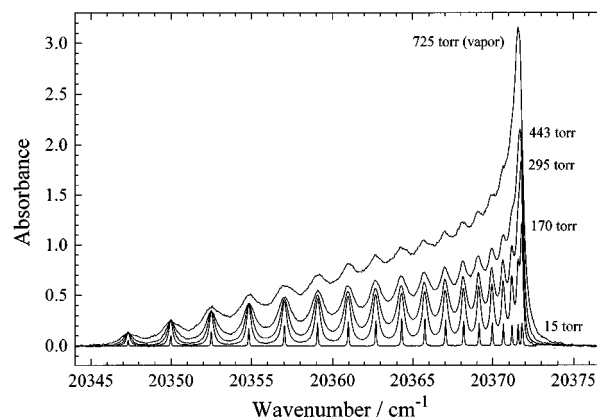


FIG. 1. Spectra of the R branch of the $106\leftarrow 000$ overtone transition in HCN, taken at different pressure values.

under the whole spectrum should be linearly proportional to the pressure even in the presence of extensive line mixing.

III. THE W MATRIX FORMALISM

In this section we give a quick outline of the W matrix formalism, which constitutes the formal and computational link between the population transfer rates and the pressure broadened and ‘‘line-mixed’’ rovibrational spectrum.

As discussed in Ref. 6, a binary-collisions theory has been developed to relate absorption spectra affected by line-mixing to the more basic population transfer rates.³⁻⁵ This theory gives a relatively simple algorithm to calculate the spectral profile from the W matrix, defined as

$$W_{JK} = \gamma_J + i\Delta\nu_J \quad \text{if } J=K$$

$$W_{JK} = -R_{J\rightarrow K} \quad \text{if } J \neq K, \quad (1)$$

where $R_{J\rightarrow K}$ are the state-specific population transfer rates, and $\Delta\nu_J$ and γ_J are the pressure shift and broadening coefficients, respectively. The transfer rates are constrained by the detailed-balance principle:

$$R_{J\rightarrow K}/\rho_K = R_{K\rightarrow J}/\rho_J, \quad (2)$$

where ρ_J is the thermal population in the state J . The line shift coefficients are usually taken to be state independent. In HCN, these coefficients have been found to be at least 10 times smaller than the pressure broadening, and they can be neglected.¹³ The broadening coefficients can be written in terms of the total depopulation rates, plus dephasing contributions γ_J^d which are also assumed to be negligible,

$$\gamma_J = \sum_{K \neq J} R_{J\rightarrow K} + \gamma_J^d. \quad (3)$$

It should be noticed that no information is available about the imaginary part of the off-diagonal W matrix elements. Therefore, rather arbitrarily, it is customary to set these to zero. Up to here we have considered only one vibrational state. As we are modeling a transition between two vibrational states, the W matrix has to be averaged over these

states. In any case it should be noticed that the values in the W matrix typically change only a few percent going from the lower to the upper state.

If the vibrational dephasing can be neglected, the W matrix formalism is a good approximation in the treatment of isotropic Raman scattering. In this case, identical forces effect both the upper and lower state of each optical transition and thus a single semiclassical path can be expected for each coherence transfer process. However, the successful application of this theory to vibrational transitions has been found to require an additional empirical scaling factor F for the off-diagonal elements of W ,^{6,14–16}

$$W_{JK} = -FR_{J \rightarrow K} \quad \text{if } J \neq K. \quad (4)$$

The empirical factor F has been often found to be close to 0.6, with some variation from system to system and depending on which fitting law is applied to calculate the transfer rates.⁶ Making reference to Eq. (3), $F=1$ implies that broadening is due only to inelastic collisions and that the coherence removed from one transition is completely transferred to other transitions. For a single collisional event, with well-defined values for both the initial and final quantum numbers of the collision partner (including translational degrees of freedom between the molecules), the unitarity of the collisional S matrix assures the conservation of coherence.

It is instructive to note that in the limiting case $F=0$ the W matrix is diagonal, and the equations for the spectral profile reduce to a sum of Lorentzian lines. An $F < 1$ may indicate that contributions to pressure broadening besides rotationally inelastic collisions are important, such as elastic dephasing, rotational re-orientation, vibrational relaxation, etc. These processes are usually considered to be much slower than rotationally inelastic transitions in collisions between highly polar molecules. It is also likely that in the thermal average over the quantum numbers of the collision partner there can be some “washing out” of the coherence transfer, which unlike population transfer, need not be positive definite, or even real. The coherence transfer per collision can be written in terms of a thermal trace over products of off diagonal S matrix elements.²⁰ As we mentioned above, PL interpret the $F \sim 0.6$ value that optimizes their simulations by suggesting that $\sim 40\%$ of the collisions may change the e, f symmetry of the rotational level. Considerations of “gyroscopic stability” would predict that at least at high J , such transitions would be unlikely, but they may be quite important for the low J levels that dominate line mixing in the Q branch.

The role of the fitting laws is to model the whole W matrix by a smooth and simple functional form. Since the models used have few parameters, fitting the W diagonal elements alone is already sufficient to determine all the matrix elements. The diagonal elements γ_J can be obtained at pressures low enough that only pure line broadening is effective.⁶ After W has been determined in this way, the band profile, including line mixing, can be calculated at higher pressure and compared with the experiment. If the profile is correctly reproduced over the full pressure range, then it is usually assumed that the fitting law is physically

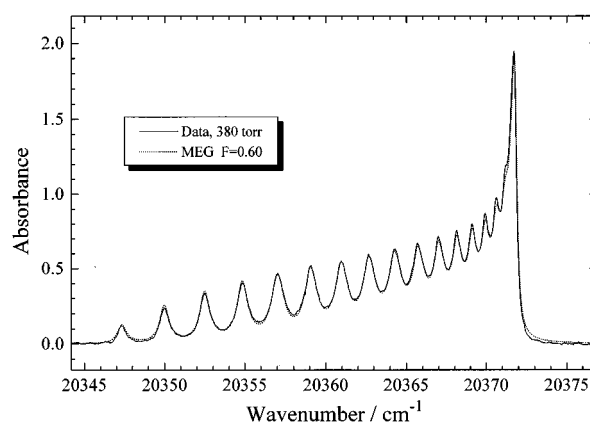


FIG. 2. Comparison of the 380 torr HCN 106–000 spectrum with a MEG simulation for $F=0.60$.

meaningful. This is not a very different argument from that used in fitting potential energy surfaces to transition frequencies. A smooth functional form with some reasonable features is chosen and then a successful fit of the data is assumed to indicate the correctness of the functional form. This argument is clearly not rigorous, and it is often the case that empirical laws are not satisfactory when extrapolated to compare with new data. In the present case, it is clear that J -resolved state-to-state rates, as recently measured by Wu *et al.* for a limited range of J values,¹⁸ would add important new information, and may allow one to choose the “right” fitting law in a direct way.

IV. DISCUSSION: MEG AND ECS SIMULATIONS

In this section we compare our R branch overtone spectra to the same empirical fitting laws tested by PL on infrared Q branch spectra of HCN.⁶ PL determined very accurate pressure broadening coefficients, which agree within the error bars for the three bands they studied. These values also agree with previous experiments and with our overtone spectra. Therefore, we did not fit the γ_J coefficients to the various empirical laws, instead we used the same parameters determined by PL. The pressure broadening coefficients calculated from these rate laws accurately reproduce the P branch of our spectra, where line mixing is unimportant. A program provided by A. S. Pine and used for the simulations of perpendicular bands, was slightly modified and used for the present case of a parallel band.

Of the fitting laws considered by PL, we found that a partially decoupled MEG law performs reasonably well in simulating our data (see Figs. 2 and 3), but that the ECS law, which is the best model for the bend-stretch Q branches,⁶ does not exhibit enough line mixing or intensity at the band head (see Fig. 4). We will also show later that a linear combination of MEG and ECS yields a good representation of our data with $F=1$ (Fig. 9).

The MEG law⁹ is determined only by the three parameters a_i ($i=1,2,3$),

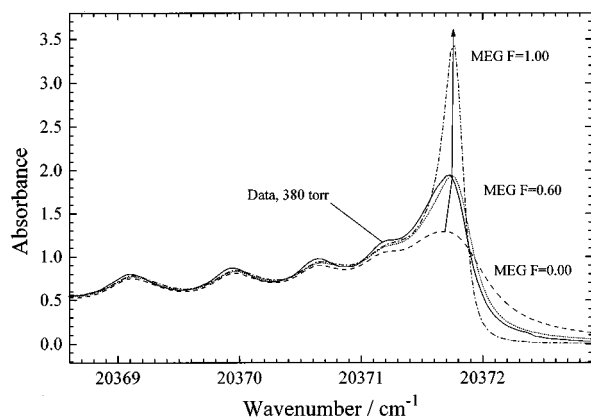


FIG. 3. Detail of the band head of the 380 torr HCN 106←000 spectrum is shown together with MEG simulations for $F=0.00$, 0.60, and 1.00. The positive shift of the band head with increasing F can be appreciated.

$$R_{J \rightarrow K} = a_1 \left[\frac{1 + 1.5(E_J/a_2 kT)}{1 + 1.5(E_J/kT)} \right]^2 \exp\left(-a_3 \frac{E_K - E_J}{kT}\right), \quad (5)$$

where E_J is the rotational energy of level J , and $J < K$. The rates for $J > K$ are given by the detailed balance principle, Eq. (2).

ECS is given by a more complex form, where all the rates depend only on those from $J=0$ to the other rotational levels (base rates),¹²

$$R_{J \rightarrow K} = (2K+1) \exp\left(-\frac{E_K - E_J}{kT}\right) \times \sum_L (2L+1) \begin{pmatrix} JKL \\ 000 \end{pmatrix}^2 \times \left[\frac{1 + [a_4(E_L - E_{L-1})]^2/B_g kT}{1 + [a_4(E_K - E_{K-1})]^2/B_g kT} \right]^2 R_{L \rightarrow 0}, \quad (6)$$

where the standard 3- J symbol ($:::$) has been employed.

For the base rates $R_{L \rightarrow 0}$ we make the same choice as PL to use the PEG form^{6,8}:

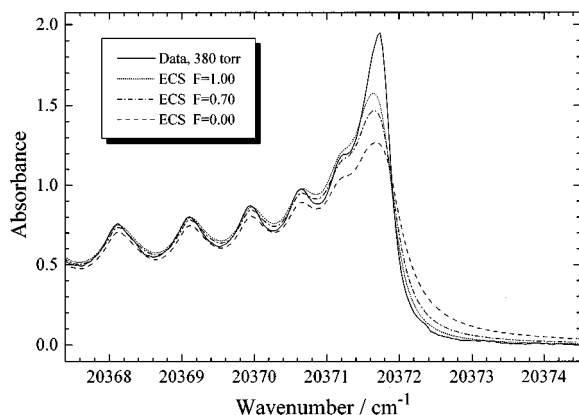


FIG. 4. Comparison of the 380 torr HCN 106←000 spectrum with ECS simulations at $F=0.00$, 0.70, and 1.00. ECS does not fit the peak of the band head, where mixing is more extensive, for any value of F .

$$R_{L \rightarrow 0} = a_1 \left(\frac{E_L}{B_g} \right)^{-a_2} \exp\left(-a_3 \frac{E_L}{kT}\right). \quad (7)$$

Therefore, ECS has four degrees of freedom. Given the strong selection rules predicted by dipole-dipole coupling, one would expect that only a few base rates would be sufficient to describe the collisions. Following a suggestion made by S. L. Coy, we attempted to fit to an ECS model using a few base rates as free parameters. However, these fits failed to converge on to a solution that reproduced the observed line broadening parameters. Likely, this is because the ECS model does not include the internal structure of the collision partner, which is essential for treating the dipole-dipole forces.

The values of the MEG and ECS parameters determined by PL are⁶

	a_1 (cm ⁻¹ /atm)	a_2	a_3	a_4
MEG	0.257 45(314)	0.316 28(628)	8.218(126)	—
ECS	0.020 66(200)	0.3431(173)	0.2912(78)	2.002(279)

where the uncertainties in parentheses are equal to one standard deviation of the fit. The spectroscopic constants fitted to the 106←000 line positions are: $\Delta B = -75.69 \pm 0.06 \times 10^{-3}$ cm⁻¹, $\Delta D = -0.13 \pm 0.24 \times 10^{-6}$ cm⁻¹ (practically zero). The fits were done with the ground-state constants fixed to the accurate experimental values $B_g = 1.478221834$ and $D_g = 2.9099 \times 10^{-6}$.²¹

In comparing the simulations to the experimental spectra, we still have to adjust a free scaling parameter for the total intensity. The best way we found to determine this factor is to normalize the total integral of the simulated spectrum to the experimental one. This is done for all the simulations shown here. It should be noticed that the integral intensity is independent of the rate model and the F value, so that the scaling can be determined once and for all.

We have measured spectral profiles for several pressure values between 100 torr (limited by laser resolution) and vapor pressure, which is about 725 torr at room temperature. We will consider only the intermediate 380 torr case and the vapor pressure case. Simulations we did at other pressure values do not seem to add any further insight to the problem.

In Fig. 2 we compare the MEG simulation for $F=0.60$, that optimizes the overlap with the data. The sensitivity to F is such that a change of 10% is sufficient to make the overlap visibly worse. The values of F that we report should therefore be considered good to about ± 0.03 . Adjustments of this parameter were done quite efficiently by manual adjustment, without need for a fitting routine. In Fig. 3 we also examine in detail the band head and the MEG simulations for $F=0.00$, 0.60, and 1.00. For $F=0$ the simulated profile is much too broad. Note in particular the region above the band head. As we commented before, for $F=0$ the W matrix procedure is exactly equivalent to overlapping independent Lorentzian lines with their linear pressure broadening. Therefore, this comparison makes evident how dramatic the line mixing is in these spectra. In this figure it is also clear that the band head peak shifts to higher frequencies as F is increased. The opposite tendency is found in the ECS

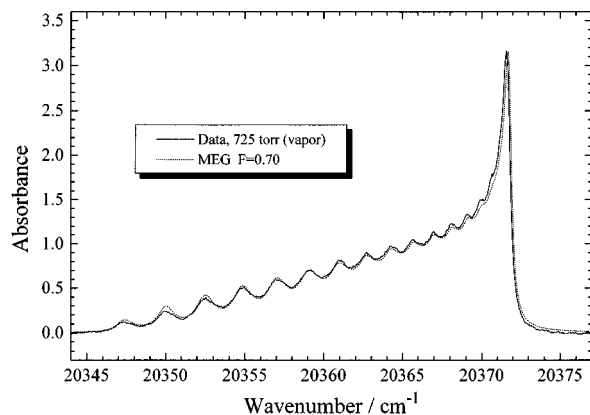


FIG. 5. Best fit of vapor-pressure HCN 106←000 spectrum by a MEG simulation with $F=0.70$.

simulations, as in Fig. 4. This is due to the stronger propensity for processes with small ΔJ in the MEG description. If each line mixes only with its close neighbors, the lines closest to the band head will not mix with lines outside it. In the case of ECS, larger ΔJ have substantial rates, and therefore the lines in the band head mix with lines closer to the band center. The effect of this line mixing is to shift the band head peak towards the band center. Given this dependence of the peak position on the rate model and on the F parameter, the mismatch of the peak position at $F=0.60$ might be considered as a failure of the MEG model. It is also possible that adding a phase shift to the coherence transfer rates (which were rather arbitrarily assumed to be real in the model) could lead to an enhanced pressure shift when line-mixing is important.

Fig. 4 is for the ECS model at the same 380 torr pressure. The overall match to the data is not very good, especially at the band head, whose intensity is underestimated even for $F=1.00$. We notice that the simulated band profile is much less sensitive on variation of F than in the MEG case. This is because most of the inelastic collisions are predicted to occur between states whose transitions have little overlap, and thus weak line mixing.

In Figs. 5 and 6 we show that MEG is still performing reasonably well at the room temperature vapor pressure, with some problems at low J 's and a larger shift of the peak position. The best F in this case is slightly larger: 0.70. This change of F is to be regarded with suspicion, as it may be an adjustment induced by an inadequacy of the MEG model. In particular, the greater pressure makes more lines near the band head to overlap significantly so that the band shape is sensitive to inelastic rates over a wider ΔJ range. The change in F could also reflect a breakdown of the binary collision model on which the W matrix formalism is based. In fact, at 725 torr we calculate that the mean molecular distance is close to the collisional radius obtained from the pressure broadening ($\sim 24 \text{ \AA}^6$). In particular, an F value increasing with pressure should indicate that long-range processes responsible for the dephasing and inelastic non-resonant collisions are decreasing in efficiency relative to

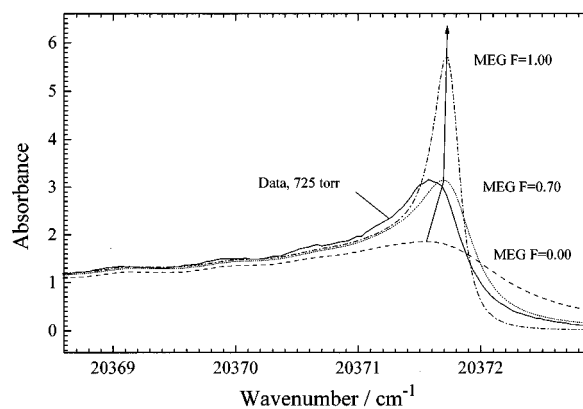


FIG. 6. Detail of vapor-pressure HCN 106←000 spectrum and MEG simulations with $F=0.00$, 0.70, and 1.00.

resonant inelastic collisions. It is difficult to understand if there are any simple reasons that justify such a trend. For example, the increased chance for three body interactions should favor non-resonant population changes with larger transfer of rotational to translational energy, which would give a *smaller* F . Alternatively, if we consider the dipolar interaction as dominant, three body interactions will decrease the effective binary coupling, and will induce a smaller effective line broadening. The MEG model, to compensate for the narrower widths, would need a higher F value.

It is instructive to consider the rates given by the MEG and the ECS models as a function of ΔJ , as already discussed by Pine.¹⁷ In Fig. 7 are the rates for the MEG model, from the selected initial states $J=0,5,\dots,25$ to final J' states, plotted as a function of $\Delta J=J'-J$. In Fig. 8 are the rates for the ECS case. From these graphics, it is clear that in the MEG model there is a strong preference for collisions that change J only by ± 1 . This is consistent with dipole-dipole scattering in the first order Born approximation, and also with the recent experimental work of Wu *et al.*,¹⁸ who observed about 70% of population transfer to be due to $\Delta J = \pm 1$ collisions. On the other hand, the fitted ECS model gives significant rates for larger ΔJ . As a result, ECS does

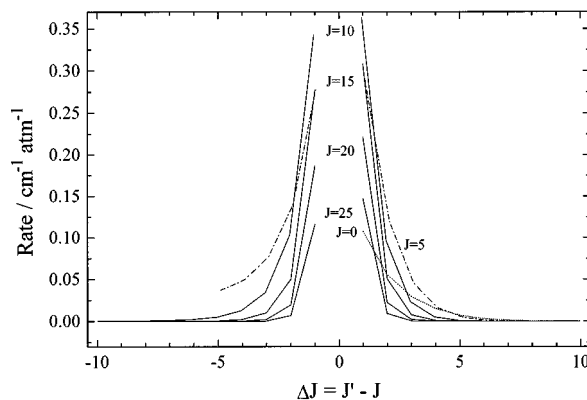


FIG. 7. Rates given by the MEG model, from the selected initial states $J=0,5,\dots,25$ to final J' states, plotted as a function of $\Delta J=J'-J$. It is clear that processes with $\Delta J > 1$ are inefficient.

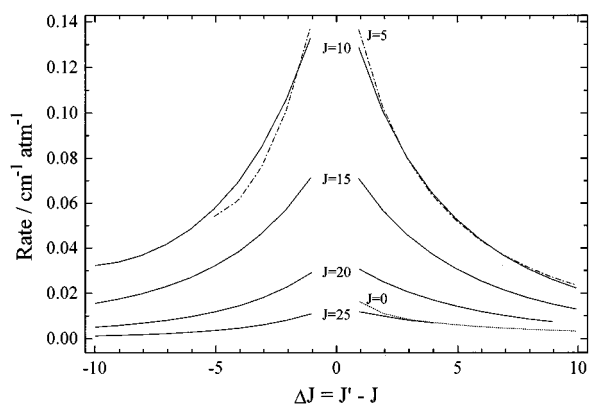


FIG. 8. Rates for the ECS model, from the initial states $J=0, 5, \dots, 25$ to final J' states, plotted as a function of $\Delta J = J' - J$. Notice the propensity for ΔJ larger than 1.

not predict enough line mixing to match the data, even for $F=1$. The simple qualitative understanding that we propose is the following. At low J values, which are important in Q branch line mixing, ECS describes the transfer rates more accurately, while at higher J , important for the overtone R branch, the MEG model is better. This would be consistent with the fact that collisions with $\Delta J > 1$ become less efficient as J increases, a kind of “gyroscopic effect.” This picture *seems* to be consistent with the observation that the vapor-pressure MEG simulation does not fit very well the low- J lines of the spectrum (see Fig. 5). However, this last observation is not correct, since the ECS simulation at vapor pressure gives almost exactly the same low- J 's profile as the MEG.

Last, in Fig. 9, we show that an excellent simulation with $F=1$ is given using the linear convex ($a+b=1$) combination of the MEG and ECS rates:

$$W = a \times W_{\text{ECS}} + b \times W_{\text{MEG}}. \quad (8)$$

The convexity guarantees that the pressure broadening coefficients (on the diagonal of the W matrix) are automatically fitted by this linear combination. The agreement with the

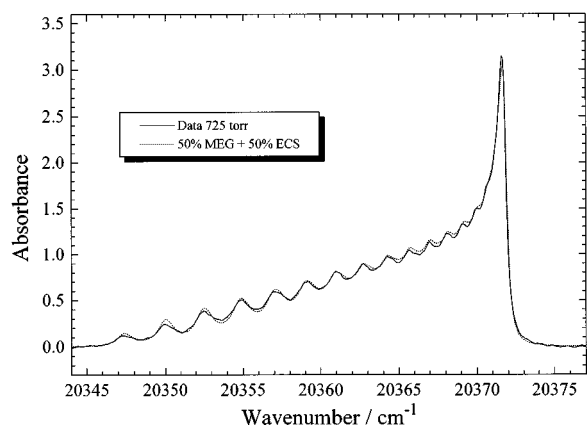


FIG. 9. Vapor-pressure HCN 106-000 spectrum compared with simulation done using 50% ECS+50% MEG with $F=1$.

data is actually slightly better than in the MEG case, since the position of the R branch peak is reproduced more accurately (since ECS “pulls” in the opposite direction as MEG).

V. CONCLUSION

In the infrared perpendicular transitions studied by PL, the upper state possesses an $e-f$ sublevels structure due to l doubling, which allows for symmetry changing collisions to induce dephasing and quench the coherence transfer. The final effect would be a decreased extent of line mixing, modeled by the introduction of the empirical F factor. In fact, PL interpret their $F \sim 0.6$ value as indicating a 40% propensity for collisions that change f into e sublevels.^{6,14,17}

Since $106 \leftarrow 000$ is a $\Sigma-\Sigma$ transition, no l doubling applies. Still, when we test the fitting laws with the same values of the parameters obtained by PL, we obtain the same optimal value of F , even if the best fitting law in this case is the MEG law. Therefore, our data would indicate that a value of F in the range 0.5–0.7 is caused by dephasing processes other than $e-f$ changing collisions. This is also consistent with the results of Wu *et al.*,¹⁸ who directly measured some of the collisional population transfer rates in HCN. They found that population transfer accounts for only $\sim 70\%$ of the pressure broadening rate, while the remaining 30% should correspond to optical collisional dephasing. Since the rate laws used by PL reproduce the pressure broadening assuming it all comes from rotationally inelastic collisions, these models will overestimate the degree of both inelastic population and coherence transfer.

In conclusion, the success of the ECS model in HCN is far from complete, since it underestimates the observed degree of line mixing in the overtone R band heads. The MEG rate law can successfully reproduce the observed R band heads, but only with the introduction of an empirical dephasing factor $F \sim 0.6$ which damps the coherence transfer predicted by the model. A similar dephasing value was found by PL to be required to fit the observed line mixing of Q branches in IR perpendicular bands. We have argued that in strongly polar systems such as HCN, dephasing in long-range inelastic collisions is expected to cause a loss of coherence which can be crudely modeled by introduction of the F dephasing factor. However, we find that the line mixing in the R band heads can be reproduced by a model with no dephasing ($F=1$), but with a rate law that averages the inelastic rates predicted by the ECS and MEG rate laws. Thus, it appears that no definite conclusions can be drawn about the degree of coherence transfer in HCN self-collisions without comparison with measurement or calculation of the state to state population transfer rates. The limited state to state population relaxation measurements reported by Wu *et al.*¹⁸ are in agreement with the MEG rate law prediction that the preponderance of collisions change J by at most ± 2 . Further, the observed total rate of depopulation was found to be only 70% of that predicted from the measured pressure broadening coefficients, assuming negligible dephasing. We hope that these measurements can be repeated for initial J

levels that make up the R band head studied in this work, since this will allow for our data to be analyzed using observed inelastic rates. We would also like to encourage theoretical determination of coherence transfer rates from full S matrix calculations for the important case of molecule-molecule scattering.

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