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Experimental and theoretical study of line mixing in methane spectra.

IV. Influence of the temperature and of the band

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Line-mixing effects are studied in infrared bands of CH₄ perturbed by N₂ at various pressures. The effects of temperature are investigated in the ν_3 region whereas spectral shapes of the ν_2 , ν_4 , and ν_3 bands are compared at room temperature. The theoretical approach proposed in preceding papers is used in order to model and analyze the influence of collisions on the spectral shape. *All model parameters are now fixed* to values determined in the previous studies. Comparisons between measurements and spectra computed with and without the inclusion of line mixing are made. They show that our approach satisfactorily accounts for the effects of temperature, pressure, and of rotational quantum numbers on the absorption by the ν_3 band. Furthermore, the effects of collisions on spectra in the ν_4 region at room temperature are also correctly calculated. On the other hand, the proposed approach fails in modeling the evolution with increasing pressure of absorption in the spectral range containing the ν_2 band. This result is attributed to the Coriolis coupling between the ν_2 and ν_4 vibrational states and to a contribution whose physical origin remains unclear. The latter, which is negligible when CH₄-He mixtures are considered, behaves as collision-induced absorption. © 2000 American Institute of Physics. [S0021-9606(00)00736-4]

I. INTRODUCTION

The present paper is the last of a series devoted to the study of line-mixing effects on methane spectra. In the first work,¹ a model was proposed for the construction of the relaxation matrix starting from state-to-state rates calculated with a semiclassical approach. Comparisons were made with infrared spectra of CH₄-N₂ mixtures in the ν_3 band at room temperature. They showed that our approach satisfactorily accounts for the influence of line coupling in wide pressure and rotational quantum number ranges. This work was completed by a second study² in which the pressure range was extended up to 1000 atm and where collisions with He and Ar were considered. This enabled the analysis of the effects of mixing between different manifolds and branches and the study of differences between spectral shapes obtained with the two perturbers considered. The third paper³ was devoted to the Raman Q branch of the ν_1 band.

The present work completes these studies by investigating the effects of temperature and of the vibrational transi-

tion. Measurements have been made for CH₄-N₂ mixtures in a wide range of pressures. The ν_3 band is studied at various temperatures between 200 and 300 K, whereas absorption in the ν_4 and ν_2 regions is investigated at room temperature. Calculations are made with the model developed previously and *no adjustable parameter*. The comparisons between measured and calculated spectra show that our approach accounts for most effects of temperature and pressure on the spectral shape in the ν_3 band. Furthermore, both the ν_4 and ν_3 transitions are correctly predicted at room temperature, but large discrepancies appear when the ν_2 region is considered for CH₄-N₂ mixtures. This failure is similar to what was observed for CH₄-Ar in Ref. 4. It might result from the effect of the strong Coriolis coupling between the ν_2 and ν_4 bands and from the contribution of collision-induced absorption processes.

The remainder of the paper is organized in four sections. The measurements, the theoretical model, and the data used are briefly described in Sec. II. The influence of temperature in the ν_3 band is studied in Sec. III. Results obtained in the ν_4 region are presented in Sec. IV, and the case of the ν_2 band is discussed in Sec. V.

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FIG. 1. Measured and calculated absorption in the ν_3 band for $\text{CH}_4\text{-N}_2$ at two temperatures and the same density of $\approx 72 \text{ Am}$. $\bullet$ are measured values, whereas — and - - - have been calculated with and without the inclusion of line mixing, respectively. (a) 200 K and 53 atm; (b) 300 K and 79 atm.

II. MEASUREMENTS, THEORETICAL MODEL, AND DATA USED

A. Measured spectra

The spectra used in the present work have been recorded with the setups and procedures described in Ref. 1. In the ν_3 region, they include temperature-dependent (200–300 K) measurements made at low pressure ($< 2 \text{ atm}$) with a high-resolution Fourier transform instrument and a tunable difference frequency spectrometer, as well as recordings at higher density (25–100 atm) obtained with a 0.1 cm^{-1} resolution Fourier transform spectrometer (FTS). The ν_4 and ν_2 regions have been investigated at room temperature for pressures above 15 atm. In all measurements, highly diluted mixtures have been used, making the contribution of $\text{CH}_4\text{-CH}_4$ collisions to the spectral shape negligible. The quantity deduced from measurements and presented in the following is $\alpha(\sigma, T, d_{\text{CH}_4}, d_X)/d_{\text{CH}_4}$ where $\alpha(\sigma, T, d_{\text{CH}_4}, d_X)$ is the absorption coefficient at wave number σ for a $\text{CH}_4\text{-X}$ mixture at temperature T with densities d_{CH_4} and d_X ($d_{\text{CH}_4} \ll d_X$).

B. Theoretical model and data used

The theoretical approach used here is identical to that presented in Refs. 1 and 2, where all needed equations are given.

The spectroscopic data used have been taken from the HITRAN database.⁵ The line-broadening parameters for $\text{CH}_4\text{-N}_2$ and their temperature dependences have been derived from both experimental and theoretical results as explained in Ref. 2. The off-diagonal elements of the relaxation matrix are constructed, as before, from state-to-state rates and a few empirical parameters $A(X, Y)$ [see Eqs. (2)–(7) of Ref. 2]. The latter have been deduced previously from absorption in the ν_3 band at room temperature. In the following, we assume that these parameters do not depend on the temperature and that all the temperature dependence of the line-coupling terms is contained in the state-to-state rates [Eq. (2) of Ref. 2]. The latter have been computed for a set of values between 200 and 300 K, as explained in Ref. 1. Fur-

thermore, we also assume that the $A(X, Y)$ parameters do not depend on the vibrational band considered. Hence, all the empirical parameters of our model are fixed to values previously determined in the ν_3 band at room temperature. The comparisons between measured and computed spectra presented thereafter thus use no adjustable quantity and are a significant test of the model consistency. Note that since de-

FIG. 2. Evolution of relative deviations between measured and computed spectra in the ν_3 band with temperature for a total density of $\approx 72 \text{ Am}$. — and - - - have been calculated with and without the inclusion of line mixing, respectively. (a) 200 K and 53 atm; (b) 250 K and 66 atm; (c) 300 K and 79 atm.

FIG. 3. Measured and calculated absorption in the $R(10)$ manifold of the ν_3 band for $\text{CH}_4\text{-N}_2$ at two temperatures and the same density of ≈ 1.84 Am. $\bullet$ are measured values, whereas — and - - - have been calculated with and without the inclusion of line mixing, respectively. (a) 300 K and 2.01 atm; (b) 195 K and 1.31 atm.

tailed analysis of line mixing processes has been made in Refs. 1 and 2, it is not repeated here.

III. THE ν_3 BAND AT DIFFERENT TEMPERATURES

Comparisons between measured and computed $\text{CH}_4\text{-N}_2$ spectra in the ν_3 band at high pressure for various temperatures are made in Figs. 1 and 2. The density d in amagat (Am) units is defined by the ratio of the molecule number densities under the considered conditions and at standard temperature and pressure (STP). For a perfect gas, it is related to pressure P (in atm) by $d(\text{Am}) = P(\text{atm}) \times 273/T(\text{K})$. They show that line-mixing effects remain qualitatively similar regardless of temperature, and that predictions with our line-mixing model are satisfactory both in the central and wing regions of the band. In all cases, neglecting line coupling leads to a strong overestimation of the widths of the spectral features (Q branch, P and R manifolds) and of absorption in the troughs, as observed previously.^{1,2} The main quantitative differences between spectra at 200 and 300 K are due to the evolution of line intensities with increasing temperature which results in the decrease of absorption in the central region (low J lines) and increase of the wings (high J lines). As a result, the relative contribution of nearby transitions to absorption in the troughs between high rotational quantum number P and R lines is reduced at low tempera-

FIG. 4. Same as Fig. 3 but for the $R(14)$ manifold.

ture. This emphasizes the strongly sub-Lorentzian behavior that results from the far wings of the low J intense lines as shown in Fig. 2.

The influence of temperature on the shapes of manifolds at low pressure is illustrated in Figs. 3 and 4. These show that our approach leads to satisfactory results for the $R(10)$ manifold, whereas this is not the case for the $R(14)$. This result can have two explanations. The first is that the temperature dependence of the half-width of these lines, which has not been studied and is a “guessed” value,⁵ might be wrong. The second is that the temperature dependence of the line-coupling elements themselves is expected to be very approximate. This is likely particularly the case for the high J lines for which use of semiclassical state-to-state rates is highly questionable.

Note that a further test of our model at low temperatures has been made in Ref. 6 using balloon-borne measurements of stratospheric transmission. Comparisons between measured and computed spectra in the ν_3 band have confirmed the quality of our approach under conditions involving air masses at temperatures around 210 K.

IV. THE ν_4 BAND

Results obtained in the ν_4 band for total pressures of 25 and 100 atm are plotted in Figs. 5 and 6. They evidence, for the first time, the influence of line mixing in this spectral region. It is worth noting that our approach, whose parameters have been determined in the ν_3 band, satisfactorily predicts the absorption shape in the ν_4 region. This result justifies the use of the same set of $A(X,Y)$ parameters for both

FIG. 5. Measured absorption and deviations with respect to calculations in the ν_4 band for $\text{CH}_4\text{-N}_2$ at room temperature for total pressures of (a) 25 atm; (b) 100 atm.

bands. This is expected since the relative dipole reduced matrix elements (line intensities) of the ν_3 and ν_4 transitions are quite similar and almost unperturbed by any (Fermi or Coriolis) coupling. Hence, the effects of line mixing are, again, the narrowing of the spectral features, the enhancement of peak absorptions, and a significant lowering of the band wings. Nevertheless, there are quantitative differences between the shapes of the ν_3 and ν_4 bands for a given pressure, which are due to the spectral distribution of the lines. This is illustrated in Fig. 7, where spectra recorded in both regions for the same total pressure of 50 atm are compared in ranges including the $P(12)$ to $R(12)$ lines. This figure calls for two remarks: the first is that the spectral extension of the ν_4 band is significantly narrower than that of the ν_3 band. This is a well-known consequence of the Coriolis coupling that affects the energies of the ν_4 rotational levels;⁷ this reduces the separation between P (or R) lines of successive rotational quantum number J from about 10 cm^{-1} for slightly perturbed bands (e.g., ν_3) to about 5 cm^{-1} for the ν_4 transitions. Another consequence is that, for the 50 atm pressure of Fig. 7 where line half-widths are of typically 2.5 cm^{-1} , the rotational structure remains distinguishable in the ν_3 band whereas it is masked by line overlapping in the ν_4 region. The second remark is that, for the considered pressure, line coupling has weaker effects on the high J $R(J)$ manifolds of ν_4 than on those of ν_3 . This is expected since the Coriolis coupling that affects the ν_4 states leads to a larger spreading of the energy levels of a given rotational quantum number J , contrary to those of the ν_3 vibrational level which remain closely spaced. Hence, the lines belonging to high J , P or R manifolds are much more closely spaced in the ν_3 band than in the ν_4 band and hence show more coupling for the same pressure. The positions of the most intense $R(10)$ lines, for instance, are spread over less than 1 cm^{-1} and about 10 cm^{-1} in the ν_3 and ν_4 bands, respectively. Note that this does not hold for the Q branches whose lines extend over a few wave numbers in both bands and hence behave similarly under the effects of collisions.

V. THE ν_2 BAND

The proposed approach, which has, up to now, proved successful in modeling the effects of collisions on the spectral shape for $\text{CH}_4\text{-N}_2$ mixtures, is less successful for the

FIG. 6. Measured and calculated absorption in the Q and R branches of the ν_4 band for $\text{CH}_4\text{-N}_2$ at room temperature for total pressures of (a) 25 atm; (b) 100 atm. $\bullet$ are measured values, whereas — and — — have been calculated with and without the inclusion of line mixing, respectively.

FIG. 7. Comparison between spectra in the $P(12)$ – $R(12)$ range of the ν_3 and ν_4 bands for CH_4 – N_2 at room temperature and a total pressure of 50 atm. Measured absorption is plotted together with relative deviations (%) with respect to calculations, where — and — — have been calculated with and without the inclusion of line mixing, respectively.

region of the ν_2 band. This failure has two different manifestations which have been pointed out previously in the case of CH_4 –Ar.⁴

The first problem comes from a still-unidentified absorption structure which grows under the ν_2 band with increasing perturber density when CH_4 – N_2 mixtures are considered, contrary to what is observed for CH_4 –He. This is demon-

strated in Fig. 8, which shows that the helium broadened band shape qualitatively behaves as that of the ν_3 band, i.e., the Q -branch peak decreases with increasing density, whereas those of the P and R branches remain roughly constant. On the other hand, the N_2 broadened ν_2 band is carried by a background that strongly increases with the perturber density as has been observed previously for CH_4 –Ar.⁴ In order to quantify this phenomenon, we have determined the density normalized integrated intensity in the region between 1410 and 2000 cm^{-1} , i.e.,

$$S_{1410-2000}(d_X) = \frac{1}{d_{\text{CH}_4}} \times \int_{1410}^{2000} \alpha(\sigma, d_{\text{CH}_4}, d_X) d\sigma, \quad (1)$$

where $\alpha(\sigma, d_{\text{CH}_4}, d_X)$ is the absorption coefficient at wave number σ for a CH_4 – X mixture with densities d_{CH_4} and d_X ($d_X \gg d_{\text{CH}_4}$). The values obtained from measured spectra for CH_4 –He and CH_4 – N_2 are plotted in Fig. 9. Recall that, in the absence of any CH_4 – X dimer, of neither collision induced absorption nor far wing contributions, the value of $S_{1410-2000}$ would simply be given by the sum of the integrated intensities S_l of the lines l centered in the considered spectral range, i.e.,

$$S_{1410-2000}^0 = S_{1410-2000}(d_X \rightarrow 0) = \sum_{\sigma_l=1410}^{\sigma_l=2000} S_l. \quad (2)$$

Use of the spectroscopic data given in the HITRAN data base gives the value $S_{1410-2000}^0 = 1.70 \text{ cm}^{-2}/\text{Am}$, which is consistent with the zero density intercepts in Fig. 9. With increasing density, the results obtained for the two perturbers are very different. For CH_4 –He, $S_{1410-2000}$ is basically independent of d_{He} , indicating that absorption is dominated by the contribution of the local allowed transitions. For CH_4 – N_2 , on the contrary, the increasing “background” observed in Fig. 8 leads to a strong linear increase of $S_{1410-2000}$ with a slope of about $0.013 \text{ cm}^{-2}/\text{Am}^2$. The physical mechanism responsible for this phenomenon is not clear, and, unfortunately, due to a second problem which is discussed in the next paragraph, we have not been able to deduce the shape of

FIG. 8. Measured absorption coefficients in the ν_2 region for mixtures with He (—) and N_2 (---) under various total pressures of (a) 60 atm; (b) 120 atm; (c) 300 atm.

FIG. 9. Integrated intensity [see Eq. (1)] in the 1410–2000 cm^{-1} spectral region versus perturber density. $\bullet$ and $\circ$ have been obtained from measured spectra for $\text{CH}_4\text{-N}_2$ and $\text{CH}_4\text{-He}$, respectively. — gives the value predicted using Eq. (2) and the HITRAN database line intensities ($1.7 \text{ cm}^{-2}/\text{Am}$), whereas — — is the linear fit (slope $0.013 \text{ cm}^{-2}/\text{Am}^2$) of the $\text{CH}_4\text{-N}_2$ results.

the background structure by removing the contribution of the local lines from measured data. Nevertheless, three different processes may be responsible for this integrated intensity that grows linearly with increasing perturber density when collisions with Ar and N_2 are considered and is absent when He is considered. (i) The first reason that can be invoked is the contribution of the far wing of the nearby intense ν_4 band. This is unlikely when considering the results in Fig. 10, where experimental data are compared with calculations in which line mixing between the ν_4 lines has been accounted for. Indeed, the theoretical results, which are validated by their precision in the central and near wing regions of the ν_4 band, indicate that the contribution of far wings is negligible below the ν_2 band and cannot explain the “anomalous” absorption in the 1400–2000 cm^{-1} range. (ii) The second possibility is the contribution of allowed transition of $\text{CH}_4\text{-X}$ complexes. This explanation is consistent with the fact that no anomalous absorption is observed for $\text{CH}_4\text{-He}$. Indeed, since the well of the methane–X interac-

tion potential is very shallow for X=He , contrary to X=N_2 and Ar, much fewer dimers are expected to be formed. Unfortunately, although $\text{CH}_4\text{-X}$ van der Waals molecules have been the subject of numerous studies (e.g., Ref. 8 and those cited therein), there is, to our knowledge, no data on this subject in the spectral region considered here. Furthermore, the question of the amount of complexes under the present experimental conditions should also be solved. (iii) Finally, collision-induced absorption (or double transitions) may also be an explanation that is consistent with the results of Fig. 9. Unfortunately, the studies dealing with this problem in methane are limited to the rototranslational part of the spectrum which lies below 600 cm^{-1} (e.g., Refs. 9–11 and those cited therein). Although this needs confirmation, collision-induced absorption in the ν_2 region is likely dominated by the N_2 quadrupole-induced dipole since the ν_2 band is Raman active.

Besides the unexplained increasing background contribution observed for $\text{CH}_4\text{-N}_2$, the shape of the ν_2 band itself causes a second problem that was also observed previously for $\text{CH}_4\text{-Ar}$.⁴ Indeed, even after a rough “empirical” removal of the background contribution, calculations of the band shape with our approach fail. The background $B(\sigma)$ has been modeled by a straight line $B(\sigma) = a\sigma + b$ whose parameters a and b are chosen such that calculated and measured absorptions are identical on the sides of the ν_2 band, near 1400 and 1700 cm^{-1} . For instance, the predicted Q branch is much too narrow at elevated density, even when line-mixing effects are disregarded, as is demonstrated in Fig. 11. For a further demonstration of this effect and quantitative comparison between different bands, we have determined the effective broadening parameters γ^{eff} of N_2 -broadened Q branches in the ν_2 , ν_3 , and ν_4 bands at room temperature. This was done using measured and calculated spectra by determining the Q branch half-width at mid height $\Gamma_Q(d)$ for different perturber densities d . A fit of $\Gamma_Q(d)$ by a linear law then gives the effective broadening coefficient γ^{eff} as explained in Eq. (17) of Ref. 1. The values obtained, given in Table I, clearly show the specificity of the ν_2 band, whereas the ν_3 and ν_4 transitions have similar be-

FIG. 10. Measured and calculated absorption in the ν_4 and ν_2 bands for $\text{CH}_4\text{-N}_2$ at room temperatures and the pressure of 100 atm. $\bullet$ are measured values, whereas — and — — have been calculated including all lines and those of the ν_4 band only, respectively.

FIG. 11. Measured and calculated absorption in the ν_2 band for $\text{CH}_4\text{--N}_2$ at room temperature for total pressures of: (a) 50 atm; (b) 200 atm. $\bullet$ are measured values from which the background contribution has been empirically removed; — and — — — have been calculated with and without the inclusion of line mixing, respectively.

haviors and are correctly predicted. We propose two explanations to this failure of our approach in the ν_2 band. The first, if the background contribution discussed above is due to collision-induced absorption, might be modification of the shape of allowed transitions due to interferences between the allowed and induced lines. This “intracollisional interference” process,¹² which has been neglected in our calculations, has been observed in HD spectra¹³ where it results in large modifications of the line shapes. However, to interfere the induced dipole and allowed dipole have to have the same angular symmetry. The second reason lies in the effects of the Coriolis coupling between the ν_2 and ν_4 levels, which is incorrectly accounted for by our model. Indeed, the relaxation operator elements that couple lines have been constructed on the basis of the lower states only, neglecting any influence of the upper vibrational levels involved.¹ This, which seems reasonable for slightly perturbed bands, is likely a crude approximation for the ν_2 transition. Further-

TABLE I. Effective N_2 broadening parameters ($\text{cm}^{-1}/\text{atm}$) of the Q branch of the ν_2 , ν_3 , and ν_4 bands of CH_4 at room temperature (see the text).

	Measured	Calculated line mixing	Calculated no line mixing
ν_2	0.07	negligible	0.055
ν_3	0.032	0.036	0.055
ν_4	0.035	0.036	0.055

more, calculations assume that all off-diagonal relaxation matrix elements are negative and that the dipole reduced matrix elements are hence all positive. Again, this is true for unperturbed transitions but breaks down when the Coriolis coupling induces large changes in the line intensities. An example is given for CO_2 in Ref. 14 and it is clearly also the case in the ν_2 band which should be forbidden in the infrared and only exists due to the coupling between the ν_2 and ν_4 vibrational levels. Note that, due to this process that mixes the wave functions, line mixing will occur not only within the ν_2 and ν_4 bands, but also between these two vibrational transitions.

Correct modeling of absorption by methane–nitrogen mixtures in the ν_2 region at elevated density hence raises very difficult theoretical problems. Indeed, a much more sophisticated line-coupling model first needs to be built in which the effect of the Coriolis coupling must be accounted for correctly. A possible solution may lie in approaches derived from the infinite order sudden approximation.¹⁵ This is not an easy task, since it first requires the calculation of the basic parameters $Q(L, M_a, M_b)$ that are the fundamental parameters of this approach, but also a full knowledge of the CH_4 rovibrational wave functions. Besides modeling of the collisional shape of the ν_2 transitions, another question is related to the background contribution whose physical origin remains unclear. Measurements at low temperature and pressure, giving information on dimer absorption, would be of interest. Furthermore, much help may be brought by theoretical predictions, provided a satisfactory potential surface can be found, both on collision-induced absorption and van der Waals contributions.

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