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Line mixing calculation in the ν_6 *Q*-branches of N_2-broadened CH_3Br at low temperatures

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Abstract:

In an early study [Tran H, Jacquemart D, Mandin JY, Lacome N, JQSRT 2008;109:119-31], line mixing effects of the ν_6 band of methyl bromide were observed and modeled at room temperature. In the present work, line mixing effects have been considered at low temperatures using state-to-state collisional rates which were modeled by a fitting law based on the energy gap and a few fitting parameters. To validate the model, several spectra of methyl bromide perturbed by nitrogen have been recorded at various temperatures (205-299K) and pressures (230-825 hPa). Comparisons between measured spectra and calculations using both direct calculation from relaxation operator and Rosenkranz profile have been performed showing improvement compared to the usual Lorentz profile. Note that the temperature dependence of the spectroscopic parameters has been taken into account using results of previous studies.

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1. Introduction

Methyl bromide is the major contributor to bromine in the stratosphere and the main organobromide in the lower atmosphere. Atmospheric CH_3Br main anthropogenic sources are fumigation processes used in agriculture and automobiles using leaded petrol [1], and some natural ones are the oceans [2, 3] and the biomass burning [4, 5]. This molecule significantly contributes to ozone depletion since CH_3Br is dissociated by UV radiation, producing Br radicals that catalyze the destruction of ozone [6]. These bromine atoms are 50-60 times more destructive of ozone than the chlorine atoms coming from the chlorofluorocarbons compounds (CFCs) [7]. For this reason, since 2005 the use of CH_3Br has been phased out under the Montreal protocol.

As the CH_3Br ν_6 band is located in an atmospheric window (band center at 954.86 cm^{-1}), it is the best candidate for possible atmospheric remote sensing. For this reason, this band is the subject of numerous laboratory spectroscopic studies in order to determine spectroscopic constants [8-12], as well as different line parameters (positions, intensities, broadenings) [13-17]. In particular, a complete set of measured line parameters (positions, intensities, room temperature air- and self-broadenings) for the CH_3Br ν_6 band is given in Ref. [15], and the temperature dependence of the N_2- and self-broadening coefficients can be found in Ref. [17]. However, it is well known that *Q*-branch absorption is significantly affected by line mixing effects when the pressure increases. In a previous study performed at room temperature in the ν_6 region of CH_3Br [16], significant deviations were observed when comparing the sum of individual line contributions with Lorentz (or Voigt) profiles and measured spectra even at moderate pressures. A theoretical approach was thus proposed to model line mixing effects within the ν_6 *Q*-branches of N_2- and self- perturbed CH_3Br at room temperature. It was validated by comparing calculations with measured spectra at different conditions of pressure and at room temperature. The results showed great improvement with respect to Lorentz lineshapes.

In order to complete these studies, this work is dedicated to the calculation at low temperatures of line mixing effects in the ν_6 *Q*-branches of CH_3Br. The theoretical model described in Ref. [16] has been extended for different temperatures. Comparisons between the experiments and the calculations have been performed. Measured spectra and experimental considerations are presented in Section 2. The theoretical model is described in Section 3.

Data used and comparisons between calculations and measured spectra are presented in Section 4.

2. Experimental measurements

The rapid scan Bruker IFS 120 HR interferometer of the Laboratoire de Dynamique, Interactions et Réactivité (LADIR) was used to record N_2-broadened spectra of CH_3Br at low temperatures. The unapodized spectral resolution (FWHM) used is about 5.5×10^{-3} cm^{-1}, corresponding to a maximum optical path difference of 90 cm. The interferometer was equipped with a Ge/KBr beamsplitter, a MCT photovoltaic detector, a Globar source, and an optical filter covering the 800 - 1100 cm^{-1} spectral region. The experimental conditions of the recorded spectra are summarized in Table 1. Under these conditions, the rotational structure of CH_3Br transitions is not completely resolved, as it can be observed on Fig. 1 which presents the whole studied spectral domain. For all spectra, the whole optical path, outside the cell, was under vacuum. A White-type cell of 1 m base length with a total absorption path of 415 cm was used with KCl windows. The commercial gas sample, purchased from Fluka, with a stated purity of 99.50% in natural abundances, was used without further purification. In order to obtain low temperatures, a continuous circulation through the secondary envelop of the cell of methylcyclohexane cooled by liquid nitrogen was used. The pressure of the gas was measured with a capacitance MKS Baratron manometer with an accuracy estimated to be ±1%. Averaging the 100 scans, the signal to noise ratio is nearly equal to 100.

As a result, 9 high-resolution spectra of CH_3Br/N_2 mixtures were recorded at different total pressures (~ from 230 to 825 hPa) and temperatures (from 205 to 299 K) (see Table 1).

3. Theoretical model

To model line mixing (LM) effects, a similar theory as what was done in Ref. [16] is used. Impact approximation and binary collisions are assumed. The Doppler width is neglected compared with the collisional broadening in the studied pressure range. Within this frame and accounting for line mixing (LM) effects, the absorption coefficient, α^{LM}, in cm^{-1}(CGS system), for CH_3Br diluted in N_2 at wavenumber σ and temperature T is given by:

$$\begin{aligned}\alpha^{LM}(\sigma, P_{CH_3Br}, P_{N_2}, T) &= \frac{8\pi^2\sigma}{3hc} P^{iso}_{CH_3Br}[1-\exp(-hc\sigma/k_BT)] \\ &\times \sum_k \sum_\ell \rho_k(T) d_k d_\ell \times \mathrm{Im}\left\{\left\langle \ell \left| [\Sigma - \mathrm{L}_0 - i(P_{CH_3Br}\mathrm{W}_{CH_3Br/CH_3Br}(T) + P_{N_2}\mathrm{W}_{CH_3Br/N_2}(T))]^{-1} \right| k \right\rangle\right\}\end{aligned}, \qquad (1)$$

where k_B is the Boltzman constant, and the summation is over all k and ℓ absorption lines. P_{CH3Br} and P_{N2} are respectively CH_3Br and N_2 partial pressures. Note that, P_{CH3Br} is the total pressure of two isotopologues, $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$. $P^{iso}_{CH_3Br}$ corresponds to the partial pressure of the considered absorbing isotopologue (i.e iso = 79 or 81, respectively 50.54 or 49.46 % of the total pressure of CH_3Br). As the two isotopologues have similar abundances and absorb in the same spectral region, they have to be calculated simultaneously, so that the whole absorption coefficient is actually the sum of the absorption coefficients due to each isotopologue. **Σ**, $\mathbf{L_0}$ and **W** are operators in the Liouville (line) space and $\langle\langle \ell \| \ldots \| k \rangle\rangle$ designate a matrix element. ρ_ℓ and d_ℓ are the relative population of the initial level and the dipole matrix element of line ℓ. The latter is related to the integrated intensity S_ℓ by the following expression:

$$S_\ell(T) = \frac{8\pi^3}{3hc} \rho_\ell(T) \times \sigma_\ell \times \left[1 - \exp\left(-hc\sigma_\ell / k_B T\right)\right] \times d_\ell{}^2 . \qquad (2)$$

Σ and $\mathbf{L_0}$ are diagonal and respectively associated with the current wavenumber and the position σ_ℓ of individual transitions, i.e.:

$$\left\langle\left\langle \ell \left| \mathbf{\Sigma} \right| k \right\rangle\right\rangle = \sigma \times \delta_{k,\ell}\, , \qquad \left\langle\left\langle \ell \left| \mathbf{L}_0 \right| k \right\rangle\right\rangle = \sigma_k \times \delta_{k,\ell}\, . \qquad (3)$$

where $\delta_{k,l}$ is the Kronecker symbol and W is the relaxation operator which contains information on the effects of collisions on the spectral line shape, it depends on the vibrational band, on the temperature, and on the collision partner. Its off-diagonal elements account for the interferences between absorption lines (line mixing) whereas the real and imaginary parts of the diagonal ones are respectively the collisional broadening and shifting coefficients, γ_ℓ and δ_ℓ

$$\langle\langle \ell | \mathbf{W}(T) | \ell \rangle\rangle = \gamma_\ell(T) - \mathrm{i}\delta_\ell(T). \tag{4}$$

Since the pressure of CH_3Br is very small compared to the N_2 pressure (0.24-0.4% of the total pressure), the term taking into account the line mixing due to the self-perturbation of CH_3Br in Eq. (1) is neglected. Therefore, the $\mathbf{W}_{\mathrm{CH3Br/CH3Br}}$ matrix becomes diagonal and only line mixing effects due to collisions of CH_3Br with N_2 are considered. The real off-diagonal elements of $\mathbf{W}_{CH_3Br/N_2}$ (the imaginary part is neglected), are modeled using the state-to-state inelastic collisional rates of the lower states as

$$\langle\langle \ell | \mathbf{W}_{CH_3Br/N_2}(T) | k \rangle\rangle = -A_{\ell,k} \times K(i_\ell \leftarrow i_k, T) \quad \text{, with } (k \neq \ell), \tag{5}$$

where $K(i_\ell \leftarrow i_k, T)$ are the collisional transfer rates from the initial level, i_k, of the k line to the initial level, i_ℓ, of the ℓ line (k and ℓ belonging to the same isotopologue). The empirical $A_{\ell,k}$ parameters which relate state-space to line-space depend in general on the considered k and ℓ lines. In order to simplify the problem, $A_{\ell,k}$ is considered to depend only on the type of the considered band and on the buffer gas. Furthermore, we assumed that A is independent of the temperature, so that the value of the preceding work at room temperature [16] has been retained, i.e. $A = 0.7$ for all Q-branches of the ν_6 band.

In order to model the state-to-state collisional rates $K(i_\ell \leftarrow i_k, T)$, a Modified Exponential Gap (MEG) fitting law [18-20] has been used

$$K(i_\ell \leftarrow i_k, T) = a_1 \left(\frac{1 + a_4 \left(E_k / a_2 k_B T \right)}{1 + a_4 \left(E_k / k_B T \right)} \right)^2 \exp\left(-\frac{a_3 |E_k - E_\ell|}{k_B T} \right) \left(\frac{T}{T_0} \right)^n . \tag{6}$$

where a_1, a_2, a_3, a_4 and n are fitting parameters and T_0 is a reference temperature. Equation (6) is applied for the downward rates, i.e., $E_\ell \langle E_k$, where E is the rotational energy of the initial level of line (ℓ or k). The upward rates are calculated by using the detailed balance

$$K(i_k \leftarrow i_\ell, T) = \frac{\rho_k(T)}{\rho_\ell(T)} K(i_\ell \leftarrow i_k, T), \tag{7}$$

Since the value of T_0 is 296 K, n was ignored in the preceding work [16] performed at room temperature. The values of a_1, a_2, a_3 and a_4 parameters are kept unchanged from those obtained at room temperature [16] by least-squares fitting the sum rule to the γ_k values for the ${}^RQ_0$ branch. Note that the values of a_1, a_2, a_3 and a_4 are the same for all ν_6 Q-branches and for the two isotopologues. The value of n is then obtained by manually fitting the sum rule using the N_2-broadenings coefficients for the ${}^RQ_0$ branch obtained at low temperatures [17], i.e.

$$\gamma_k^{CH_3Br/N_2}(T) = \frac{1}{2}\left(\sum_{\ell \neq k} K(i_\ell \leftarrow i_k, T) + \sum_{\ell \neq k} K(f_\ell \leftarrow f_k, T)\right), \tag{8}$$

with $K(i_\ell \leftarrow i_k, T)$ given by Eqs. (6,7).

In order to simplify computations for possible atmospheric applications, the absorption coefficient was also calculated using the Rosenkranz profile [21]. Expanding Eq. (1) to first order, we obtain:

$$\alpha^{LM}(\sigma, P_{\mathrm{CH_3Br}}, P_{\mathrm{N_2}}, T) = \frac{1}{\pi} P_{\mathrm{CH_3Br}} \sum_{\ell} S_\ell(T) \frac{\sigma}{\sigma_\ell} \frac{\gamma_\ell + (\sigma - \sigma_\ell) Y_\ell}{(\sigma - \sigma_\ell)^2 + \gamma_\ell^{\,2}}, \tag{9}$$

where Y_ℓ is a line mixing parameter representing the coupling between line ℓ and all other lines of the same branch. The Y_ℓ's are given by:

$$Y_\ell = 2 P_{N_2} \sum_{k \neq \ell} \frac{d_k}{d_\ell} \frac{\langle\langle k | \mathbf{W}_{\mathrm{CH_3Br/N_2}}(T) | \ell \rangle\rangle}{\sigma_\ell - \sigma_k}\ . \tag{10}$$

Calculations using the Lorentz lineshapes, the direct calculation (Eq. (1)) and the Rosenkranz profile (Eqs. (9-10)) have been performed. Comparisons between these calculations and the experimental spectra are presented in the next section.

4. Data used, results and discussion

In this work, the low temperature line mixing effects in the Q-branches of ν_6 band have been investigated using the line parameters obtained in Ref. [15] at 296 K together with the average temperature dependence of the self- and N_2-broadening coefficients of Ref. [17]. Note that this set of parameters corresponds to the actual data of the GEISA and HITRAN 2008 editions. For the temperature dependence of line intensities, the following expression has been used:

$$S_\ell(T) = S_\ell(T_0)\exp\left[-\frac{hcE_\ell}{k_B}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]\frac{\left[1-\exp\left(\frac{hcE_\ell}{T}\right)\right]}{\left[1-\exp\left(\frac{hcE_\ell}{T_0}\right)\right]}\frac{Q_{tot}(T_0)}{Q_{tot}(T)}, \qquad (11)$$

where $Q_{\mathrm{tot}}(T)$ and $Q_{\mathrm{tot}}(T_0)$ are the total partition functions of CH_3Br at temperatures T and T_0 respectively. Partition functions for a given temperature T have been obtained as the product of the vibrational (Q_{vib}) and rotational (Q_{rot}) partition functions, and using spectroscopic constants of Ref. [11].

For the broadening parameters at temperature T, the following equations have been used:

$$\begin{aligned}
&\gamma_\ell^{CH_3Br/CH_3Br}(T) = \left(\frac{T_0}{T}\right)^{n_\ell^{CH_3Br/CH_3Br}} \gamma_\ell^{CH_3Br/CH_3Br}(T_0)\\
&\gamma_\ell^{CH_3Br/N_2}(T) = \left(\frac{T_0}{T}\right)^{n_\ell^{CH_3Br/N_2}} \gamma_\ell^{CH_3Br/N_2}(T_0) \qquad ,\\
&\gamma_\ell(T) = P_{CH_3Br}\gamma_\ell^{CH_3Br/CH_3Br}(T) + P_{N_2}\gamma_\ell^{CH_3Br/N_2}(T)
\end{aligned} \qquad (12)$$

where $\gamma_\ell^{CH_3Br/CH_3Br}(T_0)$ and $\gamma_\ell^{CH_3Br/N_2}(T_0)$ are the self- and N_2-broadening coefficients for CH_3Br at 296K (taken from Ref. [15]), and $n_\ell^{CH_3Br/CH_3Br}$ and $n_\ell^{CH_3Br/N_2}$ their temperature dependence modelled by a J-dependent polynomial function (Eqs. (4,5) of Ref. [17]).

Using Eqs. [6-8] and the values of $\gamma_\ell^{CH_3Br/N_2}$ (T), the parameter n (see Eq. (6)) has been found equal to 1.43±0.05. As a_1, a_2, a_3 and a_4 parameters, n is also assumed to be independent on the considered branch. The calculated line broadening coefficients obtained in this way are presented in Fig. 2 for the ${}^RQ_0$ and ${}^PQ_1$ branches at different temperatures. As it can be observed, a good agreement is found, validating the fitted parameters of the MEG model. However, this agreement is not perfect, so that the renormalization procedure [22,23] has been performed.

For the calculation of the spectra, the apparatus function has been neglected because of the high pressures used in this work. Both isotopologues have been calculated using line mixing for transitions of the strong Q-branches (ΔK=0, K=0-6) and Lorentz profiles for the other transitions.

Comparisons between the measurements and calculations with and without the line-mixing effects are shown on Figs. 1, 3 and 4. A detailed view of the $^RQ_0$ branch in various conditions of pressures and temperatures is presented in Fig. 3, whereas the whole spectrum is shown on Fig. 1. As it can be observed in Fig. 3, Lorentzian lineshapes strongly underestimate absorption in the low J region of the Q-branch whereas the direct calculation (Eq. (1)) and the Rosenkranz profile (Eq. (9)) lead to better agreements. Similar results are obtained for all other Q-branches, as can be observed in Fig. 1 for the whole set of Q-branches, or in Fig. 4 where detailed view of $^RQ_2$, $^RQ_0$ and $^PQ_2$ is shown. Note that under the pressure range considered in this work, the use of the Rosenkranz profile leads to almost same results as those obtained by the direct calculation.

5. Conclusion

Several spectra of CH_3Br perturbed by N_2 have been recorded at different temperatures (from 205 to 299 K) and pressures (from 230 to 825 hPa) using a Bruker 120 FTIR spectrometer. For the calculation of the spectra, the relaxation matrix has been built including temperature dependences. Both direct calculation and Rosenkranz profile have been used to model the experimental spectra. In both cases, the residuals are considerably reduced compared to the ones obtained by using Lorentz lineshapes. It is then clear that line mixing must be accounted for to correctly model the ν_6 Q-branches of CH_3Br.

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FIGURE CAPTIONS

Figure 1. Overview of the ν_6 band for the experimental spectrum of CH_3Br/N_2 at T = 234 K (P_{CH3Br} = 1.52 hPa and P_{tot} = 476.1 hPa). The residuals (obs-calc) have been plotted in the lower panels using Lorentz lineshapes (a), direct calculation of the relaxation operator (b), and Rosenkranz profile (c).

Figure 2. Comparison between N_2-broadening coefficients of CH_3Br calculated by the MEG model (open circles) at different temperatures and those obtained using Refs. [15,17] (solid squares).

Figure 3. Comparison between measured transmissions (●) of CH_3Br diluted in N_2 in the ν_6 $^{R}Q_0$ region and calculations without (---) (Lorentz lineshapes) and with (—) line-mixing effects using direct calculation (Eq. (1)). The corresponding residuals are plotted in the middle panels. For comparison, residuals with calculations using Lorentz (---) and Rosenkranz (—) profiles (Eqs. (9,10)) are shown in the lower panels.

Figure 4. Comparisons for different branches between the calculations without (---) (Lorentz lineshapes) and with (—) taking into account line mixing effect (direct calculation). The experimental spectrum (■) corresponds to T=265 K, P_{CH3Br}=1.74 hPa, and P_{tot}=545.50 hPa.

Figure 5. Measured transmissions (●) of CH_3Br diluted in N_2 in the ν_6 $^{R}Q_0$ region at different temperatures and pressures and calculations with (—) and without (---) line-mixing effects using the Rosenkrantz approximation. In lower panels are represented the corresponding (obs-calc).

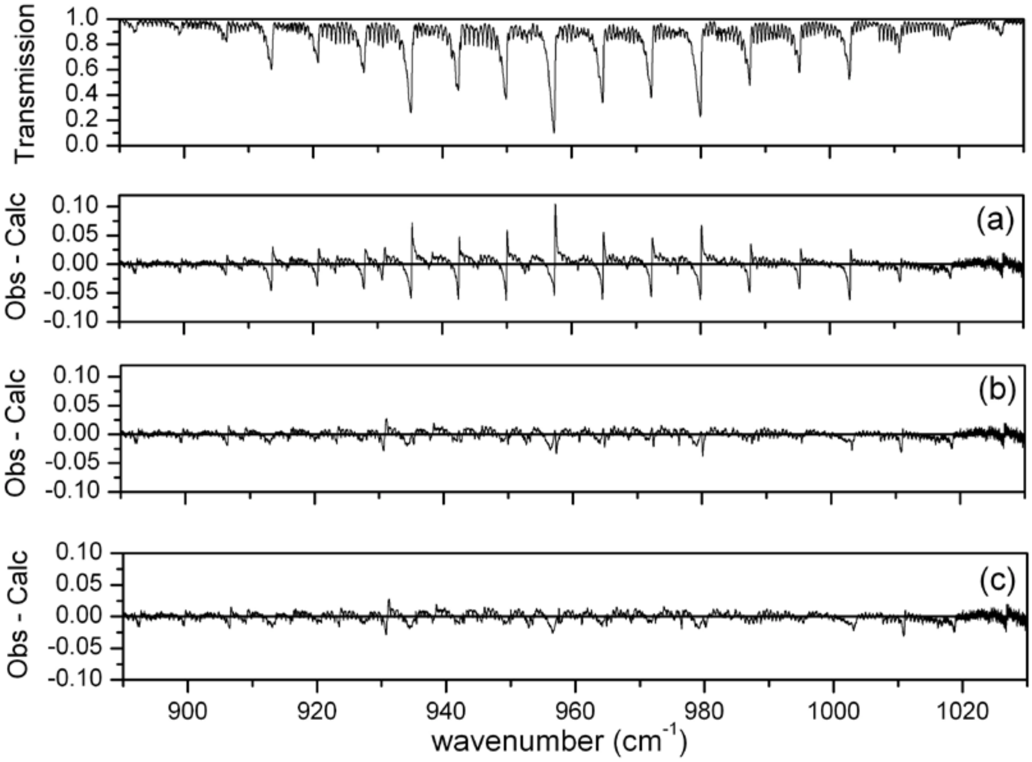
TABLE CAPTIONS

Table 1. Experimental conditions and characteristics of the recorded spectra

Table 1. Experimental conditions and characteristics of the recorded spectra

Unapodized apparatus function	
Maximum optical path difference	90 cm
FWHM	≈ 5.5×10^{-3} cm^{-1}
Absorbing sample	
Natural CH_3Br	50.54 % of $CH_3{}^{79}Br$ 49.46 % of $CH_3{}^{81}Br$ (about 1 % of ^{13}C isotopologues neglected)
Stated purity	99.50 %
Experimental conditions	
S/N ratio	≈ 100

CH_3Br pressure (hPa)	N_2 pressure (hPa)	Temperature (K)
1.4973	308.1	299
1.1489	236.4	264
1.7384	545.5	265
1.5188	476.1	234
1.9624	822.0	233
1.7356	726.2	209
1.5040	634.6	263
1.3393	565.1	237
1.1359	479.3	205



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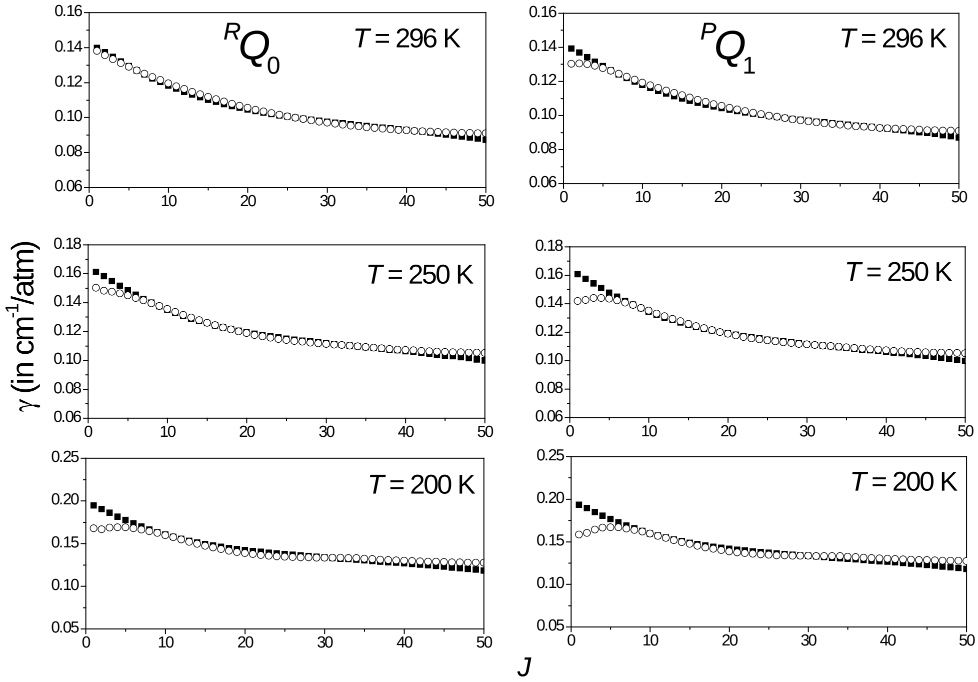

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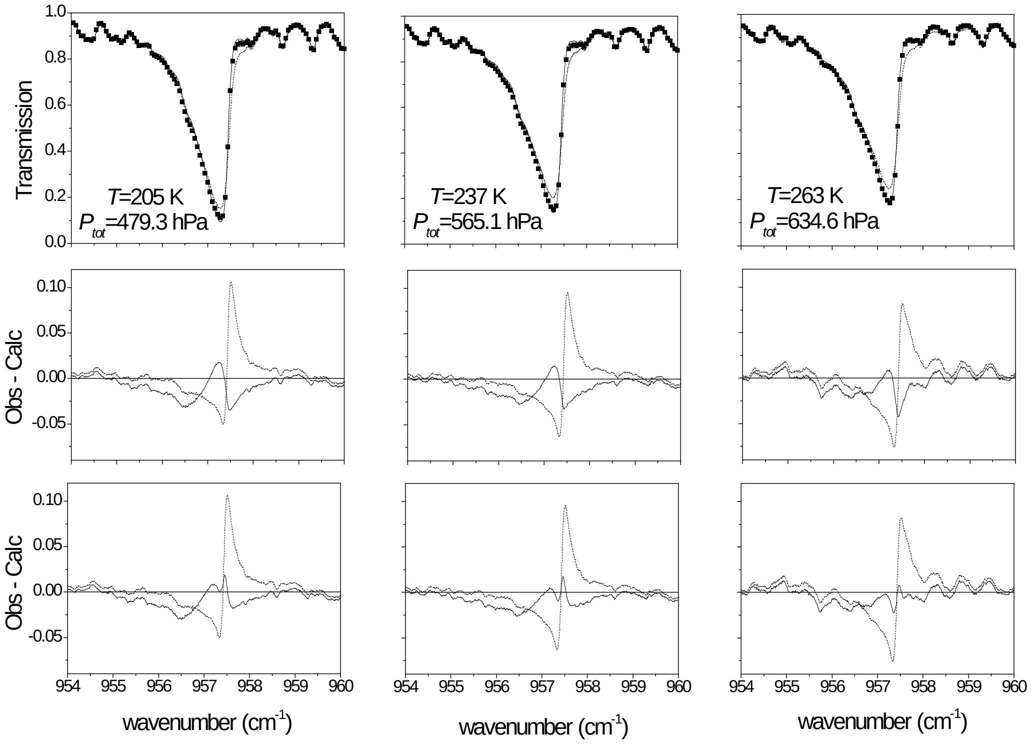

Figure 3. Comparison between measured transmissions (•) of CH$_3$Br diluted in N$_2$ in the ν_6 $^RQ_0$ region and calculations without (---) (Lorentz lineshapes) and with (—) line-mixing effects using direct calculation (Eq. (1)). The corresponding residuals are plotted in the middle panels. For comparison, residuals with calculations using Lorentz (---) and Rosenkranz (—) profiles (Eqs. (9,10)) are shown in the lower panels.

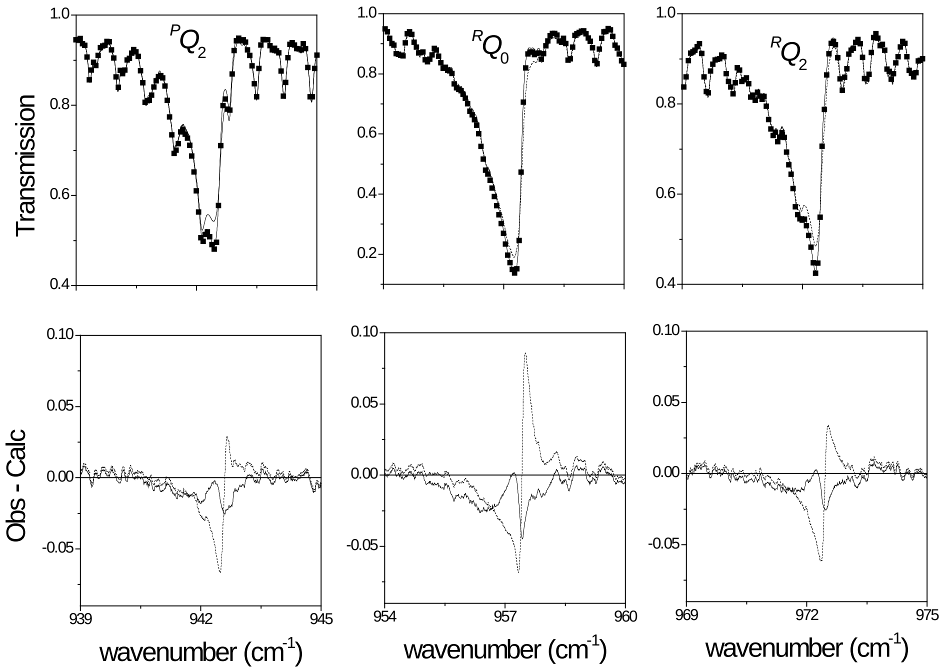

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Figure 5. Measured transmissions (•) of CH_3Br diluted in N_2 in the ν_6 $^{R}Q_0$ region at different temperatures and pressures and calculations with (—) and without (---) line-mixing effects using the Rosenkrantz approximation. In lower panels are represented the corresponding (obs-calc).