INFRARED LINE COLLISIONAL PARAMETERS OF PH₃ IN HYDROGEN: MEASUREMENTS WITH SECOND-ORDER APPROXIMATION OF PERTURBATION THEORY

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Room-temperature absorption by PH₃–H₂ mixtures in the ν₂ and ν₄ bands of phosphine (PH₃) has been measured for low pressures. Fits of these spectra are made to determine the width of isolated lines and line mixing in a first-order Rosenkranz approximation. From the previous determinations, we deduce remarks on the lack of accuracy of predicting the collisional process. With the first-order Rosenkranz approximation, the collisional parameters are considered linear with pressure. In this work, we have considered spectra recorded for three doublets: A₁ and A₂ lines in the ν₂ and ν₄ bands of PH₃ diluted with higher H₂ pressure. We show that the line shifts are nonlinear with perturber pressures, which requires testing the fits of the recorded spectra with profiles developed in the second-order approximation of the perturbation theory. Consequently, the first- and second-order mixing coefficients are determined and discussed. Throughout this study, we also show that the change in the intensity distribution is provided by the population exchange between low energy levels for the two components of doublets A₁ and A₂ lines and is described through the second-order mixing parameter. Thereby, we show the mixing effect on line width.

Keywords: first-order Rosenkranz approximation, second-order approximation, perturbation theory.

Introduction. Phosphine is a molecule observed in the atmosphere of Jupiter and Saturn [1–4] and is composed mainly of hydrogen and helium. In addition, the study of its broadened spectra by H₂ pressure can be useful in modeling planetary atmospheres. Therefore, it is of astrophysical interest. Moreover, the study of their overlapping lines can provide information on the collisional dynamics of this molecule as well as on the radiative transfer between relative transitions, which are of fundamental interest.

To model a rovibrational spectrum, different procedures and approximations have been established to adjust the spectral lines of some molecules in the infrared (IR) region. In the framework of isolated line approximation, the absorption lines of the ν₂ and ν₄ bands of phosphine (PH₃), recorded using a diode-laser spectrometer, are fitted with the Voigt, Rautian, and speed-dependent Rautian profiles [5–10]. In the framework of a first-order Rosenkranz approximation, some experimental spectra of the same ν₂ and ν₄ bands of PH₃ diluted with hydrogen (H₂) at room and low temperatures were analyzed with nonlinear least-squares multipressure fitting procedures based on the collisional Rosenkranz profile [11, 12]. In other works, the rovibrational spectra of other molecules, such as CH₄, NH₃, CH₃Br, and C₃H₄, are fitted using the same procedures [13–16].

The collisional line width shows a linear regression with the perturber pressure. The same applies to the intensity parameter versus the pressure of the active gas. Conversely, in some papers, the line shift shows a nonlinear variation with perturber pressure [14, 17, 18], which is inconsistent with the hypotheses of isolated lines and first-order Rosenkranz approximations. In fact, the reconstruction of collisional profiles is based on the diagonalization of the relaxation matrix as part of the impact approximation. A simple and well-known method of calculation is the perturbation theory used in the construction of the profiles previously mentioned. Smith [19] extended the first-order Rosenkranz approximation [20] to...
the second order in the framework of perturbation theory. His work yields a collisional profile, considering the first- and second-order parameters of line mixing effects. In this same profile expression, the line shift versus the perturber pressure has a parabolic form.

We have used the collisional profile expression given by Smith to analyze some spectra of three doublets \( A_1 \) and \( A_2 \) line recorded using a diode-laser spectrometer in the \( v_2 \) and \( v_4 \) bands of PH\(_3\) diluted with H\(_2\) at higher pressure and room temperature. Then, we specified the collisional parameters to adjust. In addition, the reconstruction of the recorded spectra justifies the need to consider second-order mixing and shifting parameters. Consequently, the first- and second-order H\(_2\)-line mixing coefficients in the \( v_2 \) and \( v_4 \) bands of PH\(_3\) are presented and discussed. Through this study, we show the line mixing effect on the intensity distributions and line widths.

**Experimental Analysis.** Experimental conditions. The absorption spectra of the PH\(_3\)-H\(_2\) mixture in the \( v_2 \) and \( v_4 \) bands of phosphine were recorded at high resolution using a tunable diode-laser spectrometer (Laser Analytics Model LS3). The experimental techniques are detailed in [21, 22]. In this work, we give the experimental conditions of the measurements, verifying our analytic procedure.

The absorption path length of the IR radiation provided by the diode-laser in the multipass white-type cell is fixed to 20.17 m. The phosphine sample is supplied by Union Carbide with a stated purity of 99.999%, and the hydrogen sample is supplied by Air Liquide with a stated purity of 99.99%. The gas pressure is measured by two Baratron MKS gauges with full-scale measurements of 1.2 and 120 mbar, with an accuracy of \( 5 \times 10^{-4} \) and \( 2 \times 10^{-2} \) mbar. All spectra are recorded at room temperature (297.2 ± 1.5 K). Table 1 summarizes the data needed for the transitions studied in this work: wave numbers, pressure of PH\(_3\) (\( P_{PH3} \)), Doppler half-width (\( \gamma_{Dop} \)), effective Doppler half-width (\( \gamma_{Deff} \)), temperature \( T \), and pressure of H\(_2\) (\( P_{H2} \)). Moreover, Fig. 1 shows an example of the recorded spectra of the doublet \( ^3R(4,3,A_1) \) and \( ^3R(4,3,A_2) \) lines of the \( v_4 \) band of PH\(_3\) diluted with pressures of H\(_2\), where the transmittance is plotted vs. the point numbers. The relative calibration of spectra is performed using a confocal etalon with an interfer fringe spacing of 0.007958 cm\(^{-1}\). The etalon fringe pattern provides a check of the laser mode’s quality for correcting the slightly nonlinear tuning of the diode-laser. Furthermore, it aids in linearization of the spectra with a constant step of 0.000121 cm\(^{-1}\). All spectra are linearized using the cubic splines techniques [23].

**Profiles and fitting procedure.** The spectra recorded using the diode-laser spectrometer allow the writing of the Beer–Lambert law:

\[
\alpha(\sigma) = (1/l) \ln \left[ \frac{l_0(\sigma)}{l(\sigma)} \right],
\]

where \( \alpha(\sigma) \) is the experimental absorbance per unit length at wavenumber \( \sigma \) in cm\(^{-1}\), \( l \) is the path length, and \( l_0(\sigma) \) and \( l(\sigma) \) are the transmitted intensities measured with the cell under a vacuum and filled with the gas sample, respectively. To fit the recorded spectra, three physical effects must be considered: weak instrumental distortion and Doppler and collisional effects. The first is implicitly considered through the effective half-width \( \gamma_{Deff} \) obtained by fitting the effective Doppler line [25] (Table 1). The Voigt profile (VP) results from the convolution of the Doppler and collisional profiles, reflecting the latter two effects. The expression of this profile depends on the extension of the collisional profile to be considered.

Consider the collisional profile proposed by Smith [19] and developed within the framework of the second-order approximation of perturbation theory:

\[
\alpha_C(\sigma) = \frac{P_{PH3}}{\pi} \sum_{\text{line}_k} S_k \left[ \frac{\gamma_k (1 + P^2 g_k) + (\sigma - \sigma_k + P^2 \delta\sigma_k) P Y_k}{(\sigma - \sigma_k + P^2 \delta\sigma_k)^2 + \gamma_k^2} \right],
\]

where the index \( k \) represents transitions in Liouville or “line” space, and \( S_k, \gamma_k, \) and \( Y_k \) are the coupled line strength, the collisional half-width, and the first-order line mixing coefficient, respectively. The wavenumber \( \sigma_k = \sigma_{0k} - \delta_k \), where \( \sigma_{0k} \) is the line center wavenumber and \( \delta_k \) is the line shift. In addition, \( g_k \) is the second-order line-mixing coefficient, and \( \delta\sigma_k \) is the second-order line-shift coefficient. We deduce the Voigt profile (VPI2) corresponding to this collisional profile as

\[
\alpha_{VPI2}(\sigma) = \frac{P_{PH3}}{\gamma_{Deff} \sqrt{\pi}} \sum_{\text{line}_k} S_k \left[ (1 + P^2 g_k) \text{Re} \left[ W(x, y) \right] + P Y_k \text{Im} \left[ W(x, y) \right] \right],
\]

where \( W(x, y) \) is the complex probability function expressed by [26]:
where \(x = (\ln 2)^{1/2}(\sigma - \sigma_k + P^2\delta \sigma_k)/\gamma_{\text{Dop}}\) and \(y = (\ln 2)^{1/2}\gamma_{k}/\gamma_{\text{Dop}}\).

It should be noted that the parameters \(\sigma_k, P^2\delta \sigma_k, \gamma_{k}, P Y_{k},\) and \(P^2 g_k\) are related to the diagonal \((W_{kk})\) and off-diagonal \((W_{kk'}\) with \(k' \neq k\)) elements of the collisional relaxation matrix \((W)\) [19]. If the second-order parameters \((\delta \sigma_k\) and \(g_k\)\) are equal to zero, then Eq. (3) reduces to the expression of the first-order Rosenkranz approximation model (VPI1) [18, 27].

To fit the observed spectra, we set the intensity parameter to the value deduced from the absolute line intensity [18]. Figure 2 shows an example of the fits for the \(A_1\) and \(A_2\) lines of the doublet \(^9R(4, 3)\) in the \(\nu_4\) band of PH\(_3\) diluted with PH\(_3\) to 0.029 mbar; 3–6) records of the broadened at pressures of H\(_2\) 70.71, 82.86, 100.77, and 116.80 mbar, respectively; 7) confocal etalon fringes pattern; 8) 0% transmission level.

**TABLE 1.** Experimental Conditions of the Recorded Spectra

| Transition | \(\sigma, \text{cm}^{-1}\) [24] | \(P_{\text{PH}_3}, \text{mbar}\) | \(\gamma_{\text{Dop}}, 10^{-3} \text{ cm}^{-1}\) | \(\gamma_{\text{Deff}}, 10^{-3} \text{ cm}^{-1}\) | \(T, \text{K}\) | \(P_{\text{H}_2}, \text{mbar}\) |
|------------|------------------|------------------|------------------|------------------|--------|------------------|
| \(^9R(3,3, A_1)\) | 1059.14042 | 0.0010 | 1.1248 | 1.1484 | 298.15 | 55.14, 65.88, 80.70, 102.29 |
| \(^9R(3,3, A_2)\) | 1059.14988 | 0.0010 | 1.1473 | 1.1734 | 297.65 | 59.13, 72.86, 86.15, 111.20 |
| \(^9R(3,3, A_1)\) | 1065.05928 | 0.0009 | 1.2220 | 1.2466 | 297.75 | 70.71, 82.86, 100.77, 116.80 |
| \(^9R(3,3, A_2)\) | 1065.07558 | 0.0009 | 1.2039 | 1.2466 | 297.75 | 70.71, 82.86, 100.77, 116.80 |

\[W(x, y) = \left(\frac{i}{\pi}\right) \int_{-\infty}^{+\infty} \frac{e^{-i^2}}{x-t+i} dt, \quad (4)\]
Results and Discussion. Line intensities. Using the absolute line intensities $S_0$ [18], the absorption path length $l$, and the constant partial pressure of PH$_3$ ($P_{\text{PH}_3}$) in the gas mixtures, we have deduced the intensity parameter $S$ for each studied transition. This parameter is fixed in the fit profiles used for all four recorded spectra broadened by four H$_2$ pressures. Consequently, we can fit the first- and second-order line mixing parameters $P_Y$ and $P^2_g$, respectively. This concept allows us to distinguish the proper line intensity from the rate of intensity transferred with the neighboring line during the overlap.

Figure 3 gives qualitative examples showing the difference between the intensity distribution in two overlapping lines: $S(1 + P^2_g)$ obtained in this work and the line intensities presented with their errors ($S \pm \Delta S$) deduced from the results [18]. These examples are presented for the $A_1$ and $A_2$ lines of the doublets $QR(8, 3)$ in the $v_2$ band and $R^2(4, 3)$ in the $v_4$ band of PH$_3$ vs. the square of the pressure of hydrogen $P^2$.

![Graph](image_url)
uncertainties of the line intensities. They also differ from Brown’s measurements [28], and they can reach 6.68% in the case of the line \( Q \)\(_{(8,3, A_1)} \).

Broadening coefficients and line mixing effects. Figure 4 shows a typical linear regression of the values of the collisional half-width measured at each of the four pressures of \( H_2 \) for the \( R(4,3) \) doublet \( A_1 \) and \( A_2 \) lines of \( PH_3 \). The collisional half-widths are measured using the VPI2 profile. The slopes of the straight lines correspond to the \( H_2 \)-broadening coefficients \( \gamma_0 \) (in \( 10^{-3} \) cm\(^{-1}\)·atm\(^{-1}\)). Here, we have systematically considered the small self-broadening contributions (represented by a point close to the origin) derived from the self-broadening coefficients calculated using the theoretical model detailed [6] and from the constant partial pressure of \( PH_3 \) in the gas mixtures. The measurements of \( \gamma_0 \) were presented in Table 3 with their errors given by the standard deviation derived from the linear least-squares fit. The average values of the broadening coefficients of the \( A_1 \) and \( A_2 \) lines are in good agreement with those obtained in [18], where the second-order mixing parameter is neglected. However, any appreciable difference between the coefficients of each line is shown as a percentage in Table 3. This behavior reflects the line mixing effect on the line widths, and it is shown by considering the second-order mixing term given by Smith’s development. In the same branch, the line mixing effect on the width decreases with the rotational quantum number \( J \), i.e., when the difference wavenumber \( \Delta \sigma \) increases (Table 3).

TABLE 2. Measured Line Intensities for the \( A_1 \) and \( A_2 \) Components of the Doublets Transition in the \( \nu_2 \) and \( \nu_4 \) Bands of \( PH_3 \) with Their Estimated Errors

| Transition | \( \sigma \), cm\(^{-1} \) [23] | \( S \pm \Delta S \) [18] | \( S' \) [28] | \( S(1 + P^2 g) \) this work | Diff, % |
|------------|-------------------------------|------------------|-----------------|---------------------|--------|
| \( Q R(8,3,A_1) \) | 1059.14042 | 21.656 ± 0.433 | 21.678 | 22.311 → 23.127 | 2.92–6.68 |
| \( Q R(8,3,A_2) \) | 1059.14988 | 21.831 ± 0.438 | 21.590 | 21.064 → 20.471 | 2.43–5.18 |
| \( Q R(9,3,A_1) \) | 1065.05928 | 16.570 ± 0.330 | 16.470 | 16.535 → 16.667 | 0.39–1.20 |
| \( Q R(9,3,A_2) \) | 1065.07558 | 16.483 ± 0.330 | 16.470 | 16.488 → 16.280 | 0.11–1.15 |

TABLE 3. Measured \( H_2 \)-Broadening Coefficients for the \( A_1 \) and \( A_2 \) Components of the Doublets Transition in the \( \nu_2 \) and \( \nu_4 \) Bands of \( PH_3 \) with Their Estimated Errors

| Transition | \( \sigma \), cm\(^{-1} \) [23] | \( \Delta \sigma \), cm\(^{-1} \) | \( \gamma_0 \), \( 10^{-3} \) cm\(^{-1}\)·atm\(^{-1} \) | \( \Delta \gamma_0 / \gamma_0 \) Av, % | \( \gamma_0 \) Av | [18] |
|------------|------------------|----------------|----------------------|-----------------|--------|--------|
| \( VPI2 \) | \( \gamma_{0A} \) | \( \gamma_{0A'} \) | \( \Delta \gamma_0 / \gamma_0 \) Av, % | \( \gamma_0 \) Av |
| \( v_2 \) band | \( \gamma_0 \) Av | \( \gamma_0 \) Av |
| \( Q R(8,3,A_1) \) | 1059.14042 | 0.00946 | 102.27 (1.07) | 100.5 (2.6) | 3.48 | 98.01 (0.76) |
| \( Q R(8,3,A_2) \) | 1059.14988 | 0.01630 | 96.34 (1.13) | 96.5 (1.1) | 0.34 | 97.31 (0.16) |
| \( Q R(9,3,A_1) \) | 1065.05928 | 102.27 (1.07) | 100.5 (2.6) | 3.48 | 98.01 (0.76) |
| \( Q R(9,3,A_2) \) | 1065.07558 | 96.67 (0.71) | 96.5 (1.1) | 0.34 | 97.31 (0.16) |
| \( v_4 \) band | \( \gamma_0 \) Av | \( \gamma_0 \) Av |
| \( R R(4,3,A_1) \) | 1174.62613 | 0.01933 | 109.97 (0.96) | 106.8 (4.8) | 5.85 | 107.15 (0.24) |
| \( R R(4,3,A_2) \) | 1174.64546 | 0.01933 | 103.72 (2.31) | 106.8 (4.8) | 5.85 | 107.15 (0.24) |

Note. \( \Delta \sigma = |\sigma(A_1) - \sigma(A_2)| \), \( \gamma_{0A'} = (\gamma_{0A} + \gamma_{0A'})/2 \), \( \Delta \gamma_0 = |\gamma_{0A} - \gamma_{0A'}| \).
Line shifting parameters. Figure 5 depicts a typical plot of the line shift $\delta$ derived from the VPI2 profile versus the H$_2$ pressure $P$ for the $^R R(4, 3, A_1)$ and $^R R(4, 3, A_2)$ lines in the $v_4$ band of PH$_3$. The point close to the origin represents the self-shifting contribution ($\delta_{\text{self}}$). The measured values show a quadratic dependence on pressure, which agrees with the theoretical analyses given by the development of Smith’s second-order perturbation theory [19]. Consequently, from the unconstrained second-order polynomial least-squares procedures, we deduce the first- and second-order coefficients of the curves, which are the first-order $\delta_0$ and second-order $\delta \sigma$ H$_2$-shift coefficients, respectively. Indeed, the line-shift parameter for each line $k$ is expressed in the framework of the development of the second-order perturbation theory as

$$\delta_k = \delta_{\text{self}} + P\delta_{0k} + P^2\delta\sigma_k,$$

Fig. 4. The linear regression of the collisional width $\gamma$ for the $^R R(4, 3)$ doublet $A_1$ and $A_2$ lines in the $v_4$ band of PH$_3$, derived from the fit of VPI2 ($\bullet$). The point close to the origin represents the self-broadening contribution.

Fig. 5. The pressure dependence of the line shifts $\delta$ for the $^R R(4, 3)$ doublet $A_1$ and $A_2$ lines in the $v_4$ band of PH$_3$, derived from the fit of VPI2 ($\bullet$). The point close to the origin represents the self-shifting contribution. The best fit curves represent the second-order polynomial functions whose first- and second-order coefficients are, respectively, the first- and second-order H$_2$-shifting coefficients for each transition.

Fig. 6. The pressure dependence of the first-order mixing parameter $P Y$ for the $A_1$ and $A_2$ components of the $^R R(4, 3)$ doublet transition in the $v_4$ band of PH$_3$, derived from the fit of VPI2 ($\bullet$). The slopes of the best-fit lines represent the first-order H$_2$-line mixing coefficients for each transition.
where the first-order coefficient $\delta_{0k}$ is related to the imaginary part of the diagonal ($W_{kk}$) elements of the collisional relaxation matrix ($W$), and the second-order coefficient $\delta\sigma_k$ is related to their off-diagonal elements ($W_{kk'}$ with $k' \neq k$) by [19]:

$$
\delta\sigma_k = \sum_{k' \neq k} \frac{W_{kk'}W_{k'k}}{\sigma_{0k'} - \sigma_{0k}}.
$$

We only present the qualitative behavior of the line-shift parameter with the perturber pressure. This behavior agrees with the hypothesis of second-order Smith’s development.

First-order line mixing parameter. Figure 6 depicts two examples of the variation of the fitted first-order line mixing parameter ($PY$) by VPI2, with $H_2$ pressure $P$ for the $A_1$ and $A_2$ lines of the $^R R(4, 3)$ doublet in the $v_4$ band of PH$_3$.

Fig. 7. Variation of the second-order mixing parameter $P^2 g$ with their bar error vs. the square of the $H_2$-pressure for the $A_1$ and $A_2$ components of the doublets transition $^Q R(8, 3)$ in the $v_2$ band and $^R R(4, 3)$ in the $v_4$ band of PH$_3$, derived from the fit of VPI2 (*). The slopes of the best-fit lines represent the second-order $H_2$-line mixing coefficients for each transition.

TABLE 4. First- and Second-Order $H_2$-Line Mixing Coefficients for the $A_1$ and $A_2$ Components of the Doublets Transition in the $v_2$ and $v_4$ Bands of PH$_3$ with Their Estimated Errors

| Transition | $\sigma$, cm$^{-1}$ [23] | $\Delta\delta$, cm$^{-1}$ | $Y$, 10$^{-3}$ atm$^{-1}$ | $g$, 10$^{-3}$ atm$^{-2}$ |
|------------|---------------------|-----------------|-----------------|-----------------|
| $^Q R(8, 3, A_1)$ | 1059.14042 | 0.00946 | VPI2 | [18]$^*$ |
| $^Q R(8, 3, A_2)$ | 1059.14988 | 1.71 (0.27) | 3.31 (0.56) | 3.30 (1.05) |
| $^Q R(9, 3, A_1)$ | 1065.05928 | -1.32 (0.04) | -1.47 (0.59) | 0.93 (0.15) |
| $^Q R(9, 3, A_2)$ | 1065.07558 | 0.92 (0.44) | 0.86 (0.27) | -1.45 (0.30) |

$v_2$ band

| Transition | $\sigma$, cm$^{-1}$ [23] | $\Delta\delta$, cm$^{-1}$ | $Y$, 10$^{-3}$ atm$^{-1}$ | $g$, 10$^{-3}$ atm$^{-2}$ |
|------------|---------------------|-----------------|-----------------|-----------------|
| $^R R(4, 3, A_1)$ | 1174.62613 | 0.01933 | VPI2 | [18]$^*$ |
| $^R R(4, 3, A_2)$ | 1174.64546 | 0.74 (0.07) | 0.76 (0.43) | -2.09 (0.95) |

$v_4$ band

Note. $\Delta\sigma = |\sigma(A_1) - \sigma(A_2)|$.

*$^*$These values correspond to the average of the measurements obtained with the two models (VP with mixing and SDRP with mixing).
The first-order $H_2$-line mixing coefficients $Y$ are deduced from the slope of the straight lines resulting from unconstrained linear least-squares procedures. These values obtained with their errors, given by the standard deviation on $Y$ derived from the linear least-squares fit, are presented in Table 4.

For the components $A_1$ and $A_2$ of the doublet lines, the first-order mixing coefficients are opposite. Except for the mixing coefficients of $Q(R(8, 3)$ doublet lines, where it is underestimated, the results presented in this work satisfactorily agree with those given in [18]. In the $Q(R$ branch, the first-order mixing coefficients show a decrease in absolute value with the rotational quantum number $J$, that is, when the difference wavenumber $\Delta \sigma$ increases (Table 4). The line mixing (off-diagonal relaxation elements) coefficients ($W_{ij}$) for the $A_1A_2$ pairs of transitions in the phosphine pentad are given by V. Malathy Devi et al. [29] are seen and compared to ours.

Second-order line mixing parameter. Two typical examples of the variation of the second-order line mixing parameter ($P^2g$) deduced by fitting with the VPI2 profile vs. the square of the pressure of hydrogen $P^2$ are shown in Fig. 7 for the $R(R(4, 3)$ doublet $A_1$ and $A_2$ lines in the $v_4$ band of PH$_3$. The second-order H$_2$-line mixing coefficients $g$ are derived from the slope of the straight lines resulting from unconstrained linear least-squares procedures. Presented in Table 4, these values are obtained with their errors, given by the standard deviation on $g$ derived from the linear least-squares fit. The measurement uncertainties are less than 31.8% for the studied transitions, except for the $Q(R(8, 3, A_1)$ and $Q(R(4, 3, A_2)$ lines, which are in the range of 53 and 45%, respectively. For each doublet line $A_1$ and $A_2$, these second-order mixing coefficients are the opposite, which reflects the rate of intensity exchange during the overlap due to the population transfer between low energy levels of the two transitions. With the pressure range considered in this work, the second-order mixing term becomes appreciable. Thereafter, it is measurable, while at lower pressures it is indistinguishable from the measured uncertainties of line intensities, such as the case of the spectra studied in [18]. Like the observed behavior of the first-order mixing parameter, the latter shows a decrease with the rotational quantum number $J$ in the $v_2$ band as the difference wavenumber $\Delta \sigma$ increases (Table 4).

Conclusions. This work presents reasonable first-and second-order mixing coefficients within the framework of the second-order approximation of perturbation theory for some lines in the $v_2$ and $v_4$ bands of PH$_3$ perturbed by H$_2$ at room temperature. To achieve these results, we used the spectra recorded at pressures ranging from 55 to 117 mbar using a diode-laser spectrometer. We also have considered the collisional profile proposed by Smith [19] and developed within the framework of the second-order perturbation theory. This allows us to deduce the VPI2 profile by convolution with the Doppler profile.

The obtained shifting parameter shows a parabolic variation with the perturber pressure, which is justified by the second-order approximation used. We have set the intensity parameter in the fit profiles; this allows us to distinguish between the appropriate line intensity and the intensity rate exchanged with the neighboring line during the overlap. Consequently, we have shown that the second-order mixing parameter is appreciable and measurable. Indeed, it expresses the rate of intensity transferred between the overlapping lines $A_1$ and $A_2$ of each doublet. During this work, we have demonstrated the line mixing effect on the line widths, which allows us to better understand the collisional dynamics of the molecules.

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