Theoretical study of CH₃Cl-N₂ line shapes in the ν_1 band. Line mixing effects in QR doublets and QQ_k sub-branches

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ABSTRACT

Line coupling and line mixing effects of CH₃Cl lines in the ν_1 band perturbed by N₂ have been investigated. We have taken into account the non-diagonality of the $\exp(-S_2)$ operator within specified line spaces as well as the k-degeneracy of the transitions (due to the double degeneracy of the j,k levels with $k \neq 0$). These transitions should be considered as doublets coupled by the line mixing process. A new problem appears in the calculation when the atom-atom potential model is introduced. In order to overcome this difficulty, a pragmatic approach is proposed. Comparisons of theoretically calculated matrix elements of W with measurements of QR(j,k) doublets as well as some QQ_k sub-branches, which are strongly affected by line mixing, have been made. The results show that the formalism improved in this way leads to rather accurate predictions.

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1. Introduction

Methyl chloride (CH₃Cl) is one of the most abundant chlorine compounds of natural origin in the Earth's atmosphere [1]. Therefore, accurate spectroscopic parameters, including of course N₂ and O₂ broadened lineshapes, are required for investigation of atmospheric spectra. Numerous experimental and theoretical studies of N₂ and O₂ broadened lineshapes have been previously reported (see Refs. [2–6] and references therein). Schematically, the available data may be classified as follows:

- Line-broadening coefficients for “isolated” rotational components belonging to various vibrational bands [2–5].
- Lineshapes for various QQ_k sub-branches, mostly affected by line mixing (LM) effects. Indeed, even under atmospheric pressures, the QQ(j,k) lines corresponding to the same k value strongly overlap [6]. Remind that the QQ sub-branches in the ν_1 band are often used for atmospheric remote sensing since they are strong and located in a relatively transparent window.

From the theoretical point of view, the most recent calculations of O₂ (Ref. [4]) and N₂ (Ref. [3]) broadened linewidths have been performed within more or less refined forms of the Robert-Bonamy (RB) semi-classical lineshape theory. Bouanich et al. [7] used the approximate parabolic trajectory model and a potential limited to

its long range components. More recently, Buldyreva et al. [3,4] improved the method by using “exact” trajectory model and a potential including short range forces through an atom-atom potential model ($V_{\text{atom-atom}}$ in the following). Regarding LM effects in the QQ sub-branches, the only previous analysis [6] was based on state-to-state inelastic rotational cross-sections represented by a statistical modified exponential gap fitting law and depending on few empirical and adjustable parameters.

For recent years, we have developed an improved semi-classical formalism allowing calculation of the whole relaxation matrix of W, starting from the intermolecular potential and taking into account the perturber's rotational degrees (Refs. [8,9] and references therein). Recently, we have applied that formalism to symmetric tops with low (NH₃) [10] and high (PH₃) [11] inversion barrier. In these studies, by following Cherkasov [12] we have taken into account the double degeneracy of the j, k levels with $k \neq 0$. Transitions between such levels should be considered as doublets whose components may be coupled by the LM process, a mechanism ignored in the previous forms of the RB formalism. At low pressures, and when the splitting between the two components is null ($E \leftrightarrow E$ transitions) or insignificant ($A_1 \leftrightarrow A_2$), the observed width of an “isolated” doublet is the sum of the diagonal element of the corresponding 2×2 line space and the intra-doublet coupling element: $W(1,1) + W(1,2)$, provided that the two components are of equal intensities. Since $W(1,2)$ is negative, it reduces the widths, up to 40% in some cases [11] as compared to a model ignoring the k degeneracy. Up to now, we had only

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applied our method to self-broadened symmetric tops with strong dipoles, allowing for limiting the potential to its main electrostatic components (dipole-dipole V_{dd} , dipole quadrupole $V_{dq} + V_{qd}$, and quadrupole-quadrupole V_{qq}).

The available extensive measurements of N_2 -broadened CH_3Cl lineshapes give us an opportunity to apply our formalism to this system comprising a non-polar diatomic perturber.

The manuscript is arranged in the following way. Section 2 gives a brief summary of the theoretical method. Section 2 is devoted to comparisons of the calculated and experimental half-widths in the QR branch of the ν_1 band and to the role of the LM process in some of the QQ_K sub-branches in the same band. Concluding remarks are given in Section IV.

2. Theory

A- short background

Within the binary collision and impact approximations and using a symmetrized form, the spectral density at the angular frequency ω can be written as [8,9]:

$$F(\omega) = \frac{1}{\pi} \text{Im} \sum_{n,l} d_l \sqrt{\rho_l} < l | \frac{1}{\omega - L_0 - iPW} | n > \sqrt{\rho_n} d_n \quad (1)$$

Here $|n\rangle \equiv |j_f k_f \varepsilon_f; j_i k_i \varepsilon_i\rangle$ is the Liouville vector in the line space associated with the transition $j_f k_f \varepsilon_f \leftarrow j_i k_i \varepsilon_i$. A background of this basis set applicable for symmetric tops is given in Section 2 and in Appendix of Ref. [11]. In Eq. (1), $\rho_n = \frac{\exp(-\beta E_n)}{Z}$ with $E_n = E(j_i k_i)$ is the matrix element of the density operator exclusive of the magnetic degeneracy and Z as the partition function, d_n is the associated transition dipole operator. In Eq. (1), $(\omega - L_0 - iPW)^{-1}$ is the resolvent operator where L_0 is a Liouville operator associated with the absorber's Hamiltonian, P is the perturber pressure, and W is the relaxation operator. The correspondence between the symmetrized form and the "usual" unsymmetrized one is recalled in Appendix A of Ref. [9].

The matrix elements of W , which is symmetric, are expressed via a second order cumulant expansion [13]:

$$W_{f'i',fi} = \frac{n_b \bar{v}}{2\pi c} \int_{r_{c,\min}}^{+\infty} 2\pi b \left(\frac{db}{dr_c} \right) \{ \delta_{f'i',fi} - \ll f'i' | e^{-S_2(r_c)} | fi \gg \} dr_c, \quad (2)$$

where n_b is the normalized number density of the bath molecules, $\bar{v}$ is the mean relative speed, b is the impact parameter, and r_c is the closest distance for a given trajectory.

Here, we would like to clarify two terminologies and their relationship. They are the line coupling (LC) and the line mixing (LM) that are used to describe effects from the non-diagonality of $\exp(-S_2)$ in Eq. (2) and the resolvent operator of $(\omega - L_0 - iPW)^{-1}$ in Eq. (1), respectively. LC and LM are closely related, but they result from two different sources. More explicitly, the source of LC is the non-diagonality of S_2 that causes the non-diagonality of $\exp(-S_2)$, and consequently, the relaxation matrix of W as well. Meanwhile, the source of LM is the non-diagonality of $\omega - L_0 - iPW$ that causes the non-diagonality of the resolvent operator. It is obvious that LC is a necessary condition of LM. Zero LC definitely means zero LM. But, a strong LC does not always mean a strong LM. In fact, how significant LM would be is not solely determined by LC itself, it also depends on the diagonal operator of L_0 , whose eigenvalues are the line frequencies ω_{fi} , and on the perturber pressure P . This fact has been mentioned in Section 1 and it will be applied in Section 3.

In our formalism, contrarily to what was assumed in all the previous analysis of CH_3Cl lineshapes (with the exception of Cherkasov [12]), S_2 and also $-S_2$ are non-diagonal operators within the line space. Then, one needs to calculate all the matrix elements

Fig. 1. Comparison of anisotropic potential radial terms (in K) with the spherical symmetry of $L_1 = 1$, $L_2 = 2$, $L = 3$, and $K_1 = 0$. V_{dq} is the dipole-quadrupole interaction and $V(1,2,3)$ is the corresponding component of the full potential. The intermolecular distance r is given in Å. The vertical line indicates the closest distance $r_{c,\min}$ (i.e., 3.5103 Å) between two colliding molecules at $T = 296$ K. For reference, the isotropic LJ model is also presented and its value at $r_{c,\min}$ is 377 K.

of the $\exp(-S_2)$ operator. In the present study, we use a straightforward way by diagonalizing the matrix of $-S_2$ to obtain its eigenvalues $G(\eta_n)$ and eigenvectors $|\eta_n\rangle$ first. Then, the matrix elements of $\exp(-S_2)$ are given by:

$$\ll f'i' | e^{-S_2(r_c)} | fi \gg = \sum_n \langle f'i' | \eta_n \rangle e^{G(\eta_n)} \langle \eta_n | fi \rangle. \quad (3)$$

The general expressions of the various contributions to S_2 (i.e., $S_{2,\text{outer-i}}$, $S_{2,\text{outer-f}}$, and $S_{2,\text{middle}}$) are given in Refs. [13,14]. Remind that the non-diagonality of S_2 solely results from the $S_{2,\text{middle}}$ term which is given in Eq. (1) of Ref. [10].

B- The intermolecular potential

In the most recent studies of the N_2 -broadened CH_3Cl linewidths [2,4], an intermolecular potential model including an atom-atom term's contribution was used for the first time. It was shown that the corresponding short range contributions to matrix elements of S_2 were important for practically all the lines. Therefore, in the present study, we have chosen to exactly use the same intermolecular potential model (V_{full} in the following). More details on the potential are given in Section 4 of Ref. [4] where the interested reader will find the values of all the parameters. Since these authors have proposed several different sets of the $V_{\text{atom-atom}}$ parameters, we have only considered that named "parameterization I". In the following calculations using that potential are labelled "full potential". For some preliminary tests, we have also considered a simple potential limited to its two strongest electrostatic components (named as $V_{dq} + V_{qq}$ in the following). The "exact" trajectories are determined by an isotropic LJ potential with the parameters given in Ref. [4]: $\varepsilon = 185$ K and $\sigma = 3.70$ Å. These values were derived with the combination rule based on the LJ parameters for CH_3Cl [7] (i.e., $\varepsilon = 368.4$ K and $\sigma = 3.584$ Å) and N_2 [3] (i.e., $\varepsilon = 92.91$ K and $\sigma = 3.816$ Å).

Figs. 1 and 2 demonstrate that for specified symmetry components, there are dramatical differences between $V_{dq} + V_{qq}$ and V_{full} . In addition, the smaller the distance is, the larger their differences are. For example, at $r_{c,\min} = 3.5103$ Å, the magnitude of $V(123)$ is about 14 times larger than V_{dq} and $V(224)$ is about 29 times larger than V_{qq} .

Finally, values of the energy levels and the line frequencies used in calculations were taken from the HITRAN 2012 data base [15].

Table 1

Spectroscopic parameters of the QR lines with $k = 3$ in the ν_1 band for $\text{CH}_3^{37}\text{Cl}$ listed in the HITRAN 2012 data base. Columns 1–6 give the rotational quantum numbers j and k and the symmetry type of the levels for the upper and lower states, respectively. Column 7 gives the line positions (in cm^{-1}). Column 8 gives the energy of the initial levels of the transitions (in cm^{-1}), while column 9 gives their integrated intensities (in $\text{cm}^2/\text{molecule}$). Finally, column 10 gives the N_2 -broadening coefficients (in $\text{cm}^{-1} \text{ atm}^{-1}$).

4	3	A1	3	3	A2	2970.816650	48.1707	9.74E-22	0.108
4	3	A2	3	3	A1	2970.816650	48.1707	9.74E-22	0.108
5	3	A1	4	3	A2	2971.704102	51.7173	1.74E-21	0.113
5	3	A2	4	3	A1	2971.704102	51.7173	1.74E-21	0.113
6	3	A2	5	3	A1	2972.591309	56.1504	2.40E-21	0.116
6	3	A1	5	3	A2	2972.591309	56.1504	2.40E-21	0.116
7	3	A2	6	3	A1	2973.478516	61.4700	2.97E-21	0.117
7	3	A1	6	3	A2	2973.478516	61.4700	2.97E-21	0.117
8	3	A1	7	3	A2	2974.365967	67.6760	3.48E-21	0.117
8	3	A2	7	3	A1	2974.365967	67.6760	3.48E-21	0.117
9	3	A1	8	3	A2	2975.253174	74.7683	3.91E-21	0.116
9	3	A2	8	3	A1	2975.253174	74.7683	3.91E-21	0.116
10	3	A1	9	3	A2	2976.140869	82.7467	4.28E-21	0.114
10	3	A2	9	3	A1	2976.140869	82.7467	4.28E-21	0.114
11	3	A1	10	3	A2	2977.028320	91.6111	4.58E-21	0.113
11	3	A2	10	3	A1	2977.028320	91.6111	4.58E-21	0.113
12	3	A2	11	3	A1	2977.915771	101.3614	4.82E-21	0.112
12	3	A1	11	3	A2	2977.915771	101.3614	4.82E-21	0.112
13	3	A1	12	3	A2	2978.803223	111.9975	5.02E-21	0.111
13	3	A2	12	3	A1	2978.803223	111.9975	5.02E-21	0.111
14	3	A1	13	3	A2	2979.690430	123.5191	5.14E-21	0.109
14	3	A2	13	3	A1	2979.690430	123.5191	5.14E-21	0.109
15	3	A2	14	3	A1	2980.577637	135.9261	5.22E-21	0.108
15	3	A1	14	3	A2	2980.577637	135.9261	5.22E-21	0.108
16	3	A2	15	3	A1	2981.465820	149.2182	5.25E-21	0.107
16	3	A1	15	3	A2	2981.465820	149.2182	5.25E-21	0.107
17	3	A1	16	3	A2	2982.352539	163.3953	5.23E-21	0.105
17	3	A2	16	3	A1	2982.352539	163.3953	5.23E-21	0.105
18	3	A1	17	3	A2	2983.239258	178.4571	5.16E-21	0.104
18	3	A2	17	3	A1	2983.239258	178.4571	5.16E-21	0.104
19	3	A2	18	3	A1	2984.125977	194.4034	5.06E-21	0.103
19	3	A1	18	3	A2	2984.125977	194.4034	5.06E-21	0.103

Fig. 2. The same as Fig. 1 except for the spherical symmetry of $L_1 = 2$, $L_2 = 2$, $L = 4$, and $K_1 = 0$. V_{qq} is the quadrupole-quadrupole interaction and $V(2,2,4)$ is the component of the full-potential.

3. Results and discussions

A- Widths of QR lines in the ν_1 band

In the first step we have considered the measurements made by Bray et al. in the ν_1 band [2]. From Table 1 of Ref. [2], it appears that the maximum perturber pressure P is 120 mbar, leading to a collisional linewidth around $19 \times 10^{-3} \text{ cm}^{-1}$. Meanwhile, For QR lines of CH_3Cl , the energy gap between two adjacent doublets is around $2B \approx 0.88 \text{ cm}^{-1}$. By using the first order Rosenkranz approximation, one can show that LM with the other doublets is neg-

ligible. A more detailed estimation has been already given in Ref. [11] (Eq.(7)) and will not be repeated here. Thus, even if significant LC could happen among many lines, non-negligible LM occurs only between two lines belonging to the same doublet. In other words, as one calculates LM in this range of perturber pressures, a doublet can be considered well “isolated” from its neighbors. As a result, $(\omega - L_0 - iPW)^{-1}$ in Eq. (1) can be restricted to a 2×2 sub-space for each doublet.

Moreover, contrarily to NH_3 and PH_3 previously analyzed, for CH_3Cl lines with $k = 3n$ ($n = 1, 2, \dots$) there is no A_1/A_2 splitting existing between the two components of a doublet. This fact is clearly demonstrated by Table 1 extracted from HITRAN 2012 [15]. Therefore, as already recalled, the observed width should be compared to $W(1,1) + W(1,2)$, where 1 and 2 corresponds to the $A_1 \leftarrow A_2$ and $A_2 \leftarrow A_1$ transitions, respectively. When $k \neq 3n$, the $E \leftarrow E$ transitions are also degenerate doublets and the treatment is totally similar.

3.1. Construction of the line space

The ν_1 band is parallel so that the radiative dipolar selection rule is $\Delta k = 0$. From our previous studies [13] and [14], we know that all the electrostatic components of the potential have exactly the same collisional selection rule. Note that with the choice of the axis of the CH_3Cl frame made in Ref. [3] and also in the present work, all of the spherical components of the full potential lead also to $\Delta k = 0$. Consequently, the whole line space can be divided into uncoupled sub-blocks corresponding to their specified values of k . In the present study we have considered five cases with $k = 2, 3, 4, 5$ and 10.

Moreover, an analysis of the coupling strength factors appearing in the non-diagonal elements of $S_{2,\text{middle}}$ (Eq. 11 of Ref. [13]) shows

Table 2

Calculated halfwidths γ and matrix elements of W (in $10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$) based on $V_{dq} + V_{qq}$ in the sub-space $k = 2$. The QR doublets are labeled by their initial quantum numbers. Experimental data from Ref. [2].

j_i, k_i	$\gamma_{\text{expt}}^{(1)}$	γ_{calc} without LC	$W(1,1)$ with LC	$W(1,2)$ with LC	$W(1,1) + W(1,2)$
2,2	123/120	121.4	116.7	-16.0	100.7
3,2	124/124	122.5	116.0	-11.6	104.4
4,2	-	123.6	115.7	-9.3	106.4
5,2	123/118	124.4	115.5	-7.7	107.8
6,2	122	124.9	115.2	-6.5	108.7
7,2	126	125.0	114.5	-5.5	109.0
8,2	122/120	124.6	113.6	-4.7	108.9
9,2	120	123.9	112.4	-4.1	108.3
10,2	117	122.8	110.9	-3.5	107.4
11,2	114 / 116	121.5	109.3	-3.1	106.2
12,2	112	120.0	107.6	-2.7	104.9
13,2	112/110	118.4	105.9	-2.4	103.5
14,2	-	116.7	104.1	-2.2	101.9
15,2	103/110	115.0	102.4	-2.0	100.4
16,2	106/108	113.4	100.8	-1.8	99.0
17,2	106	111.8	99.3	-1.6	97.7
18,2	107	110.3	98.6	-1.4	97.2
19,2	104	103.8	96.5	-1.0	95.5

⁽¹⁾ The two values correspond to the results for the two isotopes. Their difference gives an order of magnitude of the data accuracy.

that for the QR lines, the inter-branch QR-QP and QR-QQ couplings can be reasonably neglected. Then, the line space with a given k can be restricted to the $QR(j,k)$ lines given in HITRAN 2012. Similar conclusion is also valid for the QQ lines.

For the five values $k = 2, 3, 4, 5$ and 10, we have retained j_i values from k to 19. For example, for the QR sub-block with $k = 3$, there are 17 doublets containing 34 lines. In calculating the W matrix, energy levels of molecules, especially the absorber's energy levels, are important input values in calculating the off-diagonal elements of $S_{2,\text{middle}}$ because the averaged energy and the frequency gaps (see Eq. 11 of Ref. [13]) rely on these values. Poorer energy values could lead to an extra uncertainty. Therefore, we prefer to use accurate energy levels of CH_3Cl provided by HITRAN. With HITRAN 2012, we can obtain complete energy values $E(j,k)$ with $j \leq 21$.

In addition, our main goal is to show LC (and consequently LM) could lead to rather different values of the widths in comparison with that obtained from the RB model which ignores LC [3,4]. As it is shown in the present work, as well as in our previous studies of both NH_3 and PH_3 , the effect of LC and LM reaches the maximum at $j_i = k$, then decreases as j_i increases. We have chosen $j_i = 19$ as a compromise: if you consider the results obtained with the full potential, at least for the small values of k (i.e., 2, 3, 4, and 5), the difference between our theory and the RB formalism for lines with j_i around 19 is of the order of $1 \times 10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$ (see Tables 7-11). In other words, as j_i is much greater than k , the LC effect on the calculated widths becomes smaller than the experimental and theoretical (speed average, etc....) uncertainties.

3.2. Preliminary calculations with $V_{dq} + V_{qq}$

In a first step, we have restricted the potential to its main long range multipole interactions consisting of V_{dq} and V_{qq} . Accordingly, the one dimensional and two dimensional correlation functions required in calculations are (1002) and (2002) with the labeling of (L_1, K_1, K_1', L_2) [16,17]. With these correlation functions, one can calculate the whole relaxation matrix W including the widths represented by the diagonal elements of W . Comparisons between the observed and calculated widths are given in Tables 2-6.

The above tables show a very significant effect from the non-diagonality of S_2 through a double mechanism: (1) a small decrease of the diagonal element (resulting from LC; comparing columns 3 and 4) and (2) a more significant effect of the $W(1,2)$ element (resulting in LM; comparing columns 3 and 5) that strongly

depends of the j_i, k_i values. The decrease of calculated widths without and with LC and LM reaches its maximum as $j_i = k_i$ and increases with increasing k_i . Then, for a given k_i value, this difference decreases as j_i increases. These behaviors, already observed for the NH_3 and PH_3 molecules, can be easily understood by analyzing the amplitudes of the off-diagonal elements of $S_{2,\text{middle}}$. Since this analysis is rather similar to that detailed for PH_3 in Ref. [11], it will not be detailed here.

Finally, note that the theoretical widths $W(1,1) + W(1,2)$ (column 6) are systematically smaller, by about 10%, than the observed ones (column 2), indicating that one needs to take into account components associated with a shorter range potential. Note also that by only comparing the observed widths and those calculated without LC, one can't draw this conclusion.

3.3. Calculations with full potential

Then, we tried to consider the full potential. In this case, besides (1002) and (2002), the one and two dimensional correlation functions of (1000) and (2000) are needed. As explained previously, in order to calculate the matrix elements of W , we have to evaluate the matrix elements of $\exp(-S_2)$ first. At this step, we were confronted with an unexpected difficulty. According to Eq. (3), evaluation of the matrix elements of $\exp(-S_2)$ requires a preliminary determination of the eigenvalues and eigenvectors of $-S_2$. However, mainly due to contributions from $V_{\text{atom-atom}}$, the components of V_{full} at small r_c region become so strong (cf. Figs. 1 and 2) that it causes an existence of large positive eigenvalues. The latter leads to a divergence in the calculations through the factor of $e^{G(\eta_n)}$ in Eq. (3). An illustration is given in Fig. 3 (red curve). Note that this difficulty did not appear in the preliminary calculation when the potential was limited to $V_{dq} + V_{qq}$, which is much weaker than V_{full} . In that case, the S_2 matrices are always positive definite [18] and consequently, all of the eigenvalues of $(-S_2)$ remain negative (see the black curve of Fig. 3). As a result, no blowout could happen because the values of $e^{G(\eta_n)}$ are always less than 1.

The origin of that failure is unclear. It is related with no doubt to the large amplitude of the short range potential. Several hypotheses might be invoked to explain the problem:

The most likely origin should be a failure of the perturbation expansion (cumulant expansion limited to the second order) of the scattering operator S due to the strong interaction occurring at short collision distances. It is well known that this intrinsic

Table 3The same as Table 2 except for the sub-space $k = 3$.

j_i, k_i	$\gamma_{\text{expt}}^{(1)}$	γ_{calc} without LC	W(1,1) with LC	W(1,2) with LC	W(1,1) + W(1,2)
3,3	114/115	121.6	115.2	-20.7	94.5
4,3	–	122.8	115.6	-15.7	99.9
5,3	123/119	123.8	115.9	-12.7	103.2
6,3	120/121	124.4	115.9	-10.6	105.3
7,3	123/122	124.6	115.6	-9.1	106.5
8,3	122/122	124.4	114.8	-7.9	106.9
9,3	117/118	123.8	113.7	-7.0	106.7
10,3	119/122	122.8	112.4	-6.2	106.2
11,3	116/110	121.5	110.8	-5.6	105.2
12,3	115/118	120.0	109.1	-5.0	104.1
13,3	113/117	118.5	107.3	-4.6	102.7
14,3	113	116.8	105.6	-4.1	101.5
15,3	–	115.2	103.8	-3.8	100.0
16,3	109/112	113.6	102.1	-3.5	98.6
17,3	108/109	112.0	100.6	-3.2	97.4
18,3	108	110.5	99.7	-2.8	96.9
19,3	103/107	104.0	97.2	-2.0	95.2

⁽¹⁾ The two values correspond to the results for the two isotopes. Their difference gives an order of magnitude of the data accuracy.**Table 4**The same as Table 2 except for the sub-space $k = 4$.

j_i, k_i	$\gamma_{\text{expt}}^{(1)}$	γ_{calc} without LC	W(1,1) with LC	W(1,2) with LC	W(1,1) + W(1,2)
4,4	–	121.6	113.6	-24.2	89.4
5,4	114	122.9	114.8	-19.0	95.8
6,4	117	123.8	115.5	-13.4	102.1
7,4	120	124.1	115.8	-13.0	102.8
8,4	119	124.1	115.2	-11.2	104.0
9,4	118/120	123.6	114.4	-9.8	104.6
10,4	118	122.6	113.2	-8.8	104.4
11,4	110	121.5	111.8	-8.0	103.8
12,4	106	120.0	110.2	-7.3	102.9
13,4	–	118.6	108.5	-6.6	101.9
14,4	–	117.0	106.8	-6.1	100.7
15,4	112	115.4	105.1	-5.7	99.4
16,4	117/115	113.8	103.4	-5.3	98.1
17,4	104	112.2	101.8	-4.9	96.9
18,4	107	110.7	100.8	-4.3	96.5
19,4	–	104.3	98.1	-3.2	94.9

⁽¹⁾ The two values correspond to the results for the two isotopes. Their difference gives an order of magnitude of the data accuracy.**Table 5**The same as Table 2 except for the sub-space $k = 5$.

j_i, k_i	γ_{expt}	γ_{calc} without LC	W(1,1) with LC	W(1,2) with LC	W(1,1) + W(1,2)
5,5	–	121.6	112.0	-27.0	85.0
6,5	119	122.8	113.9	-21.4	92.5
7,5	116	123.4	114.8	-17.6	97.2
8,5	113	123.6	114.9	-14.9	100.0
9,5	116	123.3	114.4	-13.0	101.4
10,5	105	122.5	113.5	-11.5	102.0
11, 5	113	121.5	112.3	-10.4	101.9
12,5	116	120.2	110.4	-9.5	100.9
13,5	114	118.7	109.4	-8.7	100.7
14,5	111	117.2	107.7	-8.1	99.6
15,5	104	115.6	106.1	-7.6	98.5
16,5	–	114.0	104.4	-7.1	97.3
17,5	105	112.5	102.9	-6.6	96.3
18,5	111	111.0	101.8	-5.9	95.9
19,5	109	104.7	99.0	-4.6	94.4

weakness could cause a blowout in calculations. To overcome the blowout, a lot of efforts had been made during the course of developing the semi-classical lineshape theory. For example, as Anderson developed his theory in 1949 [19], he introduced a cut-off for the impact parameter b by assuming $S(b \text{ small}) = 1$ or averaged to 1. Later on, Robert and Bonamy applied the linked cluster theorem [20] to avoid Anderson's cut-off. More explicitly, as shown by Eq. (2), the diagonal elements of W (i.e., the width in the RB formalism) is mainly determined by an integrand fac-

tor of $\{1 - \langle f_i | e^{-S_2(r_c)} | f_i \rangle\}$. Based on the isolated line approximation introduced by these authors, the latter is replaced by $\{1 - e^{-\langle f_i | S_2(r_c) | f_i \rangle}\}$. Note that the diagonal matrix elements of S_2 are always positive and a strong interaction at small r_c leads to their large magnitudes such that $e^{-\langle f_i | S_2(r_c) | f_i \rangle} \rightarrow 0$. Consequently, equivalent to Anderson's assumption of $S(b \text{ small}) = 1$, the integrand factor $\{1 - e^{-\langle f_i | S_2(r_c) | f_i \rangle}\} \rightarrow 1$. Thus, without explicitly introducing Anderson's cut-off, the blowout is automatically gone in the RB formalism.

Table 6The same as Table 2 except for the sub-space $k = 10$.

(The experimental data are the smoothed values as given by Eq. (3) of Ref. [2]).

j_i, k_i	γ_{expt}	γ_{calc} without LC	W(1,1) with LC	W(1,2) with LC	W(1,1) + W(1,2)
10,10	109.5	120.5	104.8	-36.1	68.7
11,10	108.4	120.7	108.2	-29.5	78.7
12,10	107.3	120.3	109.4	-25.3	84.1
13,10	106.2	119.5	109.6	-22.3	87.3
14,10	105.2	118.5	109.1	-20.0	89.1
15,10	104.1	117.3	108.3	-18.3	90.0
16,10	103.1	116	107.2	-16.4	90.8
17,10	102.0	114.6	106.0	-15.8	90.2
18,10	101.1	113.3	105.0	-14.6	90.4
19,10	100.1	108	102.3	-12.6	89.7

Table 7

The same as Table 2 except for using the full potential and enforcing the sufficient condition.

j_i, k_i	$\gamma_{\text{expt}}^{(1)}$	γ_{calc} without LC	W(1,1) with LC	W(1,2) with LC	W(1,1) + W(1,2)
2,2	123/120	129.4	127.6	-8.3	119.3
3,2	124/124	130.1	127.6	-6.0	121.6
4,2	-	130.7	127.8	-4.6	123.2
5,2	123/118	130.9	127.8	-3.7	124.1
6,2	122	130.8	127.5	-3.1	124.4
7,2	126	130.3	126.9	-2.6	124.3
8,2	122/120	129.3	126.0	-2.2	123.8
9,2	120	128.0	124.3	-1.8	122.5
10,2	117	126.5	123.5	-1.5	122.0
11,2	114 /116	124.7	121.9	-1.2	120.7
12,2	112	122.8	120.3	-1.0	119.3
13,2	112/110	120.8	118.6	-0.8	117.8
14,2	-	118.8	116.8	-0.7	116.1
15,2	103/110	116.9	115.0	-0.6	114.4
16,2	106/108	115.0	113.3	-0.5	112.8
17,2	106	113.3	111.6	-0.4	111.2
18,2	107	111.5	109.8	-0.4	109.4
19,2	104	105.0	104.0	-0.4	103.6

⁽¹⁾ The two values correspond to the results for the two isotopes. Their difference gives an order of magnitude of the data accuracy.**Table 8**The same as Table 7 except for the sub-space with $k = 3$.

j_i, k_i	$\gamma_{\text{expt}}^{(1)}$	γ_{calc} without LC	W(1,1) with LC	W(1,2) with LC	W(1,1) + W(1,2)
3,3	114/115	129.4	127.3	-10.2	117.1
4,3	-	130.2	127.5	-7.9	119.6
5,3	123/119	130.6	127.7	-6.4	121.3
6,3	120/121	130.7	127.6	-5.4	122.2
7,3	123/122	130.2	127.1	-4.5	122.6
8,3	122/122	129.4	126.3	-3.8	122.5
9,3	117/118	128.1	125.2	-3.2	122.0
10,3	119/122	126.6	123.0	-2.7	121.2
11,3	116/110	124.9	122.4	-2.3	120.1
12,3	115/118	123.0	120.7	-1.9	118.8
13,3	113/117	121.0	119.0	-1.6	117.4
14,3	113	119.1	117.2	-1.3	115.9
15,3	-	117.2	115.4	-1.2	114.2
16,3	109/112	115.3	113.7	-1.0	112.7
17,3	108/109	113.5	112.0	-0.9	111.1
18,3	108	111.8	110.2	-0.8	109.4
19,3	103/107	105.4	104.4	-0.8	103.8

⁽¹⁾ The two values correspond to the results for the two isotopes. Their difference gives an order of magnitude of the data accuracy.

Nevertheless, we believe the intrinsic weakness of the perturbation expansion can't be removed by the linked cluster theorem at all. In fact, it is the isolated line approximation used in the RB formalism that temporarily blocks the blowout to show up. After removing the isolated line approximation and considering LC, the blowout in calculations could appear again. In the present case, it could reappear as one evaluates the matrix elements $\langle f' | i' | e^{-S_2(r_c)} | f \rangle$ when the matrix of $(-S_2)$ has large positive eigenvalues.

But, the semi-classical frame underlying the model may also contribute to the failure. Is it possible to isolate the translational

motions from the rotational ones when there is such a disproportion between the isotropic and anisotropic parts of the potential? We find an indication of this assumption in our previous study of LC effects in the isotropic

Raman spectra of N_2 [9]. In that case, all the eigenvalues of $(-S_2)$ were negative, but the comparison with benchmark close-coupling calculations (using the same potential) had still shown that the off-diagonal elements of W , and consequently of S_2 , were systematically overestimated. Unfortunately, fully quantum calculations remain impossible for the CH_3Cl-N_2 system.

Table 9The same as Table 7 except for the sub-space with $k = 4$.

j_i, k_i	$\gamma_{\text{expt}}^{(1)}$	γ_{calc} without LC	W(1,1) with LC	W(1,2) with LC	W(1,1) + W(1,2)
4,4	–	129.3	126.9	–11.4	115.5
5,4	114	130.1	127.2	–9.3	117.9
6,4	117	130.3	127.2	–7.8	119.4
7,4	120	130.0	126.9	–6.7	120.2
8,4	119	129.3	126.3	–5.7	120.6
9,4	118/120	128.2	125.3	–4.9	120.4
10,4	118	126.8	124.3	–4.2	119.9
11,4	110	125.1	122.6	–3.6	119.0
12,4	106	123.3	121.1	–3.0	118.1
13,4	–	121.4	119.4	–2.6	116.8
14,4	–	119.4	117.6	–2.2	115.4
15,4	112	117.5	115.9	–2.0	113.9
16,4	117/115	115.7	114.1	–1.7	112.4
17,4	104	113.9	112.4	–1.6	110.8
18,4	107	112.2	110.7	–1.4	109.3
19,4	–	105.9	105.0	–1.3	103.7

⁽¹⁾ The two values correspond to the results for the two isotopes. Their difference gives an order of magnitude of the data accuracy.**Table 10**The same as Table 7 except for the sub-space with $k = 5$.

j_i, k_i	γ_{expt}	γ_{calc} without LC	W(1,1) with LC	W(1,2) with LC	W(1,1) + W(1,2)
5,5	–	129.1	126.6	–12.4	114.2
6, 5	119	129.8	126.7	–10.3	116.4
7,5	116	129.8	126.5	–8.9	117.6
8,5	113	129.3	126.0	–7.8	118.2
9,5	116	128.3	125.1	–6.8	118.3
10,5	105	127.0	124.0	–5.9	118.1
11, 5	113	125.4	122.7	–5.1	117.6
12,5	116	123.6	121.3	–4.4	116.9
13,5	114	121.8	119.7	–3.8	115.9
14,5	111	119.9	118.0	–3.3	114.7
15,5	104	118.0	116.3	–2.9	113.4
16,5	–	116.2	114.6	–2.6	112.0
17,5	105	114.4	112.9	–2.4	110.5
18,5	111	112.7	111.2	–2.2	109.0
19,5	109	106.6	105.6	–2.0	103.6

Table 11The same as Table 7 except for the sub-space with $k = 10$.

j_i, k_i	γ_{expt}	γ_{calc} without LC	W(1,1) with LC	W(1,2) with LC	W(1,1) + W(1,2)
10,10	109.5	127.6	124.4	–16.7	107.7
11,10	108.4	127.1	123.5	–15.0	108.5
12,10	107.3	126.1	122.2	–13.8	108.4
13,10	106.2	124.8	120.8	–12.7	108.1
14,10	105.2	123.3	119.5	–11.7	107.8
15,10	104.1	121.6	118.1	–10.7	107.4
16,10	103.1	120.0	116.8	–9.7	107.1
17,10	102.0	118.3	115.5	–8.8	106.7
18,10	101.1	126.6	111.4	–8.1	103.3
19,10	100.1	111.6	110.0	–7.4	102.6

Table 12Calculated matrix elements W_{ln} (in $10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$) with a specified row index $n = 3, A2$ in the sub-space $k = 3$ constructed by the QR doublets. Lines are identified by j_i and their symmetry.

l	3,A2	3,A1	4,A2	4,A1	5,A1	5,A2	6,A1	6,A2
$W_{ln}^{(1)}$	115.2	–20.7	–5.8	–12.8	–3.4	–4.0	–2.4	–2.3
$W_{ln}^{(2)}$	127.3	–10.2	–7.7	–6.3	–1.6	–3.6	–0.98	–0.93

⁽¹⁾ Calc. based on $V_{dq} + V_{qq}$ only.⁽²⁾ Calc. based on full potential and enforcing the sufficient condition.**Table 13**The same as Table 12 except for the row index $n = 7, A1$.

l	4,A2	5,A1	5,A2	6,A1	6,A2	7,A2	7,A1	8,A2	8,A1	9,A2	9,A1	10,A2	10,A1
$W_{ln}^{(1)}$	–2.7	–5.7	–4.0	–5.7	–19.5	–9.1	115.6	–20.1	–5.3	–3.8	–6.6	–3.7	–2.7
$W_{ln}^{(2)}$	–1.2	–4.8	–1.9	–5.6	–9.3	–4.5	127.1	–9.4	–4.7	–1.6	–4.1	–1.4	–1.0

Table 14The same as Table 12 but for the row index $n = 16, A2$.

l	13,A1	14,A1	14,A2	15,A1	15,A2	16,A2	16,A1	17,A2	17,A1	18,A1	18,A2	19,A1
$W_{ln}(1)$	-4.9	-2.3	-8.1	-19	-2.7	102.1	-3.5	-2.5	-18.7	-1.9	-8.2	-5.0
$W_{ln}(2)$	-0.4	-0.3	-1.3	-6.5	-0.9	113.7	-1.0	-0.7	-6.2	-0.2	-1.1	-0.3

Table 15Comparison of the narrowing parameter τ for various QQ_k sub-spaces.

k	Experiment*	Calc. ⁽¹⁾	Calc. ⁽²⁾
2	1.25	5.24	1.52
3	1.31	5.46	1.52
4	1.35	6.45	1.54
5	1.50	6.6	1.53
10	1.30	6.45	1.53

* Experimental data come from spectrum 3 of Ref. [6] at $P(N_2) = 698.2$ mbar.⁽¹⁾ Calculated result based on $V_{dq} + V_{qq}$ only.⁽²⁾ Calculated result based on full potential with enforcing the sufficient condition. **Fig. 3.** Comparison of eigenvalues of the $(-S_2)$ matrix at $r_c = 3.524$ Å calculated with $V_{dq} + V_{qq}$ and with the full potential. The sub-space is constructed by the 34 QR lines with $k = 3$. Because the eigenvalues for $V_{dq} + V_{qq}$ are small, they have been multiplied by 100.

Up to now, we don't know whether the S_2 matrix should be in any case a positive definite or not. But, we know that after adding $V_{atom-atom}$, the S_2 matrix is no longer positive definite and this could cause the blowout happening in the calculations. In addition, we know that the sufficient condition for a matrix A to be positive definite is [18]:

$$A_{n,n} > \sum_{l \neq n} |A_{l,n}|. \quad (4)$$

Then, in order to overcome that difficulty we have adopted a pragmatic procedure to force the S_2 matrix to be positive definite. More explicitly, the procedure is for each of the r_c values,

- We calculate the ratio $X_n = \frac{|S_{2,nn}|}{\sum_{l \neq n} |S_{2,ln}|}$ for each column n of the S_2 matrix.
- We determine the smallest one among these X_n values and call it as X_{min} .
- Then, we multiply amplitudes of all its off-diagonal elements by a factor slightly smaller than X_{min} (i.e., $X_{min} - 0.0001$ for example).
- With this way, the modified matrix of S_2 remains positive definite and also symmetric.

The blue curve in Fig. 3 shows that after enforcing the sufficient condition, the eigenvalues of $(-S_2)$ derived with V_{full} are now systematically negative.

Tables 7-11 give the comparison between the observed widths and those calculated with the full potential and enforcing the sufficient condition (Eq. (4)).

By comparing the calculated diagonal element of W with and without LC for $(V_{dq} + V_{qq})$ and V_{full} , it appears that effect of LC is weaker with the full potential. But the main feature is the great difference between the amplitudes of the intra-doublet coupling $W(1,2)$ calculated without and with short range forces (and enforcing the sufficient condition in that case). It can be easily explained through the role played by the integrand factor $\{\delta_{i'i} \delta_{f'f} - \ll f'i' | e^{-S_2(r_c)} | fi \gg\}$ in Eq. (2). Our numerical calculations show that after using V_{full} with enforcing the sufficient condition, all the calculated matrix elements of $\ll f'i' | e^{-S_2(r_c)} | fi \gg$ are less than 0.0001 as long as $r_c < 3.89$ Å. As a result, it leads to $\{\delta_{i'i} \delta_{f'f} - \ll f'i' | e^{-S_2(r_c)} | fi \gg\} \rightarrow \delta_{i'i} \delta_{f'f}$ in this region. This implies that in the integral of Eq. (2), starting from the low limit (i.e., $r_{c,min} = 3.5103$ Å) to 3.89 Å, the integrand of Eq. (2) makes maximum contributions to the diagonal elements of W and nothing to the off-diagonal elements.

It is interesting to note that $\{\delta_{i'i} \delta_{f'f} - \ll f'i' | e^{-S_2(r_c)} | fi \gg\} \rightarrow \delta_{i'i} \delta_{f'f}$ looks somehow like an extended version of Anderson's assumption $S(b \text{ small}) = 1$. It also implies that besides enforcing the sufficient condition, there may be an alternately way to avoid the blowout. Similar to Anderson, with an argument that a saturation occurs at a small r_c region where the interaction is so strong, one can introduce a cut-off $r_{c,cut}$ and simply assume that $\ll f'i' | e^{-S_2(r_c)} | fi \gg = 0$ for $r_c \leq r_{c,cut}$.

Beyond these arguments, we can obtain now a better agreement with the experimental data, justifying in some sense our enforcing procedure.

We observe a similar behavior for the inter-doublet couplings, as it appears from Tables 12-14. Note that, when j becomes higher than k , the inter-doublet couplings becomes stronger than the intra-ones for $V_{dq} + V_{qq}$ or V_{full} . However the available data, which is limited to low pressures, did not allow any analysis of their influence on the spectra. But, some interesting measurements of QQ_k lineshapes are available which allow us going a step further.

- Line mixing effect in the QQ_k sub-branches in the v_1 band

As is well known, the structure of these sub-branches is narrow and LM effects between all the $QQ(j,k)$ doublets belonging to a given k -sub-branch, can be easily observed under atmospheric pressures. This gives us the opportunity to apply our formalism to some of the QQ_k sub-branches lineshapes measured by Bray et al. [6]. In this case, contrarily to the QR one, both the inter and intra doublet couplings should be simultaneously taken into account. Therefore, for a given k -sub-branch and with neglecting only the inter-branch coupling (i.e., QQ -QR and QQ -QP), the lineshape is restricted to the $QQ(j,k)$ doublets with j varying from k to 19. Then the spectral density was obtained from Eq. (1), with the two models: (1) $V_{dq} + V_{qq}$ and (2) V_{full} with enforcing the sufficient condition. We have considered five QQ_k sub-branches: $k = 2, 3, 4, 5$ and 10.

Figs. 4 and 5 and Table 15 allow one to compare the results obtained with these two potential models as well as to the experiments. In order to summarize the narrowing effect, we have in-

Fig. 4. Spectral density in the sub-block constructed by the 34 QQ lines with $k = 3$ at $P(N_2) = 698.2$ mbar. The spectral density for the two isotopes have been added and the corresponding potential is $V_{dq} + V_{qq}$.

Fig. 5. The same as Fig. 4 except that the potential is the full potential with enforcing the sufficient condition.

roduced a narrowing coefficient define by: $\tau = A_{LM}/A_{WLM}$ where A_{LM} and A_{WLM} are the maximum peak absorptions calculated with LM and without LM, respectively.

As it appears immediately, a potential limited to $V_{dq} + V_{qq}$ leads to an unrealistic narrowing due to an overestimation of the amplitudes of the W off-diagonal elements. On the opposite, the full potential leads to a reasonable agreement with the experimental data since it dramatically reduces the amplitudes of the off-diagonal elements. We find here, in some sense, another justification of the empirical procedure proposed to avoid negative eigenvalues of S_2 . On that basis, there is little doubt that a slight adjustment of the atom-atom parameters (which is outside the objectives of the present work) will lead to a much better agreement.

Finally, note that this type of measurements is, by far, a more severe test of the potential model than the simple analysis of the coupling between the two components of a QR (or QP) doublets which only probes the intra-doublet coupling.

4. Conclusion

The most intriguing feature of the present work is certainly the emergence of larger positive eigenvalues of the $(-S_2)$ matrix when the potential reaches very high values at short collisional distances.

Its origin is not clear. The problem may result from a failure of the perturbation expansion of the scattering operator S for strong interactions happening at short distances and/or partly from the semi-classical approach. In the present work, in order to avoid the blowout, we enforce the sufficient condition of the positive definite matrix (Eq. (4)) on the S_2 matrix. Although this choice is by no means unique, it allows the extension of our formalism to systems requiring consideration of short range forces. In the present case, it leads to a good explanation of the LM effects observed in N_2 -broadened CH_3Cl spectra. But there is no doubt that the physical nature of this enforcing approach remains an open question that requires to be investigated.

Declaration of Competing Interest

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

CRediT authorship contribution statement

Q. Ma: Conceptualization, Formal analysis, Supervision. **C. Boulet:** Conceptualization, Formal analysis, Supervision.

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