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Molecular dynamics simulations for CO₂ spectra. IV. Collisional line-mixing in infrared and Raman bands

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Ab initio calculations of the shapes of pure CO₂ infrared and Raman bands under (pressure) conditions for which line-mixing effects are important have been performed using requantized classical molecular dynamics simulations. This approach provides the autocorrelation functions of the dipole vector and isotropic polarizability whose Fourier-Laplace transforms yield the corresponding spectra. For that, the classical equations of dynamics are solved for each molecule among several millions treated as linear rigid rotors and interacting through an anisotropic intermolecular potential. Two of the approximations used in the previous studies have been corrected, allowing the consideration of line-mixing effects without use of *any* adjusted parameters. The comparisons between calculated and experimental spectra under various conditions of pressure and temperature demonstrate the quality of the theoretical model. This opens promising perspectives for first principle *ab initio* predictions of line-mixing effects in absorption and scattering spectra of various systems involving linear molecules. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4811518>]

I. INTRODUCTION

The accurate modeling of pure CO₂ spectra is essential for various applications, in particular for atmospheric remote sensing and radiative transfer studies. In a number of circumstances, the collision-induced transfers of rotational populations, and thus the exchanges of intensity within the spectrum (line-mixing (LM)), have to be taken into account in order to reach the required accuracies on the properties (pressure, temperature, etc.) retrieved from fits of remote sensed spectra.¹ These LM effects yield an enhancement of the intense regions of the spectrum when the lines overlap significantly, a reduction of the band wings, and a filling of the gaps between doublets lines. Furthermore, the effects near the band or branch centers are more important when the collision-broadened optical transitions overlap significantly.¹ As a result, LM in CO₂ has to be considered for the modeling of the infrared absorption/emission in the deep atmosphere of Venus (about 96.5% of CO₂) where the pressure is high (up to 90 bar). Similarly, narrow infrared (e.g., Refs. 1–3) and Raman (e.g., Refs. 1 and 4–6) CO₂ Q branches are generally strongly affected by LM, even at low pressures, with consequences for remote sensing.^{1,7–9} Furthermore, although the effects of LM within and between CO₂ P and R branches are small at atmospheric pressure, they must be accurately

modeled for a proper treatment of infrared atmospheric spectra.^{10,11}

A quite exhaustive review of the models proposed to describe LM and of their applications to various molecular systems is given in Chap. IV of Ref. 1. Many studies have been devoted to mixtures involving CO₂ with a few for the pure gas in the infrared at high pressure^{12–17} and Raman Q branches.^{4–6,18–20} Let us mention at this step that all LM models proposed up to now¹ are partly empirical and that *ab initio* predictions starting from the intermolecular potential have not yet been made. Finally note that the most used¹ and accurate approach to describe LM effects is that based on the so-called Energy Corrected Sudden (ECS) approximation, with applications to pure CO₂ in Refs. 6, 12, 16, 19, and 20, and references therein. Despite that first principle quantum models have been proposed for the calculation of the relaxation matrix involved in the description of LM from the interaction potential,¹ none are tractable nowadays (due to computer limitations) for CO₂-CO₂. Recently, a new approach was proposed for the *ab initio* calculation of different absorption shape features without any adjusted parameters, based on Classical Molecular Dynamics Simulations (CMDS). It has been successively and successfully applied, for pure CO₂, to the predictions of line broadening coefficients,²¹ of collision-induced absorption,²² of the far wings of absorption and scattering bands,^{21,23} of individual line shapes,²⁴ and to the collisional dissipation of laser-induced molecular alignment.^{25,26}

In the present paper, properly requantized Classical Molecular Dynamics Simulations (rCMDS) are used for

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calculations of spectra under conditions which make line-mixing effects important, a topic to which this approach had not yet been applied. We thus present thereafter the first *ab initio* calculation of line-mixing for pure CO₂ and compare their results with experiments. This is done, for various pressures and temperatures, for two infrared bands and the 2ν₂ isotropic Raman Q branch. Section II describes the theoretical model and the modifications that have been made to properly take into account the line-mixing effects through rCMDS. This model is validated in Sec. III by comparisons with measured spectra and concluding remarks are given in Sec. IV.

II. THEORETICAL MODEL AND DATA USED

A. Spectral shape

As is well known,¹ the absorption coefficient resulting from the interaction of a molecular intrinsic (i.e., *not* interaction induced^{1,27}) dipole \vec{d} with an electromagnetic field of angular frequency ω and wave vector $\vec{k} = (\omega/c)\vec{z}$ is given by

$$F(\omega) = \text{Re} \left\{ \frac{1}{\pi} \int_0^{+\infty} \Phi(\omega, t) e^{-i\omega t} dt \right\}, \quad (1)$$

where $\Phi(\omega, t)$ is the autocorrelation function (ACF) of the dipole $\vec{d}(t)$

$$\Phi(\omega, t) = \langle e^{-i\vec{k}(\omega) \cdot \vec{q}(t)} \vec{d}(t) \cdot \vec{d}(0) e^{+i\vec{k}(\omega) \cdot \vec{q}(0)} \rangle. \quad (2)$$

In Eq. (2), $\langle \dots \rangle$ denotes an average over the molecular system, $\vec{q}(t)$ is the molecule position, and the exponential terms result from the Doppler effect associated with the translational motion. This contribution is included in Eq. (2) for its completeness although the Doppler effect plays no role under the pressure conditions of the spectra considered in this study. Using the ACF of the isotropic polarizability $\alpha(0)$ [i.e., replacing $\vec{d}(t) \cdot \vec{d}(0)$ by $\alpha(t) \cdot \alpha(0)$ in Eq. (2)], Eq. (1) yields the isotropic Raman scattering spectrum.

B. Classical molecular dynamics

The approach used here for the calculation of $\Phi(\omega, t)$ is based on requantized classical molecular dynamics simulations. In these calculations, the force and torque applied to each molecule, treated as a linear and rigid rotor, by its surrounding sisters are computed classically at each time.^{21–24} This provides the center of mass position $\vec{q}_m(t)$ and velocity $\dot{\vec{q}}_m(t)$, the unit vector $\vec{u}_m(t)$ along the molecule axis, and the rotational angular momentum $\vec{\omega}_m(t)$ for each molecule m at each time t . Note that if no requantization is made, the Fourier-Laplace transform of the relevant autocorrelation function leads to a continuous spectrum with no line structure.^{21,23} Most details of the method and of its implementation can be found in Ref. 24 and those therein. Nevertheless, the approach used in Refs. 24 and 28 suffered two limitations that were of no consequences for the studies made because the latter considered isolated lines. The first is that calculations were done for a single branch implicitly assuming identical P and R branches. This resulted from the fact that the information on the direction in which each molecule rotates was not used. The second is that the positions and intensities of

the lines were incorrect since calculated for a strictly rigid rotor and neglecting centrifugal distortion. These inaccuracies must obviously be corrected for the prediction of the spectral shapes of entire bands or branches when the lines overlap significantly and are not isolated anymore.

C. New requantization scheme

In order to explain the new approach, let us start by considering dipole absorption for which we first focus on the calculation of the phase $\eta_m(t)$, such that $\vec{d}_m(t) = \exp[i\eta_m(t)]\vec{d}_m(0)$. We then use the following four steps procedure for each molecule m . (i) We first determine the rotational quantum number from the correspondence principle for rotational energy. In other words, we find the even (for CO₂) integer $J_m(t)$ for which $\frac{\hbar^2}{2I} J_m(t)[J_m(t) + 1]$ is the closest to $\frac{1}{2} I \|\vec{\omega}_m(t)\|^2$ (I being the CO₂ molecule moment of inertia). This provides the value of J for the lower state of the optical transition to which molecule m contributes at time t . (ii) In order to now know which specific line $L_m(t)$ ($L = R$ or P) is involved, we consider, following Ref. 29, the direction in which the molecule rotates. We hence look at the sign of the projection of the rotational angular momentum $\vec{\omega}_m(t)$ along the fixed axis x , deciding that positive and negative signs correspond to $L = R$ and $L = P$ branches, respectively. Due to isotropy, the choices of the projection axis and sign-to-branch correspondence are of no consequence. (iii) We can then calculate the true angular frequency corresponding to the line of initial rotational quantum number $J_m(t)$ in branch $L_m(t)$, from

$$\omega_{L_m[J_m(t)]} = \omega_{vib} + \omega_{Rot}^{Up}[J_m(t) + \Delta J_m(t)] - \omega_{Rot}^{Low}[J_m(t)], \quad (3)$$

where $\Delta J_m(t) = -1$ for $L_m(t) = P$ and $\Delta J_m(t) = +1$ for $L_m(t) = R$. In Eq. (3), ω_{vib} is the vibrational frequency for the considered band and $\omega_{Rot}^{Low}(J)$ and $\omega_{Rot}^{Up}(J)$ are rotational energies in the lower and upper states. The latter are calculated from the proper rotational constants B , D , and H through

$$\omega_{Rot}^{Up/Low}(J) = B^{Up/Low} J(J+1) - D^{Up/Low} [J(J+1)]^2 + H^{Up/Low} [J(J+1)]^3. \quad (4)$$

(iv) Finally, we calculate the phase $\eta_m(t)$ from

$$\eta_m(t) = \int_0^t \omega_{L_m[J_m(t)]} \times \cos[\theta_m(t)] dt \quad \text{with} \\ \cos[\theta_m(t)] = \left| \frac{\vec{\omega}_m(t) \cdot \vec{u}_m(0)}{\|\vec{\omega}_m(t)\|} \right|, \quad (5)$$

where $\cos[\theta_m(t)]$ takes into account the angle between the plane in which the molecule rotates and the $\vec{d}_m(0)$ reference axis [recall that the dipole $\vec{d}(t)$ for the asymmetric stretching of CO₂ is carried by the molecular axis $\vec{u}(t)$]. Now that we know the phase and on which absorption line molecule m absorbs at time t , the autocorrelation function is calculated from

$$\Phi^{absorption}(\omega, t) = \frac{1}{N_T} \sum_{m=1, N_T} (d_{L_m[J_m(t)]})^2 e^{-i\vec{k}(\omega) \cdot [\vec{q}_m(t) - \vec{q}_m(0)] + i\eta_m(t)}, \quad (6)$$

where N_T is the total number of molecules, and $d_{L(J)}$ is the dipole transition moment of the line of branch L of initial rotational quantum number J . Its value is directly obtained¹ from the line integrated intensity $S_{L(J)}$ through $d_{L(J)} = \sqrt{S_{L(J)}/p(J)}$ where $p(J)$ is the relative population of level J . These two quantities are easily calculated from the data provided in the used spectroscopic database (see Sec. II D).

For isotropic Raman scattering, the same procedure and equations are used except that $\cos[\theta_m(t)]$ is removed from Eq. (5) (due to isotropy) as are $S_{L_m[J_m(t)]}$ and $\rho_{J_m(t)}$ in Eq. (6) [since this ratio is line independent]. Note that the considered $2\nu_2$ Q branch shows a significant spectral shift Δ_{vib} and broadening Γ_{vib} (HWHM) due to vibrational effects (both linear vs density).¹⁸ Since these cannot be predicted by the rCMDS, they have been *a posteriori* introduced in the auto-correlation function. The latter is then given by

$$\Phi^{Raman}(\omega, t) = \frac{1}{N_T} \sum_{m=1, N_T} e^{-i\vec{k}(\omega) \cdot [\vec{q}_m(t) - \vec{q}_m(0)] + i\eta_m(t)} e^{i\Delta_{vib}t - \Gamma_{vib}t}. \quad (7)$$

Note that the procedure described above, which provides the phase $\eta_m(t)$ and autocorrelation function $\Phi(\omega, t)$, is carried at *each time step* of the rCMDS. Also recall that the molecules' rotations are left unchanged as the requantization applied in Refs. 24 and 28 is not made anymore since it is now unnecessary.

D. Data used and implementation

Various input data are needed for calculations using the above described approach. The molecular parameters of CO₂ and CO₂-CO₂ intermolecular potential³⁰ are the same as those used in Ref. 24. ω_{vib} and the B , D , and H molecular constants in Eqs. (3) and (4) are from Ref. 31, while, for the

infrared bands, the infrared spectroscopic parameters (line intensities and relative populations) were taken from Ref. 32 and converted to the temperature of the study. For the $2\nu_2$ isotropic Raman Q branch, the density-normalized vibrational broadening and shifting coefficients γ_{vib} and δ_{vib} were taken from Ref. 18.

Practical computations were made as described in Ref. 24 using the same initialisation procedure, time step, and algorithm. Furthermore, a dozen sets of about 10^5 molecules were treated using the various cores of a parallel computer.

III. RESULTS AND DISCUSSION

This section is devoted to comparisons between measured spectra and those *ab initio* calculated using the rCMDS approach. In addition to these, we also present spectra calculated neglecting LM in order to show the influence of this process. This was done independently of the rCMDS by simply summing the contributions of the individual lines, each of them having a Voigt profile. The input line intensities, populations, and line positions are the same as those used in the rCMDS while the broadening coefficients were taken from Ref. 16. Note that the same line widths are used for infrared and Raman lines, an approximation justified in Ref. 33.

A. $3\nu_3$ and $2\nu_1 + 2\nu_2 + \nu_3$ infrared bands regions at room temperature

For simplicity, rCMDS have been made *only* for the most intense band in each of the two spectral ranges considered in this work, i.e., the $3\nu_3$ (around 6972.58 cm^{-1}) and $2\nu_1 + 2\nu_2 + \nu_3$ (near 6347.85 cm^{-1}) bands. This is due to the treatment of molecules as linear rotors which prohibits simulations when the bending mode of CO₂ is involved. Hence, the relatively small contributions of minor bands (e.g., the first

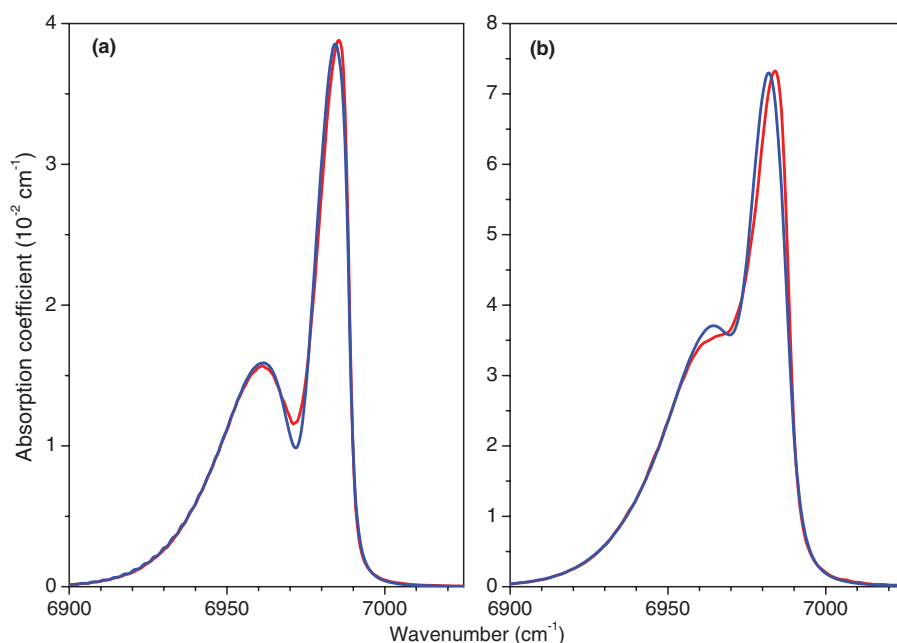


FIG. 1. Absorption coefficient of pure CO₂ at 296 K due to the single $3\nu_3$ band calculated with the present rCMDS model (red line) and the ECS approach of Ref. 16 (blue line) for the densities of (a) 22.65 Am and (b) 51.28 Am.

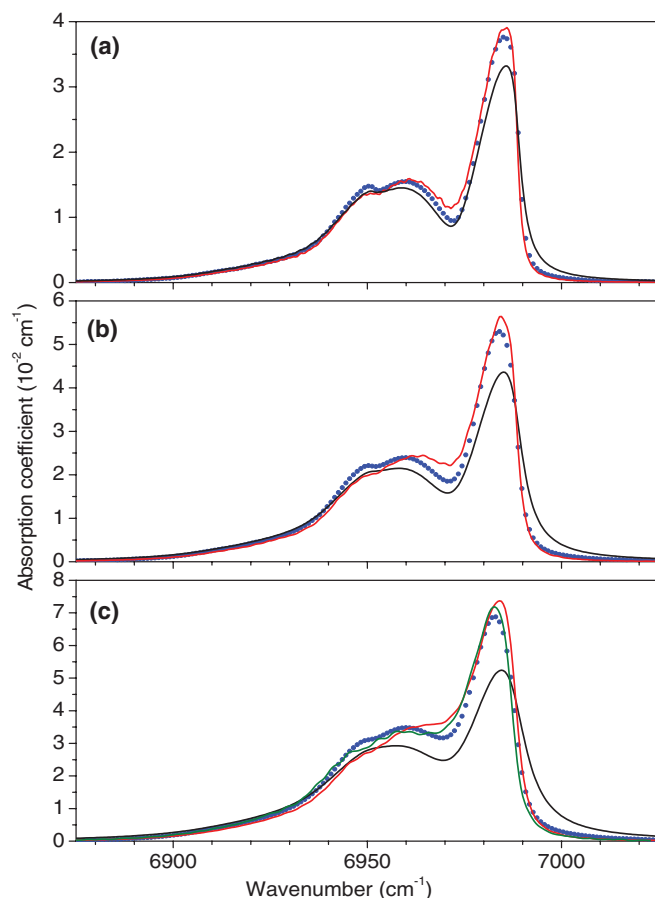


FIG. 2. Absorption coefficients of pure CO₂ in the region of the $3\nu_3$ band at 294 K for densities of (a) 22.7 Am, (b) 35.5 Am, and (c) 51.3 Am. The blue circles are measured values¹⁶ while the lines are calculated results obtained with the rCMDS model (red) and neglecting line-mixing (black). The olive curve in (c) has been obtained from rCMDS after the introduction of spectral shifts of opposite signs in the P and R branches (see text).

hot band $3\nu_3 + \nu_2 - \nu_2$) have been calculated independently and added to the rCMDS results. This was done using the ECS model and tools of Ref. 16 which have been successfully validated in the same reference. Note that the comparisons, in Fig. 1, between ECS-calculated spectra and those obtained from rCMDS for the single $3\nu_3$ band show the good agreement between these two completely independent approaches. A similar agreement is obtained for the $2\nu_1 + 2\nu_2 + \nu_3$ band.

Calculated and measured¹⁶ spectra at 294 K in the region of the $3\nu_3$ band for three gas densities are presented in Fig. 2. As expected from previous studies (see Refs. 16 and 17 and, more generally, Ref. 1), line-mixing has a significant influence that increases with pressure. The widths (respectively absorption peak) of the branches are overestimated (respectively underestimated) when this process is not taken into account with effects more pronounced in the $3\nu_3$ R branch due to the presence of a band-head around R(40). Figure 2 shows a satisfactory agreement, for all pressures, between the measured spectra and the rCMDS predictions, a result which validates the proposed model. However, some discrepancies remain, although they are much smaller than those obtained if LM is neglected. The most obvious is that the calculations underestimate the spectral distance between the maxima of the P and R branches and consequently overestimate the absorption

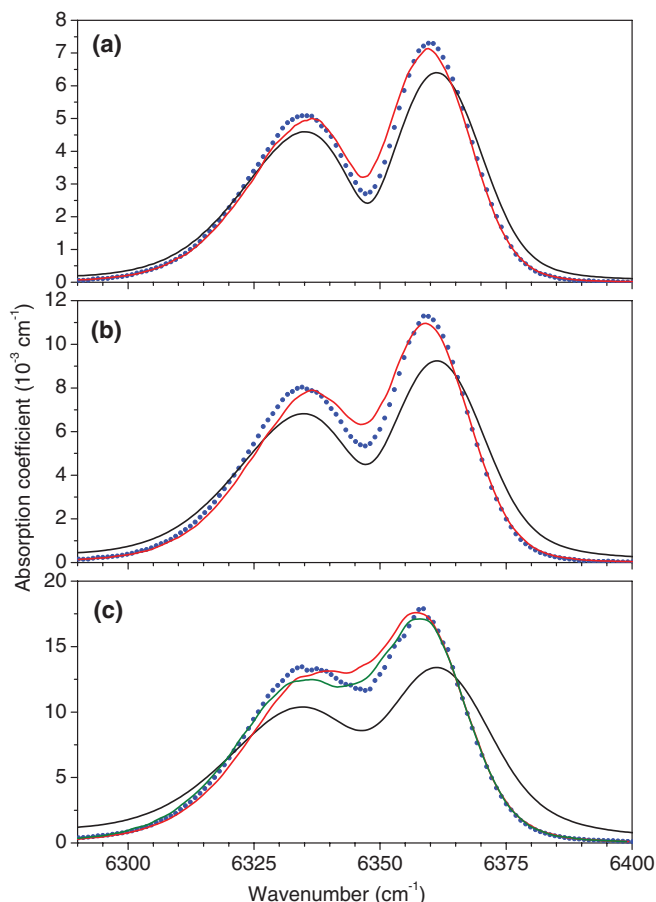


FIG. 3. Same as Fig. 2 but for the $2\nu_1 + 2\nu_2 + \nu_3$ band region and densities of (a) 20.6 Am, (b) 33.0 Am, and (c) 56.7 Am.

near the band center. This discrepancy, which increases with the gas density, is likely due to the fact that the influence of the spectral shifts is not taken into account in the rCMDS. Indeed, as analyzed in Ref. 34, these lead, through the off-diagonal imaginary elements of the relaxation matrix, to spectral shifts of the P and R branches with respect to the band center of opposite signs. Hence the branches shift away from each other as the pressure increases, a process not taken into account in the rCMDS that likely explains the discrepancies in Fig. 2. In order to check this, and following Ref. 34, we have introduced spectral shifts independent of the transition but of opposite signs for P and R transitions by simply multiplying the autocorrelation functions in Eq. (6) by $\exp[i \int_0^t \Delta_{L_m(t)} dt]$ with $\Delta_{L_m(t)} = \Delta$ if $L_m(t) = R$ and $\Delta_{L_m(t)} = -\Delta$ if $L_m(t) = P$. As can be seen from the examples at elevated pressure in Figs. 2 and 3, this greatly improves the results.

The results for the region of the $2\nu_1 + 2\nu_2 + \nu_3$ band at 295 K are presented in Fig. 3 with measured spectra from Refs. 16 and 32. They lead to the same conclusions as those drawn above from the $3\nu_3$ band region.

B. $2\nu_2$ isotropic Raman Q branch at room temperature

Comparisons between calculated spectra and measured ones⁴ in the $2\nu_2$ isotropic Raman Q branch of pure CO₂ for three gas densities are shown in Fig. 4. The rCMDS are in striking agreement with the experimental spectra under

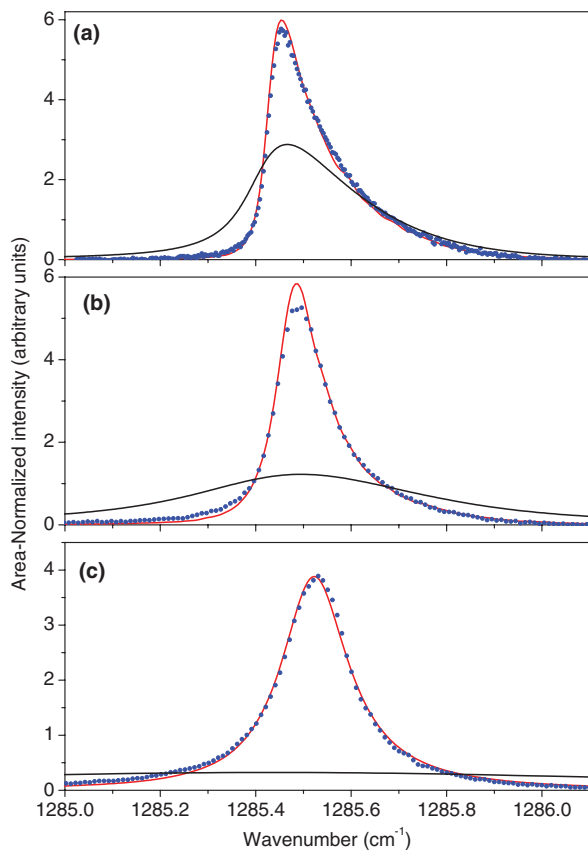


FIG. 4. Area-normalized intensities (in arbitrary units) in the $2\nu_2$ isotropic Raman Q branch of pure CO_2 at 295 K for the densities of (a) 0.5 Am, (b) 2.0 Am, and (c) 10.0 Am. The blue circles are measured values⁴ while the lines are calculated results obtained with the rCMDS model (red) and neglecting line-mixing (black).

conditions for which neglecting line-mixing leads to a considerable overestimation of the Q branch width. This last statement is explained by the well known fact¹ that LM leads to a strong narrowing of isotropic Raman Q branches that can result in their collapse if no vibrational width is considered.

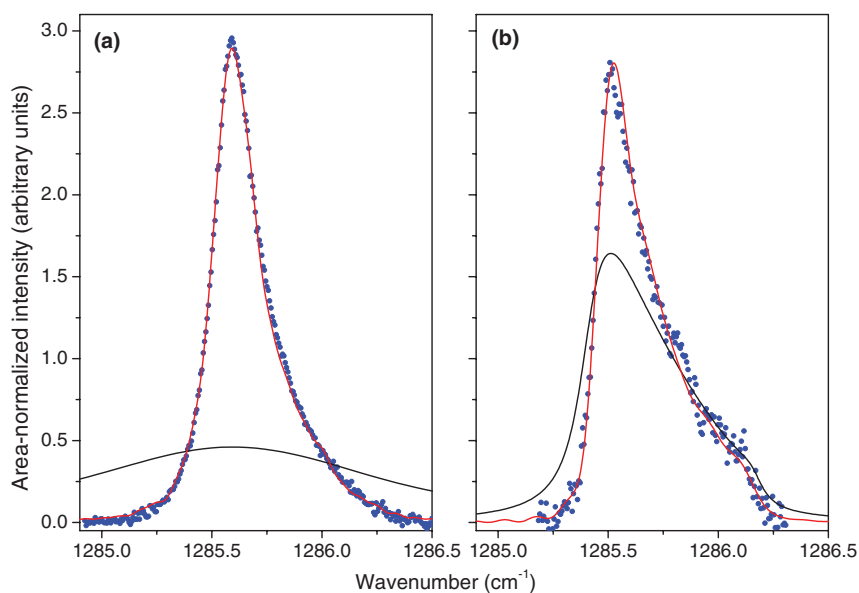


FIG. 6. Same as Fig. 4 but for 700 K and densities of (a) 5 Am and (b) 1 Am.

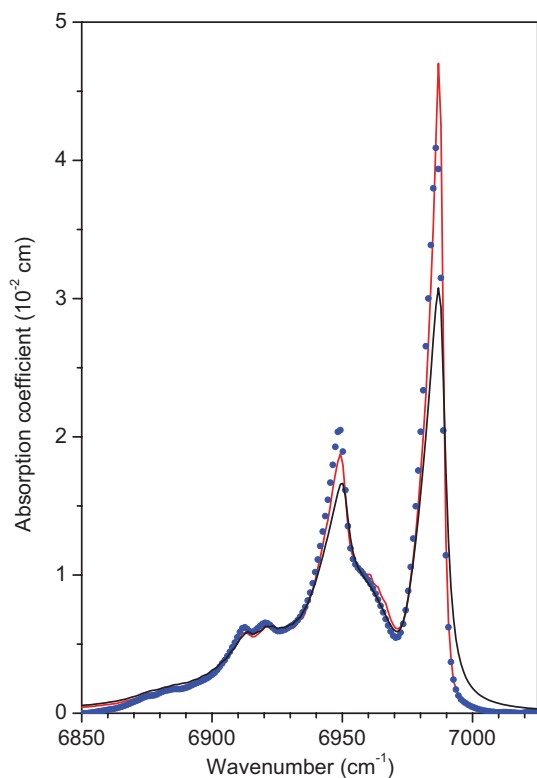


FIG. 5. Same as Fig. 2 but for 473 K and a density of 23.63 Am.

C. Temperature effects

For a final test of the rCMDS ability to describe the spectral effects of line-mixing, calculations were also made at higher temperatures. Comparisons between calculated spectra and those measured in the $3\nu_3$ infrared region at 473 K¹⁶ and in the $2\nu_2$ Raman Q branch at 700 K¹⁸ are presented in Figs. 5 and 6, respectively. For the $3\nu_3$ band (Fig. 5), the significant contribution of several hot bands was, as mentioned above, taken into account using the ECS approach of

Ref. 16. Figures 5 and 6 again show that the rCMDS leads to much better agreement with experiments than the model neglecting line-mixing. Nevertheless, while very satisfactory results are obtained for the Raman Q branch, the quality of predictions in the infrared is poorer than at room temperature. The predicted R branch is too narrow, a finding for which we have no explanation that deserves further investigations. Finally note that, thanks to a requantization that now rigorously includes the line positions, the small “bump” near 1286.18 cm^{-1} in Fig. 6(b), due to the Q branch head at $J = 80$, is well reproduced.

IV. CONCLUSION

In this paper, we present what are, to the best of our knowledge, the first *ab initio* calculations of molecular spectra under conditions for which line-mixing significantly affects the spectral shape. The comparisons between predicted and measured infrared absorption and isotropic Raman scattering spectra demonstrate the quality of the proposed rCMDS model. Together with previous similar exercises for line-broadening,²¹ collision-induced absorption,²² wings of entire bands,²³ and isolated line-shapes,²⁴ this demonstrates that rCMDS are a robust and flexible tool for the description of the consequences of inter-molecular collisions on CO₂ spectra.

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