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Molecular dynamic simulations of N₂-broadened methane line shapes and comparison with experiments

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Absorption spectra of methane transitions broadened by nitrogen have been calculated for the first time using classical molecular dynamic simulations. For that, the time evolution of the auto-correlation function of the dipole moment vector, assumed along a C–H axis, was computed using an accurate site-site intermolecular potential for CH₄–N₂. Quaternion coordinates were used to treat the rotation of the molecules. A requantization procedure was applied to the classical rotation and spectra were then derived as the Fourier-Laplace transform of the auto-correlation function. These computed spectra were compared with experimental ones recorded with a tunable diode laser and a difference-frequency laser spectrometer. Specifically, nine isolated methane lines broadened by nitrogen, belonging to various vibrational bands and having rotational quantum numbers J from 0 to 9, were measured at room temperature and at several pressures from 20 to 945 mbar. Comparisons between measured and calculated spectra were made through their fits using the Voigt profile. The results show that *ab initio* calculated spectra reproduce with very high fidelity non-Voigt effects on the measurements and that classical molecular dynamic simulations can be used to predict spectral shapes of isolated lines of methane perturbed by nitrogen. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4976978>]

I. INTRODUCTION

Methane is one of the most important greenhouse gases in the Earth's atmosphere. It is also an important constituent of atmospheres of various planets and satellites in the solar system. An accurate knowledge of methane spectroscopic parameters is essential for current atmospheric methane remote sensing missions with unprecedented precision requirements.^{1–5} For isolated transitions (no collisional line mixing),⁶ deviations of measured methane line shapes with respect to the usual Voigt profile have been pointed out in many studies (see Ref. 7 and references therein). As it is well known, they are due to various refined effects neglected in the Voigt line shape, such as the molecules' center-of-mass velocity changes (VCs)^{8,9} and the speed dependence (SD) of the broadening and shifting coefficients^{10,11} induced by collisions. Several models⁶ have been proposed in order to describe these effects and their eventual temporal correlations. However, these approaches are often based on oversimplified descriptions of both VC (hard¹² or soft⁹ collisions) and SD (quadratic¹³ or confluent hypergeometric¹⁰ laws). Therefore, first-principle approaches are needed to provide reference benchmarks and to understand the different mechanisms affecting the line shape.

Requantized classical molecular dynamics simulations (rCMDSs) have proved to be a powerful tool to predict the

line shapes of linear molecules such as CO₂, O₂, and HCl.^{14–19}

From reliable intermolecular potentials, the evolution of a system involving a large number of molecules can be computed, including the time dependence of the position of the center of mass, of the translational and angular velocities, and of the orientation of each molecule. The auto-correlation function of the molecular dipole moment can be also computed. The corresponding absorption spectrum can then be calculated as the Fourier-Laplace of this auto-correlation function. As described and discussed in detail in Ref. 15, various collisional effects affecting the spectral line shape, such as the collision-induced velocity changes and the speed dependence of the collisional parameters, are taken into account in rCMDS. Comparisons between these *ab initio* calculations and experimental spectra of several lines for different linear molecules, measured in a large pressure range, showed very good agreements. Specifically, the measured spectral shapes and their evolution with pressure are satisfactorily reproduced by the calculations.^{14–19} Classical molecular dynamic simulations (CMDSSs) were also successfully applied to non-linear molecules as for the case of pure H₂O^{20,21} and H₂O diluted in N₂.²² In these situations, quaternion coordinates were used to treat the rotation of the molecules. The spectral shapes, computed by using a kinetic equation¹² with velocity changes rates predicted using CMDSS, were shown to be in very good agreement with measured spectra.

In this study, rCMDSs are used for the first time to compute absorption spectra of isolated transitions of CH₄ diluted in N₂. Starting from accurate intermolecular potentials,^{23–25} the

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time evolution of the auto-correlation function of the dipole moment vector assumed along a C–H axis is computed, CH₄ being considered as a linear molecule. Methane spectra are then derived as the Fourier-Laplace transform of this auto-correlation function. The computed spectra are compared with experimental data, recorded with two different instruments. More specifically, room temperature spectra of 9 isolated lines of CH₄ diluted in N₂, located in 4 vibrational bands, and with different rotational quantum numbers, are recorded for large pressure ranges (from 20 to 945 mbar). Comparisons between measured and calculated spectra are then made through their fits using the Voigt profile, retrieved parameters and fit residuals being compared.

The remainder of this paper is divided into four sections. Sections II and III describe, respectively, the rCMDS and the experimental details. The data analysis procedure and the obtained results are presented and discussed in Sec. IV while some conclusions are drawn in Sec. V.

II. RE-QUANTIZED CLASSICAL MOLECULAR DYNAMICS SIMULATIONS

Classical molecular dynamics simulations (CMDSs)²⁶ were carried out for the CH₄–N₂ gas mixture at room temperature and 1.09 bar. The molecules are considered as rigid rotors. Each molecule m is then characterized by its center-of-mass position $\vec{q}_m(t)$ and velocity $\dot{\vec{q}}_m(t)$, by a unit vector $\vec{u}_m(t)$ along a molecular axis and by its rotational angular velocity $\vec{u}_m(t)$. Note that unlike linear molecules,^{15–19} methane is a spherical top with 4 hydrogen atoms evenly distributed on the surface of a sphere with a carbon atom located at its center. The molecular axis ($\vec{u}_m(t)$) of methane is therefore chosen to lie along a given C–H bond. The evolution with time of this gas mixture is governed by interactions among all molecules which can be separately described by three types of molecular-pair interactions: CH₄–CH₄, N₂–N₂, and CH₄–N₂. Accurate site-site interaction potential functions^{23–25} are used for these pairs, the nine- and five-site models²⁵ being, respectively, used to describe methane and nitrogen molecules. Based on these intermolecular potentials and on the initial conditions ($\vec{q}_m(0)$, $\dot{\vec{q}}_m(0)$, $\vec{u}_m(0)$, and $\dot{\vec{u}}_m(0)$), the time evolution of the CH₄–N₂ system was then computed using the classical dynamics simulation approach.

The calculations have been made on the IBM Blue Gene/P computer of the *Institut du Développement et des Ressources en Informatique Scientifique*. The CH₄ and N₂ molecules are initially randomly placed inside 4096 cubic boxes (corresponding to 4096 cores) with periodic boundary conditions;²⁶ each box contains 2000 molecules leading to a total of $N_T \approx 8 \times 10^6$ molecules. The size L of each box is deduced from the number of molecules, temperature, and density using the perfect gas law. In order to ensure that unphysical strong intermolecular interactions are absent at $t = 0$, the initial center-of-mass distances between the molecules are imposed to be larger than 9 Å. The initial orientations of the translational and angular velocities of all molecules have been randomly chosen while their modulus obeys the Maxwell-Boltzmann distribution. Quaternion coordinates are used to treat the rotation of the methane molecules.²⁶ After several tests, a temporization

time²⁶ of about 20 ps and a time step of 1 fs were retained. At each time step, the force and torque applied to each molecule by its neighbors are computed. The center-of-mass position $\vec{q}_m(t)$ and velocity $\dot{\vec{q}}_m(t)$ as well as the molecule orientation $\vec{u}_m(t)$ and its angular velocity $\dot{\vec{u}}_m(t)$ are determined at each time step.

In this study, the dipole moment vector of each methane molecule at any time is assumed to be along its molecular axis. The $\Phi^{CMDS}(\omega, t)$ auto-correlation function of the dipole moment of all molecules at angular frequency ω and wave vector $\vec{k}(\omega) = (\omega/c)\vec{z}$ is then given by

$$\Phi^{CMDS}(\omega, t) = \frac{1}{N_T} \sum_{m=1}^{N_T} e^{-i\vec{k}(\omega) \cdot [\vec{q}_m(t) - \vec{q}_m(0)]} \cdot [\vec{u}_m(t) \cdot \vec{u}_m(0)]. \quad (1)$$

The exponential term in Eq. (1) is related to the Doppler effect associated with the translational motion. As mentioned in Ref. 15, at atmospheric pressure, absorption of a line centered at angular frequency ω_0 is significant only in a narrow frequency interval, one may thus safely replaced $\vec{k}(\omega)$ by $\vec{k}(\omega_0)$ in Eq. (1). It means that at each rCMDS step, one can calculate the auto-correlation functions $\Phi^{rCMDS}(\omega_0, t)$ for several values of ω_0 with a negligible extra computation cost. In this study, eleven wave vectors corresponding to wave numbers ($\sigma_0 = \omega_0/2\pi c$) varying from 0 to $4 \times 10^5 \text{ cm}^{-1}$ were used. With these choices, the Lorentz to Doppler half-width ratio Γ_L/Γ_D has a large range from infinite (collisional regime) to 0.06 (close to the Doppler regime).

The normalized absorption coefficient of methane is then directly calculated as the Fourier-Laplace transform of this auto-correlation function,^{6,15}

$$F(\omega) = \text{Re} \left\{ \frac{1}{\pi} \int_0^\infty \Phi^{CMDS}(\omega, t) e^{-i\omega t} dt \right\}. \quad (2)$$

As shown previously,^{27,28} the Fourier-Laplace transform in Eq. (2) leads to continuous spectra with no line structure. A requantization procedure is thus necessary in order to obtain a line-structure. The requantization scheme described in Ref. 19 has been applied here to the CH₄ angular momentum $\vec{\omega}_m(t)$. Specifically, one considers the angle $\theta_m(t)$ between $\vec{u}_m(0)$ and $\vec{u}_m(t)$. This angle is calculated for each time step by

$$\theta_m(t + dt) = \left\{ \theta_m(t) + \text{sign} \omega_m^{req}(t) dt \right\} \times \cos [\vec{u}_m(t), \vec{u}_m(0) \times \vec{u}_m(t + dt)], \quad (3)$$

where ω_m^{req} is the requantized value of the classical rotational angular momentum ω_m , i.e., $\vec{\omega}_m^{req} = \vec{\omega}_m \frac{\sqrt{J_m(J_m+1)}\hbar/I}{|\vec{\omega}_m|}$ with J_m the corresponding rotational quantum number. In Eq. (3), *sign* is the sign of the projection of the vector product of the rotational angular velocity $\vec{u}_m$ and the molecular axis $\vec{u}_m(t)$ along the fixed axis x .^{16,29} $\theta_m(t)$ and thus the auto-correlation function of the dipole moment (carried by the molecular axis) are then calculated for each time step using this requantization procedure. The other parameters such as $\dot{\vec{u}}_m$ and $\vec{u}_m(t)$ are kept unchanged with respect to their classical values and follow the classical evolution of the system. Note that this requantization procedure does not take into account the complex fine structure of the CH₄ manifolds due to their different symmetry; only a line will be calculated for each rotational quantum number J .

Therefore, the present rCMDS-calculated spectra can only be used to test the spectral shapes of isolated methane lines. Also, line mixing effects⁶ for lines belonging to the same manifold cannot be investigated by the present method.

III. EXPERIMENTAL DETAILS

In order to test the rCMDS, room temperature absorption spectra of 9 N₂-broadened methane lines (Table I) were measured with two different instruments. These lines were carefully chosen so that the influence of neighbouring lines and line-mixing on their absorption spectrum can be neglected. Spectra of each line were recorded for a large pressure range corresponding to a wide range of the Lorentz to Doppler half-widths, Γ_L/Γ_D ratio (from 0.1 to 10, see Table I).

Spectra of 8 isolated methane lines broadened by N₂ were recorded with a difference frequency laser spectrometer (DFLS)^{19,30} at IEM-CSIC in Madrid, Spain. Briefly, tunable IR radiation is produced by difference frequency mixing of an Ar⁺ laser and a tunable ring dye laser in LiNbO₃ crystals. For most of the lines, a periodically poled crystal with different grating periods was used, but for the line at 4430 cm⁻¹, it was replaced by a single x-cut LiNbO₃ crystal. Both lasers are operated single mode, and the Ar⁺ laser is actively locked to the a₃ hyperfine component of the 43-0 P(13) transition of the ¹²⁷I₂ molecule, resulting in a jitter-limited linewidth of less than 1 MHz (rms) and similar long term stability. This laser is also used to calibrate a solid state wave meter (High Finesse Ultimate WSU-10), with a manufacturer stated accuracy of 3.3 MHz rms. The wavemeter provides a wavenumber reading for the ring dye laser synchronously with the spectrum data acquisition in just 1 ms. The IR frequency scale is calculated directly as the difference between the known Ar⁺ frequency and the wavemeter reading at each experimental data point and has an absolute accuracy and precision

limited by the wavemeter (3.3 and 1 MHz, respectively). The IR radiation is split into two beams, one traversing the sample cell and the second one serving as intensity reference, and both are detected by InSb detectors, fed to the current input of two lock-in amplifiers. As shown in Ref. 31, time constant effects must be carefully accounted for in line profile analysis. In the present experiments, the frequency scans are typically 1 cm⁻¹ wide, scan speed is 0.01 cm⁻¹/s, and detection time constant is 10 ms at 6 db/oct roll-off. With these conditions, for CH₄ at 2847 cm⁻¹ and 300 K, one Doppler full width at half maximum (FWHM) is scanned in more than 80 time constants, so line shape distortions due to detection bandwidth effects are minimized. Although the determination of absolute line positions is not the goal of this work, the small delay introduced by the time constant (equivalent to $\sim 10^{-4}$ cm⁻¹ according to Ref. 31) is corrected by applying an exponential average low pass filter³² with the same time constant to the vector containing the frequency scale. Two different dye solutions were necessary to cover the spectral region spanned by this study: Rhodamine 6G in ethylene-glycol for the lines at 2848 and 2856 cm⁻¹ and DCM in ethylene-glycol/ethyl-phenyl-ether for the rest.

CH₄ was supplied by Air Liquide and N₂ was supplied by Contse. Since both had purities >99.995%, they were used without further purification. Mixtures were prepared in steel cylinders at least one day in advance to allow for a homogeneous mixing of the gases, and their partial pressures were monitored with a capacitance manometer for CH₄ and a piezo ceramic sensor for N₂, both with an accuracy of 0.5% of their readings. The target concentration was a 2% of CH₄ in the mixture, although some mixtures were only 1.8%. The sample cell was a Specac 20350 White type cell set to an absorption path length of 1.8 m.

Spectra were taken at room temperature that ranged from 24 to 26 °C but was constant within 0.1 °C for each line. Target pressures for the spectra were 1000, 800, 600, 400, 200, 100, 50, and 20 mbar and were measured with a capacitance gauge

TABLE I. Experimental conditions of the measured spectra. The line positions were taken from the HITRAN database.³³

Vibrational band	Transition	Line position (cm ⁻¹)	T (K)	L (cm)	P (mbar)	P _{CH4} /P (%)	Γ_L/Γ_D range	Spectrometer
v ₄	P(3)A2	1287.813 279	296.5 ± 0.2	417.0	30.9, 70.0, 78.9, 103.2, 157.5, 205.8, 296.3, 399.9	0.040-0.067	0.88-12.24	TDLS
v ₂ + v ₄	R(0)A1	2847.719 101	299.3 ± 0.1	180.0	20.2, 50.7, 99.4, 199.7, 391.0, 599.3, 799.3, 910.0	2.020	0.24-12.31	DFLS
v ₂ + v ₄	R(1)F1	2856.963 094	299.5 ± 0.1	180.0	20.1, 49.7, 99.6, 200.5, 400.3, 600.2, 793.4, 924.7	1.790	0.25-13.16	DFLS
v ₂ + v ₄	R(6)A2	2908.331 351	299.5 ± 0.1	180.0	20.1, 50.7, 99.0, 199.6, 398.8, 598.1, 792.4, 926.0	1.790	0.24-12.49	DFLS
v ₃ + v ₄	P(9)A1	4161.051 852	299.0 ± 0.1	180.0	20.1, 50.8, 98.4, 200.7, 399.2, 599.9, 800.4, 924.8	1.790	0.13-7.91	DFLS
v ₃ + v ₄	P(8)F1	4168.483 790	297.3 ± 0.1	180.0	20.0, 49.9, 99.5, 200.6, 400.1, 599.9, 800.4, 924.7	1.990	0.16-8.40	DFLS
v ₁ + v ₄	Q(1)F1	4324.933 076	297.5 ± 0.1	180.0	20.0, 50.0, 100.8, 200.5, 400.7, 598.7, 799.8, 925.7	1.996	0.15-8.62	DFLS
v ₃ + v ₄	Q(2)F2	4330.107 883	297.7 ± 0.1	180.0	20.1, 49.8, 100.1, 200.4, 399.8, 599.5, 800.5, 925.3	1.996	0.15-8.80	DFLS
v ₃ + v ₄	R(7)F1	4427.816 365	298.0 ± 0.1	180.0	19.9, 50.1, 100.4, 200.6, 399.9, 600.2, 799.6, 945.4	1.996	0.14-8.61	DFLS

FIG. 1. A sample of calculated (a) and measured (b) spectra and their corresponding Voigt fit residuals. The inset in Fig. 1(b) shows the measured spectrum before (black) and after (red) subtraction of the synthetic background (blue).

with an accuracy of 0.5% of the reading. The cell had some tendency to produce interference fringes that drifted slowly with time during the pressure sequence, so empty cell spectra were taken before, at the middle and at the end of the pressure sequence. The smoothed empty cell spectra were used to calculate synthetic background spectra for each pressure, by interpolation according to the elapsed time between traces. Nevertheless when the empty cell spectra showed differences of more than a few percent, the whole sequence was disregarded and repeated. The transmission and background traces were converted to Napierian absorbance and subtracted. An example corresponding to the $\nu_2 + \nu_4$ R(6)A2 line at a total pressure of 0.098 atm, before and after subtraction of the synthetic background, is given in Fig. 1. The rms noise level in the final spectra ranged between 8×10^{-4} and 5×10^{-4} absorbance units.

In addition to these 8 lines, spectra of the ν_4 P(3)A2 ($\sigma_0 = 1287.813279 \text{ cm}^{-1}$) line were also recorded using a tunable diode laser spectrometer (TDLS) at LLS in Namur, Belgium. The experimental setup is the same as that used in Ref. 7 where detailed descriptions of the spectrometer, the experimental setup, and material supplies can be found. Note that, the influence of the small but asymmetric instrumental distortion which could be due to the detection time constant³¹ was modelled by an asymmetric Lorentzian apparatus function as done in Ref. 7.

IV. DATA ANALYSIS AND RESULTS

For the analysis of both the measured and calculated spectra, we used the same approach as done in some previous studies.^{15–19} For each considered transition and pressure, the absorption spectrum was fitted with the Voigt profile and a baseline. The Doppler half width Γ_D is fixed to its

theoretical value, calculated at the considered temperature while the line area S , the collisional half-width $\Gamma_L(P)$, the effective line-center position $\sigma_0(P)$, and the baseline parameters were adjusted together in the fit.

A sample of measured and calculated absorption spectra and their Voigt fit residuals is shown in Fig. 1. These spectra and their residuals were normalized by their corresponding absorption peak values (at the effective line-center positions). As it is well known, these Voigt residuals have a “W” shape characteristic of a line narrowing. The (maximum-minimum) amplitude of these residuals, indicated by W (see Fig. 1), is a first non-Voigt signature for quantitative comparisons between calculation and measurements. For the measured spectra, the

N_2 -broadening coefficient, $\gamma_L^{N_2}(P_{N_2}) = \frac{\Gamma_L^{N_2}(P_{N_2})}{P_{N_2}}$, is obtained by subtracting from total linewidth the self-broadening contribution [i.e., $\Gamma_L^{N_2}(P_{N_2}) = \Gamma_L(P) - \gamma^{CH_4} \cdot P_{CH_4}$]. Note that the self-broadening contribution is calculated using the CH_4 self-broadening coefficient³³ and the partial pressure of CH_4 , that is, in turn, determined from the retrieved line area and the line intensity given in the HITRAN database.³³ The pressure dependence of $\gamma_L^{N_2}(P_{N_2})$ (see Fig. 2(a) for instance) is a second signature of the non-Voigt effect on the spectral shape.

The value of the measured broadening/shifting coefficients estimated as usual by the slope of the linear fit of the collisional broadening/effective line center position vs pressure (Fig. 2(b)) is reported in Table II. Note that fitting the values of $\Gamma_L(P)$ by the linear law ($\gamma \times P$) generally gives the false impression that $\Gamma_L(P)/P$ is constant (see panel (a)). However, the pressure broadening coefficient γ obtained from such linear fit is essentially determined by the highest pressures for which our obtained value of $\Gamma_L(P)/P$ is almost constant. The comparison between these values and previous determinations shows very good agreement (Table II). Note that

FIG. 2. The pressure dependence of the broadening coefficients (a) and the linear fit of the linewidth versus pressure (b), deduced from the measured spectra of the $\nu_2 + \nu_4$ R(6)A2 line.

the large uncertainties of the measured shifting coefficients of some lines are due to the lower signal to noise ratio of their measured spectra and to the contribution of neighboring lines which was estimated using spectroscopic data of Ref. 33. From the rCMDS spectrum computed without any Doppler contribution (i.e., $\omega_0 = 0$, only the collisional effect is taken into account), the broadening coefficient is deduced by fitting this spectrum with Lorentz profiles. The obtained values are also reported in Table II. Note that in our rCMDS, as we neglect all vibration dependence of the intermolecular potential, there is no pressure shift in the rCMDS calculated spectra. As can be observed in Table II, the calculated broadening coefficient decreases much more quickly with the rotational quantum number m than the measured one. The broadening

parameters deduced from rCMDS calculated spectra are quite close to those obtained from experiments at high values of m but they are much larger (up to 35%) than the corresponding measured ones when m is small. These results are probably due to the classical treatment of the molecule rotation and to the fact that we consider CH_4 as linear molecules in our requantization procedure. Nevertheless, we will see in the following that these rCMDS calculated spectra reproduce very closely the non-Voigt effects observed on the measured spectra.

The amplitudes of the normalized Voigt-fit residuals W (see Fig. 2) of all considered transitions are plotted into 6 panels in Fig. 3; each panel corresponds to a value of $|m|$ (with $m = J + 1$, $m = -J$, and $m = J$ for R, P, and Q branch lines, respectively). The uncertainties of W are estimated based on

TABLE II. Shifting- and broadening-coefficients of the considered lines of CH_4 in N_2 and comparison with previous published values. Values for air-broadening and air-shifting coefficients were converted to those for N_2 using the multiplicative factors given by Pine and Gabard.³⁴ All coefficients are given in $10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$ and the uncertainties of our values (in parentheses, in the same unit as the last digit) are estimated as three times the standard deviation. All measured values refer to the Voigt profile.

Band	Transition	m	$\sigma_0 \text{ (cm}^{-1}\text{)}$	δ^{meas}	δ^{Refs}	δ^{HITRAN}	γ^{meas}	γ^{Refs}	γ^{HITRAN}	γ^{calc}
$\nu_1 + \nu_4$	Q(1)F1	1	4324.933 076	-7.97(6)	-6.96(99) ³⁵ -8.05(40) ³⁶	-8.31	64.76(48)	62.45(10) ³⁵ 66.39(71) ³⁶	65.99	87.63
$\nu_2 + \nu_4$	R(0)A1		2847.719 101	-3.41(2)	-3.4(6) ³⁷	-3.78	61.97(36)	63.5(13) ³⁷	57.77	
$\nu_2 + \nu_4$	R(1)F1	2	2856.963 094	-3.48(8)	-3.5(4) ³⁷	-6.26	65.22(54)	66.4(8) ³⁷	66.09	81.08
$\nu_3 + \nu_4$	Q(2)F2		4330.107 883	-7.55(7)	-6.66(99) ³⁵ -7.55(30) ³⁶	-7.71	66.01(24)	64.67(10) ³⁴ 67.00(81) ³⁶	65.58	
ν_4	P(3)A2	3	1287.813 279		-2.91(9) ³⁸	-2.88	62.29(42)	60.88(15) ³⁸ 59.67(112) ⁷	61.73	76.48
$\nu_2 + \nu_4$	R(6)A2	7	2908.331 351	-6.63(75)	-7.4(2) ³⁷	-6.86	63.07(51)	61.9(4) ³⁷	64.16	57.71
$\nu_3 + \nu_4$	P(8)F1	8	4168.483 790	-10.89(45)	-10.14(30) ³⁶	-9.65	60.85(42)	64.78(71) ³⁶	60.91	51.75
$\nu_3 + \nu_4$	R(7)F1		4427.816 365	-3.62(10)	-3.48(20) ³⁶	-3.58	65.08(57)	66.29(91) ³⁶	64.26	
$\nu_3 + \nu_4$	P(9)A1	9	4161.051 852	-9.74(28)		-10.43	57.15(72)		58.48	48.72

FIG. 3. Peak-absorption-normalized amplitude of the residuals obtained from fit of the measured (red and blue) and calculated (black) spectra with the Voigt profile.

the spectral noises (experimental or numerical noise levels). Within these uncertainties, the values of W deduced from rCMDS calculations are in very good agreement with those obtained from measured spectra. W has the same evolution versus the Γ_L/Γ_D ratio for all considered lines: Its value firstly increases with Γ_L/Γ_D when Γ_L/Γ_D is small, it then reaches a maximum (when Γ_L/Γ_D is around 1), and finally decreases when Γ_L/Γ_D increases and becomes a constant at high values of Γ_L/Γ_D . This evolution of W with Γ_L/Γ_D has been observed for many other molecular systems.^{14–22} As can be seen in Fig. 3, the rotational quantum number dependence of W is not clear when m is small ($m = 1, 2, 3$) but it seems to be more obvious when m is large ($m = 7–9$): W increases with

increasing rotational quantum number. Nevertheless, a larger range of investigated m is needed to confirm this dependence.

The pressure dependence (Fig. 2(a)) of nitrogen broadening coefficients for all measured methane lines is shown in Fig. 4. In order to compare these results with values deduced from calculated spectra, these broadening coefficients are plotted versus the Lorentz to Doppler widths ratio, Γ_L/Γ_D , instead of pressure. Note that these broadening parameters are normalized by their corresponding values obtained at the highest values of the Γ_L/Γ_D ratio. This Γ_L/Γ_D dependence is due to all non-Voigt effects which are not taken into account in the Voigt profile. As well known, fits with the Voigt profile provide underestimated linewidths.⁶ This underestimation

FIG. 4. Γ_L/Γ_D dependence of broadening coefficients. These broadening parameters were normalized by their corresponding values (γ) obtained at the highest values of the Γ_L/Γ_D ratio.

increases when the pressure (or the Γ_L/Γ_D ratio) decreases. The Γ_L/Γ_D dependences of the measured line broadening coefficients are satisfactorily predicted by the rCMDS calculated spectra (Fig. 4). Similar to the case for W, we can observe here that the Γ_L/Γ_D dependence of the broadening coefficient increases with increasing value of m .

These results show that our calculations correctly predict non-Voigt effects on the measured line shapes of CH₄ in N₂ in a large pressure range. These calculations can thus be used as a benchmark for line shape studies of isolated methane lines as well as to determine the relative contribution of velocity changing and of speed dependence. For instance, spectra simulated with rCMDS can be used in order to test various empirical line shape models.⁶ They can therefore help to choose the most appropriate line shape model to describe measured spectra of CH₄ in N₂, as it was done for H₂O for instance.²¹ Once the appropriate model is chosen, rCMDS calculated spectra can also be used to predict the different line shape parameters, especially the high order line shape parameters such as those used to describe the collision-induced velocity changes, the speed dependence of the linewidth, as well as their pressure and temperature dependences, as what was done for CO, for instance.³⁹

V. CONCLUSIONS

Requantized classical molecular dynamic simulations have been used for the first time to calculate the spectral shapes of isolated methane transitions broadened by nitrogen. The calculated spectra have been compared with experimental data recorded with two different laser spectrometers for a large pressure range. The measured lines span a large range of the rotational quantum number, thus providing a meaningful test of the calculations. Comparisons between measured and calculated spectra show that *ab initio* calculated spectra reproduce with very high fidelity the non-Voigt effects observed in the measurements and that classical molecular dynamic simulations can be used to predict spectral shapes of isolated lines of methane perturbed by nitrogen.

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