Isolated line shapes of molecular oxygen: Requantized classical molecular dynamics calculations versus measurements

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We present comparisons between measured isolated line shapes of molecular oxygen in air at various pressures and those calculated, free of any adjusted parameter, using requantized classical molecular dynamics simulations (rCMDS). The measurements have been made for the R1Q2, P9P9, P11P11, P13P13, and P15Q14 transitions in the O$_2$ singlet-$\Delta$ band $[a^1\Delta_s \leftarrow X^3\Sigma_-^+(0,0)]$ by the frequency-stabilized cavity ring-down spectroscopy technique. This work extends a previous study made for a single oxygen line [Phys. Rev. A 87, 032510 (2013)] and confirms the quality of this theoretical approach over broad ranges of pressure and rotational quantum number. Indeed, not only the collisional broadening coefficients but also the (small) deviations of observed line shapes with respect to the Voigt profile are accurately predicted. These results illustrate the viability of using the rCMDS method as a benchmark for the development and testing of simpler parametrized line profiles that are suitable for the analysis of underlying physical mechanisms and for atmospheric remote sensing applications.

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I. INTRODUCTION

There are numerous remote sensing applications which probe the absorption spectra of molecular oxygen and which typically exploit the constant mixing ratio of this species in the Earth’s atmosphere. Commonly probed absorption features include the $\gamma^-$- (0.63 $\mu$m), $B$- (0.69 $\mu$m), and $A$- (0.76 $\mu$m) rovibronic bands of O$_2$, which have been used for wind measurements [1], in the determination of surface pressure [2–4] and aerosol and cloud properties [5–8], and for the retrieval of vertical profiles of pressure and temperature [9,10]. Among the various remote sensing experiments, those targeting the quantification of greenhouse gas concentrations (e.g., GOSAT [11], OCO-2 [12,13], CarbonSat [14]) are the most demanding because they require a relative standard uncertainty of less than 0.3% [12] in the atmospheric pressure profile retrieved from the O$_2$ $A$ band. It is thus obvious that an accurate (better than a few times 0.1% relative uncertainty) forward model for O$_2$ absorption coefficients is required [15]. From this perspective, it has been demonstrated that line mixing and collision-induced absorption effects must be taken into account [16], a problem for which software and data [2] are available. However, the latter models use Voigt profiles of isolated lines, which, as is well known (see Ref. [17] and those therein), is an approximation leading to biases that significantly exceed the required uncertainty.

It is now well known from studies of molecular line shapes that the effects of velocity changes (VC) and of the speed dependence (SD) of the collisional parameters (neither of which is modeled by the Voigt profile) must be taken into account [18]. Nevertheless, the situation for O$_2$ remains uncertain despite the numerous laboratory studies. Indeed, among the many available approaches [18], the reasons given by different authors for choosing specific line shape models are not always clearly stated. In some oxygen line-shape studies, transitions have been analysed using Galatry [19–26] or Rautian [22,23,26] profiles thus taking into account only VC but disregarding the effects of SD. The opposite assumption has also been made; the speed-dependent Voigt model being thus used while effects of VC are disregarded [22,25–27]. Several alternative line shapes based on combinations of various VC and SD models have also been tested, as in [25,26]. One must then rely on the quality of the fit of experimental spectra for a conclusion on the physical processes involved and the model adequacy. Hence, there is a compelling need for a physically based approach to predict the respective contributions of the VC and SD effects on O$_2$ line shapes. This step must be resolved before an appropriate line profile is proposed for practical applications. To this end, we envisage that the relative contributions of these mechanisms can be calculated through requantized classical molecular dynamics simulations (rCMDS), since recent results [28–30] indicate that rCMDS yield accurate calculations of line profiles free of any adjustable parameters. These simulations could be used as the starting basis for line shape calculations similar to those made in Refs. [31–34]. In this semiclassical approach, the line shape is calculated from a kinetic equation that drives the dipole autocorrelation function in which VC and SD effects (and their eventual correlation) are explicitly included. For the calculation of O$_2$ line shapes, we have thus adopted the strategy proposed in Ref. [28], which involves several steps. First, we will validate the rCMDS method by comparing calculated and measured line shapes. Second, we will input VC and SD parameters (extracted from rCMDS) into a kinetic equation for the autocorrelation function (likely similar to that used in Ref. [32]) of the considered line to yield a simpler model for the spectral line shape. This step will be followed by tuning the broadening coefficient used in this simpler model through comparisons with measured spectra. Finally, we will define a parametrized line profile, which is readily calculable using input data (to be) stored in spectroscopic databases and which

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is suitable for atmospheric radiative transfer calculations. We note that the line profile proposed in Ref. [33] incorporates VC, SD, as well as correlation effects and is expected to solve this last problem.

This paper addresses the first step described above which involves experimental validation of rCMDS. By considering various lines of molecular oxygen in air, the present work extends the previous study of Ref. [29] in which only the P11P11 transition was investigated and calculations were made for the case of pure oxygen. This is done using new measurements made, at various pressures, for the R1Q2, P9P9, P11P11, P13P13, and P15Q14 transitions in the O2 singlet-Δ band \([a^1Δ_g ← X^3Σ_g^−(0,0)]\) by the frequency-stabilized cavity ring-down spectroscopy technique. The remainder of this paper is divided into three sections. These comprise descriptions of the experimental and the rCMDS-calculated spectra and their analyses in Sec. II, a comparison of measured and predicted results (in particular the non-Voigt effects) in Sec. III, and concluding remarks given in Sec. IV.

II. EXPERIMENTAL AND THEORETICAL SPECTRA AND THEIR ANALYSES

A. Experimental spectra

Room-temperature absorption spectra of individual transitions of the O2 singlet-Δ band, \(a^1Δ_g ← X^3Σ_g^−(0,0)\), were acquired at the National Institute of Standards and Technology (NIST) using the frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) technique as described in Refs. [35,36]. The present FS-CRDS system consists of an actively length-stabilized ring-down cavity having a finesse of \(~6 \times 10^4\) and minimum detectable absorption coefficient (1 s averaging time) of \(~2 \times 10^{-10}\) cm\(^{-1}\). We measured the R1Q2, P9P9, P11P11, P13P13, and P15Q14 transitions, which were chosen to span a wide range of rotational quantum numbers and yield high signal-to-noise ratios. The rotational identifications correspond to \(ΔN^JΔJJ′′\), where \(J\) is the total rotational quantum number given by the sum of the rotational \(N\) and the spin \(S\) quantum numbers, and the double prime refers to the lower state quantum numbers. For the \(a^1Δ_g ← X^3Σ_g^−(0,0)\) band \(S′′ = 1\), Spectra were acquired by step scanning the laser to sample successive longitudinal modes of the ring-down cavity and averaging 200 ring-down decay constants at each step. For a peak single-pass absorbance of \(~5 \times 10^{-5}\), the relative combined standard uncertainty of the averaged, baseline-corrected peak absorption signal was \(~0.03\%\). We used a continuous wave, transverse-mode-matched laser beam (\(~2\) mW incident power) from an external cavity diode laser to probe individual transitions. Signal acquisition and laser scanning and relocking took about 30 s per step. With this scheme, the sampling interval of the spectrum detuning axis corresponds to the cavity free spectral range (FSR), with a resolution limited by the long-term stability (\(~500\) kHz) of the reference HeNe laser to which the cavity is locked. The FSR of the empty cavity was measured to be 201.4516(8) MHz and corrected for the slight dependence on the sample density and refractive index. Accounting for the systematic uncertainty in FSR and variations in the reference laser frequency, the combined standard uncertainty of the spectrum detuning axis was \(~250\) kHz. All spectra were acquired on static samples of synthetic air (79.28% N\(_2\), 20.72% O\(_2\)) over the pressure range 6.7 to 100 kPa. As previously discussed [28] the relatively broad spectrum sampling interval does not permit one to probe all line shape details. Nevertheless, fits of measured spectra enabled accurate and precise determinations of the Doppler and Lorentz widths. Indeed, based on measurements made in the low pressure limit, we estimate a relative bias of less than 0.05% for the measured Doppler width, thus quantifying the magnitude of residual spectrometer-induced effects on the line shape.

B. Calculated spectra

As is well known [18], the normalized absorption coefficient resulting from the interaction of a molecule’s intrinsic transition moment with an electromagnetic field of angular frequency \(ω\) is given by the Fourier-Laplace transform of the autocorrelation function (ACF) of the transition moment. This ACF is calculated here using requantized classical molecular dynamics simulations (rCMDS). This is done exactly as described in [28,29], but in the present case for a mixture of O\(_2\) (20%) and N\(_2\) (80%). In these rCMDS, the force and torque applied to each molecule by its surrounding neighbors are computed classically. This provides the center-of-mass position and velocity, the unit velocity vector \(\vec{u}_m(t)\) along the molecular axis, and the rotational angular momentum for each molecule \(m\) at each time \(t\). The dipole ACF is then directly obtained by the average over all molecules of the scalar product \(\vec{u}_m(0) \cdot \vec{u}_m(t)\). Since details of this approach can be found in [28,29] and references therein, only the specific features for the present oxygen-in-air calculations are described here. A total number \(N_T = N_M N_B\) of rigid O\(_2\) and N\(_2\) molecules is considered, distributed among \(N_B\) independent boxes. Each of these boxes contains 0.2N\(_M\) O\(_2\) molecules and 0.8N\(_M\) N\(_2\) molecules and is treated with periodic boundary conditions by the core of a parallel supercomputer. For the present analysis, 24 \times 10^6\) molecules of O\(_2\) were considered using \(N_B = 4096\) boxes with \(N_M = 30,000\). The calculations were carried out to \(t_{\text{max}} = 400\) ps with a time step of 2 fs and a temperization time of 50 ps for thermalization. All intermolecular interactions were described by pairwise 6-12 Lennard-Jones atom-atom potentials complemented by Coulombic forces between fictitious charges that were introduced to reproduce the electric quadrupoles of the molecules. The atom-atom data for O\(_2\)-O\(_2\) and N\(_2\)-N\(_2\) were taken from Refs. [29] and [37], respectively, and the corresponding parameters for O\(_2\)-N\(_2\) were deduced from the standard combination rules [38]. The requantization procedure proposed in Ref. [28] was applied and the electronic spin of O\(_2\) was neglected. Thus, the rotational quantum number \(N''\) is equal to the total rotational quantum number \(J''\) and PP and PQ transitions are identical (as for RR and RQ). We note that this approximation is likely of small consequence because differences between the half-widths of the various transitions with the same \(N''\) (e.g., PP and PQ for example) are small [24]. In order to simulate spectra for various Doppler widths, calculations were made at room temperature (296 K) and at a total pressure of 203 kPa for various values of the wave vector, as in Ref. [28]. Thirteen wave vectors were considered (corresponding to wave numbers from 0 to about 26 \times 10^4\) cm\(^{-1}\).
yielding values of the Lorentz-to-Doppler-width ratio $\Gamma_L/\Gamma_D$ from about 0.1 to infinity. The results thus span the domain from the nearly Doppler limited to the purely collisional regime.

C. Analysis of spectra

In the present analysis the experimental and theoretical (rCMDS) spectra were fit using Voigt line profiles, as previously reported in Refs. [28,29,39,40], whereas the Doppler widths $\Gamma_D$ were fixed to their theoretical values according to the considered transitions and measured temperature. This fitting procedure yielded the position $\gamma_0$, the integrated intensity $S$, the Lorentz half-width at half maximum (HWHM) $\Gamma_L$, and a linear baseline. For fits to the calculated spectra, we chose wave number intervals that were 4 cm$^{-1}$ wide and centered on individual lines. In the case of the experimental spectra, the entire measured interval was considered in the fits. Below we compare the pressure-normalized Lorentz HWHMs $\Gamma_L/P$ as well as the shape and amplitude of the Voigt fit residuals for the experimental and theoretical cases.

III. RESULTS AND DISCUSSION

A. Line broadening coefficients

A first test of the theoretical model is made here by considering the pressure-normalized Lorentz broadening coefficients $\gamma^0 = \Gamma_L/P$ obtained in the purely collisional regime (i.e., for $P$ and $\Gamma_L/\Gamma_D \to +\infty$). Indeed, as widely shown (e.g., Refs. [28,29] and Sec. III B) $\Gamma_L/P$ depends on $P$ but tends to an asymptotic value when $P \to \infty$. The theoretical values have thus been obtained from Voigt fits to the rCMDS-calculated spectra for $\Gamma_D = 0$. Recall (Sec. II A) that the present measurements of the R1Q2, P9P9, P11P11, P13P13, and P15Q14 transitions were made for pressures up to $P_{\text{max}} \approx 100$ kPa. For this pressure, $\Gamma_L/\Gamma_D \approx 6$, which is significantly greater than unity so that the asymptotic value is practically reached. In addition to these experimental broadening coefficients, we also consider the values of [41], the results of Refs. [27] and [42] in which a Voigt profile was used, and those of [24] where a Galatry profile was employed. This data compilation, plotted in Fig. 1, shows the quality of the rCMDS predictions and the consistency of the various measurements (within about $\pm 2\%$ up to $|m| = 20$, where $|m| = N''$ or $N'' + 1$ for P and R branch, respectively). Note that as PP and PQ (or RR and RQ) transitions are identical in the calculations, but not in the measurements, there may be two values of $\gamma^0$ for each $|m|$ value. Finally, despite the fact that the results of Refs. [24,27,42] are for the $A$ band [$b^1\Sigma^+_g \leftrightarrow X^3\Sigma^+_g (0,0)$], they have been considered in this study as they are the most recent and accurate results available in the literature. In addition, the band dependence is expected to be small.

B. Non-Voigt effects

For a first test of how well the rCMDS predict non-Voigt effects, we compared values of the pressure broadening coefficient $\gamma_L(P) = \Gamma_L/P$ obtained from measured and calculated spectra. The results are presented in Fig. 2 where the $\gamma_L(P)$ value of each line is normalized by the corresponding highest-pressure value. This normalization enables comparison of the various transitions and corrects for the (small) differences

![image1](image1.png)

**FIG. 1.** (Color online) Pressure normalized Lorentz HWHM $\gamma^0$ (see text) versus the rotational quantum number $|m|$ ($=N''$ for P lines and $N''+1$ for R lines). The (black) line shows the results obtained from fits of the rCMDS-calculated spectra. The symbols are data from the HITRAN database [41] (green down triangles) and Ref. [24] (red stars), and values obtained from Voigt fits of measured spectra from the present work (black circles), and Refs. [27] (magenta squares) and [42] (blue triangles). The calculations, the present measurements and the data from Ref. [41] are for the $O_2$ singlet-$\Delta$ band [$a^1\Delta_g \leftrightarrow X^3\Sigma^+_g (0,0)$], whereas the other measurements are for the $A$ band [$b^1\Sigma^+_g \leftrightarrow X^3\Sigma^+_g (0,0)$]. The error bars for $|m| = 0$ and 30 correspond to $\pm 5\%$.

![image2](image2.png)

**FIG. 2.** (Color online) Observed (symbols) and theoretical (lines) collisional broadening coefficient $\Gamma_L(P)/P$ normalized by the value at the highest pressure. The results are for the R1Q2 (blue, open circles), P9P9 (black, squares), P11P11 (red, full circles), P13P13 (olive, up triangles), and P15Q14 (magenta, down triangles) transitions of the $O_2$ singlet-$\Delta$ band [$a^1\Delta_g \leftrightarrow X^3\Sigma^+_g (0,0)$]. The error bar on the left side corresponds to $\pm 2\%$. 

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between the measured and calculated asymptotic values (see Fig. 1). As expected from similar studies \cite{28,29,40}, we find that $\gamma_L(P)$ is not constant. This pressure dependence is a signature of non-Voigt effects \cite{28} and is well predicted by the rCMDS except for in the limit $\Gamma_L \ll \Gamma_D$. However, this apparent discrepancy may not be real and could be explained by the fact that at low-pressure the line shape is almost purely Gaussian. The contribution of $\Gamma_L$ to the line shape is then very small making its determination (from both calculated and experimental spectra) highly uncertain. Note that, interestingly, both the experimental and theoretical values in Fig. 2 show a small variation (within an uncertainty of 1%–2%) of the non-Voigt effects from line to line (i.e., vs the rotational quantum numbers). The calculated values indicate that the reduction in normalized $\gamma_L(P)$ with decreasing pressure increases with increasing rotational quantum number. However, this effect remains too small to make a definitive conclusion regarding its validity.

A second signature of non-Voigt effects that can be used to test the rCMDS calculations lies in the residuals of the Voigt fits. As is well known, they have a “W” shape \cite{28,29} that captures the fact that the true line shape is narrowed due to both VC and SD. Typical residuals of the fit of the rCMDS-calculated and measured spectra of the P9P9 line are presented in Fig. 3 for three pressures, with the same $x$ and $y$ scales. As can be seen, the agreement is quite satisfactory for both the amplitude and width of the W residuals. Recall that the “noise” in the rCMDS results is caused by the limited number of molecules treated, resulting in not-fully-converged statistics as discussed in Ref. \cite{28}. This particularly affects the residuals for the limiting cases $\Gamma_L \gg \Gamma_D$ and $\Gamma_L \ll \Gamma_D$, where non-Voigt effects (and the W amplitude) are small. Also note that the measured spectra are somewhat undersampled at low pressure for reasons explained in Sec. II A and Ref. \cite{29}.

Finally, and as done before in Refs. \cite{28,29,39}, an overall view can be obtained by considering the amplitude of the W residuals relative to the peak absorption, i.e., $A_W/\alpha(\sigma_0)$, where $A_W$ is the maximum-minimum amplitude of the W residuals and $\alpha(\sigma_0)$ is the peak value of the absorption. The results plotted in Fig. 4 show a good agreement between experimental and theoretical results, for both the amplitude of $A_W/\alpha(\sigma_0)$ and its dependence on $\Gamma_L/\Gamma_D$. As previously observed for CO$_2$ \cite{28}, H$_2$O \cite{32,40}, and the P11P11 line of O$_2$ \cite{29}, the relative deviation from the Voigt profile has a maximum around $\Gamma_L/\Gamma_D \approx 1$ and decreases toward zero when approaching the Doppler limit ($\Gamma_L/\Gamma_D \ll 1$). Asymptotic nonzero values are expected \cite{28,29} in the collisional regime ($\Gamma_L \gg \Gamma_D$) which cannot be clearly discerned with the present data but which are likely around 0.5%. Discussing the line to line variations from the results would be very hazardous for two reasons. For the theoretical results, the previously mentioned noise on rCMDS-calculated spectra (see Fig. 3) induces an uncertainty on the determination of the W amplitude. It can be estimated as about ±0.2% around the peaks near $\Gamma_L/\Gamma_D \approx 1$ and explains why a determination for the weak R1Q2 line could not be made, except near the maximum. For the experimental determination,
IV. CONCLUSION

The long-term goal of this research is to propose an accurate and readily calculable line profile for molecular oxygen, which is more general than the Voigt profile yet suitable for spectroscopic measurements of isolated air-broadened oxygen lines. Line shapes were calculated based on restandardized classical molecular dynamics simulations (rCMDS) for air (20% O2 + 80% N2), and high-precision absorption spectra were acquired on the near-infrared 1Δ band of O2 using the frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) technique. This comparison of calculated and measured pressure-broadened spectra (through fits using Voigt profiles) demonstrates that the rCMDS can be used to predict subtle but often-observed departures from the Voigt profile. These results validate the first step of our strategy as discussed in the Introduction, which is aimed at understanding the most important mechanisms that affect line shape in air-broadened oxygen spectra. The second step is currently under investigation and involves determination of the parameters quantifying velocity changes and speed dependent broadening due to collisions, both of which can be extracted from rCMDS. These results will be incorporated into a kinetic equation that describes the time evolution of the transition dipole autocorrelation function, from which the line shape can be more easily calculated. The resulting line profiles will then be compared with those based on rCMDS and high-precision spectroscopic measurements. The validation of the simpler approach is expected to facilitate routine quantitative analysis of the physical processes that influence the line shape.

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