Bulk viscosity of CO$_2$ from Rayleigh-Brillouin light scattering spectroscopy at 532 nm

Yuanqing Wang, Wim Ubachs, and Willem van de Water

ARTICLES YOU MAY BE INTERESTED IN

Two-body interatomic potentials for He, Ne, Ar, Kr, and Xe from ab initio data
The Journal of Chemical Physics 150, 134504 (2019); https://doi.org/10.1063/1.5085420

Dispersion truncation affects the phase behavior of bulk and confined fluids: Coexistence, adsorption, and criticality
The Journal of Chemical Physics 150, 154104 (2019); https://doi.org/10.1063/1.5085431

Thermofield theory for finite-temperature quantum chemistry
The Journal of Chemical Physics 150, 154109 (2019); https://doi.org/10.1063/1.5089560
Bulk viscosity of CO$_2$ from Rayleigh-Brillouin light scattering spectroscopy at 532 nm

Yuanqing Wang,$^{1}$ Wim Ubachs,$^{1,2}$ and Willem van de Water$^2$

ABSTRACT

Rayleigh-Brillouin scattering spectra of CO$_2$ were measured at pressures ranging from 0.5 to 4 bars and temperatures from 257 to 355 K using green laser light (wavelength 532 nm, scattering angle of 55.7°). These spectra were compared to two line shape models, which take the bulk viscosity as a parameter. One model applies to the kinetic regime, i.e., low pressures, while the second model uses the continuum, hydrodynamic approach and takes the rotational relaxation time as a parameter, which translates into the bulk viscosity. We do not find a significant dependence of the bulk viscosity with pressure or temperature. At pressures where both models apply, we find a consistent value of the ratio of bulk viscosity over shear viscosity $\eta_b/\eta_s = 0.41 \pm 0.10$. This value is four orders of magnitude smaller than the common value that is based on the damping of ultrasound and signifies that in light scattering only relaxation of rotational modes matters, while vibrational modes remain "frozen."

I. INTRODUCTION

The light scattering properties of carbon dioxide remain of interest, both from a fundamental perspective studying the relaxation in molecular gases and for determining their thermodynamic properties, as well as from an applied perspective. Details of Rayleigh-Brillouin (RB) phenomena, scattering spectral profiles of CO$_2$ gas at differing pressures and temperatures, as well as its cross section, are of relevance for current and future remote sensing exploration of the planetary atmospheres where CO$_2$ is the main constituent, either under high-pressure and high-temperature conditions as on Venus or under low pressure and low-temperature conditions as on Mars. The fact that carbon dioxide is the prime greenhouse gas has spurred large-scale activity in the transformation of this gaseous species, through catalytic hydrogenation, and electrochemical conversion into renewable energy, as well as in plasma-driven dissociation for the synthesis of fuel from CO$_2$. Apart from issues of capture, fixation, and transformation of terrains of carbon dioxide, its storage and transport, either in the liquid or gas phase, forms an important challenge. For these purposes, the study of the transport coefficients of CO$_2$ gas, such as thermal conductivity, heat capacity, and shear viscosity, is of practical importance. Light scattering is an elegant way to determine the thermodynamic properties of a gas because the Rayleigh scattering phenomenon resulting in the elastic peak is connected to entropy fluctuations, while the Brillouin-side peaks are associated with density fluctuations or sound. The macroscopic gas transport coefficients govern the scattering spectral profiles and can in turn be deduced from the measurement of such profiles. This holds for both spontaneous RB-scattering and coherent RB-scattering.

The bulk viscosity, $\eta_b$, is the most elusive transport coefficient. It is associated with the relaxation of internal degrees of freedom of the molecule, i.e., rotations and vibrations. The bulk viscosity is commonly measured from the damping of ultrasound at frequencies of the megahertz domain. It can also be retrieved from the light scattering spectrum of molecular gases. This was demonstrated by Pan et al. and recently for N$_2$, O$_2$, and air by Gu and Ubachs and for N$_2$O gas by Wang et al. In light scattering, the frequencies $f_i$ involved are those of sound with wavelengths comparable to that of light, three orders of magnitude larger than the frequencies used to measure $\eta_b$ from ultrasound experiments. The bulk viscosity of CO$_2$...
from light scattering is found to be four orders of magnitude smaller than that from ultrasound experiments. A simple explanation is that at high (hypersound) frequencies the relaxation of vibrational modes of the CO₂ molecule no longer plays a role, i.e., the vibrational energy stays frozen in.

The bulk viscosity can be expressed in terms of relaxation times of intramolecular degrees of freedom

\[ \eta_b = \frac{p}{(3 + \sum N_i i^2)} \sum N_i \tau_i, \tag{1} \]

where \( p \) is the pressure, \( N_i \) is the number of degrees of freedom of mode \( i \) (rotations, vibrations), and \( \tau_i \) is the relaxation time \( (\tau_{\text{rot}}, \tau_{\text{vib}}) \).\(^3\) A frequency-dependent version of this formula, depending on the product \( f_i \tau_i \), was given by Meijer.\(^3\) Carbon dioxide is a linear molecule with 2 rotational degrees of freedom. In the case of frozen vibrations \( (\tau_{\text{rot}}, \tau_{\text{vib}}) \gg 1 \), Eq. (1) reduces to

\[ \eta_b = \frac{4}{25} p \tau_{\text{rot}}. \tag{2} \]

The vibrational relaxation time strongly decreases with temperature, and so does the bulk viscosity. In a simple model, Landau and Teller proposed an exponential dependence of the chance of relaxation on the ratio of the collision interaction time and the vibration period.\(^3\) This leads to a scaling prediction for the temperature dependence of the bulk viscosity which agrees with the experiment.\(^3\) On the other hand, a classical analysis of collisions of rigid rotors by Parker\(^3\) results in a scaling expression for \( \tau_{\text{rot}} \) which predicts an "increase" in \( \tau_{\text{rot}} \) with increasing temperature.

The bulk viscosity changes with temperature motivated the present study in which laser-based light scattering measurements in CO₂ gas are carried out in a pressure regime of 0.5–4 bars and in a temperature regime of 257–355 K. Accurate, highly spectrally resolved and high signal-to-noise scattering line profiles are measured at a scattering angle of 55.7° and a wavelength of \( \lambda_s = 532 \) nm, a wavelength commonly used in Lidar applications. Under these conditions of a longer wavelength and a smaller scattering angle than in a previous study,\(^1\) the Brillouin-side peaks become more pronounced in the scattering spectrum.

Experimental data are analyzed in the context of two models for the spectral line shape. One model applies at low pressures, the kinetic regime where the mean free path between collisions is comparable to the wavelength of light,\(^3\) while the other one is valid in the hydrodynamic regime.\(^3\) Values of the bulk viscosity are determined using a least squares method by comparing model spectra to the measured ones.

The remainder of this article consists of an experimental section, a section discussing the bulk viscosity and model descriptions for RB-scattering, a presentation of results in the context of applicable models to describe the scattering spectrum, followed by a conclusion.

II. EXPERIMENT

The experimental apparatus for measuring the RB-scattering spectral profiles of CO₂ is displayed in Fig. 1. The laser source provides continuous wave radiation at \( \lambda_s = 532.22 \) nm at a bandwidth of less than 5 MHz. RB-scattered light is produced from the laser beam of 5 W intensity traversing a gas cell equipped with a gas inlet valve and a pressure sensor. Brewster-angled windows are mounted at the entrance and exit ports, and black paint covers the inside walls, to reduce unwanted scatter contributions. A temperature control system equipped with Peltier elements is employed for heating, cooling, and keeping the cell at a constant temperature with uncertainty less than 0.1 °C. RB-scattered light is captured at a scattering angle \( \theta = (55.7 \pm 0.3)^\circ \) defined by the setting of a slit in the scatter beam path (see Fig. 1), which also limits the opening angle for collecting RB-scattered light to less than 0.5°. The exact scatter angle and uncertainty are determined with

![FIG. 1. Schematic of the experimental apparatus. A Verdi-V5 laser provides continuous wave light at 532.22 nm at a power of 5 W and a bandwidth less than 5 MHz. The laser light is split into two beams. The pump beam crosses the RB-scattering gas cell producing scattered light that is captured under an angle \( \theta = (55.7 \pm 0.3)^\circ \) defined by the setting of a slit in the scatter beam path (see Fig. 1), which also limits the opening angle for collecting RB-scattered light to less than 0.5°. The exact scatter angle and uncertainty are determined with](attachment://fig1.png)
a rotatable stage operated as a goniometer. A reference beam as depicted in Fig. 1 is used for aligning the collection and detection system. The scattering angle determines the scattered light wave vector \( k_{\text{sc}} \)

\[
k_{\text{sc}} = \frac{2\pi}{\lambda_i} 2 \sin(\theta/2),
\]

with \( n \) being the index of refraction.

The scattered light propagates through a bandpass filter (Materion, \( T > 90\% \) at \( \lambda_i = 532 \text{ nm} \), bandwidth \( \Delta \lambda = 2.0 \text{ nm} \)) onto a Fabry-Pérot interferometer (FPI) via an optical projection system consisting of a number of lenses and pinholes to reduce stray light and contributions from Raman scattering. Finally, the scattered photons are detected on a photomultiplier tube (PMT), processed, and stored in a data acquisition system. The FPI is half-confocal, the curved mirror having a radius of curvature of \( r = -12.5 \text{ mm} \). Mirror reflectivities are 99\%. The FPI has an effective free spectral range (FSR) of 2.9964 GHz, which is determined through frequency-scanning a laser (a narrowband tunable cw-ring dye laser) over more than 1000 modes of the FPI while measuring the laser wavelength by a wavelength meter (Toptica HighFinesse WSU-30), hence yielding an uncertainty in the FSR below 1 MHz. The instrument width, yielding a value of \( \sigma_{\epsilon,\text{FWMH}} = 58.0 \pm 3.0 \text{ MHz} \) (FWHM), is determined by using the reference beam while scanning the piezo-actuated FPI, following the methods discussed by Gu et al.\(^{37}\) It includes the bandwidth of the incident laser. The instrument function is verified to exhibit the functional form of an Airy function, which may be well approximated by a Lorentzian function during data analyses.

RB-scattering spectral profiles were recorded by piezo-scanning the FPI at integration times of 1 s for each step, usually over 18 MHz. Typical detection rates were \( \sim 2000 \text{ counts/s} \) for conditions of 1 bar pressure. A full spectrum covering lots of consecutive RB-peaks and 10 000 data points was obtained in about 3 h. The piezo-voltage scans were linearized and converted to frequency scale by fitting the RB-peak separations to the calibrated FSR-value. The linearization procedure also corrects for frequency drifts of the laser, which were measured to amount to 10–100 MHz/h, depending on temperature drifts in the laboratory. Finally, a collocated spectrum was obtained by cutting and adding all individual recordings over \( \sim 60 \) RB-peaks.\(^{37}\) In a final step, the RB scattering profiles were averaged to improve the signal to noise ratio. This procedure yields a noise level of \( \sim 0.4\% \) (with respect to peak height) for the 1 bar pressure case. A single typical light scattering spectrum recorded at 1 bar and room temperature, measured in a typical recording time of \( \sim 3 \text{ h} \), is displayed in Fig. 2. Figure 2 and its inset demonstrate the signal-to-noise ratio attainable in the present setup.

III. RB-SCATTERING AND LINE SHAPE MODELS

In light scattering, the key quantity is the uniformity parameter \( y \), which—up to a constant—is defined as the ratio of the scattering wavelength over the mean free path between collisions, which can be shown to equal

\[
y = \frac{p}{k_{\text{sc}} v_0 \eta_b},
\]
with thermal velocity \( v_0 = \left(\frac{2k_B T}{m}\right)^{1/2} \), where \( k_B \) is the Boltzmann constant, \( m \) is the molecular mass, and \( \eta_s \) is the shear viscosity.

Values \( y = \mathcal{O}(1) \) pertain to the kinetic regime, and models must be based on the Boltzmann equation. There, spectra do not deviate strongly from the Rayleigh (Maxwellian) line shape. At larger values of \( y \), many mean free paths fit in a wavelength and a hydrodynamic, continuum approach applies. The Brillouin-side features become more and more prominent with increasing \( y \) and occur at frequency shifts \( f_s = \pm \upsilon s k_{sc}/2\pi \), with \( \upsilon s \) being the speed of sound.

Our data are in the interval \( y = [0.7–9] \) and, therefore, range from the kinetic into the hydrodynamic regime.

### A. The Tenti model

The Tenti model, originally developed for analyzing RB-scattering in molecular hydrogen and diatomic molecules, is a widely used model for light scattering spectra in the kinetic regime. It uses the Wang Chang–Uhlenbeck eigentheory which takes known values of the macroscopic transport coefficients as input. This input consists of values for the shear viscosity \( \eta_s \), thermal conductivity \( \lambda_{th} \), the molar heat capacity \( C_{int} \) of internal modes of motion (rotations, vibrations), and the bulk viscosity \( \eta_b \). The model agrees well with experiments, where it was established that the six-mode version of the Tenti model (hereafter called the Tenti-S6 model) is widely used for light scattering spectra in the kinetic regime.

### TABLE I. Datasets for RB-scattering measurements in CO₂ gas recorded under conditions as indicated. The uniformity parameter is \( y \). For values of the temperature-dependent \( \eta_s \) and \( \lambda_{th} \), we used the values Boushehri et al. and Eq. (3), respectively. The bulk viscosity and the ratios \( \eta_b^T/\eta_s \) are derived in a fit to the experimental data. The bulk viscosity \( \eta_b^T \) is based on the Tenti-S6 model, while \( \eta_b^H \) is based on the Hammond–Wiggins hydrodynamic model.

| Dataset | \( p \) | \( T \) | \( \eta_s \times 10^{-5} \) | \( \lambda_{th} \times 10^{-3} \) | \( \eta_b^T \times 10^{-5} \) | \( \eta_b^T/\eta_s \) | \( \eta_b^H \times 10^{-5} \) | \( \eta_b^H/\eta_s \) | \( y \) |
|---------|--------|--------|----------------|-----------------|-----------------|----------------|----------------|----------------|--------|
| Unit    | bars  | K      | Pa s           | W/m k           | Pa s            | W/m k         | Pa s            | W/m k          |       |
| 0.5 bar | 0.500 | 273.2  | 1.37           | 13.4            | 0.64            | 0.47          | 0.30            | 0.23            | 1.03   |
|         | 0.500 | 293.2  | 1.47           | 14.3            | 0.72            | 0.49          | 0.30            | 0.23            | 0.93   |
|         | 0.505 | 313.2  | 1.56           | 15.3            | 0.91            | 0.58          | 0.35            | 0.28            | 0.85   |
|         | 0.508 | 333.2  | 1.66           | 16.2            | 1.65            | 0.99          | 0.30            | 0.20            | 0.78   |
|         | 0.503 | 353.2  | 1.75           | 17.1            | 1.79            | 1.02          | 0.30            | 0.19            | 0.71   |
| 1 bar   | 1.033 | 258.1  | 1.30           | 12.7            | 0.50            | 0.38          | 0.30            | 0.23            | 2.32   |
|         | 1.038 | 274.3  | 1.38           | 13.4            | 0.46            | 0.33          | 0.24            | 0.18            | 2.13   |
|         | 1.055 | 312.9  | 1.56           | 15.2            | 0.69            | 0.45          | 0.31            | 0.20            | 1.79   |
|         | 1.048 | 330.8  | 1.65           | 16.1            | 0.77            | 0.47          | 0.33            | 0.20            | 1.62   |
|         | 1.028 | 353.2  | 1.75           | 17.1            | 0.67            | 0.38          | 0.34            | 0.19            | 1.46   |
| 2 bars  | 2.012 | 257.4  | 1.29           | 12.6            | 0.47            | 0.37          | 0.49            | 0.38            | 4.54   |
|         | 2.037 | 274.5  | 1.38           | 13.4            | 0.46            | 0.34          | 0.45            | 0.33            | 4.18   |
|         | 2.000 | 293.2  | 1.47           | 14.3            | 0.40            | 0.27          | 0.37            | 0.25            | 3.71   |
|         | 2.047 | 312.9  | 1.56           | 15.2            | 0.60            | 0.38          | 0.47            | 0.30            | 3.47   |
|         | 2.050 | 331.8  | 1.65           | 16.1            | 0.70            | 0.42          | 0.51            | 0.31            | 3.15   |
|         | 2.042 | 354.8  | 1.76           | 17.1            | 0.64            | 0.36          | 0.40            | 0.23            | 2.89   |
| 3 bars  | 3.012 | 257.1  | 1.29           | 12.6            | 0.66            | 0.51          | 0.73            | 0.57            | 6.80   |
|         | 2.996 | 273.2  | 1.37           | 13.4            | 0.65            | 0.47          | 0.63            | 0.46            | 6.18   |
|         | 3.037 | 295.7  | 1.48           | 14.4            | 0.66            | 0.45          | 0.68            | 0.46            | 5.59   |
|         | 3.050 | 313.7  | 1.56           | 15.3            | 0.77            | 0.49          | 0.75            | 0.48            | 5.15   |
|         | 3.064 | 332.4  | 1.65           | 16.1            | 0.98            | 0.59          | 0.89            | 0.54            | 4.76   |
|         | 3.021 | 354.4  | 1.76           | 17.1            | 0.75            | 0.43          | 0.61            | 0.35            | 4.28   |
| 4 bars  | 4.026 | 258.1  | 1.29           | 12.6            | 0.98            | 0.76          | 1.07            | 0.83            | 9.04   |
|         | 4.052 | 274.9  | 1.34           | 13.5            | 0.70            | 0.51          | 0.79            | 0.57            | 8.29   |
|         | 4.048 | 295.2  | 1.48           | 14.4            | 0.61            | 0.41          | 0.70            | 0.47            | 7.46   |
|         | 4.041 | 313.1  | 1.56           | 15.3            | 0.73            | 0.47          | 0.78            | 0.50            | 6.84   |
|         | 4.042 | 332.7  | 1.65           | 16.2            | 0.86            | 0.52          | 0.86            | 0.52            | 6.27   |
|         | 4.000 | 353.5  | 1.75           | 17.1            | 0.94            | 0.54          | 0.89            | 0.51            | 5.68   |
We use the values for a temperature dependent shear viscosity \( \eta_s(T) \) for \( \text{CO}_2 \) from the work of Boushehri et al.\(^{39} \) Of the transport coefficients needed in the model, \( \lambda_{\text{th}} \), \( C_{\text{int}} \), and \( \eta_b \) depend on the participation of intramolecular modes of motion. We assume that at the frequencies associated with light scattering, only rotations participate in the exchange of internal and kinetic energy so that \( C_{\text{int}} \) for the linear \( \text{CO}_2 \) molecule becomes \( C_{\text{int}} = 2/2 R \) with \( R \) being the gas constant.

For the thermal conductivity \( \lambda_{\text{th}} \), Uribe et al.\(^{15} \) listed temperature-dependent values. As in the present study only the thermal conductivity associated with “rotational” relaxation is considered, these values are not straightforwardly applicable to RB-scattering data. We need a value that reflects rotational internal energy only. For polyatomic gases, a high-frequency value for \( \lambda_{\text{th}} \) was estimated from the Eucken relation, which expresses \( \lambda_{\text{th}} \) as a function of the shear viscosity \( \eta_s \), the diffusivity \( D \), and the heat capacity \( C_{\text{int}} \) of internal motion

\[
\lambda_{\text{th}} = \frac{5}{2} \eta_s C_{\text{int}} + \rho D C_{\text{int}},
\]

with \( C_{\text{t}} = 3/2 R \), the heat capacity of kinetic motion, \( C_{\text{int}} = 2/2 R \) and the temperature-dependent diffusivity \( D \) taken from the work of Boushehri et al.\(^{39} \) At temperature \( T = 296.55 \, \text{K} \), the low-frequency value is \( \lambda_{\text{th}} = 1.651 \times 10^{-2} \, \text{W/m K} \) (Ref. 15), whereas Eq. (3) predicts a high-frequency value \( \lambda_{\text{th}} = 1.452 \times 10^{-2} \, \text{W/m K} \). As will be demonstrated below, the smaller value indeed produces a better fit of the kinetic model. The bulk viscosity \( \eta_b \), our prime quantity of interest, is determined using a least squares procedure.

**B. The Hammond–Wiggins model**

At the other end of the uniformity scale, we seek confrontation with a hydrodynamic, continuum model by Hammond and
Unlike the Tenti model, which is built on (tensorial) eigenvectors of the linearized collision operator, the hydrodynamic model is built on (tensorial) moments of the space-time distribution function, i.e., hydrodynamic quantities. The hydrodynamic model takes the shear viscosity $\eta_s$, the diffusivity $D$, and the heat capacity of internal motion $C_{\text{int}}$ as parameters. The rotational relaxation time $\tau_{\text{rot}}$ is determined using a least squares procedure, from which the bulk viscosity $\eta_b$ is computed using Eq. (2). Allowance for rotational relaxation only is done through the choice of $C_{\text{int}} = 2/2 \, R$.

The evaluation of both kinetic and hydrodynamic models can be done extremely quickly. Where their range of validity overlaps, the derived values of the bulk viscosity should agree.

IV. RESULTS AND DISCUSSION

In this section, we will first present experimental data on light scattering in CO$_2$, followed by an analysis in terms of two complementary spectral line models. We finally summarize the results of the temperature-dependent bulk viscosity.

A. Measurements: Light scattering in CO$_2$

Measurements of the RB-scattering spectral profile of CO$_2$ gas were performed for conditions of 0.5–4 bars pressure and temperatures in the range between 258 and 355 K, as listed in Table I. In Table I, the accurately measured $p$ and $T$ conditions for 29 $(p, T)$ measurement combinations as well as the temperature-dependent transport coefficients are listed: shear viscosity $\eta_s$ and thermal conductivity $A_{\text{th}}$. For all measurements, a value for the internal molecular heat capacity of $C_{\text{int}} = 2/2 \, R$ is adopted.

In Fig. 3, the RB light spectra for the 29 different $(p, T)$ combinations are graphically displayed. A qualitative inspection shows, when comparing profiles from the top-row down, the pressure $p$ is increased and therewith the $y$-parameter is increased, and hence, the spectra show more pronounced Brillouin-side peaks. Indeed, at higher uniformity parameters $y$, the hydrodynamic regime is
approached resulting in well-isolated acoustic side modes. Similarly, while going from left to right along the columns, the temperature $T$ is increased, associated with a lowering of the $y$-parameter, and hence, the Brillouin-side peaks become less pronounced. In the following, the experimental profiles will be compared to the Tenti-S6 model and the Hammond–Wiggins hydrodynamic model.

B. Comparison with the two models

For a quantitative analysis of the data, a comparison is made with the Tenti-S6 model, which was developed into a code\textsuperscript{25,40} that was included in fitting routines for analyzing both spontaneous and coherent RB-scattering.\textsuperscript{24,26} In comparing model and experiments, the bulk viscosity $\eta_b$ was determined using a least-squares procedure, minimizing the mean squared deviation

$$\chi^2 = \frac{1}{N} \sum_{i=1}^{N} \left[ \frac{I_e(f_i) - I_m(f_i)}{\delta^2(f_i)} \right]^2,$$

where $I_e(f_i)$ and $I_m(f_i)$ are the experimental and modeled amplitude of the spectrum at (discrete) frequency $f_i$, and $N$ is total number of the experimental data. The error $\delta(f_i)$ of $I_e(f_i)$ is estimated as the square root of the number of collected photons.

First, an analysis is made of the spectrum presented in Fig. 2. Least-squares fits are performed for determining the value of the bulk viscosity $\eta_b$, invoking two values for the thermal conductivity: first $\lambda_{th} = 14.3$ mW/m K as resulting from the modified Eucken approach and second the value obtained from a direct measurement at acoustic frequencies $\lambda_{th} = 16.2$ mW/m K.\textsuperscript{39} The residuals plotted in Fig. 2 show that in the first approach a peak residual of 3% is found, where in the latter approach the peak deviation amounts to 5%. This supports the validity of the treatment of thermal...
conductivity following the modified Eucken relation in this study conducted at hypersound frequencies. In such an approach focusing on hypersound, the internal heat capacity is set at $C_{\text{int}} = 2/2 R$, signifying that two rotational degrees of freedom are involved and vibrational relaxation is “frozen.”

Least-squares fitting procedures based on the Tenti-S6 model were applied to the large body of 29 datasets on CO$_2$ for $(p, T)$ values, as displayed in Fig. 3. With inclusion of values for the transport coefficients as listed in Table I, optimized values for $\eta^b_s$ were derived. The resulting values are listed in Table I. Based on these fits and optimized $\eta^b_s$ values, residuals between experimental data and the Tenti-S6 model description are calculated and displayed in Fig. 4. These residuals provide insight into the quality of the fit, its accuracy, and the applicability of the model.

Similarly, the hydrodynamic model is used to compare the experimental and model spectra for the data of pressures above 1 bar. Here, the rotational relational time $\tau_{\text{rot}}$ was adopted as a free parameter, from which the bulk viscosity was calculated using Eq. (2).

Figure 5 displays the residual between the experimental data and this model.

C. Bulk viscosities

Our main result, the ratio $\eta^b_b/\eta^b_s$ as a function of temperature and pressure is summarized in Fig. 6. At $p = 0.5$ bar, the spectral line shape is not very sensitive to variation of $\eta^b_b$; at the highest pressure, the models deviate significantly from the experiment. At $p = 1$ bar (corresponding to $y = [1.4–2.3]$), the hydrodynamic model does not yet apply, and the values of $\eta^b_b/\eta^b_s$ of the two models differ significantly.

Figure 6 also shows the prediction of the Landau–Teller scaling, which captures low-frequency experimental data. However, with a crucial proviso: “it is scaled down by a factor” $10^4$. This vividly illustrates the dramatic effect of high frequencies on the ratio $\eta^b_b/\eta^b_s$.

At these high frequencies, only rotational relaxation remains. Based on the analysis of classical trajectories, Parker$^{33}$ derived a scaling expression for the ratio $\eta^b_b/\eta^b_s$

$$\eta^b_b/\eta^b_s \propto \left[ 1 + \frac{x^{3/2}}{2} \left( \frac{T^*}{T} \right)^{1/2} + \left( \frac{x^2}{4} + \pi \right) \frac{T^*}{T} \right]^{-1}$$

with $T^* = 82.6$ K, the temperature associated with the well depth of the O–O interaction potential.$^{15}$ This prediction, scaled on $\eta^b_b/\eta^b_s = 0.5$ at $T = 250$ K, is also shown in Fig. 6.

We find no significant dependency on pressure or temperature. At pressures where both kinetic and hydrodynamic models apply, we find an average $\eta^b_b/\eta^b_s = 0.33 \pm 0.06$ at $p = 2$ bars and $\eta^b_b/\eta^b_s = 0.48 \pm 0.06$ at $p = 3$ bars. These averages, together with their uncertainty, are also indicated in Fig. 6. Our present numbers are consistent with the finding obtained from the light scattering experiments on CO$_2$ in the UV-range ($\lambda = 366.8$ nm) covering the parameter space $y = [0.9–3.7]$, and yielding $\eta^b_b = (5.7 \pm 0.6) \times 10^{-6}$ Pa s$^2$, which gives rise to $\eta^b_b/\eta^b_s = 0.39 \pm 0.04$. These values should be compared to $\eta^b_b = 4.6 \times 10^{-6}$ Pa s (for $y = [3.3–8.2]$) by Lao et al.$^{1}$ corresponding to $\eta^b_b/\eta^b_s = 0.31$, and $\eta^b_b = 3.7 \times 10^{-6}$ Pa s for $y = [0.44–3.54]$ by Pan et al.$^{1}$, for which the ratio $\eta^b_b/\eta^b_s = 0.25$.

V. DISCUSSION AND CONCLUSION

In this paper, we study Rayleigh-Brillouin scattering over a range of pressures with the aim of determining the bulk viscosity using two different types of models for the spectral line shape. Where the range of applicability of these two models overlaps, we find consistent values of the bulk viscosity.

At low frequencies, the bulk viscosity depends strongly on temperature, which is caused by the temperature dependence of the vibrational relaxation rate. We do not find a significant temperature dependence, not even the one predicted for the increase in the bulk viscosity with the temperature due to the increase in the rotational relaxation time. We find $\eta^b_b/\eta^b_s = 0.41 \pm 0.10$ at pressures of 2 and 3 bars.
For $N_2$, a measurement of sound absorption at low pressure yielded a value of the bulk viscosity, expressed relative to the shear viscosity as $\eta_b/\eta_s = 0.73$ (Ref. 42). Cramer 47 showed that this ratio should increase from 0.4 to 1 as the temperature changes from 100 K to 420 K. Indeed, Gu and Ubachs 43 experimentally determined a ratio of $\eta_b/\eta_s = [0.46–1.01]$ from RB-scattering for the temperature range 254.7–336.6 K. Hence, for measurements at lower sound frequencies ($f_{sl}$) and at hypersonic frequencies ($f_{sh}$), this ratio yields a similar value. The vibrational relaxation time of $N_2$ is longer than $10^{-3}$ s at room temperature, thus $f_{sl}T_{vib} >> 1$ as well as $f_{sh}T_{vib} >> 1$. In other words, the vibrational degrees remain frozen under both conditions.

For $CO_2$, a different situation is encountered. At atmospheric pressure, the vibrational relaxation time is $\tau_{vib} = 6 \times 10^{-18}$ s, while the rotational relaxation time is $\tau_{rot} = 3.8 \times 10^{-16}$ s (Refs. 3 and 46). Hence, for sound frequency measurements (at the megahertz scale), $f_{sl}T_{vib} \approx 1$ and $f_{sl}T_{rot} << 1$, which means that both rotation and vibration are excited and take effect during energy exchange with translation in collisions. The method of sound absorption delivers an experimental ratio of bulk viscosity to shear viscosity ($\eta_b/\eta_s$) of $O(10^3)$ (Refs. 42, 47, and 48). For hypersonic frequencies (at the gigahertz scale), $f_{sh}T_{vib} >> 1$, causing the vibrational modes not to take effect.

In order to describe macroscopic flow phenomena on time scales ranging from microseconds to nanoseconds, the used value of the bulk viscosity will range over four orders of magnitude. An example of such a flow phenomenon is a shock in a high Mach number flow. The comparison of scattered light spectra to kinetic and hydrodynamic models in this paper shows that this dramatic frequency dependence of the bulk viscosity is due to the to the (gradual) cessation of vibrational relaxation.

ACKNOWLEDGMENTS

This research was supported by the China Exchange Program jointly run by the Netherlands Royal Academy of Sciences (KNAW) and the Chinese Ministry of Education. Y.W. acknowledges support from the Chinese Scholarship Council (CSC) for his stay at VU Amsterdam. W.U. acknowledges the European Research Council for an ERC-Advanced grant under the European Union’s Horizon 2020 Research and Innovation Programme (Grant Agreement No. 670168). The core part of the code that computes the Tenti models has been kindly provided to us by Xingguo Pan.

REFERENCES

1. Q. H. Lao, P. E. Schoen, and B. Chu, “Rayleigh-Brillouin scattering of gases with internal relaxation,” J. Chem. Phys. 64, 3547 (1976).
2. K. D. Pan, M. N. Shneider, and R. B. Miles, “Power spectrum of coherent Rayleigh-Brillouin scattering in carbon dioxide,” Phys. Rev. A 71, 045801 (2005).
3. Z. Gu, W. Ubachs, and W. van de Water, “Rayleigh-Brillouin scattering of carbon dioxide,” Opt. Lett. 39, 3301 (2014).
4. M. Snee and W. Ubachs, “Direct measurement of the Rayleigh scattering cross section in various gases,” J. Quant. Spectrosc. Radiat. Transfer 92, 293 (2005).
5. S. I. Rasool and C. De Bergh, “The runaway greenhouse and the accumulation of CO$_2$ in the Venus atmosphere,” Nature 226, 1037 (1970).
6. O. Aharonson, M. T. Zuber, D. E. Smith, G. A. Neumann, W. C. Feldman, and T. H. Prettyman, “Depth, distribution, and density of CO$_2$ deposition on Mars,” J. Geophys. Res. E: Planets 109, E05004, https://doi.org/10.1029/2003je002223 (2004).
7. T. Sakakura, J.-C. Choi, and H. Yasuda, “Transformation of carbon dioxide,” Chem. Rev. 107, 2365 (2007).
8. G. J. van Rooij, H. N. Akoe, W. A. Bongers, and M. C. M. van de Sanden, “Plasma for electrochemical industry: A case study on CO2 reduction,” Plasma Phys. Control. Fusion 60, 041019 (2018).
9. W. Wang, S. Wang, X. Ma, and J. Gong, “Recent advances in catalytic hydrogenation of carbon dioxide,” Chem. Soc. Rev. 40, 3703 (2011).
10. D. R. Kauffman, J. Thakkar, R. Siva, C. Matranga, P. R. Ohodnicki, C. Zeng, and R. Jin, “Efficient electrochemical CO2 conversion powered by renewable energy,” ACS Appl. Mater. Interfaces 7, 15626 (2015).
11. E. V. Kondratenko, G. Mul, J. Ruhnusasitis, G. O. Larrazabal, and J. Pérez-Ramírez, “Status and perspectives of CO2 conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes,” Energy Environ. Sci. 6, 3112 (2013).
12. W. Bongers, H. Bouwmeester, B. Wolf, F. Peeters, S. Welzel, D. van den Bekerom, N. den Harder, A. Goede, M. Graswinkel, P. W. Groen et al., “Plasma-driven dissociation of CO2 for fuel synthesis,” Plasma Processes Polym. 14, 1600126 (2017).
13. M. Mikkelsen, M. Jørgensen, and F. C. Krebs, “The teraton challenge. A review of fixation and transformation of carbon dioxide,” Energy Environ. Sci. 3, 43 (2010).
14. M. E. Boot-Handford, J. C. Abanades, E. J. Anthony, M. J. Blunt, S. Brandani, N. Mac Dowell, J. R. Fernandez, M.-C. Ferrari, R. Gross, J. P. Hallett et al., “Carbon capture and storage update,” Energy Environ. Sci. 7, 130 (2014).
15. F. J. Uribe, E. A. Mason, and J. Kestin, “Thermal conductivity of nine polyatomic gases at low density,” J. Phys. Chem. Ref. Data 19, 1123 (1990).
16. R. D. Trengove and W. A. Wakeham, “The viscosity of carbon dioxide, methane, and sulfur hexafluoride in the limit of zero density,” J. Phys. Chem. Ref. Data 16, 175 (1987).
17. S. Bock, E. Bich, E. Vogel, A. S. Dickinson, and V. Vesovic, “Calculation of the transport properties of carbon dioxide. I. Shear viscosity, viscomagnetic effects, and self-diffusion,” J. Chem. Phys. 117, 2131 (2002).
18. J. W. Strutt and Lord Rayleigh, “On the transmission of light through an atmosphere containing small particles in suspension, and the origin of the blue of the sky,” Philos. Mag. 47, 375 (1899).
19. L. Brillouin, “Diffusion de la lumière et des rayons X par un corps transparent homogène. Influence de l’agitation thermique,” Ann. Phys. 9(17), 88 (1922).
20. E. Mandelstam, “Light scattering by inhomogeneous medium,” Zh. Russ. Fiz-Khim. Ova. 58, 381 (1926).
21. J. O. Hirschfelder, R. B. Bird, and E. L. Spitz, “The transport properties for non-polar gases,” J. Chem. Phys. 16, 968 (1948).
22. L. Letamendia, P. Joubert, J. Rouch, C. Vaucamps, C. D. Boley, S. Yip, and S. H. Chen, “Light-scattering studies of moderately dense gases. II. Nonhydrodynamic regime,” Phys. Rev. A 25, 481 (1982).
23. W. Marques, Jr. and G. Kremer, “Spectral distribution of scattered light in polyatomic gases,” Physica A 197, 352 (1993).
24. M. O. Vitez, E. J. van Djuin, W. Ubachs, B. Witschas, A. Meijer, A. S. de Wijn, N. J. Dam, and W. van de Water, “Coherent and spontaneous Rayleigh-Brillouin scattering in atomic and molecular gases, and gas mixtures,” Phys. Rev. A 82, 043836 (2010).
25. K. Pan, M. N. Shneider, and R. B. Miles, “Coherent Rayleigh-Brillouin scattering in molecular gases,” Phys. Rev. A 69, 033814 (2004).
26. A. S. Meijer, A. S. de Wijn, M. F. E. Peters, N. J. Dam, and W. van de Water, “Coherent Rayleigh-Brillouin scattering measurements of bulk viscosity of polar and nonpolar gases, and kinetic theory,” J. Chem. Phys. 133, 164315 (2010).
27. M. S. Cramer, “Numerical estimates for the bulk viscosity of ideal gases,” Phys. Fluids 24, 066102 (2012).
28. F. Jaeger, O. K. Matar, and E. A. Müller, “Bulk viscosity of molecular fluids,” J. Chem. Phys. 148, 174504 (2018).
29. K. E. Herzfeld and T. A. Litovitz, Absorption and Dispersion of Ultrasonic Waves, Volume 7 of Pure and Applied Physics (Academic Press, London, 1959).
30 Z. Y. Gu and W. Ubachs, "A systematic study of Rayleigh-Brillouin scattering in air, N₂, and O₂ gases," J. Chem. Phys. 141, 104320 (2014).
31 Y. Wang, K. Liang, W. van de Water, W. Marques, and W. Ubachs, "Rayleigh–Brillouin light scattering spectroscopy of nitrous oxide (N₂O)," J. Quant. Spectrosc. Radiat. Transfer 206, 63 (2018).
32 A. Chapman and T. G. Cowling, Mathematical Theory of Non-Uniform Gases, 3rd ed. (Cambridge Mathematical Library, Cambridge, 1970), ISBN: 052140844.
33 J. G. Parker, "Rotational and vibrational relaxation in diatomic gases," Phys. Fluids 2, 449 (1959).
34 C. D. Boley, R. C. Desai, and G. Tenti, "Kinetic models and Brillouin scattering in a molecular gas," Can. J. Phys. 50, 2158 (1972).
35 G. Tenti, C. D. Boley, and R. C. Desai, "On the kinetic model description of Rayleigh-Brillouin scattering from molecular gases," Can. J. Phys. 52, 285 (1974).
36 C. M. Hammond and T. A. Wiggins, "Rayleigh-Brillouin scattering from methane," J. Chem. Phys. 65, 2788 (1976).
37 Z. Gu, M. O. Vieitez, E. J. van Duijn, and W. Ubachs, "A Rayleigh-Brillouin scattering spectrometer for ultraviolet wavelengths," Rev. Sci. Instrum. 83, 053112 (2012).
38 C. S. Wang Chang and G. E. Uhlenbeck, Research Report No. CM-681, University of Michigan, 1951.
39 A. Bousethri, J. Bzowski, J. Kestin, and E. A. Mason, "Equilibrium and transport properties of eleven polyatomic gases at low density," J. Phys. Chem. Ref. Data 16, 445 (1987).
40 J. Chem. Phys. 150, 154502 (2019); doi: 10.1063/1.5093541
41 X. Pan, Ph.D. thesis, Princeton University, 2003.
42 Z. Zhang and Z. Duan, "An optimized molecular potential for carbon dioxide," J. Chem. Phys. 122, 214507 (2005).
43 G. J. Prangsma, A. H. Alberga, and J. J. M. Beenakker, "Ultrasonic determination of the volume viscosity of N₂, CO, CH₄, and CD₄ between 277 and 300 K," Physica 64, 278 (1972).
44 Z. Gu and W. Ubachs, "Temperature-dependent bulk viscosity of nitrogen gas determined from spontaneous Rayleigh-Brillouin scattering," Opt. Lett. 38, 1110 (2013).
45 B. D. Taylor, D. A. Kessler, and E. S. Oran, "Estimates of vibrational nonequilibrium time scales in hydrogen-air detonation waves," 24th International Colloquium on the Dynamics of Explosive and Reactive Systems (Taipei, Taiwan, 2013), Paper 224. Available at http://www.icders.org/ICDERS2013/PapersICDERS2013/ICDERS2013-0223.pdf.
46 G. Emanuel, "Bulk viscosity of a dilute polyatomic gas," Phys. Fluids A 2, 2252 (1990).
47 J. D. Lambert, Vibrational and Rotational Relaxation in Gases (Clarendon Press, Oxford, 1977).
48 L. Tisza, "Supersonic absorption and Stokes’ viscosity relation," Phys. Rev. 61, 531 (1942).
49 W. E. Meador, G. A. Miner, and Lawrence W. Townsend, " Bulk viscosity as a relaxation parameter: Fact or fiction?" Phys. Fluids 8, 258 (1996).