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Rayleigh-Brillouin Scattering in Binary-Gas Mixtures

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Precise measurements are performed on spectral line shapes of spontaneous Rayleigh-Brillouin scattering in mixtures of the noble gases Ar and Kr, with He. Admixture of a light He atomic fraction results in marked changes of the spectra, although in all experiments He is merely a spectator atom: it affects the relaxation of density fluctuations of the heavy constituent, but its contribution to the scattered light intensity is negligibly small. The results are compared to a theory for the spectral line shape without adjustable parameters, yielding excellent agreement for the case of binary monatomic gases, signifying a step towards modeling and understanding of light scattering in more complex molecular media.

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The spectrum of light scattered in a gas is determined by the fluctuations of its refractive index [1] or, equivalently, by the motion of its molecules. When the mean-free path between collisions is much larger than the wavelength, the scattering spectral line shape is a pure Gaussian, to be understood as a Doppler effect. At higher pressures, collisional excitations and acoustic modes come into play, as was recognized independently by Brillouin [2] and Mandelstam [3]. In a first approximation, redshifted and blueshifted frequency components are added to the scattering spectrum with characteristic shifts $\Delta \nu = v_s k/2 \pi$, with $v_s$ the speed of sound and $k$ the size of the scattering wave vector, $k/2\pi = 2 \sin(\theta/2)/\lambda$, with $\theta$ the scattering angle and $\lambda$ the wavelength of the incident light.

Rayleigh-Brillouin scattering in dilute gases offers a sensitive probe of gas kinetics. Understanding the scattered light spectrum involves the linearized Boltzmann equation [4], and throughout the years intricate approximations to the collision integral have resulted in various kinetic models for the scattered light spectrum. These models may be viewed as a success of statistical physics. Still, discrepancies with experiments exist, and the kinetic models are generally restricted to simple gases. In contrast, the Earth’s atmosphere consists of a mixture of gases, each of which explores internal molecular degrees of freedom. An important practical application of understanding such mixtures of gases is in its connection to laser light scattering of the atmosphere [5,6], in particular the ADM-Aeolus mission of the European Space Agency for measuring the global wind profile [7].

The Tenti model is a well-known theory for the spectral line shape of scattered light in monomolecular gases [8,9]. The spectrum is determined by the communication between kinetic and internal degrees of freedom, which is characterized by a transport coefficient, the bulk viscosity $\eta_b$. The bulk viscosity is a dynamic quantity, which is not well known at the gigahertz frequencies of interest in light scattering. Therefore, $\eta_b$ was used as an adjustable parameter to describe spectral profiles in light scattering in both coherent [10–13] and spontaneous [14–16] Rayleigh-Brillouin scattering experiments. However, the Tenti model is not designed to describe light scattering in mixtures. Nevertheless, applying it to air and assuming that air is a fictitious gas with effective values for its transport coefficients and molecular mass yields fair agreement with experiments [17,18]. When devising a proper theory for air, one faces the formidable task of including both kinetic and internal degrees of freedom for several species.

As a first step in understanding light scattering in more complex gases, we will concentrate on mixtures of noble gases by using a new experimental setup which provides spectra with unprecedented statistical accuracy [19]. We will compare these spectra to models with no adjustable parameters: the only parameter needed is the atomic diameter, which follows from the well-known value of the shear viscosity of the pure noble gas [20]. All our experiments are in the kinetic regime, where the mean-free path between collisions is comparable to the scattered light wavelength. Interestingly, mixtures of gases with very different mass behave in a similar fashion as a gas of molecules with internal degrees of freedom. While the two components of the mixture briefly can have different temperatures, a molecular gas can have different temperatures associated with translational and internal degrees of freedom. It is the relaxation of these temperature differences that determines the scattered line shape.

The components of our He-Ar and He-Kr mixtures have a large mass disparity ($M_{\text{He}}/M_{\text{Ar}} = 0.1002$, and $M_{\text{He}}/M_{\text{Kr}} = 0.0478$). With these different size atoms, it is only the heavy ones that contribute to the scattered light intensity. The intensity is proportional to the square of the optical polarizabilities $\alpha$, with the ratio $(\alpha_{\text{He}}/\alpha_{\text{Ar}})^2 = 1.56 \times 10^{-2}$, and $(\alpha_{\text{He}}/\alpha_{\text{Kr}})^2 = 5.96 \times 10^{-3}$. Thus, the

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controlled gas cell. The laser is a frequency-doubled Ti:
laser is scattered off a gas contained in a temperature-
intensity of 4 W in the interaction region\[19\]. The light
amplifies the circulating power, delivering a scattering
is sealed with Brewster windows. The enhancement cavity
ment cavity, in which a scattering cell is mounted. The cell
angle of 90° from an auxiliary focus inside the enhance-
400 mW of output power. The long-term frequency drift
photomultiplier tube (PMT).

Perot interferometer (FPI) for spectral analyses and detected on a
collimated and directed onto a piezoelectrical scannable Fabry-
the scattering intensity. Scattered light at an angle of 90° is
beam (blue line) is amplified in an enhancement cavity to increase
setup for spontaneous Rayleigh-Brillouin scattering. The laser
FIG. 2 (color online). Schematic diagram of the experimental
Fig. 2. The light from a narrow band continuous-wave
spontaneous Rayleigh-Brillouin scattering is shown in
shape of the scattered light spectrum.

light atoms are spectators and influence the spectral line
shape only indirectly through collisions. Nevertheless, as
Fig. 1 illustrates, their influence can be large: adding light
atoms to a gas of heavy ones significantly changes the
shape of the scattered light spectrum.
A schematic view of the setup for the measurement of
spontaneous Rayleigh-Brillouin scattering is shown in
Fig. 2. The light from a narrow band continuous-wave laser is scattered off a gas contained in a temperature-
controlled gas cell. The laser is a frequency-doubled Ti:sa
laser delivering light at 403 nm, 2 MHz bandwidth, and
400 mW of output power. The long-term frequency drift
was measured with a wavelength meter to be smaller than
10 MHz per hour. The scattered light is collected at an
angle of 90° from an auxiliary focus inside the enhance-
cavity, in which a scattering cell is mounted. The cell
is sealed with Brewster windows. The enhancement cavity
amplifies the circulating power, delivering a scattering
intensity of 4 W in the interaction region \[19\]. The light
that passes through the FPI is detected using a PMT which
is operated in the photon-counting mode and read out by
the computer. All measurements are performed at room
temperature, 297 ± 1 K.
The scattering angle is determined to be 90 ± 0.9° by
means of the reference laser beam and geometrical relations
using sets of diaphragms and pinholes present in the optical
setup. The scattered light is filtered by a diaphragm which
covers an opening angle of 2°, collected by a set of lenses,
进一步 filtered by an extra pinhole (d = 50 μm) and then
directed into a hemispherical scanning Fabry-Perot interferometer, which is used to resolve the frequency spectrum
of the scattered light. To scan the FPI plate distance, the
spherical mirror is mounted on a piezoelectrical translator,
which is controlled by the computer.
The spectral response \( S(\nu) \) of the Fabry-Perot spectrom-
eter was measured in a separate experiment and could
be parametrized very well by the formula
\[ S(\nu) = [1 + 4(\nu/\nu_a)^2\text{sinc}^2(\pi\nu/\nu_{\text{FSR}})]^{-1}, \]
where \( \nu_{\text{FSR}} \) is the free spectral range of the etalon,
\( \nu_a = 7553 \text{ MHz}, \) and \( \nu_a = 139 \text{ MHz} \) is the Airy width
of the transmission peak. All computed model spectra were
convolved with \( S(\nu) \), and, since the free spectral range is
relatively small, it is important to allow for the periodic
nature of \( S(\nu) \).
The light scattering experiments do not provide an
absolute intensity; therefore, the experimental and computed
spectra were normalized such that
\[ \int_{\nu_{\text{min}}}^{\nu_{\text{max}}} I(\nu) d\nu = 1, \]
where the integral extends over one free spectral range
(FSR), \( \nu_{\text{b}} = \nu_{\text{FSR}}/2. \) Assuming Poissonian statistics of
registered photon counts, an estimate of the statistical error
\( \sigma(\nu_i) \) of measured spectra was obtained from the square
root of the accumulated photon count \( N_i \) at each discrete
frequency \( \nu_i \). It was verified that the fluctuations \( N_i^{1/2} \)
at each \( \nu_i \) were independent. The normalized error is then
\( \chi^2 = N^{-1} \sum_{i=1}^{N} [I_m(\nu_i) - I_e(\nu_i)]^2 / \sigma^2(\nu_i) \). If the computed
line shape model \( I_m \) would fit the measurement perfectly,
then only statistical errors remain and the minimum of \( \chi^2 \) is
unity. The difference between theory and experiment will
be expressed by \( \chi^2 \).

In the past decades, many ingenious efforts have been
undertaken to arrive at approximate solutions of the
Boltzmann equation which are relevant for light scattering.
Light scattering involves density fluctuations, with the
spectrum of scattered light equaling the Fourier transform
of the density-density correlation function. Van Leeuwen
and Yip showed that this correlation function follows from
the first moment of the solution of the linearized Boltzmann
equation \[4\].

One such effort is based on the Bhatnagar-Gross-Krook
(BGK) model, which takes a simple relaxation form for the
collision integral \[21\]:
\[ \frac{\partial f}{\partial t} + (c \cdot \nabla)f = -\sigma(f - f_r), \] (1)
increasing number of moments $N$ spectra are shown for spectra to the theory of light scattering in binary mixtures of noble gases of freedom. There, the reference distribution function needs is the hard-sphere diameter of the noble-gas atom, $a_i = (a_i + a_j)/2$ the distance between the centers of two spherical particles with diameters $a_i$ and $a_j$ at the instant of collision. With all uniformity parameters of the order of one, the experiments are in the kinetic regime. The computation of the theory now also needs the hard-sphere diameter of He, $a_{He} = 2.16 \times 10^{-10}$ m, and the atomic polarizabilities of the noble gases $\alpha_{He} = 0.227 \times 10^{-40}$ Cm$^2$V$^{-1}$, $\alpha_{Ar} = 1.82 \times 10^{-40}$ Cm$^2$V$^{-1}$, and $\alpha_{Kr} = 2.94 \times 10^{-40}$ Cm$^2$V$^{-1}$.

The measured mixture spectra are reproduced well by the theory. Although the mixture model is designed to represent the relevant interspecies relaxation processes, which become less important for asymmetric mixtures, the agreement with the measured spectra at 1 bar He and 3 bars Ar, and the reverse case, is still excellent. Early experiments on mixtures of He and Xe atoms were done by Clark [25] but were interpreted in terms of hydrodynamics, as a complete kinetic theory was still lacking. Light scattering on He-Xe mixtures in a range of pressures comparable to ours was studied by Letamendia et al. [26], and sizable differences with a kinetic mixture model [27] were found.

A striking observation is the narrowing of the mixture spectrum in Figs. 4(a) and 4(d) when the number of helium atoms is increased while keeping the number of Ar atoms the same. Collisional narrowing takes place when, for Ar, $y_i = 1/(kl_i)$ of a binary mixture involves the partial mean-free paths $l_i$ of hard-sphere atoms:

$$l_i = \left( \pi \sum_{j=1}^{2} n_j a_j^2 \sqrt{1 + M_i/M_j} \right)^{-1},$$

with $n_i$ and $M_i$ the number density and atomic mass of constituent $i$, respectively, and $a_{ij} = (a_i + a_j)/2$ the distance between the centers of two spherical particles with diameters $a_i$ and $a_j$ at the instant of collision. With all uniformity parameters of the order of one, the experiments are in the kinetic regime. The computation of the theory now also needs the hard-sphere diameter of He, $a_{He} = 2.16 \times 10^{-10}$ m, and the atomic polarizabilities of the noble gases $\alpha_{He} = 0.227 \times 10^{-40}$ Cm$^2$V$^{-1}$, $\alpha_{Ar} = 1.82 \times 10^{-40}$ Cm$^2$V$^{-1}$, and $\alpha_{Kr} = 2.94 \times 10^{-40}$ Cm$^2$V$^{-1}$.

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FIG. 4. Comparing scattered light spectra of mixtures to the mixture model of Ref. [23]. (a) Equimolar mixture He $p = 1$ bar, Ar $p = 1$ bar, uniformity parameters $y_{\text{He}} = 1.63$, $y_{\text{Ar}} = 0.54$; (b) equimolar mixture He $p = 2$ bar, Ar $p = 2$ bar, $y_{\text{He}} = 1.08$; (c) asymmetric mixture He $p = 1$ bar, Ar $p = 3$ bar, $y_{\text{He}} = 2.96$, $y_{\text{Ar}} = 1.16$; (d) asymmetric mixture He $p = 3$ bar, Ar $p = 1$ bar, $y_{\text{He}} = 3.59$, $y_{\text{Ar}} = 1.00$; (e) equimolar mixture He $p = 1.3$ bar, Kr $p = 1.3$ bar, $y_{\text{He}} = 3.28$, $y_{\text{Kr}} = 0.77$; (f) asymmetric mixture He $p = 2$ bar, Kr $p = 2$ bar, $y_{\text{He}} = 5.01$, $y_{\text{Kr}} = 1.17$. The lower line is the difference between the experiment and model. Apart from the normalization of the spectra, there are no adjustable parameters. In (d), the dashed thick (gray) line shows the purely Gaussian spectral line shape embodied both extreme cases, and it provides a near-perfect reproduction of the experimental spectrum.

We have studied Rayleigh-Brillouin scattering in mixtures of noble gases, whose constituents have a very different mass. In all cases, the addition of the light He atomic gas has a large influence on the spectral line shapes, although He atoms hardly contribute to the scattered light intensity. Density fluctuations in mixtures are dominated by the relaxation of temperature and velocity differences between the constituent gases. These relaxations appear to be captured adequately by the mixture model of Ref. [23]. This is the first time that these predictions have been tested in the kinetic regime. The model contains no adjustable parameters and reproduces all experiments excellently. The present successful comparison of the model and experiment marks a step towards a description of light scattering in mixtures of molecular gases (such as air) and emphasizes the need to account for interspecies relaxation of temperatures of both translational and kinetic degrees of freedom.

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