PHYSICAL REVIEW A **78**, 033822 (2008)

# Thermal phonon resonance in nitrogen gas observed by Brillouin scattering

Yasuo Minami,[*] Takeshi Yogi, and Keiji Sakai
*Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan*

(Received 24 April 2008; published 17 September 2008; publisher error corrected 22 September 2008)

We observed the thermal phonon resonance of nitrogen gas with optical-beating Brillouin scattering and measured the sound velocity and the absorption coefficient in the MHz region. Optical-beating spectroscopy possesses a frequency resolution of 1 kHz, which enabled us to resolve the fine structure of the thermal phonon resonance spectra. Resonance peaks of phonons were observed at every 185 kHz in the resonance cavity composed of two flat glass plates. The measurement accuracy of the sound velocity and the absorption coefficient was remarkably improved to $10^{-4}$ and $10^{-1}$, respectively.

DOI: 10.1103/PhysRevA.78.033822 PACS number(s): 42.65.Es, 78.35.+c, 33.20.Fb

## I. INTRODUCTION

Brillouin-scattering spectroscopy has attracted much attention as almost the only method of nondestructive and noncontact measurement of the acoustical properties of materials [1–6]. Recently, optical-beating spectroscopy was proposed as a technique of resolving the Brillouin-scattering spectrum with high-frequency resolution and has been used for the measurement of phonon propagation in various kinds of liquid, solid, and gas materials [7–11].

It has been difficult to measure the sound velocity and the absorption coefficient in gases accurately with the conventional ultrasonic pulse method in the frequency region above MHz, since the typical intrinsic absorption due to shear viscosity is larger than 1 $\text{mm}^{-1}$ at 1 atm in the frequency region [12–21]. It is also a technical difficulty to use hard piezoelectric devices to excite and detect ultrasonic waves in dilute gases, since the transmission efficiency is quite poor because of their huge impedance miss matching.

On the other hand, optical-beating spectroscopy is free from these problems since we detect thermally excited ultrasonic waves (called thermal phonons) with a laser probe. In the case that the propagation distance of the ultrasonic wave is shorter than the beamwidth of the probe laser, the absorption coefficient is obtained with sufficient accuracy in light-scattering experiments. Therefore, optical-beating spectroscopy is promising as an effective probe of ultrasonic waves in gases at high frequencies. However, disadvantages remain; one is that measurement of the absorption coefficient is still impossible if the propagation distance of the ultrasonic wave is longer than the beamwidth at a small scattering angle, in principle, since the laser probe could not observe the phonon decay within its width [22–24]. The problem is actually serious in the frequency region below 10 MHz for gases.

We therefore carried out the observation of the thermal phonon resonance in gas. In this study, we succeeded in measuring the ultrasonic decay in nitrogen gas in the MHz region, in which the resolution of the usual optical-beating spectroscopy is insufficient. We could also determine the sound velocity of nitrogen gas within an accuracy of $10^{-4}$.

## II. REQUIRED SPECIFICATION FOR GAS SPECTROSCOPY

The thermodynamics of ideal monoatomic gases is quite simple, through which the elasticity and the shear viscosity are theoretically predicted [25,26]. The mechanics of diatomic or polyatomic gases are, however, not very simple due to the contribution from the internal degrees of freedom of the molecule, and in general, it is difficult to predict the whole aspect of the phonon relaxation due to the coupling between the elasticity and the internal degrees.

In one of the simplest models assuming the molecule as a hard sphere, the sound velocity $v$ of monoatomic gas is represented as

$$v = \sqrt{\frac{5k_{\mathrm{B}}T}{3m}},$$

where, $k_{\mathrm{B}}$ is the Boltzmann constant, $T$ is the temperature, and $m$ is the molecular mass, respectively. The calculated velocities at 300 K of He, Ne, and Ar are 1000, 450, and 320 m/s, respectively, for example, and they agree with the literature values [25,26]. On the other hand, the viscosity of the monoatomic gas is represented as

$$\eta = \frac{1}{2\pi d^2}\sqrt{\frac{5mk_{\mathrm{B}}T}{3}},$$

where $d$ is the molecular diameter. The calculated viscosities at 300 K of He, Ne, and Ar are 12, 23, and 26 $\mu$Pa s, respectively, and they also agree with the actual values. However, we could not predict all the mechanical properties of polyatomic molecules since the time required for the relaxation to the equilibrium state is unknown. The transfer of energy plays a dominate role to determine the acoustical properties of gases. Note here that the time scale of the vibration-translation ($V$-$T$) or rotation-translation ($R$-$T$) relaxations is usually quite apart, which is typically 20 ms and 2 ns for oxygen, respectively, at 300 K at 1 atm.

The $V$-$T$ relaxation time is measured from the dispersion of the sound velocity or absorption coefficient. Since the measurement accuracy of $10^{-2}$ in the sound velocity and that of $10^{-2}$ in the absorption coefficient is required to observe $V$-$T$ relaxation in nitrogen gas, it has been impossible to observe the $V$-$T$ relaxation from the change in absorption

---

[*] yminami@iis.u-tokyo.ac.jp

coefficient with conventional optical-beating Brillouin-scattering spectroscopy. It is also difficult to observe the relaxation from the sound velocity since the accuracy of our light-scattering method is $10^{-2}$ at best [11].

In this study, we propose to apply a phonon resonance technique for the observation of the *V-T* relaxation in gases. We observed the thermal phonon resonance spectrum in nitrogen gas by optical-beating Brillouin-scattering spectroscopy and determined the sound velocity and absorption coefficient. The accuracy is as high as $10^{-4}$ in the sound velocity measurement, which is superior to those realized by conventional ultrasonic measurements [12–21].

In this method, we use a small cavity as a sample container, in which the thermal phonon resonates. The relevant phonon intersects with the probing laser light many times, which effectively increases the interaction time between the phonon and the light. The contribution of the instrumental factor to the Brillouin peak width becomes smaller.

## III. EXPERIMENT

We observed thermal phonons in gas with optical-beating spectroscopy. Optical-beating spectroscopy was previously reported in detail [11]. Here, we briefly describe the account of optical-beating Brillouin-scattering spectroscopy and its recent improvement in detection sensitivity. The beam from a frequency-doubled cw Nd:YAG laser (wavelength 532 nm) with a power of 8 W is divided once into a strong incident light and a weak reference light, and they are adjusted to intersect in the sample. The region of intersection makes the scattering volume. The scattered light collinear with the reference light is detected by a high-speed avalanche-type photodiode (S5343, Hamamatsu Photonics) and generates the optical-beating signal. The power spectrum of the scattered light is thus obtained using a spectrum analyzer, which is shown in Fig. 1(a).

The frequency resolution of the system is restricted by the width of the electrical bandpass filter of the spectrum analyzer, which is as narrow as 1 kHz in the present experiment to resolve the fine structure of resonance peaks. Recent efforts to improve detection sensitivity enabled the observation of thermal phonons propagating in poor-phonon-scattering samples, such as stiff solids and dilute gas materials [10,11,22].

The phonon resonance cavity is shown in Fig. 1(b), which is composed of two flat phonon reflectors made of glass with flatness better than 2λ set face to face with 950 $\mu$m spacing. The decay length of the phonon in nitrogen gas at 300 K, 1 atm, and a frequency of 3.4 MHz is 5 mm. Therefore, we expect that phonons make the round-trip between the two walls. Since the wavelength of the relevant phonon is much larger than the surface roughness of the phonon reflector, the phonon makes the round-trip for several times. The reflectors have a diameter of 15 mm in the length along the laser penetration. The geometry of the reflectors, reference light, incident light, and photodiode is shown in Fig. 1(a).

Of greatest importance is the parallelism of the reflectors in this study. The parallelism of the countering phonon reflector is adjusted to better than 10″ by observing the circular fringes of the adjusting laser incident perpendicular to the reflectors.

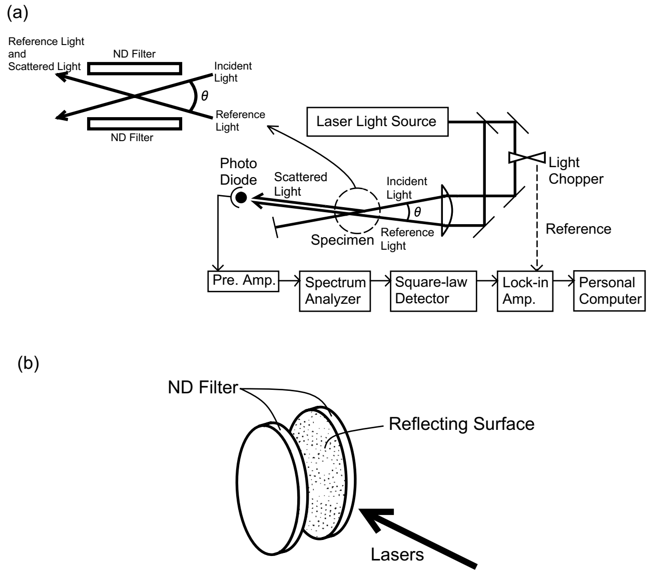

FIG. 1. Block diagram of the system and top view of the reference light, incident light, and cavity (a) and schematic view of the phonon resonator (b).

In the phonon resonance measurement, the wave number of the phonon is determined strictly by the boundary condition of the cavity, whereas the observation band is determined by the scattering wave number and its ambiguity.

In this experiment, the scattering angle is fixed to 5.2 mrad, which is precisely determined from the phonon frequency in liquid toluene observed with the same experimental configuration and its well-known sound velocity. The corresponding scattering wave number given by $k = 2K\sin(\theta/2)$ is $k = 6.2 \times 10^4\ \mathrm{m}^{-1}$. The ambiguity of the scattering wave number is induced by the focusing lens. Focusing the laser beam (wavelength λ) with an initial diameter ($2w_0$) of 2 mm by a lens with a focal length ($F$) of 1000 mm yields the ambiguity of the wave number, $\Delta k = 2\pi w_0/\lambda F \approx 1.2 \times 10^4\ \mathrm{m}^{-1}$ [27]. All experiments were carried out at 300 K and $1.0 \times 10^5$ Pa.

## IV. RESULTS AND DISCUSSION

The optical-beating Brillouin-scattering spectra observed in gas are shown in Fig. 2. Figure 2(a) shows the Brillouin-scattering spectrum observed in nitrogen gas outside the cavity. The center frequency of the peak is 3.42 MHz, which gives a phonon velocity of 347 m/s. This value agrees well with the literature value of 354 m/s. However, the ambiguity in the peak determination of 0.1 MHz directly leads to an error larger than 1%. The spot size of the laser beam at the focus is 10 $\mu$m [27], which derives the instrumental width $\Delta f_{\mathrm{inst}}$ from the finite interaction length between the phonon and the beam. The width $\Delta f_{\mathrm{inst}}$ is then estimated to $\Delta f_{\mathrm{inst}} \approx v\Delta k/2\pi \approx 670$ kHz, which roughly agrees with the half width at half maximum (HWHM) of the peak in Fig. 2(a). Note here that the HWHM of the Brillouin peak without

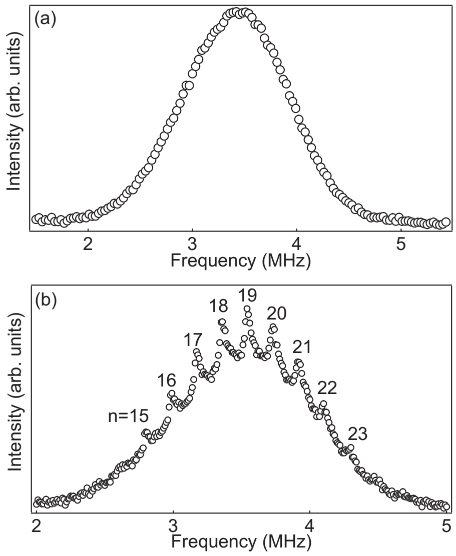

FIG. 2. Phonon spectra of nitrogen gas observed outside the cavity (a) and in the cavity (b) with optical-beating Brillouin-scattering spectroscopy. The integers in (b) indicate the resonance order. The solid line is the best-fitted line described with Eq. (2).

$\Delta f_{\mathrm{inst}}$ corresponds with the damping constant of the phonon. The expected HWHM of the peak calculated from the intrinsic absorption coefficient is 12 kHz, which is by far smaller than the present instrumental width and we cannot determine the absorption coefficient from the experimental width of the peak.

Figure 2(b) shows the Brillouin-scattering spectrum observed in the phonon resonance cavity. We can see that the resonant peaks appear and the integers in Fig. 2(b) indicate the resonance order of each peak. The acoustic impedance ratio between nitrogen gas and the resonator made of glass is more than $10^4$, and the energy transmission coefficient is less than $10^{-8}$. Therefore, the surface is an ideal reflector for the elastic wave.

The observation of the phonon resonance has an advantage that we do not have to employ the ultrasonic transducer, which more or less disturbs the boundary condition and causes imperfect ultrasonic reflection or excess damping of sound and which leads to the harmful instrumental factor. In addition, we can assign all peaks with integer $n$ to indicate the absolute resonance order, since the present condition is the perfectly fixed boundary. The resonance peaks are observed at the frequency of

$$f_n = nv/2L, \tag{1}$$

where $n$ is the resonance order and $L$ is the spacing between the countering resonator. The frequency interval between the neighboring peak is $\Delta f = v/2L$, which is 185 kHz at the present condition and agrees with the experimental result.

The power spectrum of the phonon resonance taking the instrumental factor into account is represented as

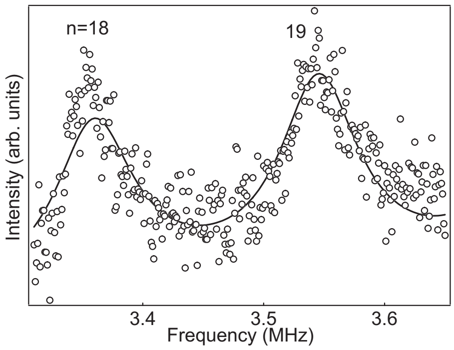

FIG. 3. Enlarged phonon resonance peak for mode $n=18,19$ shown in Fig. 2(b). The solid line is the best-fitted line described with Eq. (2).

$$S(\omega) \propto \int I(k) \frac{1}{(\omega - kv)^2 + \Gamma^2} \times \frac{1}{1 + e^{-4\Gamma L/v} - 2e^{-2\Gamma L/v} \cos 2L\omega/v} dk, \tag{2}$$

where $I(k)$ is the instrumental factor, $\omega$ is the angular frequency, and $\Gamma$ is the damping constant of the phonon, respectively. Note here that the instrumental factor $I(k)$ gives the frequency range of the phonon resonance observation. The solid lines in Figs. 2(b) and 3 are the best-fitted lines described with Eq. (2).

The detail of resonance peaks at $n=18,19$ in Fig. 2(b) is shown in Fig. 3. The phonon decay measurement has not been carried out with conventional optical-beating spectroscopy in this frequency range [11]. Observing each peak in Fig. 3 carefully, we find an asymmetry in its shape; the skirt towards the higher frequency is more gradual. The right-hand-side skirt is composed of the intrinsic absorption coefficient of ultrasound and the other instrumental factor. This instrumental factor is due to the phonon propagating off-normal to the resonator walls. Here, we estimate the width of the instrumental factor of the right-hand-side skirt. When the incident and local reference lights intersect at the scattering angle $\theta$ with the direction ambiguity $\Delta\theta$, the divergence of the scattering wave number along the direction of laser transmission is approximately given by $\Delta k_{\perp} = K\Delta\theta/2$ for $\theta \ll 1$. The resonant length of the phonon propagating off-normal to the resonator walls is represented as $L \cos \Delta\theta$, where $\Delta\theta$ is the off-normal angle which agrees with the direction ambiguity. The more gradual skirt, therefore, appears only in the higher-frequency region of the each resonant peak. We can estimate, from the equations, the frequency width of the right-hand-side skirt of the resonance peak due to the ambiguity of the scattering wave number to 10 kHz. In the actual spectrum, the frequency width is broader than the estimated value. The reason is not clear at present, however; the declination of the incident angle on the surface might lead to the increase in $\Delta k_{\perp}$. It is also plausible that the poor smoothness or the parallelism of the walls yields a distortion of the phonon, which may lead to the additional $\Delta k_{\perp}$.

We carried out the fitting of the theoretical curve to the left-hand-side skirt of the resonance peak at $n=19$ shown in

Fig. 3. The spatial absorption coefficient $\alpha$ $(=\Gamma/v)$ obtained is $\alpha/f^2=2.0\times10^{-13}$ $s^2/cm$ at 1 atm, which agrees with the value measured by the ultrasonic technique of $\alpha/f^2=1.8\times10^{-13}$ $s^2/cm$ [12–14]. We also measured the sound velocity in nitrogen gas with thermal phonon resonance in the MHz region. The peak frequency at $n=19$ is 3.545 MHz, which gives the phonon velocity of 354.1 m/s with Eq. (1). This value agrees well with the literature value of 354.3 m/s. The accuracy is thus corroborated to be $10^{-4}$.

## V. CONCLUSION

We carried out the observation of thermal phonon resonance in gas-state material. The phonon propagates without any disturbance in the resonance cavity, and we could observe a clear resonance spectrum. We measured the phonon decay in nitrogen gas in the MHz region, which has not been achieved with conventional optical-beating spectroscopy. We also measured the sound velocity of nitrogen gas with an accuracy of $10^{-4}$, which is superior to that of the traditional ultrasonic measurement in the frequency region above MHz [12–14].

The present experiment of the thermal phonon resonance will enable us to observe the dynamics of structures at the molecular level through the investigation of the fluctuation in density and other physical quantities, such as molecular orientation. Another advantage of this method is that it is applicable to the measurement of the viscosity and the sound velocity in gases over a temperature of 1000 K.

## ACKNOWLEDGMENTS

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and the Japan Society for the Promotion of Science for Young Scientists.

---

[1] B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976), Chap. 10.
[2] X. Pan, M. N. Shneider, and R. B. Miles, Phys. Rev. A **69**, 033814 (2004).
[3] R. P. C. Schram, G. H. Wegdam, and A. Bot, Phys. Rev. A **44**, 8062 (1991).
[4] W. S. Gornall, C. S. Wang, C. C. Yang, and N. Bloembergen, Phys. Rev. Lett. **26**, 1094 (1971).
[5] L. Letamendia, J. L. Cabanié, C. Vaucamps, and G. Nouchi, Phys. Rev. A **44**, 3606 (1991).
[6] S. Murata, T. Kawamoto, M. Matsukawa, T. Yanagitani, and N. Ohtori, Jpn. J. Appl. Phys., Part 1 **46**, 4626 (2007).
[7] Y. Minami, T. Yogi, S. Mitani, and K. Sakai, J. Appl. Phys. **102**, 013111 (2007).
[8] K. Sakai, K. Omata, and K. Takagi, J. Chem. Phys. **122**, 024503 (2005).
[9] H. Tanaka, K. Hattori, K. Sakai, and K. Takagi, Jpn. J. Appl. Phys., Part 2 **36**, L1415 (1997).
[10] Y. Minami, T. Yogi, H. Kutsuna, and K. Sakai, Jpn. J. Appl. Phys., Part 1 **46**, 4327 (2007).
[11] T. Yogi, K. Sakai, and K. Takagi, J. Appl. Phys. **100**, 023505 (2006).
[12] G. J. Prangsma, A. H. Alberga, and J. J. M. Beenakker, Physica (Amsterdam) **64**, 278 (1973).
[13] A. Bardow and H. C. Ottinger, Physica A **373**, 88 (2007).
[14] A. J. Zmuda, J. Acoust. Soc. Am. **23**, 472 (1951).
[15] M. Bijedic and N. Neimarlija, Int. J. Thermophys. **28**, 268 (2007).
[16] S. Lago, P. A. G. Albo, and D. M. Ripa, Int. J. Thermophys. **27**, 1083 (2006).
[17] F. W. Giacobbe, J. Acoust. Soc. Am. **94**, 1200 (1993).
[18] P. J. Kortbeek, S. N. Biswas, and J. A. Schouten, Int. J. Thermophys. **9**, 803 (1988).
[19] M. Kimura, Y. Hanayama, and T. Nishitake, Jpn. J. Appl. Phys., Part 1 **26**, 1361 (1987).
[20] E. W. Lemmon and R. T. Jacobsen, Int. J. Thermophys. **25**, 21 (2004).
[21] R. A. Dawe and E. B. Smith, J. Chem. Phys. **52**, 693 (1970).
[22] Y. Minami, T. Yogi, and K. Sakai, Jpn. J. Appl. Phys., Part 1 **45**, 4469 (2006).
[23] K. Hattori, K. Sakai, and K. Takagi, Jpn. J. Appl. Phys., Part 1 **38**, 4932 (1999).
[24] K. Sakai, K. Hattori, and K. Takagi, Phys. Rev. B **52**, 9402 (1995).
[25] R. T. Beyer and S. V. Letcher, *Physical Ultrasonics* (Academic, New York, 1969), Chap. 4.
[26] J. D. Lambert, *Vibrational and Rotational Relaxation in Gases* (Oxford University Press, Oxford, 1977), Chap. 3.
[27] A. Yariv, *Introduction to Optical Electronics* (Holt, Rinehart and Winston, New York, 1971), Chap. 3.