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Spectroscopic characterization of dragonfly wings common in Japan

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ABSTRACT

A series of Fourier Transform infrared (FT-IR) absorption, X-ray diffraction (XRD), and Brillouin light scattering (BLS) studies on the wings of six species of dragonfly common in Japan, including the largest *Anotogaster sieboldii* and much smaller *Lestes temporalis*, was performed at room temperature. XRD and FT-IR results indicate that dragonfly wing is comprised of a randomly oriented microcrystalline or an amorphous-like α-chitin. We observed a pair of longitudinal acoustic (LA) phonon peaks and a broad quasi-elastic scattering peak in backscattering BLS spectra. LA phonon frequencies and full widths at half maximum were found to be 19.5 ± 0.4 GHz and 1.0 ± 0.2 GHz for the 488 nm excitation and independent of their sizes and species.

1. Introduction

While the dragonfly is a very popular insect in this world, it has an extremely long geological history. An extinct dragonfly, known as *Meganeura*, appeared about 290 million years ago in the Carboniferous period of the Paleozoic era [1,2]. Fossils of *Meganeura* have been discovered in Europe and northern America. According to the fossils, *Meganeura* looked like existing dragonflies, but possessed two pairs of long wings with a span of over 600 mm and was much larger than any kind of existing dragonfly. Today, more than five thousand kinds of dragonflies are distributed all over the world. Existing dragonflies have developed very advanced flying capabilities like hovering, gliding, and fluttering. About two hundred kinds of dragonflies have been confirmed in Japan. Dragonflies in the family *Cordulegastridae* are the largest with a wing span of over 120 mm, while dragonflies in the family *Brachydiplacinae* are the smallest with a wing span of less than 20 mm. There is a wide variety of sizes and weights in the order *Odonata*.

Brillouin light scattering (BLS) is a powerful technique to study thermally excited acoustic phonons in a frequency range between ~1 GHz and ~100 GHz, and has been successfully applied in various fields of condensed matter physics [3,4]. We are interested in the acoustic properties of various thin film structures in thickness below 10 μm; some of them are artificial polymer films [5] and the others are naturally produced thin films. As a naturally produced thin film, we are interested in dragonfly wings, because of not only their transparent nature for visible laser light but also biological and biomechanical interests. Dragonfly wings have also attracted a wide variety of scientific and technological interest from the viewpoints of biochemical and biopolymer sciences, structural dynamics, bioengineering, aerodynamics, and so on [6].

The cuticle mainly consists of chitin, which is a nitrogenous polysaccharide given by the formula of $(C_6H_9O_4\text{—}R)_n$ ($R = NHCOCH_3$), and insoluble proteins like collagen, keratin, and so on. Chitin (or cuticle) is commonly found in the shells of crabs and shrimps, in insect integuments, and in the cell walls of fungi [7]. In insect integument, chitin is distributed in the procuticle [8]. The phylogenic origin of insect wings, a morphology of the integment, is still a subject of controversy. However, it seems to be reasonable to assume that the main constituent of insect wing is chitin (or cuticle). Actually, our preliminary Fourier Transform infrared (FT-IR) absorption study on wings of several species of cicada, which belongs to the order *Hemiptera*, gives very similar FT-IR spectra with dragonfly spectrum. Of course one can find some differences when one carefully examines both FT-IR spectra of dragonfly and cicada in detail. In order to establish the dragonfly wing as a first example of insect wings, we tried to clarify the structural, molecular vibrational, and acoustic properties of dragonfly wings.

Let us consider more details on chitin. Since chitin is structurally similar to cellulose $(C_6H_{10}O_5)_n$, which is the main constituent of plant cell walls, one can expect strong elasticity and high flexibility for chitin. It is well known that chitin single crystals possess at least two different structural forms which are described as α-chitin and β-chitin. The α-chitin is widely distributed in nature and crustacean chitin crystal belongs to an orthorhombic space group $P2_12_12_1$ with lattice parameters of $a_\alpha = 0.474$ nm, $b_\alpha = 1.886$ nm,

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and $c_\alpha = 1.032$ nm [9]. The α-chitin crystal contains two polymer chains in a unit cell and these polymer chains are arranged anti-parallel. On the other hand, β-chitin is rather rare and mainly found in squid pens. β-chitin crystal belongs to a monoclinic space group $P2_1$ with one polymer chain in a unit cell. Lattice parameters of β-chitin are found to be $a_\beta = 0.485$ nm, $b_\beta = 0.926$ nm, $c_\beta = 1.038$ nm, and $\gamma = 97.5^\circ$ [10]. It is interesting to note a lattice constant relation, $a_\beta \sim a_\alpha$, $2b_\beta \sim b_\alpha$, $c_\beta \sim c_\alpha$, between the two chitin forms.

One can readily observe a characteristic feature of dragonfly wings by using an optical microscope with a magnification power of less than 50. Veins form irregularly shaped polygons. These are mainly squares and pentagons near the front and central portions of the wing, and then gradually change into irregularly shaped hexagons near the hind and tip portions. Thin cuticle films fill up these polygons. This polygon structure of veins and the elasticity of the cuticle give mechanical strength to dragonfly wings and support the highly developed flying capabilities of the dragonfly. Unfortunately the elastic properties of the cuticle have not been investigated yet to the best of our knowledge. Because of the lower crystal symmetry of α-chitin, the elastic properties of α-chitin are expected highly anisotropic. It is a very interesting question how a material with higher elastic anisotropy can be fitted into a dragonfly wing. BLS study of dragonfly wings would be expected to give information not only on the elastic properties of the dragonfly wing cuticle but also on the elastic properties of the shells of crabs and shrimps, and insect integuments as well as the cell walls of fungi.

Information on the crystallinity of chitin will be essential for the understanding of BLS results from dragonfly wings. A powder X-ray diffraction (XRD) technique is the most convenient and powerful method for structural characterization in an atomic scale. Since chitin is a polysaccharide, FT-IR spectroscopy is also a powerful technique to characterize molecular vibrations of polymer skeleton and attached molecular groups.

2. Experimental

Every measurement in this report was performed at 297 ± 1 K. We measured a series of BLS and FT-IR spectra from wings for six common species of dragonfly in Japan. These dragonflies, at least seven samples for each species, were collected during the early summer and fall seasons of 2009, 2010 and 2011, summarized in Table 1. Fig. 1(a) shows a picture of *Anotogaster sieboldii*, which is the largest dragonfly in Japan, and Fig. 1(b) shows a picture of a much smaller dragonfly, *Lestes temporalis*.

BLS spectra were probed by the *p*-polarized 488 nm line from an Argon ion laser operated in a single-cavity mode using the standard backscattering geometry. We should reduce the laser output power well below 10 mW to protect the thin dragonfly wings from thermal damage by the focused laser beam. Inelastically scattered light was analyzed by using a 3 + 3 pass tandem Fabry–Pérot interferometer (FPI) followed by a thermoelectrically cooled photomultiplier tube and photon counting electronics [11]. BLS spectrum within a frequency range of ±70 GHz around the laser frequency was directly stored on 500 channels of a computer memory. Because of small BLS cross section of dragonfly wings and low laser output power, each BLS spectrum was accumulated 600 times (1 scan/5 s). In order to protect the photomultiplier tube from optical damage by the intense elastically scattered beam, a mechanical shutter was introduced around the Rayleigh peak and the ghost peaks.

FT-IR spectrum was recorded by using a Shimadzu IRAffinity-1 spectrometer with a resolving power of 2 cm^{-1} in a wavenumber range between 800 cm^{-1} and 4000 cm^{-1} employing the KBr disc method in the transmission configuration. Each spectrum was accumulated 20 times to improve the signal to noise ratio. We also measured powder XRD patterns for structural characterization using the Cu Kα radiation ($\lambda = 0.1542$ nm) in a 2θ range from 5° to 60°. Dragonfly XRD patterns were accumulated 9 times to improve the signal to noise ratio. For a comparison, we also measured XRD and FT-IR pattern of crab chitin powder, which is expected to be α-chitin (Nakarai Tesque. Inc.).

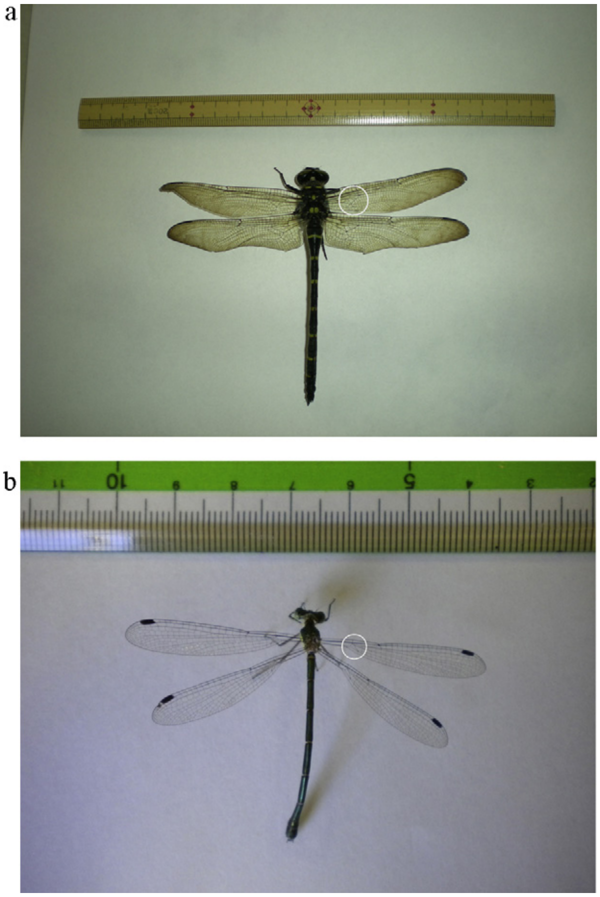

Fig. 1. Pictures of (a) *Anotogaster sieboldii* and (b) *Lestes temporalis*. The circle on each dragonfly wing indicates the area where we have performed Brillouin light scattering and thickness measurements.

In order to discriminate a set of similar dragonfly FT-IR spectra, we carried out principal component analysis (PCA) and agglomerative hierarchical cluster analysis (AHCA), both are multivariate analysis techniques [12]. We applied PCA for FT-IR spectra in a wevenumber range between 815 cm^{-1} and 3985 cm^{-1} (3288 points for each spectrum). We used Mathematica Ver. 8.0.4 software program (Wolfram Research Inc.) for both of PCA and preprocessing procedures, including the 15 points second-order Savitzky–Golay smoothing, baseline correction, mean-centering, area- and peak-normalization, and calculation of the first and second derivative spectrum. For the baseline correction we adapted the least-squares technique assuming a linear function between two regions, one is a spectral area showing a minimum in a wavenumber range between 1700 cm^{-1} and 2000 cm^{-1}, and the other is a spectrum above 3700 cm^{-1}. For the Savitzky–Golay smoothing, we examined several smoothing points between 7 and 21, and found that 15 points smoothing gives the best result. After several attempts of area-normalization and peak-normalization, we found that an area-normalization by using an integrated spectrum between 900 cm^{-1} and 1900 cm^{-1} gives the best result. Then, spectra were multiplied by a factor of 500. We also employed the PCA technique for the first and second derivative spectra. AHCA was performed for FT-IR spectra in a wavenumber region between 900 cm^{-1} and