

**RADIAL BREATHING MODES IN COSMOCHEMISTRY AND METEORITICS.** K. B. Wilson<sup>1</sup> and T. L. Wilson<sup>2</sup>, <sup>1</sup>Department of Mechanical Engineering and Materials Science, Rice University, Houston, Texas 77005, <sup>2</sup>NASA, Johnson Space Center, Houston, Texas 77058 USA.

**Introduction:** One area of continuing interest in cosmochemistry and meteoritics (C&M) is the identification of the nature of Q-phase, although some researchers in C&M are not reporting relevant portions of Raman spectral data [e.g. 1]. Q is the unidentified carrier of noble gases in carbonaceous chondrites (CCs). Being carbonaceous, the focus has been on any number of Q-candidates arising from the  $sp^2$  hybridization of carbon (C). These all derive from various forms of graphene [2-4], a monolayer of C atoms packed into a two-dimensional (2D) hexagonal honeycomb lattice that is the basic building block for graphitic materials of all other dimensions for  $sp^2$  allotropes of C.

As a basic lattice, 2D graphene can be curled into fullerenes (0D), wrapped into carbon nanotubes or CNTs (1D), and stacked into graphite (3D). These take such additional forms as scroll-like carbon whiskers [1, 5], carbon fibers [5], carbon onions, GPCs (graphite polyhedral crystals) [6], and GICs (graphite intercalation compounds) [5]. Although all of these have been observed in meteoritics [e.g. 7-8, 1], the issue is which can explain the Q-abundances [9]. In brief, one or more of the 0D-3D  $sp^2$  hybridization forms of C is Q.

For some Q-candidates, the radial breathing modes (RBMs) are the most important Raman active vibrational modes that exist, and bear a direct relevance to solving this puzzle. Typically in C&M they are ignored when present. Their importance is addressed here as “smoking-gun” signatures for certain Q-candidates and are very relevant to the ultimate identification of Q.

**Raman Spectroscopy:** Raman spectroscopy is widely used in planetary science as a technique for identifying and analyzing molecular structures such as bonds and crystal lattices. One can study vibrational, rotational, and electronic excitation modes of a molecular system induced by monochromatic light such as a laser. It is a non-invasive means of chemical and molecular analysis based upon the inelastic scattering of photons (the Raman effect).

The Raman effect derives from the scattering of incident laser light (at wavelength  $\lambda$ ) to excite energy levels and produce spectral shifts in the molecular system being studied. The molecules are excited into virtual atomic states that decay, producing new light at different frequencies. The molecules either absorb energy (Stokes scattering), emitting lower energy photons; or lose energy (anti-Stokes), emitting higher-energy photons. Since the two are usually symmetric, only the

Stokes lines are generally presented. A Raman spectrum is produced by subtracting the incident laser-light energy from that of the photons emitted, giving a shift with respect to  $\lambda$  as a function of wavenumber ( $\text{cm}^{-1}$ ).

The laser excitation induces vibrational waves in the crystal lattice (phonons) being examined, and these phonon-modes can be thought of as humming-modes. The Earth does a similar thing [10]. Because the incident Raman photon has produced a phonon, the scattering is inelastic. There is an extensive field of literature on Raman photon-phonon interactions and the associated Brillouin zones in solid state physics as these pertain to  $sp^2$  C allotropes [11-13, 5].

**Phonon Breathing Modes for Carbon:** The vibrational modes are often referred to as phonon breathing modes (Figure 1). They are modelled as simple and coupled harmonic oscillators. Like notes on a piano, basic phonon tones are produced at beat frequencies as well as harmonic overtones.

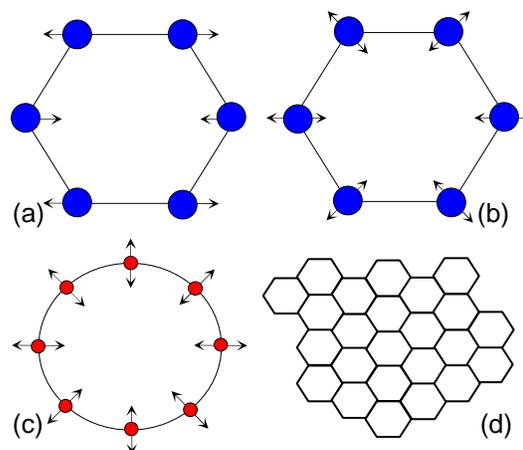


Figure 1. Phonon vibration modes for  $sp^2$  C. (a) G-band ( $E_{2g}$ ) mode, (b) D-band mode, (c) RBM ( $A_{1g}$ ) for CNTs and fullerenes, (d) graphene.

The vibrational modes are all dispersive (except for perfect crystals), being dependent upon temperature, pressure, and the number of graphene layers involved [14, 2]. The crystal lattice symmetries such as  $A_{1g}$  and  $E_{2g}$  in Figure 1 are complex but have been well-defined in numerous places [11; 13 Table 8.1; 15 Table 1]. In the case of CNTs, only two numbers ( $n, m$ ) are required to define a chiral lattice vector  $C_h \equiv (n, m)$  so that all of the geometrical properties are then determined. In particular, the diameter  $d_t$  of a CNT is  $d_t = \pi C_h$  and the

Raman shift  $\omega_{RBM}$  is found to be  $\omega_{RBM} \text{ (cm}^{-1}\text{)} \approx A/d_t + B$  where  $A=234$  and  $B \sim 10$  [13] for a limited range of  $d_t$ . This result has piqued so much interest that tremendous progress has been made regarding the general subject of Raman spectra and  $sp^2$  C lattice geometries.

It is important to note that Rao *et al.* pointed out additional Raman scattering variation effects caused by stacking or layering [15, their Ref. 11; 2]. The Raman spectrum for MWNTs (multi-walled CNTs) closely resembles that of graphite save for the RBMs appearing below  $500 \text{ cm}^{-1}$  [e.g. 6, Fig. 3 inset]. This means in C&M that a measurement of D and G alone does *not* eliminate MWNTs or any 0D-1D  $sp^2$  geometry as Q-candidates. These and CNTs in general were conjectured to be carriers of the Q-gases some time ago by Heymann [16]. A side-by-side comparison of CNTs and graphite illustrates the same thing [12, Fig. 48]. Therefore, all Raman spectra in C&M investigations of Q will find D and G modes because these are basic modes of 2D graphene (Figure 1d), not 3D graphite. D and G information discloses little regarding the nature of  $sp^2$  Q. The D mode (and its overtones) in fact is a dispersive effect created by crystal defects and is not an active Raman vibration mode at all. It disappears for pure crystal lattices.

**Carbon Nanotubes and RBMs:** We give specific examples of SWNT (single-walled CNT) RBMs below in Figure 2 adapted from Ti composite research [17]. Since Ti is of interest in CCs [18], the RBMs for a Ti-SWNT lattice are shown – along with TiC (*fcc*) in order to prove that the C involved constitutes SWNTs and not simply a TiC matrix. The  $A_{1g} (8,8)$  RBM [15] at  $208.9 \text{ cm}^{-1}$  is clearly visible along with general RBM activity. These types of RBMs would appear in Raman spectra for the insoluble organic material (IOM) of Q if SWNTs were present. 0D fullerenes have RBMs too.

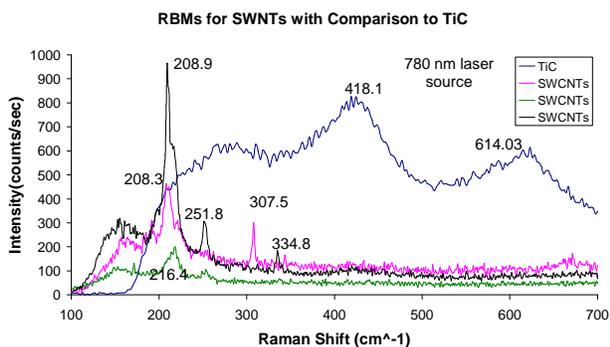


Figure 2. RBMs for SWNTs in a Ti matrix [17].

The full Raman spectrum for this example is given in Figure 3. The importance of explaining all energy modes from  $50 \text{ cm}^{-1}$  to  $3000 \text{ cm}^{-1}$  – RBMs, D and G, high-energy modes, and  $1^{\text{st}}$  overtones – cannot be over-emphasized.

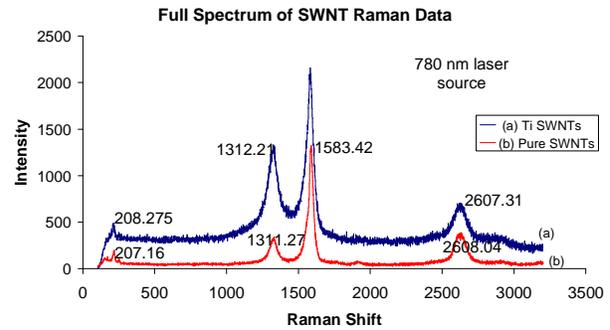


Figure 3. Full spectrum for Figure 2.

**Relevance to Q:** Without the RBM region of the Raman spectrum and the explicit definition of what features appear below  $\sim 500 \text{ cm}^{-1}$ , there actually is not very much that one can conclude about the D and G modes except to say that the material under study is a graphene derivative. All of these derivatives bear the tell-tale D and G features, in many cases almost identically [12, Fig. 48]. All of them are  $sp^2$  Q-candidates.

**Conclusions:** Without thorough experimental Raman data addressing phonon-breathing modes in cosmochemistry and meteoritics, theoretical and computational progress in the study of Q-phase is difficult. 1D Q-candidates clearly exhibit RBMs (Figure 2). Therefore, all vibrational Raman active modes (not just some) must be measured in the IOM, prior to release of the noble Q-gases. In this manner, one can eliminate  $sp^2$  C candidates that in fact are not bearing the noble gases, or cannot explain the known abundances. This will ultimately lead to an understanding of the nature of Q, without which there will be slow progress in understanding the origin and evolution of the solar system.

**References:** [1] Fries M. & Steele A. (2008) *Science* 320, 91-93. [2] Ferrari A. et al. (2006) *Phys. Rev. Lett.* 97, 187401. [3] Geim A. and Novoselov K. (2007) *Nature Mat.* 6, 183-191. [4] Katsnelson M. (2007) *Materials Today* 10.1, 20-27. [5] Dresselhaus M. & Endo M. (2001) in *CNTs, Topics in Appl. Phys.* 80, 11-28. [6] Gogotsi Y. et al. (2000) *Science* 290, 317-320. [7] Smith P. & Buseck P. (1981) *Science* 212, 322-324. [8] Buseck P. (2002) *EPSL* 203, 781-792. [9] Wilson T. & Mittlefehldt D. (2007) *LPSC XXXIX*, 1142. [10] Tanimoto T. (2008) *Science*, 452, 539-540. [11] Dresselhaus M. et al. (2005) *Phys. Rep.* 409, 47-99. [12] Dresselhaus M. & Eklund P. (2000) *Adv. Phys.* 49, 705-814. [13] Reich S. et al. (2003) *Carbon Nanotubes*, Weinheim: Wiley-VCH. [14] Ravikar N. et al. (2002) *Phys. Rev. B*, 66, 235424. [15] Rao A. et al. (1997) *Science*, 275, 187-191. [16] Heymann D. (1998) *LPS XXIX*, 1098. [17] Wilson K.E. (2008) *PhD Thesis*, Rice University. [18] Brearley A.J. (1993) *Meteoritics* 28, 590-595.