Chapter 15
Functionalized Nanomaterials to Sense Toxins/Pollutant Gases Using Perturbed Microwave Resonant Cavities

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Abstract This chapter provides an overview of the techniques and methods involving electromagnetic resonators to study the interactions of gas molecules with nanomaterials substrates. A resonant cavity operating in TE_{011} mode was employed by the author(s) to characterize the nature of interactions of a range of weakly polar to nonpolar gas molecules with carbon nanotubes loaded in the cavity. Microwave resonant cavities are special electromagnetic resonators that can have a very high quality factor, which enhances the sensitivity of the apparatus as compared to standard electrical tank circuits. By measuring shifts in the resonant frequency of these circuits and by calculating the pressure broadening of the resonant peaks, the technique developed offers a highly effective means to quantify the amount of foreign agents perturbing these resonant cylinders. By functionalizing the nanomaterials with specific antibodies and loading them as wicks in these cylinders, the technique can be engineered into a very sensitive and unique chemical and biological sensor prototype.

Keywords Carbon nanotubes, chemical and biological sensors, microwave resonance, resonant cavities

15.1 Introduction

Resonant cavities are well-known, highly sensitive devices that have been used to make measurements of fundamental properties of matter in all its phases (Hong, 1974). A resonant cavity can be considered to be multiple inductor capacitor resistance

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(LCR) circuits connected in parallel. In this chapter, we present an overview of the study done to quantify the nature of interactions of the gas molecules with the nanomaterials that act as loads in these resonant cavities. The microwave spectral response of these cavities containing different gases possessing different indices of refraction provide encyclopedic signatures of interactions of these gases in a complex dielectric medium. The cavities were loaded with different types of materials (carbon-based, silica gel, and cotton fibers). Upon energizing the cavities in their fundamental modes, a nondestructive study was performed to investigate the perturbation response of the load with several different gases. The frequency range of 9.1–9.8 GHz was used in the experiment to study the changes in the dielectric properties of the load due to the gases as well as to quantify the nature of absorption/adsorption of these gases by the nanomaterials loaded in the resonant cavities. The fact that different substrate materials interact differently with select gases enabled the study to provide information on the effect of various forces such as van der Waals (VdW) and other exchange forces that have significant contributions in the interaction behavior of gaseous molecules with the substrates.

15.2 Brief Electromagnetic Theory of Microwave Resonant Cavities

Waveguides and cavities offer an efficient method of transferring electrical energy into special media by varying electromagnetic fields, either in free space or in a contained environment. Extensive experimental, as well as theoretical, studies have been done in the past using various geometries and materials loading electromagnetic devices. Transmission lines, waveguides, and cylindrical and spherical resonators have found many applications in industries today (Harvey, 1963). These devices are highly efficient in storing energies with minimal losses, depending upon the materials used to construct them. Skin depth and Ohmic losses are two major factors in considering the leakage of the fields (Air Force manual Radar Circuit Analysis, 1950). In order to properly design electromagnetic devices solutions of Maxwell's electromagnetic wave equations with appropriate boundary conditions within these devices must be used.

The experiment in this discussion employed a cylindrical resonant cavity, which is formed by closing the ends of a cylindrical waveguide with conducting plates on its ends as shown in Fig. 15.1 (Montgomery, 1947).

A cylindrical microwave resonant cavity can be considered to be N LCR circuits arranged in parallel, where N tends to infinity. The cavity is constructed by $\lambda/4$ sections of such circuits as described in the Air Force manual Radar Circuit Analysis (1950).

In cylindrical resonant cavities there exist Electric (E) and Magnetic (B) fields orthogonal to each other. Eigenvalue solutions of the wave equation subjected to proper boundary conditions are called the modes of resonance and are labeled as either transverse electric (TE_{lmn}) or transverse magnetic (TM_{lmn}). The subscripts l,m,n define the patterns of the fields along the circumference and the axis of the cylinder. Formally, these l,m,n values are the number of full-period variations of E_r

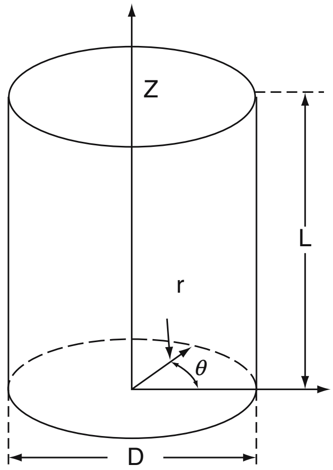


Fig. 15.1 A sketch of a cylindrical geometry coordinate system for a cylindrical resonant cavity. The dimensions are determined by the range of frequencies to be used in the studies

with respect to θ, number of half-period variations of E_θ with respect to r, and number of half-period variations of E_r with respect to the z-axis, respectively (Montgomery, 1947). In this investigation, the cylinder was tuned to oscillate in its fundamental TE_{011} mode. This convention will be used for future references in this work for the purpose of discussions.

The resonant cavities are tuned with a shorting plunger in order to obtain a selective mode frequency. The cylinders were coated with silver in order to minimize losses due to stray fields and other ohmic losses. Very high quality factor of around 20,000 can be obtained. Due to such high quality factors, the resonant devices are very sensitive to perturbation response when loaded with any external medium. Depending upon the permittivity, as well as permeability of the sample, the response of these resonant cavities will have a shift in their resonant frequencies as well as changes in their quality factors. Whenever the samples are loaded in the intense electric field of the cavity, Slater's perturbation theory (Slater, 1941) states that the shift in the resonant frequencies and change in the Q values of the resonator can then be expressed by Equations (15.1) and (15.2), respectively, as given below

$$\frac{\delta f}{f_r} \approx -\frac{(\varepsilon' - 1)}{2} \frac{\int_{\Delta \upsilon} \vec{E} * \vec{E^*} \, \mathrm{d}\upsilon}{\int_V \vec{E} * \vec{E^*} \, \mathrm{d}V} \tag{15.1}$$

where δf is the shift from the resonant frequency, ε' is the real part of the dielectric constant, $\mathrm{d}\upsilon$ is the volume of the sample perturbing the cavity, and $\mathrm{d}V$ is the cavity volume, and

$$\Delta\left(\frac{1}{Q}\right) = \varepsilon'' \frac{\int_{\Delta\upsilon} \vec{E} * \vec{E^*} \mathrm{d}\upsilon}{\int_V \vec{E} * \vec{E^*} \mathrm{d}V} \tag{15.2}$$

where ε'' is the imaginary part of the dielectric constant and Q is the quality factor of the resonator.

The above two equations then tells us that by measuring the amount of shift in the resonant frequency and by quantifying the amount of change in the quality factor of these resonators, it is possible to determine the nature and amount of material loading the cavities. Under no load conditions the resonant frequency is scaled by the dielectric constant of free space/air or vacuum depending upon the pressure conditions of these resonators. It is only when a medium with a dielectric constant (ε') different from free space is introduced within the cavity that the natural resonant frequency gets scaled as defined by equation (15.1). Also, the quality factor, which is a measurable quantity of the imaginary part of the dielectric behavior of the material, is a measure of loss. Hence, the entire concept of measuring any deviation from the unperturbed state of the medium is thus obtained from these two measurable quantities.

15.3 Can We Use This Information to Make Sensor to Detect Toxins?

In order to show how the properties of the cavity can be used to develop a chemical/biological sensor, the nature of sensor needs to be outlined. What is a sensor? In simplistic terms, it is a device that is equipped with proper electronics to quantify changes in a given state of a system. It may be an accelerometer of an automobile, emission gas temperature of a jetliner, environment, bio-metabolism of living bodies, space storms, etc. What is required is a way to detect subtle "**changes**."

The sensors must determine and quantify these changes and specify the nature of change and transmit or store information in a logical manner for proper countermeasures. An efficient and a reliable detector of a person wearing cologne or perfume is the nose. Can an electronic device be designed to mimic this property?

The natural diffusion of those aromatic compounds and essential oils quickly is detected. What is not observed is the diffusion phenomenon of Brownian motion. The ability to be able to determine which brand of cologne or perfume fragrance is in the immediate environment and how widely it is spread is not easy to be achieved. When a device is able to respond to these fundamental events of change, and is able to signaturize them, the information retrieved is what basically constitutes a sensor response.

Similarly, when the electromagnetic signals that constitute a set of orthogonally coupled Electric (**E**) and Magnetic field (**B**) vectors are introduced inside a geometrical boundary, which in the case in a cylindrical resonant cavity, electrodynamics comes into the play. Solutions to the Maxwell's equations according to the appropriate boundary conditions then define the nature of oscillations, resonance, and any impedance losses within these cylinders. By being able to tune these resonant cavities to operate in a specific mode, we are then able to define the natural state of resonance in a particular dominant mode, which can be either electric or magnetic. The experiment described below demonstrates some unique and selective results with the resonant cavities.

15.4 The Experiment

15.4.1 Experimental Setup and Sensitivity of the Apparatus

Figure 15.2a shows two tunable cylindrical resonant cavities that were phase-locked to each other for this investigation. These two cavities were maintained under high vacuum conditions in order to avoid any contamination from the environment. In this experimental setup an empirical study was made to observe and characterize the nature of interactions of various gases, both weakly polar as well as nonpolar gases, with the various substrates (S1–S5) as listed in Table 15.1. The two resonant cavities shown in Fig. 15.2a served the purpose of making comparative studies. A cavity containing no load was used as the reference cavity to characterize the nature of perturbation response of only the gas molecules, whereas, on the other hand, the second cavity was loaded with different substrates (S1–S5) progressively and the same gases were cycled through them. Six different experiments were made to characterize the responses of the cavities when gases were cycled through them.

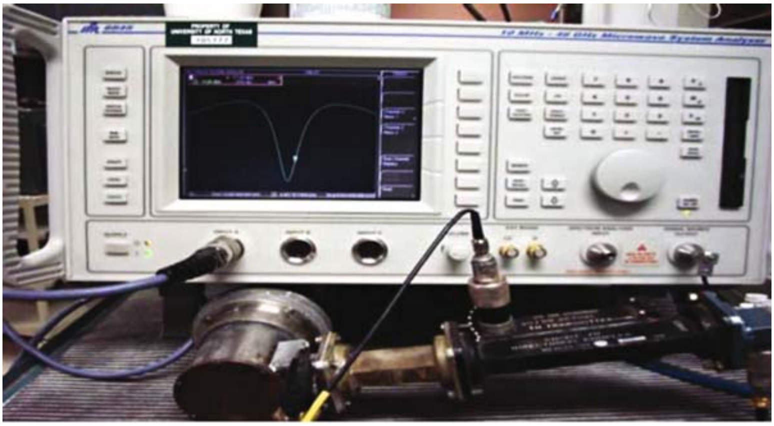
The microwave source used in this study was a microwave network analyzer model IFR 6845 shown in Fig. 15.2b (Microwave network analyzer). Integrated into this single instrument is a synthesized source, a three-input scalar analyzer, and a synthesized spectrum analyzer. Complete engineering details of this equipment is beyond the scope of this document, but the basic function of this instrument is to generate a constant

Table 15.1 Various substrates that served as gas absorbers that were loaded in the test cavity shown in Fig. 15.2a

Labeled	Various substrates in amorphous as well as fibrous forms loaded for each experiment	Form/shape/properties
S1	Untreated single-walled carbon nanotubes (SWCNT)	Amorphous powder, chirality (7.5 and 6.5) semiconducting mixed with conducting
S2	Thermally treated nanotubes	Just as S1
S3	Activated charcoal	Granular crystals
S4	Silica gel	Amorphous granules
S5	Cotton fibers	Cotton medical grade

a

Fig. 15.2a Two tunable vacuum tight cylindrical resonant cavities that were phase-locked and their impedance were matched using the impedance tuning coil. The plungers seen on the top were to aid us in tuning these cylinders to resonate in TE_{011} mode (*See Color Plates*)



b

Fig. 15.2b IFR6845 series microwave network analyzer used as the synthesized source to generate and feed the microwaves into the resonant cavities (*See Color Plates*)

(CW) output of microwaves capable of sweeping 10 MHz to 47 GHz. Depending upon the physical dimensions of the resonator and their coupling with the source, this spectrum analyzer can operate to detect the microwave absorption profile of the resonator either in the reflection or in the transmission mode. In this work the frequency range used to sweep the resonator was between 9.1 and 9.8 GHz. The synthesized source has low phase noise and 1 Hz frequency resolution. The crystal detector used to detect the absorption profile usually produces an output current such that the current–voltage characteristic is represented by $I \alpha V^2$. The output power can be approximately related to the square of the input power; hence, a small power that is input into the cavity containing some load will produce a relatively large change in the output signal. This engineering principle made it relatively simple to study the effects of both low and high concentrations of gases absorbed onto the substrate.

The test cavity loaded with substrates as labeled below and the reference cavity that was void of any substrate were then completely degassed and a vacuum was maintained around the order of 10^{-5} Torr. During individual experimental runs, fixed pressures of gases (carbon monoxide, carbon dioxide, oxygen, hydrogen, freon-13, fluorine, chlorine, and ammonia) were progressively cycled through the two resonators, and their dielectric response in both test and reference cavities was collected for spectroscopic investigation.

From the response of each substrate it is thus possible to calculate the electric displacement density (**D**) due to the polarization of the material when subjected to **E** vector.

Even though the presence of a dielectric material in an Electric (**E**) field involves phenomenon at the atomic scale, it is possible to represent the overall macroscopic effect from equations (15.1) and (15.3).

$$\begin{aligned} D &= \varepsilon_o \left(1 + \frac{P}{\varepsilon_o E} \right) E \\ &= \varepsilon_o \varepsilon_r E \end{aligned} \tag{15.3}$$

where D is the electric displacement and P is the polarization of the material, ε_r is the relative dielectric constant of the material whose real and imaginary parts can be found by simply measuring the shift in the frequency and changes in the full width of the profile at half power maximum (full width half maximum [FWHM]) by using equations (15.1) and (15.2), respectively.

Thus, it is shown how experimentally these signature changes in the spectroscopic profile of the medium tell us about the scalability of the resonance with the amount of dielectric material introduced into it.

Hence, by using the above design it is possible to sensitively (parts per million – few parts per billion) detect any changes in the resonators unperturbed response (Fig. 15.3). The remaining task is to find specificity in these changes. These changes can be due to any foreign material; until we are able to specify what material, the sole purpose of the sensor remains half complete. The next phase of the experiment is to find out how to eliminate the role of the vacuum only and to introduce chemical selectivity of the resonator for a specific toxin.

It was found that for different pressures of different gases and different types of nanomaterials, there were different responses in the shifts of the probe signal for each cycle of gassing and degassing of the cavity. This preliminary work suggests

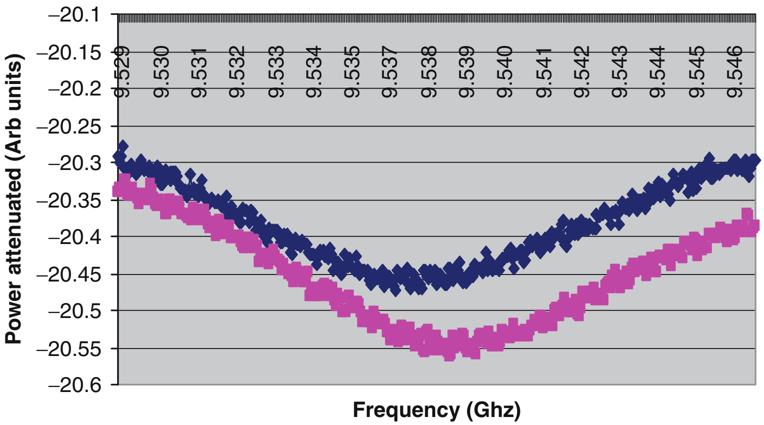


Fig. 15.3 A typical frequency response curve obtained due to the introduction of air into the resonant cavities. Shown above in pink is a typical absorption profile of the resonator under vacuum, and in blue is the shift of the resonant frequency to a lower value upon introducing air into the system (*See Color Plates*)

that microwave spectroscopy of the complex medium of gases and carbon nanotubes can be used as a highly sensitive technique in studying the complex dielectric response of different polar as well as nonpolar gases when subjected to intense electromagnetic fields within the cavity. In order to introduce the specificity of this prototype, defining the role of carbon nanotubes is imperative. Through experimental runs performed, it was determined that of all the substrates (S1–S5), carbon nanotubes show selective molecular sieving for specific gases. The results of these investigations recorded elsewhere (Anand et al., 2005; Anand, 2007) indicate that due to huge surface area to mass ratio of these novel materials, nanotubes have demonstrated excellent adsorption properties. It was interesting to note that the resonant cavities without any substrates loaded, showed no or very little response of adsorption due to surface adhesion of molecules on their walls, whereas, the cavities with very little amounts of substrates, showed significant adsorption of gas upon cycling. Out of all the substrates, single-walled carbon nanotubes showed maximum adsorption for all the gases and the amount of adsorption of these nanotubes were different for different gases.

15.4.2 Specificity That Completes the Functionality of Sensing

The resonant cavities discussed in section 15.4.1 demonstrated their sensitivity for any foreign agents introduced into them. The cavity that holds no substrates acts as a reference device which is subjected to the same conditions as the test cavity containing chemically functionalized nanotubes in it. When subjected to a certain toxin, which has a high degree of reactivity towards the functionalized nanomaterial the result will be a specific by-product with a certain degree of polarizability

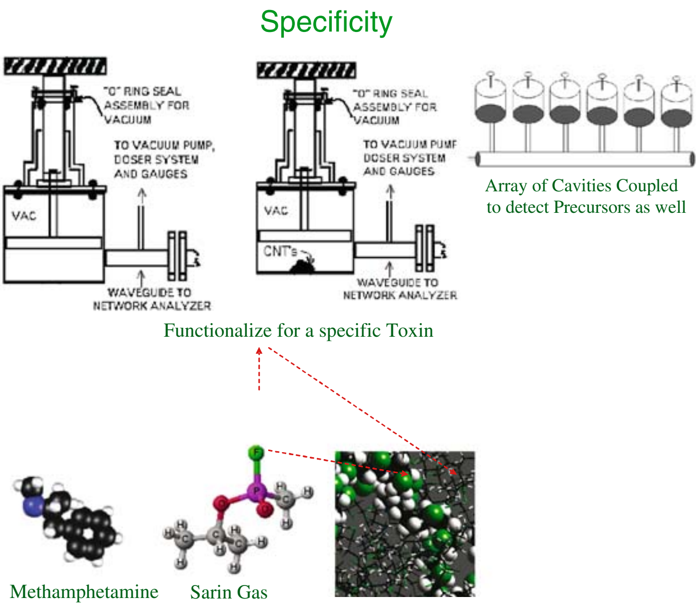


Fig. 15.4 Functionality of the prototype for specific detection (*See Color Plates*)

and dielectric response. This by-product response will be absent in the reference cavity. Thus, by measuring the resolution of shift in the frequencies of both (test and reference) cavities, it is possible to determine the specific toxin that invaded the boundaries of the prototype. The algorithmic procedure of detection capabilities of this prototype is shown in the schematic form in Fig. 15.4.

Figure 15.4 shows the loading and cycling of the samples when the resonant cavities with and without chemically functionalized sniffing wick get perturbed with the foreign agent. Both cavities show different responses to the dielectric medium. Designate the reference cavity (CR) and test cavity with functionalized nanotubes (CTFN) in their natural resonance having frequency F_{ocr} and F_{octfn} subjected to Toxin X.

In the procedure F_{ocr} is scaled due to the new dielectric material of X and this frequency is F_{1cr}. From this ΔF_{cr} is given by:

$$\Delta F_{cr} = F_{ocr} - F_{1cr} \tag{15.4}$$

Similarly, when CTFN is perturbed with the same Toxin X, simultaneously, there is a chemical change in the environment of the CTFN, but not in CR.

Where X + functionalized bonds on nanotubes produces a by-product Y inside CTFN. The new Y will scale the frequency of CTFN due to its own dielectric properties resulting in a new frequency designated as F_{yctfn}. The resultant ΔF_{ctfn} is then given by:

$$\Delta F_{ctfn} = F_{octfn} - F_{yctfn} \tag{15.5}$$

The ratio of equations 15.4 and 15.5 is basically the resultant response, which is specific to the nature of the perturber, implying:

$$\frac{\Delta f_{\mathrm{cr}}}{\Delta f_{\mathrm{ctfn}}} \rightarrow X \tag{15.6}$$

Similarly, when arrays of these test resonant cavities loaded with functionalized wicks for various toxins are phase-locked to the reference cavity as shown in Fig. 15.5 they can act as detectors for targeting various toxins as well as their precursors through an array of suitably tuned cavities with specifically functionalized nanotubes. By using the approach as demonstrated in this document, it has been shown that the apparatus can be used to successfully detect low levels of toxin vapors associated with the drug “Methamphetamine,” in a laboratory-controlled environment. Some of the results of this study are highly sensitive in nature and are not reported in this document. These results can be obtained by other avenues.

Besides the two main characteristics of sensitivity as well as specificity of a sensor, the industrial, military, and other standards demand the device to be portable, economical, autonomous, and power efficient. In order to address some of these characteristics, the authors in their respective laboratories have been working on improving the design of the prototype, as shown in Figs. 15.6 and 15.7, respectively. The necessary electronics consisting of local oscillators, beat oscillators, smaller cavities, mixers, and phase-locking loops have been assembled in prototypes. As of this date the device needs further evaluation in an operational environment to establish a set of encyclopedic data and for comparison with unknown toxins.

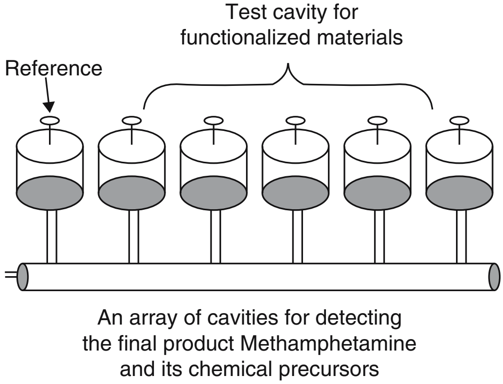


Fig. 15.5 Arrays of cavities phase-locked to the reference cavity and loaded with functionalized wicks to specifically determine the toxin and its precursors

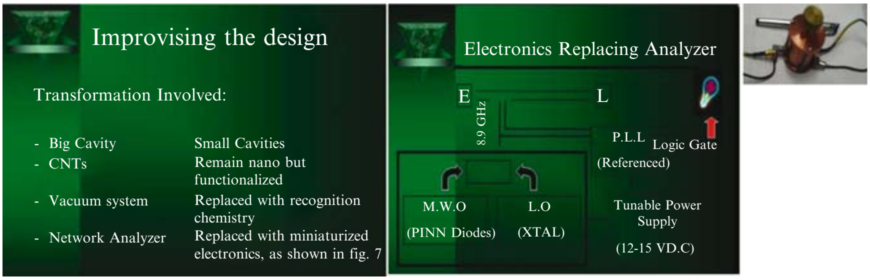


Fig. 15.6 (left) and 15.7 (right) The figures shown above describe the necessary steps taken to introduce portability into the sensor prototype. Shown on the right is the schematic involved in phase-locking the empty (E) and the loaded (L) cavity energized with a 12 V DC current-driven microwave diode. A typical electromagnetic mixer circuit has also been developed. The cavity shown at the far right is a significantly smaller than the test cavity and is comparable to today's cellular phones (*See Color Plates*)

15.5 Conclusion

The results described in this chapter provide an overview of the experimental investigation of gas interactions with carbon nanotubes inside a resonant cavity. An innovative concept of a chemical and biological sensor prototype has also been described. Using the principle of selective functionalization of carbon nanotubes, the scalability of this prototype can be extended to demonstrate sensing in military and chemical and biological industries to detect lethal, less lethal, and other industrial gases. The sensor industry is a multi-billion dollar industry world-wide and sensors have been researched for over a century. Investigators in many nations are working on sensor concepts to develop a "fool-proof" design of sensors/actuators to reduce false-positives in its operations. It is beyond the scope of this document to list all the types of sensor researches that have been done, but with the advancement in nanotechnology and development of novel nanomaterials, there exist several references in the literature (Anand, 2007; Rosa et al., 2004; Poncharal et al., 1999; Babic et al., 2003; Reulet et al., 2000; Zhao, 2001; Ye et al., 1999; Weber et al., 2000; Torrens, 2004; Insepov et al., 2006) that involve the application of nanomaterials to develop various kinds of sensors to detect toxins. It is proposed that with the further development of nanotechnology, and advancement in antibody research, there will be advancement in functionalization chemistry, which can be incorporated in sensor design to develop products with wide applications.

References

Anand A (2007) studying interactions of gas molecules with nanomaterials loaded in a microwave resonant cavity, Ph.D. dissertation, University of North Texas, Texas, USA.

Anand A et al. (2005) Select gas absorption in carbon nanotubes, loading a resonant cavity to sense airborne toxin gases. Nucl. Instrum. Meth. Phys. Res. B 241: 511–516.

Babic B, Furer J, Sahoo S, Farhangfar Sh, and Schonenberger C (2003) Intrinsic thermal vibrations of suspended doubly clampled single-wall carbon nanotubes. Nano Lett. 3:1577.

Harvey AF (1963) Microwave engineering. Academic Press, London, Ch. 5, p. 196.

Hong KH (1974) Microwave Properties of Liquids and Solids Using a Resonant Microwave Cavity as a Probe, Ph.D. dissertation, University of North Texas, Texas, USA.

Microwave network analyzer purchased through Naval Grant number – ONR-N00013-03-0880

Montgomery CG (1947) Technique of microwave measurement. McGraw-Hill, Cleveland, p. 294.

Poncharal P., Wang ZL., Ugarte D., et al. (1999) Science 283: 1513.

Radar Circuit Analysis, U.S. Air Force radar manual. Washington, 1950, Ch. 10.

Reulet B, Kasumov AYu, Kociak M, Deblock R, Khodos II, Gorbatov YuB, Volkov VT, Journet C, and Bouchiat HL (2000) Acoustoelectric effects in carbon nanotubes. Phys. Rev. Lett. 85: 2829–2832.

Rosa HMC, Carmen KMF, and Wen JL (2004) Nanotechnology 15: S672–S677.

Slater JC (1941) Microwave electronics. Rev. Mod. Phys. 441.

Torrens F (2004) Effect of type, size, and deformation on the polarizability of carbon nanotubes from atomic increments. Nanotechnology 15: S259–264.

Weber SE, Talapatra S, Journet C, Zambano A, and Migone AD (2000) Determination of the binding energy of methane on single-walled carbon nanotube bundles. Phys. Rev. B. 61: 19.

Ye Y et al. (1999) Hydrogen adsorption and cohesive energy of single walled carbon nanotubes. Appl. Phys. Lett. 74: 16.

Zeke Insepov, Dieter Wolf, and Ahmed Hassanein (2006) Nanopumping using carbon nanotubes. Nanoletters 6 (9): 1893.

Zhao, J. (2001) Gas molecules adsorption on carbon nanotubes. Mat. Res. Soc. Symp. Proc. 633: A13.48.1.