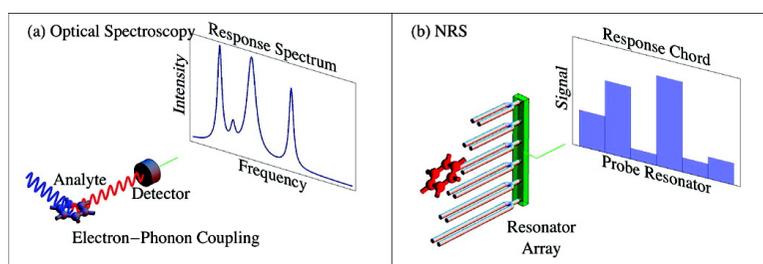


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Nanomechanical Resonance Spectroscopy: A Novel Route to Ultrasensitive Label-Free Detection

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ABSTRACT

We propose a new chemical detection technique in which an analyte's vibrational frequencies are interrogated directly using an array of nanomechanical resonators. This "nanomechanical resonance spectroscopy" (NRS) could permit label-free chemical detection, combining the high sensitivity of nanomechanical approaches with the high selectivity of traditional spectroscopy. A computational proof of principle is presented, demonstrating the central concept: exploiting resonant exchange of vibrational energy for chemical identification. Guidelines for experimental realization of NRS are discussed.

The ability to quickly and accurately detect the presence of a given biological or chemical analyte, whether gaseous or in solution, remains one of the most important challenges for a range of applications, from chemical sensing for homeland security to biomolecular recognition. Spectroscopic techniques such as Raman, infrared, and nuclear magnetic resonance spectroscopy have the great advantage of being "label-free", that is, they require no preconditioning in order to identify a given analyte. In addition, such approaches have the advantage of being highly selective, capable of distinguishing species that are chemically or functionally very similar. Yet, despite these benefits, spectroscopic methods face enormous challenges in measuring dilute concentrations of an analyte (without a purification step such as by gas chromatography) and generally involve the use of large, expensive equipment that require a laboratory setting.

Recently, different approaches to chemical detection have been developed that exploit nanomechanical phenomena, relying on simple scaling laws to achieve remarkably high sensitivities. These mechanical sensors detect either the surface stress^{1,2} or the change in resonant frequency as analyte molecules bind to the surface of a nanoscale resonator. Using the latter approach, attogram sensitivity at room temperature^{3,4} and zeptogram sensitivity at cryogenic temperatures have been achieved. Recently, subzeptogram sensitivity was demonstrated at room temperature using field emission from a vibrating carbon nanotube.⁷ Yet, despite the exceptional sensitivities of these approaches, high selectivity—one of the key advantages of optical spectroscopy—remains extremely difficult. Typically such detectors are functional-

ized with a coating that selectively binds to a desired analyte; however, the development of this functionalization chemistry can be costly and time-consuming and results in a detector that is limited in what it can detect.

In this Letter, we propose a new form of experimental detection that is based on probing the vibrational modes of an analyte molecule with nanomechanical resonators. Using molecular dynamics simulations, we demonstrate that this approach has the potential to combine the ultrahigh sensitivity of nanomechanical mass sensing with the superior selectivity and label-free aspect of optical spectroscopy. The central idea in this approach is to take advantage of resonant exchange of mechanical energy at the nanoscale, which exploits the fact that the phonon spectrum of nanomechanical probes is commensurate with the frequency ranges of the vast majority of analytes. Concomitantly, one obtains the same benefits of scaling leading to ultrahigh sensitivities. Our calculations show that the underlying requirements needed for this form of detection can be achieved, namely, (1) the analyte efficiently transfers mechanical energy resonantly with the probe, (2) this energy transfer produces an experimentally measurable signal in the probe, and (3) an appropriate distribution of probe frequencies can be experimentally realized.

To make a nanomechanical resonance spectroscopy (NRS) measurement one can imagine undertaking the following heuristic sequence. First the vibrational modes of the analyte molecules are excited thermally. A nanoscale resonator is then brought into "contact" with an analyte molecule. If the analyte and probe share a common vibrational frequency, energy will be exchanged between the resonant modes. The change in this vibrational energy in the probe resonator is

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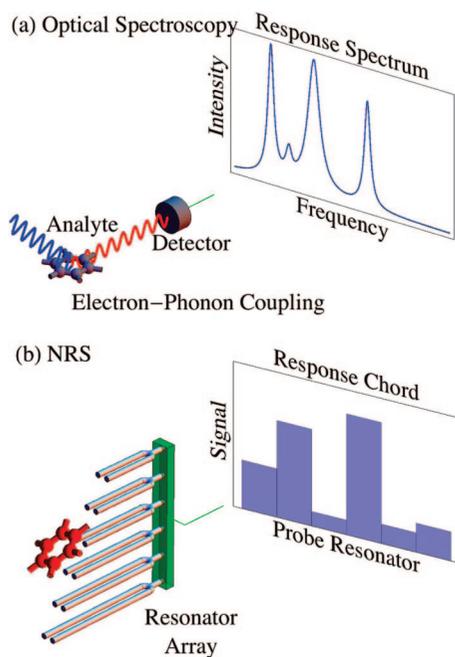


Figure 1. A schematic comparison of NRS with traditional optical spectroscopy. Panel (a) depicts in very general terms an optical spectroscopy method, in which the vibrational modes of an analyte are interrogated with a laser. Electron–phonon coupling transduces the illuminating radiation and the measured spectrum that results is used to identify the analyte. Panel (b) depicts the proposed NRS method in which a heated analyte interacts directly with a series of nanomechanical probe resonators. If a probe is in resonance with a vibrational mode in the analyte, then vibrational energy is exchanged; thus, the analyte excites a unique chord in the array of probes which can be used to identify it.

measured and recorded. This procedure is then repeated with a battery of probe resonators, each with different frequencies to build up a histogram of the nanomechanical response of the analyte. As with optical spectroscopy, to identify the analyte, the NRS histogram is compared with a library of responses for known substances.

In concept NRS is very simple and may be thought of as bringing an analyte into contact with a series of nanoscale “tuning forks” and listening to the “chord” that is excited. Figure 1 shows conceptually the NRS, and its comparison with optical spectroscopy. The feasibility of the fundamental underpinning NRS—resonant exchange of molecular vibrational energy—is demonstrated in this work using a dimer molecule with varying frequencies as the analyte and a carbon nanotube as the probe. Classical molecular dynamics simulations are performed to measure, in detail, the transfer of vibrational energy for this system.

The simulations are performed in the microcanonical ensemble with the dimer initially stretched such that upon release its mean temperature is ~ 1100 K. The (10,0) carbon nanotube is in its ground-state geometry when the stretched dimer is placed randomly alongside the tube. Interatomic interactions were modeled using Brenner’s second generation reactive empirical bond order potential (REBO),⁸ in which the van der Waal’s (vdW) interaction is treated with a Leonard-Jones 6-12 potential. Previous work demonstrated the validity of using the REBO potential for studying the

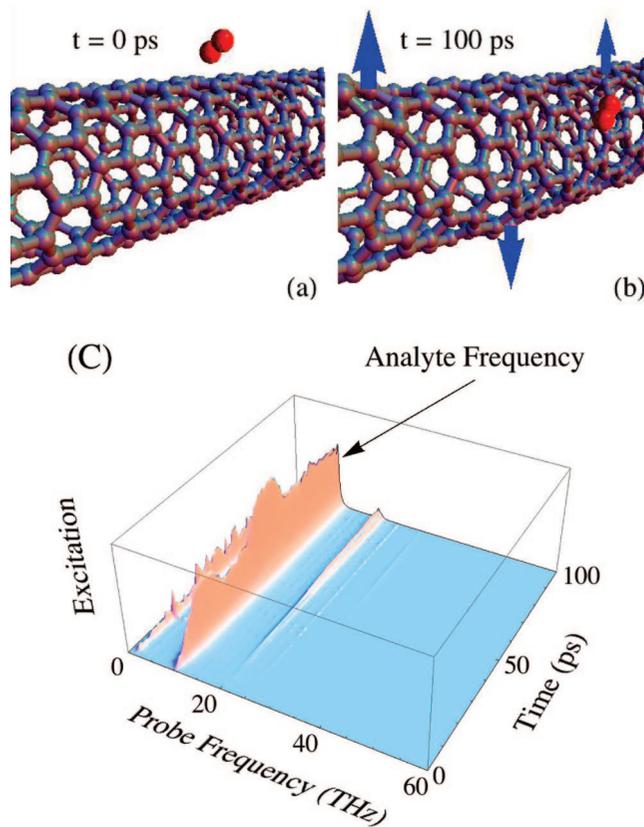


Figure 2. Simulation results for (10,0) CNT resonance probe interacting with a 10 THz dimer. Panels (a) and (b) show respectively the initial and final configurations of the system. In panel (b) the internal displacements within the CNT have been artificially amplified to show that it is a flexural mode in the tube which has been primarily activated. The surface plot in panel (c) shows the evolution of the spectrum of vibrational modes excited in the probe. The excited energy density includes both the potential and kinetic contributions to the vibrational energy of each mode.

transfer of vibrational energy⁹ between weakly interacting resonators. For each simulation the carbon nanotube (CNT) contained 400 atoms periodically repeated along its axis, and the equations of motion were integrated using the velocity Verlet algorithm with a time step of 0.1 fs, limiting fluctuations in the total energy to less than 10^{-7} of the energy of the system. In order to monitor the excitation of the probe in the presence of a given analyte, the energy in each vibrational mode of the CNT is computed at every time step, by projecting the atomic displacements and velocities of the CNT onto each of its eigenvectors, which are computed a priori using the frozen phonon method.¹⁰

When a simulation is initiated, the vibrating dimer exerts an oscillatory force on the CNT via the van der Waal’s interaction, driving the tube’s vibrational modes and transferring energy into them. As the dimer is weakly bound to the tube, it also undergoes a slower bouncing oscillation on the tube surface, causing the dimer to migrate randomly along the tube. Figure 2 shows the evolution of the spectrum of vibrations excited in a CNT that is in contact with a dimer tuned to oscillate at 10 THz. At each time-step the excited spectrum is computed from a sum of Lorentzian’s centered at each mode and weighted by the mode energy.

It can clearly be seen from Figure 2 that for a 10 THz analyte most of the vibrational energy that is transferred to the CNT occupies modes with frequencies closest to 10 THz, i.e., modes in resonance with the dimer. This demonstrates that information about the vibrational frequency of the analyte is communicated to the probe and remains localized in frequency for an experimentally measurable duration. The dissipation of energy in the excited mode in the tube is small as the tube was initially at 0 K. Simulations in which the tube has an initial background temperature show the same qualitative behavior although with increased dissipation from the excited mode.

It is interesting to note in Figure 2 that the resonant modes in the CNT become excited over the initial 10–20 ps of the simulation and does not appear to continue gaining significant energy over the subsequent 80 ps, even though the dimer remains considerably hotter than the nanotube and is still bound to it. Simulations out to 1 ns show that the energy does continue to rise slowly. This behavior arises because while it is vibrating, the dimer also slowly meanders randomly over the surface of the tube, resulting in a drift in phase space of the oscillatory force felt by the tube. This continuous dephasing of the driving force (from the dimer) and the driven mode in the probe reduces the rate of energy transfer resulting in a long transfer time. The long duration of energy transfer that we observe implies that the resonator will remain excited for nanoseconds, even if the quality factor of the probe resonator is poor. Thus, measurement of the probe energy is limited by the intensity of the excitation to be detected rather than the length of time available to detect it. Another interesting feature in Figure 2 is the small excitation of modes with twice the frequency of the dimer, indicating that an anharmonic interaction is rectifying (frequency doubling) the force that the dimer exerts on the tube.

In order to test the frequency sensitivity of the probe, we repeated this calculation for a sweep through dimer frequencies between 1 and 50 THz in 0.25 THz intervals (i.e., spanning most of the phonon density of states of the CNT). For each case the dimer was set such that its mean temperature was 1100 K and again brought into contact with the CNT. The energies in all of the phonon modes of the tube were evaluated as a function of time (as in Figure 2), and for each simulation a measure of the response of the CNT nanomechanical resonance probe was taken by averaging its excited spectrum over the final 10 ps. By repeating the simulations with dimers of different frequencies, we obtain a scan of the response of the probe to analytes spanning its entire frequency range, the first 20 THz of which is shown in Figure 3. The fact that the CNT response surface is excited primarily along the diagonal in this plot shows that the excitation of the probe remains resonant—that is, sharply localized at the dimer frequency—for all analyte frequencies. This result represents a critical proof of concept, important for a functional NRS: it ensures that when a strong signal is detected at a particular frequency in the probe, it corresponds to the presence of a molecular vibration in the analyte of the same frequency; modes in the probe are clearly

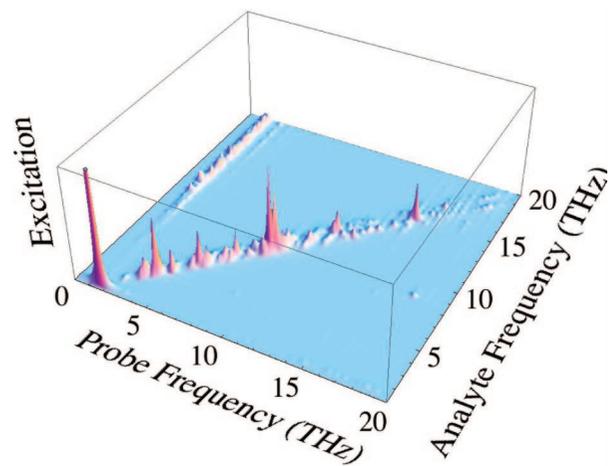


Figure 3. Scan of the excitation response of a CNT nanomechanical resonance probe to molecular vibrations with frequencies over the entire frequency range of the CNT. Only the first 20 THz of the scan are plotted, as the response of the probe at higher frequencies was negligible. The response spectrum of the probe for each analyte frequency is an average of the excited spectrum between 90 and 100 ps of the simulation.

not strongly excited by an off resonant analyte as evidenced in Figure 3. Moreover, the presence of the analyte does not strongly alter the frequency of the modes of the CNT—which would blur the frequency specificity of the probe. Unlike mass sensing approaches which rely on the analyte binding causing a frequency shift in the resonator, here the analyte is only very weakly bound to the probe through the van der Waal’s interaction which vitiates the effects of mass loading. While weak binding of the analyte to the probe is likely to be necessary for NRS, it should be noted that it is considerably more straightforward to “unfunctionalize” a resonator—making it nonselectively less binding—than to tailor a functionalization coating to bind selectively to a particular molecular species.

A second observation from Figure 3 is that the probe detects molecular vibrations over a wide range of frequencies and that the diagonal band of resonant response of the probe is not uniform but peaked at frequencies where there are more modes in the tube that can couple to the dimer. Consequently, the single CNT is acting like an array of resonance probes distributed according to its phonon density of states, and if a more complicated molecule with many vibrational modes were to interact with the probe, each of the molecule’s frequencies would be excited in the probe. If one could experimentally monitor simultaneously the excitation of all the modes of a tube, then we would be able to identify the analyte with only a single tube. Of course, if it were possible to monitor all phonon modes of the CNT, we would also be able to measure the modes of (and thus identify) the analyte, and so the NRS would be unnecessary. The dramatic simplification upon which the NRS depends is that one only requires the ability to measure the excitation of a *single* particular vibrational mode of a nanoscale object. With the ability to detect the excitation of a single resonant mode in a nanomechanical probe, one could use an array of resonant probes, each tuned to a different frequency, in order

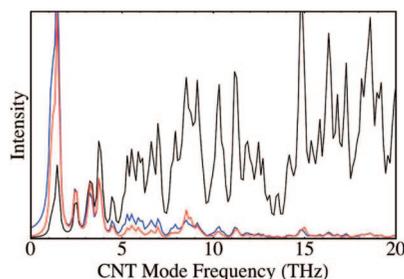


Figure 4. Low frequency portion of the integrated response of the nanomechanical resonance probe $\phi(\omega)$ (red line), the PDoS, $\rho(\omega)$, of the tube (black line), and the convoluted PDoS, $\omega^{-2}\rho(\omega)$ (blue line). The scaling in the y direction is arbitrary.

to interrogate an analyte. The combined frequency information from each of the probes would make a unique signature (like the notes in a chord) and could be used to identify the vibrational frequencies present in the analyte.

The detection capabilities required to measure the excitation within a probe will vary greatly depending on the frequency range of interest and the particular design of the resonance probe. We note that there are a number of exciting developments in experimental nanoscale characterization that could provide enabling technologies for an NRS method. For example, the technological goal of ultrasensitive mass measurement has driven the development of numerous methods for sensing vibrations in the fundamental modes of nanomechanical resonators using capacitance,¹¹ piezoresistance,¹² atomic force microscopy,^{13–15} and field emission.^{7,16} In addition, the race for the quantum limit of mechanical detection has spawned ultrasensitive position detectors using single electron transistors.^{17,18} Also, methods of cooling an individual mode of a resonator below the thermal background of the rest of its modes have been developed.^{19–21} Finally, scanning near-field spectroscopy can now identify localized nonmechanical vibrational modes of a system.²²

Given the necessity of monitoring the activity of a single mode in each resonance probe, presuming one had a choice, which mode should one measure? As the excited response of the CNT to the dimer is (largely) resonant, scanning the dimer frequency has sampled the tube's vibrational density of states (PDoS) weighted by the efficiency with which the energy transfers. Thus, we can write the response spectrum of the probe $\phi(\omega) = \sigma(\omega)\rho(\omega)$, where $\rho(\omega)$ is the density of vibrational modes in the tube with frequency ω and $\sigma(\omega)$ is a measure of the efficiency with which a dimer resonantly exchanges energy with modes in the tube of frequency ω . The CNT response spectrum, $\phi(\omega)$, is computed by integrating the response surface (Figure 3) over the dimer frequencies. Previous work⁹ has shown that the rate of resonant transfer of energy between modes (or their transmittance, $\sigma(\omega)$) is inversely proportional to the square of their frequency. Figure 4 shows the broadband response of the CNT resonance probe (red), the CNT's density of states (black), and this density weighted by $1/\omega^2$ (blue). The collapse of the data is excellent, illustrating the general nature of this result.

The $1/\omega^2$ dependence on the sensitivity of the probe to a molecular vibration implies that the tubes are effectively self-

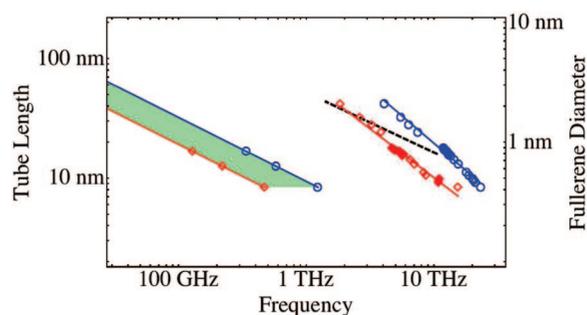


Figure 5. Mode frequency for families of nanoscale objects. The data plotted in red and blue at high frequencies show respectively the frequency of the lowest frequency mode and the breathing mode for fullerenes as a function of their diameter. The dashed black line shows the frequency of the radial breathing mode for CNTs as a function of their diameter (with data plotted using the fitting formula ω (cm⁻¹) = 244/d²(nm) from Eklund and Dresselhaus²³). The shaded region plotted at lower frequencies shows the frequencies of the lowest frequency flexural mode of single-walled CNTs as a function of length for a range of stable chiralities and diameters. The mode frequencies for both the fullerenes and CNTs were calculated using the REBO potential.

filtering. This property can be used advantageously and can help set some guidelines for the realization of a working nanomechanical resonance spectroscope. The most sensitive sampling frequency of each probe resonator is its lowest frequency mode; thus one should design the spectroscope so that one can monitor the occupation of this mode in each of the probes in the array. Additionally, this self-filtering property may relax the stringent energy detection requirements of an NRS probe. Knowing that a nanoscale object transfers heat most strongly through its lowest frequency mode means that one could simply monitor the total heat flux through a resonator, given that a large increase in the thermal flux comes from interactions with hot molecules with molecular vibrations in resonance with the fundamental mode of the probe. This one guideline vastly simplifies the process of selecting nanoscale objects to act as probe resonators, by choosing families of objects with controllable geometries that change the fundamental frequency. Several examples of this are fullerenes where the radius of the fullerene determines the frequency of its breathing and flattening modes or the fundamental mode of a suspended or cantilevered nanowire or nanotube, determined by length and radius. By way of example, the lowest frequency modes for fullerenes and the flexural modes of CNTs are plotted as a function of their tuning dimension in Figure 5. It can be seen that together these modes span nearly 3 decades in frequency space and thus, if used as nanomechanical resonance probes for NRS, could potentially permit detection of a wide range of molecular vibrations. One could envision several NRS device setups; for example, a series of CNTs of differing length (or radius) suspended over a trench, similar to the strings in a harp. Alternatively one could pass analytes through holes in graphene membranes or over substrates coated in fullerenes of different radius. The design of a practical NRS is more limited by capabilities for detecting the excitation of a vibrational mode than the ability to fabricate nanoscale devices.

In conclusion, we have proposed a novel form of chemical

detection (and characterization) that combines the advantages of mechanical chemical sensing methods with the label-free ability of traditional spectroscopic methods. While there are practical hurdles which must be overcome in order to realize experimentally a successful NRS, using the specific example of a dimer and a CNT, the results described here demonstrate the underlying principle of the device. The simulations reveal that energy is resonantly exchanged into specific modes of the probe CNT and that this energy can remain localized in frequency before dissipating to other modes of the tube. Moreover, our work indicates that *strong* excitation of a mode is only due to resonant interaction, and thus the measured signal in a resonance probe is unique and meaningful. Beyond the proof of principle, it is found that probes are not uniformly sensitive to molecular vibrations but are self-filtering and that this behavior can be exploited to simplify the construction of a functioning nanomechanical resonance spectroscopy.

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