Coláiste na Tríonóide, Baile Átha Cliath
Trinity College Dublin
Ollscoil Átha Cliath | The University of Dublin

Faculty of Engineering, Mathematics and Science

School of Chemistry

Moderatorship Examination   **Trinity Term 2016**

Nanoscience, Physics & Chemistry of Advanced Materials

Senior Sophister

SS NPCAM

(Comprehension and Problem Solving Paper)

Paper Coordinator: Prof Duesberg

Friday 6th May 2016   **SNIAM PHYS**   **09.30 – 12.30**

The Chemistry Examination Board

Complete the comprehension exercise in **Section A** and **answer 6** questions from **Section B**

Section A accounts for 40% and **Section B** accounts for 60%

Please use separate answer books for each question

Tables of physical constants and relative atomic masses and a periodic table are attached.

Spectroscopic tables, character tables, Mathematical Tables (Old) or Formulae and Tables (New) and graph paper are available from the invigilators, if required.

Non-programmable calculators are permitted for this examination – please indicate the make and model of your calculator on each answer book used.

Section A

(a)   Prepare a summary of the article "Nanotubes resound better" (on the next page) and describe its key findings.

(b)   Discuss how miniaturization of mechanical systems leads to:

       (i)   Improvement of Q-factor

       (ii)   Suppression of Q-factor

(c)   **(i)**   Determine the bandwidth for the resonator "Ref.1" in Fig 1 of the article.

       (ii)   Determine the damping ratio and describe if the system is over or under-damped.

       (iii)   What is the timescale for amplitude decay in this resonator?

NANOMECHANICS

Nanotubes resound better

Advanced measurement techniques combined with a tightly controlled noise environment have enabled the creation of carbon nanotube-based mechanical resonators with quality factors of up to five million.

Ilya Khivrich and Shahal Ilani

Nanoscale mechanical resonators can be used as extremely sensitive force and mass detectors and have promising prospects as devices operating in the quantum mechanical regime. In all such applications, their performance depends crucially on the mechanical quality factor, Q — the ratio between the energy stored in the resonator and the energy lost in a single oscillation cycle. Writing in *Nature Nanotechnology*, Adrian Bachtold and collaborators at the Institut de Ciencies Fotoniques in Barcelona and Michigan State University demonstrate a significant improvement in the quality factor of carbon nanotube-based mechanical resonators to a record value of 5 million (ref. 1), paving the way for ultrasensitive mass and force detection, and for the development of quantum bits with long coherence times based entirely on mechanical motion.

Over the past centuries, society has relied on clocks based on mechanical oscillators for accurate timekeeping. The operating principle is intuitive (Fig. 1a): counting the oscillations translates directly into a measure of time. For precise operation, the number of cycles made before the oscillator's energy decays (the quality factor) should be as high as possible. In pendulum clocks, the decay

problem was solved by the invention of the escapement mechanism that feeds energy into the oscillator without affecting the phase of the oscillations. An equally important factor in maintaining accurate timing is the stability of the clock's frequency of oscillation. For sailors in the eighteenth century, such frequency stability was a matter of life and death, because precise timing in conjunction with the observation of celestial motion was the only way to navigate the open sea. Early sea clocks employed a simple pendulum design, but because the oscillation frequency of a pendulum depends on the local gravity and weather, this design was unsuitable for long travels, and only more stable designs made global navigation safe. Bachtold and collaborators address a similar problem of frequency stability, but in much tinier nanotube-based mechanical resonators.

The miniaturization of resonators that took place in the last few decades has expanded their use far beyond the realm of timekeeping. Compared with their larger ancestors, micro- and nanoscale resonators provide greatly enhanced sensitivity to external forces and changes in mass, and are thus excellent detectors for these quantities. However, as these lithographically defined resonators are

made smaller, their Q generally degrades owing to increased dissipation by surface defects and imperfect clamping (Fig. 1b). Consequently there are ongoing efforts to increase Q using materials engineering methods such as surface treatments[2], improved crystalline purity[3] and built-in stress[4].

Recently, an alternative scheme for creating nanoscale resonators from the bottom up has emerged. One example is a mechanical 'string' resonator made out of a carbon nanotube, which is mechanically clamped at its two ends by metallic electrodes and is free to oscillate above a gate electrode (Fig. 1a). With no dangling bonds at the surface and an almost ideal clamping at the contact electrodes, carbon nanotube-based resonators were expected to reach record high quality factors. However, although early experiments demonstrated unprecedented frequency tunability[5], they reported disappointingly low Q of not more than a hundred, suggesting the presence of hidden mechanisms of dissipation.

The first breakthrough in the quest for high-Q nanotube resonators came from experiments at cryogenic temperatures[6], yielding values as high as 1.5×10^5. The low temperatures helped unravel two of the mechanisms responsible for the low
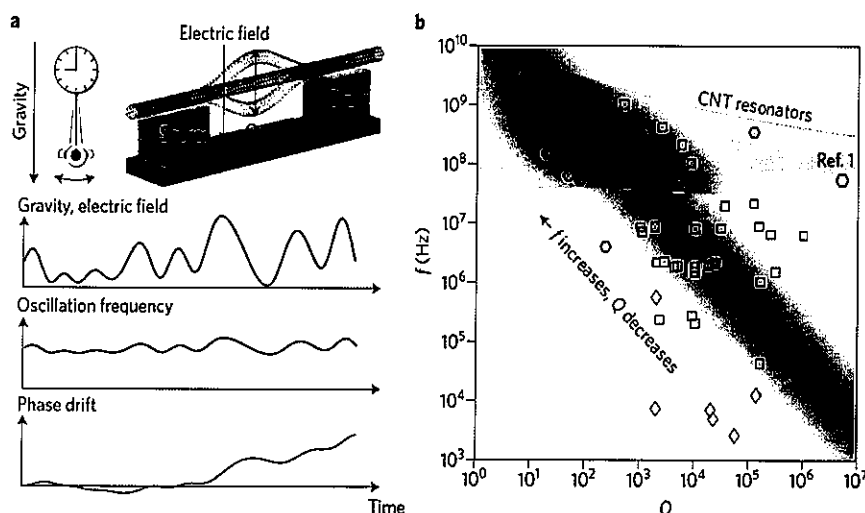
news & views

Figure 1 | Improving the quality factor of carbon nanotube mechanical resonators. **a**, The motion of a nanoscale mechanical resonator, composed of a carbon nanotube (CNT) suspended above a gate electrode, can be compared to the motion of a clock's pendulum. Just as changes in gravity will cause variations in a clock's oscillation period, electric field fluctuations (top graph) will induce fluctuations in the CNT tension and correspondingly in its resonant frequency (middle graph). In both cases, this will lead to accumulating phase drift in the time domain (bottom graph). Viewed from the frequency domain, these fluctuations manifest as broadening of the resonance peak and mask the intrinsic Q, despite not being associated with additional energy dissipation. **b**, The lowest resonance frequency (f) and the corresponding Q of nanomechanical resonators based on cantilevers (diamonds), beams (squares) and CNT beams (hexagons) reported in the literature[3,4,10]. While higher frequency resonators tend to have lower Q (shown by the purple shading), recent advances in CNT resonators suggest that in this system, extremely high Q can be achieved (red shading). The experiment reported by Bachtold and collaborators[1] establishes a new record for a resonator combining both high frequency and high Q. Image of clock, © mysondanube/iStock/Thinkstock.

Q observed in previous experiments. The first is the dissipation due to phonon–phonon scattering that occurs because of the extreme nonlinearity of the nanotube's mechanical motion, which is an effect that intensifies with increasing temperatures. The second mechanism is the dissipation of mechanical vibration energy into the motion of electrons due to the strong coupling between these two degrees of freedom. Only by suppressing the electronic motion using the phenomenon known as the Coulomb blockade did the resonators show high Q.

Now, Bachtold and colleagues report the next breakthrough, in which the quality factors in carbon nanotube resonators (Fig. 1a) have soared to a value of 5 million. Two key elements were essential for achieving such a high Q. The first is the ability to probe the resonators without any external actuation. Typically, a measurement of a mechanical resonance involves its actuation by an external drive and the monitoring of its coherent response. However, given the strong nonlinearity of nanotube resonators, even the smallest actuation hampers the achievement of high quality factors. The

researchers avoided this pitfall altogether by measuring instead the oscillations produced by the thermal motion of the nanotube. Since thermal motion is stochastic, they had to probe the motional noise at the resonance frequency, and with remarkably careful measurements, they could detect thermal motion down to an effective temperature of 44 mK.

Second, the researchers realized that the limiting factor in the measurement of such high Q is not energy dissipation, but rather the frequency stability of the resonator. The researchers discovered that the width of the resonant peak depends on how fast they measure it — being narrower when measured faster. This signalled a possible smearing by a fluctuating environment. In analogy to the frequency drift of a sailor's pendulum clock that resulted from fluctuations in gravitation, changes in the resonance frequency of the nanotube resulted from tiny fluctuations in the electric field emanating from the gate, which randomly pulls the nanotube down and changes its tension. To alleviate this problem, Bachtold and collaborators operated the nanotube resonator in a conductance regime that was the least

sensitive to the gate voltage. Still, even the tiny fluctuations in state-of-the-art voltage sources were significant enough to induce large frequency fluctuations and substantially reduce the measured Q. Only when batteries were used to gate the device was the resonance frequency stable enough for the resonator to unveil its intrinsic Q — a 30-fold improvement over the previous record[6].

The observed high values of Q are remarkable given the small nanotube mass, hinting at the potential for significant improvement in their already exceptional mass- and force-detection sensitivity. Large Q could also have a significant effect on the performance of nanotube resonators operating in the quantum limit of mechanics, allowing them to survive in their quantum state for an extended period of time. An intriguing possibility is the creation of a quantum bit based entirely on mechanical motion of the nanotube, whose logical 0 and 1 states correspond to two mechanical oscillation modes[7,8]. The ability to tailor the electron–phonon coupling in nanotubes[9] should allow to selectively couple these modes to electronic degrees of freedom and populate exactly a single phononic excitation in one of these modes. Further coherent manipulation[7,8] could then put this single phonon into a quantum superposition state between the modes. It will be exciting to see whether the low energy dissipation and long classical coherence times reported by Bachtold and collaborators will translate to similar times in their quantum analogues. If such long coherence times would be observed, this could open a new era of long-lived quantum information processing in nanotubes based entirely on mechanical motion. □

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References
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Section B

Question 1

(a) Calculate the value of ΔS if one mole of an ideal gas is expanded reversibly and isothermally from 10 dm^3 to 20 dm^3. Explain the sign of S.

(b) You open the door of a fridge in a perfectly isolated room. What will happen to the temperature in the room? Explain with the laws of thermodynamics.

[10 marks]

Question 2

The hydrogen molecule, H_2, vibrates with a frequency corresponding to a wavenumber of 4400 cm^{-1}. What would the vibration wavenumber be if one H atom is replaced by a Li one?

[The mass of Li is $7m_H$, m_H is the mass of H].

[10 marks]

Question 3

Given the solubility product of CaF_2 is $K_{sp} = 1.7 \times 10^{-10}$ mol^3 dm^{-3}, estimate the solubility (in mol dm^{-3}) of CaF_2 in:

(i)   pure water;

(ii)   0.01 M $Ca(NO_3)_2$.

[10 marks]

Question 4

A particle with mass $m = 9.1 \times 10^{-31}$ kg is confined within a one-dimensional potential box with length L and infinite potential on both sides. Sketch the first five energy levels, their spacings and their associated wavefunction. Starting from the ground state ($n = 1$), among the spectral lines that the particle can absorb at room temperature are two adjacent spectral lines whose wavelengths are 1.0304×10^{-7} m and 5.4953×10^{-8} m. Find the length L.

[10 marks]

Question 5

An ideal gas is taken through the three processes, A→B, B→C and C→A in the figure below, where the process described by B→C is isothermal.
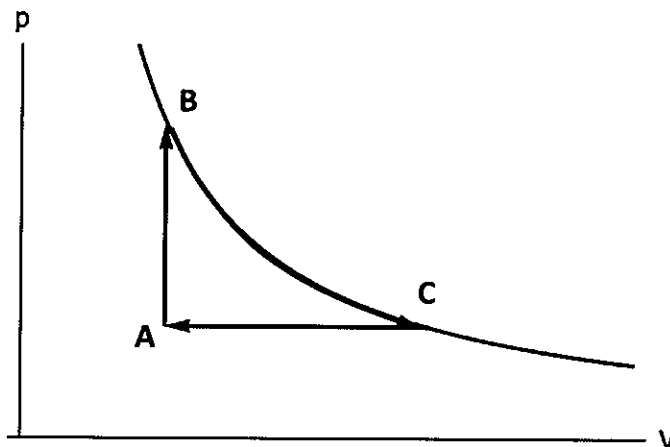
(a) The temperature of the isotherm is 298 K and the gas has p = 2.8 bar, V = 1 L at point B. Calculate the number of moles of the gas.

[2 marks]

(b) Complete the five missing entries in the table below:

	ΔU	Q	W
A→B	a	+148 J	b
B→C	c	d	-210 J
C→A	e	f	+132 J

Where U is the internal energy, Q is the heat exchanged and W is the work done by or on the ideal gas.

[6 marks]

(c) Process B→C is run reversibly at 298 K. Calculate the change in entropy of the universe, the ideal gas and its surroundings.

[2 marks]

Question 6

Estimate the number of hydrogen nuclei in human brain. Suppose that an MRI medical diagnostic machine applies a static magnetic field of 2T to the brain, at room temperature. Classically, how much more likely is it that the magnetic moment of a hydrogen nuclei magnetic moment is aligned with this field than anti-aligned with it? In the brain under these conditions, on average, how many more hydrogen nuclei are present that have their spins aligned with the field, than those that have their spins anti-aligned with it?

[10 marks]

Question 7

A schematic phase diagram for a one component system is shown below.
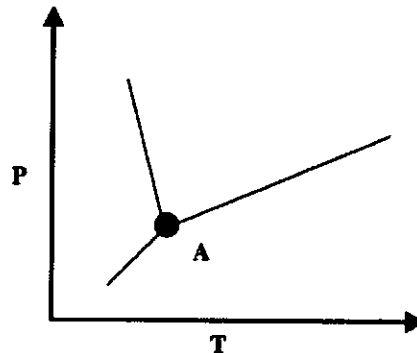
(i)   Label regions where you would expect to find pure solid, pure vapour and pure liquid phases.

[2 marks]

(ii)   Label the lines representing the Solid-Liquid and Liquid-Gas equilibria.

[2 marks]

(iii)   What phases are present at the point marked **A**?

[2 marks]

(iv)   Starting from the Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta H_m}{T \Delta V_M}$$

Derive the equation for the Solid-Liquid equilibrium on the phase diagram for a one component system. State clearly any assumptions used and comment on their validity.

[4 marks]

Question 8

A researcher studies metal clusters deposited on a flat substrate. Estimate the size of a metal cluster at which the quantisation of the energy levels of the particle can be observed. Assume the experiment is carried out at room temperature.

Hint: consider the particle to be a cube-shaped quantum well.

[10 marks]

Question 9

NH_3 belongs to the C_{3v} point group. Determine the reducible representation for the modes of motion in NH_3, reduce the representation and identify which irreducible representations correspond to vibrations. Identify which vibrational modes are i.r. active and which are Raman active; give reasons for your choices.

[10 marks]

Question 10

Make an estimate of how many 12 V lead-acid car batteries, each of capacity 50 A h, are required to give the same energy as the combustion of 1 kg of paraffin fuel $((CH)_n)$, given that the heat of formation of H_2O is 235 kJ $mole^{-1}$ and of CO_2 is 390 kJ $mole^{-1}$.

Why will a practical combustion engine give less than the ideal amount of useful energy from the above values? Comment on the implications of your answer for the batteries required for longer range electric vehicles.

[10 marks]

Question 11

Calculate the pH of a 2×10^{-7} M solution of H_2SO_4 (aq). (pK_w = 14).

Question 12

The low temperature specific heat of diamond varies with temperature as:

$$c_p = 124 \left(\frac{T}{\Theta_D} \right)^3 \text{ kJ kg}^{-1}\text{K}^{-1}$$

where the Debye temperature Θ_D = 1860 K. The Debye temperature of graphite is Θ_D = 1500 K, and

$$c_p = 89 \left(\frac{T}{\Theta_D} \right)^3 \text{ kJ kg}^{-1}\text{K}^{-1}$$

What is the entropy change of 1 g each, of diamond and graphite respectively, when it is heated at constant pressure from 4 K to 300 K? Thermodynamically, is graphite more or less stable with respect to diamond at room temperature? Does the equation for specific heat satisfy the Third Law of thermodynamics?
(The atomic weight of carbon is 12)

[10 marks]

School of Chemistry

Use the following values for fundamental constants, conversion factors, relative atomic masses and other data for examination purposes:

Constants

Gas Constant	$R = 8.314 \; J \; K^{-1} \, mol^{-1}$
Boltzmann's Constant	$k_B = 1.381 \times 10^{-23} \, J \; K^{-1}$
Planck's Constant	$h = 6.626 \times 10^{-34} \, J \; s$
	$\hbar = h/2\pi = 1.055 \times 10^{-34} \, J \; s$
Velocity of light	$c = 2.998 \times 10^8 \; m \; s^{-1}$
Charge of electron	$e = -1.602 \times 10^{-19} \, C$
Rest mass of electron	$m_e = 9.109 \times 10^{-31} \, kg$
Rest mass of proton	$m_p = 1.673 \times 10^{-27} \, kg$
Atomic Mass Unit	$1 \; u = 1.66054 \times 10^{-27} \, kg$
Vacuum permittivity	$\varepsilon_0 = 8.854 \times 10^{-12} \, J^{-1} \, C^2 \, m^{-1}$
Vacuum permeability	$\mu_0 = 4\pi \times 10^{-7} \, J \; s^2 \, C^{-2} \, m^{-1}$
Bohr magneton	$\beta = 9.274 \times 10^{-24} \, J \; T^{-1}$
Nuclear magneton	$\beta_n = 5.051 \times 10^{-27} \, J \; T^{-1}$
Rydberg constant	$R_\infty = 2.178 \times 10^{-18} \, J = 1.097 \times 10^5 \; cm^{-1}$
Avogadro's constant	$N_A = 6.022 \times 10^{23} \, mol^{-1}$
Faraday constant	$F = N_A e = 9.648 \times 10^4 \; C \; mol^{-1}$
Bohr radius	$a_0 = 5.292 \times 10^{-11} \, m$
Molar volume at S.T.P.	$M_v = 22.414 \; dm^3 \, mol^{-1}$

Conversion factors etc.

$1 \; eV = 1.602 \times 10^{-19} \, J = 9.648 \times 10^4 \, J \; mol^{-1}$

$1 \; cm^{-1} = 1.986 \times 10^{-23} \, J = 11.96 \; J \; mol^{-1} = 1.240 \times 10^{-4} \, eV$

$1 \; \text{Å} = 0.1 \; nm = 10^{-10} \, m$

1 standard atmosphere $= 1.013 \times 10^5 \; N \; m^{-2} \; (Pa) = 760 \; torr = 1013 \; mbar$

$1 \; L = 1 \; dm^3 = 10^{-3} \, m^3$

$1 \; \text{Debye (D)} = 3.336 \times 10^{-30} \, C \; m$

1 calorie $= 4.184 \; J$

$R = 8.314 \; J \; K^{-1} \, mol^{-1} = 8.206 \times 10^{-2} \, L \; atm \; K^{-1} \, mol^{-1}$
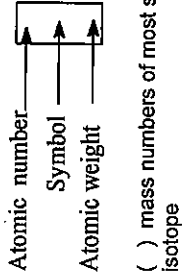
Approximate values of relative atomic masses

(Values in brackets are mass numbers of longest lived isotopes).

Ac	(227)	Ge	72.6	Po	(209)
Ag	107.9	H	1.0	Pr	140.9
Al	27.0	He	4.0	Pt	195.1
Am	(243)	Hf	178.5	Pu	(244)
Ar	40.0	Hg	200.6	Ra	(226)
As	74.9	Ho	164.9	Rb	85.5
At	(210)	I	126.9	Re	186.2
Au	197.0	In	114.8	Rh	102.9
B	10.8	Ir	192.2	Rn	(222)
Ba	137.3	K	39.1	Ru	101.1
Be	9.0	Kr	83.8	S	32.0
Bi	209.0	La	138.9	Sb	121.8
Bk	(247)	Li	6.9	Sc	45.0
Br	79.9	Lu	175.0	Se	79.0
C	12.0	Lw	(257)	Si	28.1
Ca	40.1	Md	(258.1)	Sm	150.4
Cd	112.4	Mg	24.3	Sn	118.7
Ce	140.1	Mn	54.9	Sr	87.6
Cf	(242.1)	Mo	95.9	Ta	180.9
Cl	35.5	N	14.0	Tb	158.9
Cm	(247)	Na	23.0	Tc	(97.9)
Co	58.9	Nb	92.9	Te	127.6
Cr	52.0	Nd	144.2	Tl	204.4
Cs	132.9	Ne	20.2	Th	232.0
Cu	63.5	Ni	58.7	Ti	47.9
Dy	162.5	No	(259.1)	Tm	168.9
Er	167.3	Np	(237)	U	238.0
Es	(252.1)	O	16.0	V	50.9
Eu	152.0	Os	190.2	W	183.9
F	19.0	P	31.0	Xe	131.3
Fe	55.9	Pa	(231)	Y	88.9
Fm	(257)	Pb	207.2	Yb	173.0
Fr	(223)	Pd	106.4	Zn	65.4
Ga	69.7	Pm	(145)	Zr	91.2
Gd	157.3				

The Periodic Table of the Elements

Key

Atomic number
Symbol
Atomic weight

( ) mass numbers of most stable isotope

1	2	3 3d, 4d, 5d	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.0079																	2 **He** 4.0026
3 **Li** 6.941	4 **Be** 9.01218											5 **B** 10.81	6 **C** 12.011	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.9984	10 **Ne** 20.179
11 **Na** 22.98977	12 **Mg** 24.305											13 **Al** 26.9815	14 **Si** 28.0855	15 **P** 30.9738	16 **S** 32.06	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.0983	20 **Ca** 40.08	21 **Sc** 44.9559	22 **Ti** 47.88	23 **V** 50.9415	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.847	27 **Co** 58.9332	28 **Ni** 58.69	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.9059	40 **Zr** 91.22	41 **Nb** 92.9064	42 **Mo** 95.94	43 **Tc** (97.9)	44 **Ru** 101.07	45 **Rh** 102.9055	46 **Pd** 106.42	47 **Ag** 107.868	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.69	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.9045	54 **Xe** 131.29
55 **Cs** 132.9054	56 **Ba** 137.33	57 **#La** 138.9055	72 **Hf** 178.49	73 **Ta** 180.9479	74 **W** 183.85	75 **Re** 186.207	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.9665	80 **Hg** 200.59	81 **Tl** 204.383	82 **Pb** 207.2	83 **Bi** 208.9804	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0254	89 ***Ac** 227.0278															

LANTHANUM SERIES

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce 140.12	**Pr** 140.9077	**Nd** 144.24	**Pm** (145)	**Sm** 150.36	**Eu** 151.96	**Gd** 157.25	**Tb** 158.9254	**Dy** 162.50	**Ho** 164.9304	**Er** 167.26	**Tm** 168.9342	**Yb** 173.04	**Lu** 174.967

* ACTINIUM SERIES

90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th 232.0381	**Pa** 231.0359	**U** 238.0389	**Np** 237.0482	**Pu** (244)	**Am** (243)	**Cm** (247)	**Bk** (247)	**Cf** (242.1)	**Es** (254)	**Fm** (257)	**Md** (258.1)	**No** (259.1)	**Lr** (260)