Examination #4
"Spectroscopy"

Handout Monday, 12/06/04 in lecture.
Submit Wednesday, 12/08/04, 11am.

Name:
Answer Key

Question 1. Human Body MRI.	20	
Question 2. Spitzer Observation of Kuiper Belt Objects.	10	
Question 3. Methane on Mars.	20	
Total	50	

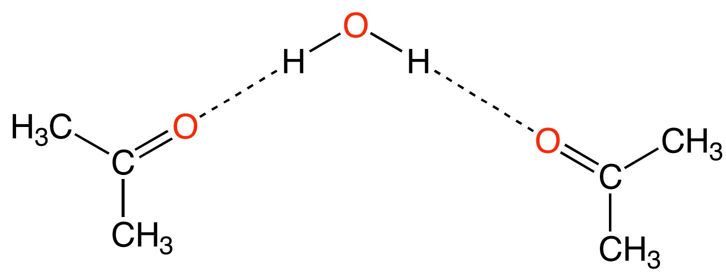
Question 1. Human Body MRI. (20 points)

In Hornak's *Basics of MRI*, in the section on *Imaging Principles*, one learns that "radiologists are most interested in looking at the NMR signal from **water** and **fat**, the major hydrogen containing components of the human body." Go to the online *SDBS Integrated Spectral Data Base System for Organic Compounds* and find the NMR spectra of water (#4544) and of stearic acid (our fat model, find it yourself, SDBS#: _**1493**_) and answer the following questions. (1 point)

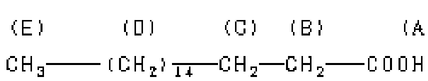
(a) The chemical shifts of **water** depend on the solvent. List the chemical shifts measured in various solvents. Explain why water is deshielded so much in acetone. [Hint: How does a water molecule get "solvated" by acetone? E.g. draw a water molecule and at least two molecules of acetone.] (8 points)

In chloroform: 1.58
In benzene: 0.44
In acetonitrile: 2.17
In acetone: 2.83
In DMSO: 3.65

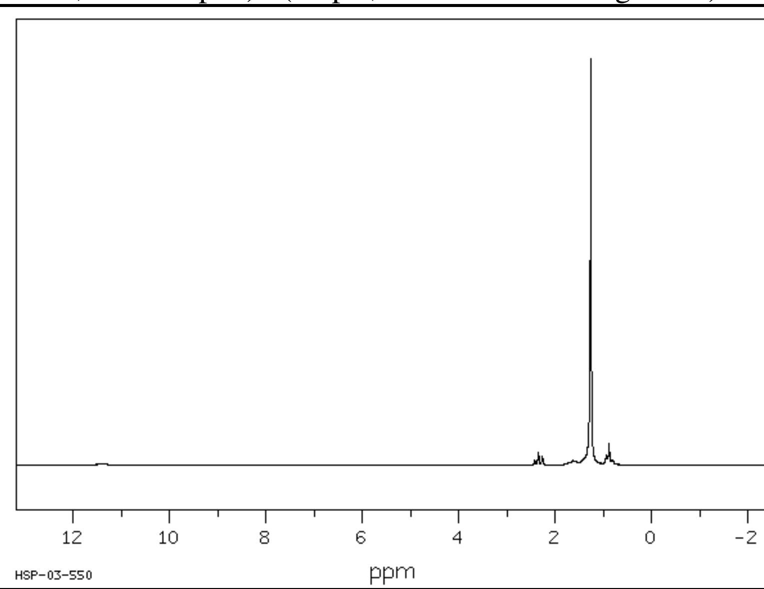
Explanation:



(b) Find the SDBS spectrum of stearic acid and reproduce it below as nicely as possible. Draw the structure of stearic acid. For each peak, indicate which H-atoms cause the peak (e.g. alpha-methylene, beta-methylene, … terminal methyl), how many H-atoms cause the peak (e.g. 1H, 2H, 3H, etc), and indicate the peak's multiplicity (singlet, doublet, … multiplet). (11 pts, -1 for each missing items)



A: 11 ppm, Singlet, 1H, COO<u>H</u>
B: 2.32 ppm, Triplet, 2H, α-CH_2
C: 1.64 ppm, Multiplet, 2H, β-CH_2
D: 1.26 ppm, Multiplet, 28H, $(CH_2)_{14}$
E: 0.88 ppm, Triplet, 3H, CH_3.

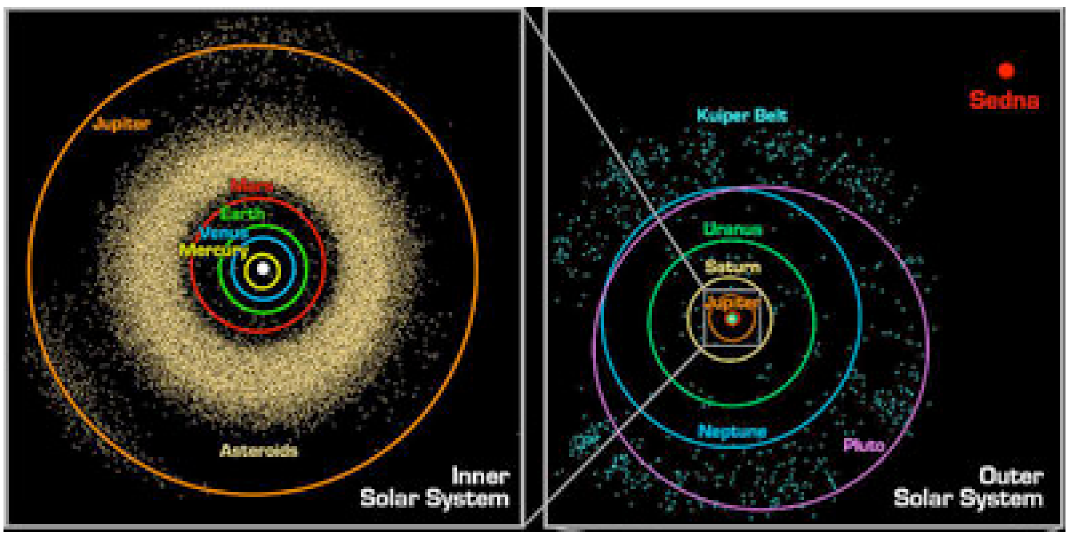


Question 2. Is Pluto a Planet? (10 points)

The **New York Times**
November 16, 2004 Tuesday, Late Edition - Final
SECTION: Section F; Column 2; Science Desk; Pg. 4
LENGTH: 401 words
HEADLINE: Pluto, the Maybe Planet, Gets Another Look
BYLINE: By JOHN NOBLE WILFORD
BODY:

So maybe Pluto is a planet after all.

Astronomers in recent years were having doubts. Perhaps Pluto, small, distant and poorly observed, should be downgraded from true planet to a mere Kuiper Belt Object, or K.B.O., one of the thousands of icy bodies orbiting beyond Neptune that probably are leftovers from the creation of the outer solar system.



''People were finding all these K.B.O.'s that were huge, literally half the size of Pluto or larger,'' said Dr. John Stansberry, an astronomer at the University of Arizona. ''But those supposed sizes were based on assumptions that K.B.O.'s have low albedos, similar to comets.''

Albedo is a measure of how much light an object reflects. The more light it reflects, the higher its albedo and the smaller its size needs to be.

In a report last week at a meeting of planetary scientists in Louisville, Ky., Dr. Stansberry said a recently discovered K.B.O., first estimated to be 932 miles in diameter, appeared in new observations to be no more than 435 miles wide. It was a matter of the albedo -- 18 percent, instead of the assumed 4 percent for previous calculations.

The measured object, designated 2002 AW197, is one of the largest nonplanet bodies in the solar system, and yet is only about 30 percent as large as the 1,400-mile-wide Pluto.

As more K.B.O. albedos are studied, astronomers should find out if the first object is typical, or an oddball, and if Pluto appears to be significantly different from these smaller objects.

A planned survey of 30 such objects, Dr. Stansberry said, ''will help us determine what their compositions are, how they evolve, how massive they are, what their real size distributions and dynamics are -- and how Pluto fits into the whole picture.''

Dr. Michael Shara, chairman of the astrophysics department at the Hayden Planetarium in New York, said the Spitzer telescope's infrared observations ''appear rock-solid and a terrific piece of work.''

The planetarium has had a leading role in reclassifying Pluto. In its exhibition hall, eight planets are prominently displayed, and the supposed ninth, Pluto, rates only a plaque, casting doubt on its status as a planet.

''We remain convinced that Pluto is not a planet, but one of the Kuiper Belt Objects,'' Dr. Shara said. But, he allowed, the new observations could eventually restore Pluto's planetary status.

URL: http://www.nytimes.com

LOAD-DATE: November 16, 2004

Related URL: http://www.atlasaerospace.net/eng/newsi-r.htm?id=1755
Figure Source: http://spaceflightnow.com/news/n0403/15sedna/
Read the article and visit the NASA web site and let's try to understand what is going on here.

(a) What is the temperature of "minus 370 degrees Fahrenheit" in absolute temperature, that is, in units of Kelvin? _**49.81**_ K. (2 points) [Computed at http://www.onlineconversion.com/temperature.htm]

(b) How large are the distances from the Sun to Earth, Pluto, and "Stansberry's KBO" in billion kilometers. Earth: _**0.150 bkm**_. Pluto: _**5.9 bkm**_. Stransberry's KBO: _**7 bkm**_. (3 points)

(c) A major issue is the reflectivity of the KBOs. The IR radiation that is not reflected is absorbed. Find out what KBOs are mostly made of (which major molecule, do not worry about the "dirt") and write down for which range of IR wave numbers you expect significant absorption. Give approximate wave numbers, peak strengths (weak, medium, strong, broad, etc), and assignment (what vibrates?). (5 pts)

KBOs are "dirty snowballs". Water ice and rocks. Mostly water!

Very broad and very strong absorption for HO stretching modes, in H-bonding environment.

(d) Why does one have to this sort of analysis with IR light rather than visible light? The answer is not obvious and requires a bit of physics. Give it a shot. (2 extra points).

Black body radiation maximum depends on temperature.
The universe is much warmer than it is bright. (And "warmer" is relative. There are more IR photons in the universe than there are UV/Vis photons.)

Question 3. Methane on Mars. (20 points)

Methane in Martian Air Suggests Life Beneath the Surface

By Kenneth Chang, *The New York Times*, November 23, 2004

A third team of scientists has now reported a seemingly simple discovery on Mars: its atmosphere contains methane.

But that finding has potentially profound implications, including the possibility of present-day microbes living on Mars.

Speaking this month at the American Astronomical Society's Division for Planetary Sciences meeting in Louisville, Ky., Dr. Michael Mumma, a senior scientist at NASA's Goddard Space Flight Center in Greenbelt, Md., reported three years of observations had provided strong evidence for methane.

"We are 99 percent confident," Dr. Mumma said. "It surprised all of us, actually. We really are still scrambling to understand what it means."

Methane, the simplest of hydrocarbon molecules with one carbon and four hydrogen atoms, is fragile in air and easily broken apart when hit by ultraviolet light. Calculations indicate that any methane in the Martian air must have been put there within the past 300 years.

That then raises the question: What is putting methane into the Martian air?

There seem to be only two plausible explanations. One is geothermal chemical reactions involving water and heat like those that occur on Earth in the hot springs of Yellowstone or at hydrothermal vents on the bottoms of oceans.

That would intrigue planetary geologists. Although frozen water is known to exist, there are no signs that any volcanism has occurred there for millions of years. Also, an instrument aboard NASA's Mars Odyssey looked for warm spots on Mars' surface and did not find any.

The other, more intriguing, is life. On Earth, a class of bacteria known as methanogens breathes out methane as a waste product. The discovery, if confirmed, suggests that perhaps Martian life arose on a presumably more hospitable Mars billions of years ago and survives to this day underground, beneath the cold, dry landscape.

Dr. Vladimir Krasnopolsky of Catholic University in Washington, the leader of one of the teams, said he believed bacteria to be the "most plausible source."

Others are more cautious. "Three difficult detections, or marginal detections, don't equate to one really strong one," said Dr. Philip R. Christensen, a professor of geological sciences at Arizona State University.

Dr. Krasnopolsky's findings, relying on observations from the Canada-France-Hawaii Telescope in Hawaii, were first reported at a conference in Europe this year and will be published in the journal Icarus.

In January, scientists working on the European Space Agency's Mars Express mission also reported the detection of the methane. A few months later, that group, led by Dr. Vittorio Formisano of the Institute of Physics and Interplanetary Science in Rome reported that the methane appeared to be more plentiful in regions where frozen water is known to exist underground.

All three teams of astronomers looked for methane molecules in the Martian air by examining the rainbow of light reflected by the planet. Different molecules absorb different, very specific colors, producing a bar-code-like series of black lines blotting out part of the rainbow spectrum. The widths of the lines tell the quantity. Dr. Krasnopolsky and Dr. Formisano based their claims on a single dark line.

The journal Science published the Mars Express results this month. Dr. Christensen of Arizona State said he was unconvinced by it. "I must confess I'm surprised it was published," he said. "I think it's just instrument noise. This detection is right at the noise level of the instrument."

Dr. Mumma said his ground-based observations from Hawaii and Chile spotted two separate dark lines corresponding to methane and performed other checks. "Mike's a really careful guy," said Dr. Steven W. Squyres, principal investigator for the rovers now on Mars, who attended Dr. Mumma's talk. "It was to me, by a significant margin, the most compelling argument that I've seen."

There is a new wrinkle in Dr. Mumma's findings: some regions of Mars near the equator possess surprisingly high levels of methane, up to 250 parts per billion, while areas near the poles had 20 to 60 parts per billion. Earth air, by comparison, contains about 1,700 parts per billion of methane. Dr. Mumma's readings are considerably higher than those reported by the other two groups.

Scientists have generally thought that methane, if present, would quickly distribute evenly through the atmosphere, so the clumps of high concentration suggest that not only are there sources emitting methane, but perhaps some process is also destroying methane over the poles.

The methane findings on current-day Mars come as planetary scientists are again rethinking their ideas about long-ago Mars. Geological carvings on the surface, from ones that look like meandering river channels to gigantic canyons, gave rise to the notion that Mars had been a tropical paradise, perhaps warmed by a thick heat-trapping blanket of carbon dioxide in its atmosphere.

But climatologists found that it was hard for their computer models to provide that much warming, and scientists shifted to a picture of Mars as wet, but cold. Many of the features could have been cut by glaciers or transitory hellish deluges when ice was melted by meteor strikes.

Mars also possesses few carbonates, the minerals in limestone that would be expected to form in the presence of water, but does have much olivine, a mineral that falls apart when exposed to moisture.

This year, however, the rover Opportunity, which landed at a site called Meridiani Planum, found minerals and salts that indicate that that part of Mars at least had once been soaked in water, although when and for how long remain uncertain. Dr. Squyres also noted that while the minerals indicate liquid water, "We see nothing that looks like wave ripples" in the layers of sediments preserved in the rocks.

The other rover, Spirit, on the other side of Mars, initially found only volcanic rocks that appear almost unchanged for billions of years. It has since rolled to nearby hills, which appear to be slightly older, where the rocks seem to have been significantly changed by water.

The rover findings and others presented last month in Jackson Hole, Wyo., at a conference about early Mars have led some to think again of the planet long ago as warm and wet.

Even Dr. James F. Kasting, a climatologist at Penn State whose models helped convince people that Mars had not been warm, has changed his mind. Dr. Kasting is now investigating methane, a more potent greenhouse gas than carbon dioxide, as a cause of warming. His initial simulations show methane cooling the planet but he thinks the error is in his calculations, not his hypothesis.

"I think it's our problem, not Mars' problem," he said. "I think the evidence keeps mounting that it was warm. I think it has to be stably warm."

The opinion is not unanimous, but the idea of early oceans is gaining favor. Some scientists, like Dr. Stephen M. Clifford of the Lunar and Planetary Institute in Houston, said that four billion years ago the decay of radioactive elements in the core of Mars would have produced enough heat to melt ice from below, producing an ice-covered ocean. Acidic waters could explain the lack of carbonates.

Dr. Daniel J. McCleese, chief scientist for Mars exploration at the NASA's Jet Propulsion Laboratory, said that during discussions someone said, "So we all believe there were oceans on early Mars?"

Dr. McCleese said: "Nobody spoke against that. Then someone said, 'What about a warm climate?' And then a tumultuous exchange began."

(a) Does the article state whether UV-, VIS-, or IR-spectroscopy was used in the methane detection? NO: _X_. YES: ___-spectroscopy. (1 points)

(b) The methane "line" usually observed corresponds to an absorption at a wave number of about 3000 cm^{-1}. Compute the corresponding wave length (in nm) and frequency (in Hz, MHz, or GHz). State whether this line occurs in the UV, VIS, or IR region. (3 points)

Wave length: 3,333 nm	**Frequency: 90.90 Ghz**	**Region: IR**

(c) Find the *Science* article by Formisano et al. Provide its complete citation in ACS format. Read the article and list the two dominant sources of methane on Earth. Write down the average concentrations of methane on Earth and Mars in parts per billion by volume and, for comparison, provide the approximate concentration of the oxygen molecule on Earth in these ppbv units. (6 points)

Detection of Methane in the Atmosphere of Mars **Formisano, V.; Atrya, S.; Encrenaz, T.; Ignaziev, N.; Giuranna, M.** Sciencexpress / www.sciencexpress.org / 28 October 2004 / Page 4/ 10.1126/science. 1101732		
Two Main Methane Sources on Earth: Termites, cattle		
Methane on Mars: **10±5 ppbv**	**Methane on Earth:** **1700 ppbv**	**Oxygen on Earth:** **200,000,000 ppbv**

(d) It is one hypothesis that the methane on Mars is due to "chemolithotropic microbes." Write down the metabolic reaction that is thought to create methane. Briefly explain why this reaction is an example of a "disproportionation reaction." (6 points)

Metabolic Reaction: $4\,CO + 2\,H_2O \rightarrow CH_4 + 3\,CO_2$
Why Disproportionation?   **C(+II) in CO turns into lower (C(-IV) in methane) and higher Oxidation State (C(+IV) in carbon dioxide)**

(e) How is methane broken up in the Mars atmosphere? Provide the equation for the reaction and indicate clearly the energy source that causes this break-up. Explain why methane can exist much longer in the Earth atmosphere without being broken up? (4 points)

Methane Decomposition on Mars: CH_4 + light $\rightarrow$ •CH_3 + •H
Longer Lifetime on Earth because …   **Less UV light! Thank you, ozone! (While you still exist up there.)**