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http://dx.doi.org/doi:10.1017/S1473550406003363

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UV-Vis spectroscopy of stardust

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Abstract: NASA’s Stardust mission flew through the coma of comet Wild 2 in January 2004, capturing dust grains as it did so. The grains were returned safely to Earth in January 2006, and are in the process of being distributed to investigators. As members of the Spectroscopy Preliminary Examination Team, we are preparing to analyse Stardust grains. Our contribution is to measure the spectrum of the grains between 200 nm (in the near ultraviolet) and 800 nm (near infrared). The purpose of the measurement is to provide an additional technique for characterizing the grains, one that is complementary to other spectroscopic techniques and one that produces results that can be matched directly with spectra acquired remotely (with telescope or spacecraft instrumentation). As part of the preparation for analysis of Stardust materials, we are producing a database of spectra from appropriate minerals, and are honing the technique through analysis of primitive meteorites.

Received 30 June 2006, accepted 28 August 2006

Key words: Stardust, comets, UV/Vis spectroscopy, meteorites.

Introduction

Dust in our Solar System comes from several different sources, including fragmentation of asteroids, activity of comets and collisions in the Kuiper Belt (Mann et al. 2006). A stream of ‘fresh’ interstellar dust entering the Solar System was detected by the Ulysses spacecraft (Grun et al. 1993). Interstellar dust grains constitute most of the solid matter in the Galaxy. They are the building blocks for the formation of stars and planets including asteroids, comets and Kuiper Belt objects. After the dust particles are condensed in red giants, supernovae and novae, they are injected into the interstellar medium (ISM). They keep growing by condensation, collisional accretion and coagulation. At the same time stellar ultraviolet (UV) radiation causes chemical reactions leading to the formation organic refractory material in icy condensates.

Comets and the Stardust mission

Comets are believed to be the most primitive bodies in the Solar System. They formed approximately 4.57 Gyr ago from the presolar nebula in the same processes that led to the formation of the Sun and planets. The composition of comets is dominated by ice, and so it is assumed that they formed at a distance from the Sun where ice could condense. The largest population of comets associated with the Solar System inhabits the outermost fringes, where they compose the Oort cloud (Dones et al. 2004). The Oort cloud, approximately 10,000 to 50,000 AU from the Sun, has never been viewed directly, but its existence is inferred from observations of the orbits of long period comets. Much closer to the Sun is the Kuiper Belt, stretching beyond Neptune, from ~30 to 60 AU, which is a reservoir of comets with shorter orbital periods, measured in years rather than hundreds of years (Gladman 2005).

Because comets formed on the outer fringes of the Solar System, they are thought to be pristine in composition. This means that they have not been greatly altered by thermal or fluid processing. As a comet draws closer to the Sun, surface ices begin to sublime; the resulting jets and streams of gas form a tail, carrying with them the dust particles that had been embedded within the ices. Each time a comet approaches the Sun, and tail formation takes place, additional material is lost, gradually resulting in a decrease in size of the nucleus. This evolutionary sequence, however, is not believed to process material within the nucleus, as material is constantly removed rather than being altered in situ, and so the cometary nucleus remains pristine. Unlike planets and asteroids, the composition of comets has not changed since their formation, and they are believed to be the most primitive bodies in the Solar System. Comets can thus provide information on the original material from which the Solar System formed.

There have been several missions to comets over the past 20 years. The first was ESA’s Giotto mission, which flew by Halley’s comet in 1985, and took the first image of a cometary nucleus (Reinhard 1986). One of the most significant findings of this mission was that the comet was richer in organics relative to ice than had been expected (Kissel et al. 1986). ESA followed up the success of the Giotto mission with the Rosetta mission (Ferri & Schwehm 2005). This is the first mission planned to chase, rendezvous with and land on a
comet; the spacecraft, launched in March 2004, will land on the nucleus of comet 67P/Churyumov-Gerasimenko in 2014. NASA has also had two successful cometary missions. Deep Impact, launched in January 2005, fired a 360 kg copper-rich projectile into comet 9P/Temple 1 in July 2005, creating a crater and liberating vast amounts of ice, gas and dust in the process. This allowed us the first sight of the sub-surface of a comet.

NASA’s other successful cometary mission was Stardust, launched on 7 February, 1999 to comet 81P/Wild 2. Up until 1974, when it experienced a close encounter with Jupiter, comet Wild 2 had an elongated orbit, with aphelion at 25 AU, perihelion \( \sim 5 \) AU and a period of 57 years (Sekanina 2003). Its new period of 6.4 years means that comet Wild 2 has completed five orbits of the Sun since encounter with Jupiter. Even so, the comet is thought to still be pristine. One of the goals of the Stardust mission was to collect samples from the comet Wild 2 as well as from the stream of interstellar dust that enters the Solar System (Brownlee et al. 2003). The spacecraft was equipped with an aerogel grid, which collected samples from the comet on one side of the collector and from interstellar dust on the other side of the collector. The spacecraft made three orbits around the Sun before the encounter, passing through the interstellar dust stream and collecting samples as it did so. It encountered comet Wild 2 on 2 January, 2004, passing in front of the comet, and collected samples from the coma. The sample return capsule landed safely in the Utah desert on 15 January, 2006. Figure 1(a) is an illustration of the path taken by the Stardust mission. An image taken by the Stardust spacecraft (Fig. 1(b)) shows the nucleus to have an irregular surface that is cratered in appearance.

Meteorites and interplanetary dust particles

Meteorites can be sub-divided into two large divisions: differentiated and undifferentiated materials. The former come from parent bodies that have been subject to planetary processes of melting and segregation, leading to fractionation of elements and minerals at a variety of scales from the macroscopic to sub-micrometre. Differentiated meteorites include irons (composed of nickel-rich iron metal), stony-irons (sub-equal mixtures of nickel-rich iron and silicates) and achondrites (silicate-rich meteorites). Undifferentiated meteorites, or chondrites, are of specific relevance to this study. They are silicate-rich meteorites that emanate from parental sources that have not suffered episodes of major melting and fractionation, although some have been altered by thermal and aqueous processes. The grains from which meteorites initially aggregated were interstellar silicates, processed through a molecular cloud prior to accretion in the protoplanetary disc. Although chondrites have experienced some thermal and hydrothermal processing since accretion, the most primitive of chondrites still retain a record of the original primordial cloud. Chondrites also contain minor components that have distinct origins: over the past 20 years, interstellar and circumstellar grains have been separated from meteorites. These grains of (dominantly) diamond, graphite and silicon carbide have been linked to production in various extra-solar environments including supernovae, novae and AGB stars (Hoppe & Zinner 2000; Zinner 2003).

Dust grains from comets (and asteroids) have been captured from Earth’s atmosphere through collection on plates carried on U2 planes flying through the stratosphere (Brownlee 1985). These interplanetary dust particles (IDPs) have been classified into anhydrous and hydrated types; the former are thought to be cometary, whilst the latter are more likely to be asteroidal in origin (Bradley & Brownlee 1986; Sandford & Bradley 1989). The study of anhydrous IDPs has given us a picture of the material from which the solid components of comets are composed: primary silicates (predominantly the orthopyroxene, enstatite, but olivine and clinopyroxenes do occur), organics and glass with embedded metal and sulphides (GEMS). This last component is thought to be original interstellar material.
Visible reflectance spectroscopy has been applied to IDPs, in order to compare them with primitive meteorites and with astronomical data (Bradley et al. 1996).

**Rationale of the study**

As members of the Spectroscopy Preliminary Examination Team, we are preparing to examine Stardust grains. Our contribution is to measure the spectrum of the grains between 200 nm (in the near UV) and 800 nm (near infrared (IR)). The purpose of the measurement is to provide an additional technique for characterizing the grains, one that is complementary to other spectroscopic techniques and one that produces results that can be matched directly with spectra acquired remotely (with telescope or spacecraft instrumentation). As part of the preparation for analysis of Stardust materials, we are producing a database of spectra from appropriate minerals, and are honing the technique through analysis of primitive meteorites. This paper describes the technique of ultraviolet-visible (UV-Vis) spectroscopy that we are applying to cometary particles, captured in aerogel and aluminium foil. By comparing the returned Stardust samples from comet Wild 2 and interstellar dust with primitive meteorites and IDP, we will have an insight into the materials, environments and processes that occurred from the central to the outer regions of the Solar System and around other stars.

Measurement of the UV-Vis spectra of objects (dust grains, asteroids) is a technique that allows recognition of specific features that can be associated with particular materials: organic species, water, silicates, etc. There are two compelling reasons for studying the spectra of extraterrestrial materials between 200 and 850 nm. First, along every line-of-sight through the Galaxy there is an adsorption feature at 217.5 nm. The cause of this absorption band has not been identified but is thought to be from the presence of very small, organic-rich dust grains. A feature with similar spectral characteristics has recently been reported from an IDP (Bradley et al. 2005). The second interest comes from reflectance spectroscopy of planetary surfaces: missions reliant on a remote sensing technique to identify the composition of planetary (asteroidal) surfaces require comparison with known materials for calibration and identification purposes. So, for example, asteroids are classified into groups and families on the basis of their spectral reflectance properties (Cellino et al. 2002). Comparison of asteroid spectra obtained by telescope with laboratory-derived spectra of meteorites and individual mineral species has been instrumental in relating asteroid families with meteorite groups (Burbin et al. 2002).

One of the aims of our study is to observe whether or not there is an absorbance present that can be compared with the 217.5 nm interstellar absorption band. We also intend to make qualitative analyses of the presence (or otherwise) of organic molecules in the grains and assign bond identities, and assess the relative abundances of hydrated and anhydrous minerals within grains on the basis of OH features.

**Technique and samples**

**UV-Vis spectroscopy**

Electronic spectroscopy is a technique that records changes of energy that occur within and between atoms. Energy changes can be brought about by rotation, bending, stretching and vibration of bonds within molecules, and these motions lead to spectra with features in the IR and sub-millimetre regions of the electromagnetic spectrum ($\lambda > 1 \mu m$). Near UV-Vis spectroscopy concerns the excitation of valence electrons within an atom, where transitions between energy levels result in absorptions (or emission) of energy at wavelengths below ~1 $\mu m$. The electronic transitions taking place are from movement of electrons. This can be either within the molecular orbitals formed during bonding (most significant for organic compounds) or by charge transfer between cations (inorganic compounds). So, for example, in saturated organic species with singly bonded carbon atoms (C—C, C—H, etc.), the only transitions that can occur involve the $\sigma$ molecular orbitals, and the $\sigma$—$\sigma^*$ transitions generally occur at $\lambda < 150$ nm. In contrast, bonding in unsaturated organic species (C=C, C==C, C==O, etc.) involves electrons in the $\pi$ molecular orbitals, and there are many transitions that can take place giving features at wavelengths between 200 nm and ~1 $\mu m$. In inorganic compounds, electronic transitions are dominated by charge-transfer effects. These effects are particularly significant in mineral species, where the ‘cages’ of SiO$_4$” are held together by arrays of metal ions (Mg$^{2+}$; Ca$^{2+}$, etc.). Charge-transfer effects generally yield spectra at slightly higher wavelengths than the molecular orbital effect, producing features in the visible part of the spectrum.

Spectra can be acquired in transmission (a technique that is usually used for gas-phase studies) or reflectance. Because this study is to become the basis of a more detailed comparison of remotely derived UV-Vis reflectance spectra of planetary surfaces and interplanetary and interstellar dust, we have acquired data mainly in reflectance mode. In general, a spectrophotometer is an optical instrument for measuring the change in light intensity with wavelength after the light has interacted with a sample. The microspectrophotometer acts as a combination of both a microscope and a precision spectrometer, thus allowing magnification of a sample image enabling analysis of extremely small samples. This allows the distribution of organics or mineral types within small clumps of materials to be determined simply by selecting the specific area from which to gather the spectral data. We used an optical microspectrophotometer system supplied by Craic Technologies (San Dimas, Ca). The system is based on a Leica DMR microscope, with the regular objective lenses removed and fitted with Cassegrain reflecting mirrors. The light source is a 75 W xenon lamp. The square aperture through which light was focused varied in size with selected magnification, from $10 \times 10 \mu m^2$ to $2 \times 2 \mu m^2$.

The system allows non-destructive measurement of spectra across the UV-Vis range in both transmittance and reflectance of samples presented as powders, single grains or polished mounts. Measurements were made over the range...
200 to 850 nm at a spectral resolution of 2 nm. Prior to every period of data collection, the system was calibrated using the National Institute of Standards and Technology white standard number. Here we are reporting relative reflectance data, rather than absolute reflectance.

**Samples**

**Aerogel.** Aerogel is a very-low-density silica gel produced by precipitation from a solvent. Pieces of flight-spare aerogel from the Stardust mission were made available for analysis. The purpose was to determine the spectral properties of aerogel, to see if they were either (a) sufficiently featureless or (b) sufficiently specific such that data acquired from Stardust particles embedded within aerogel could have the aerogel component subtracted away, to leave a ‘clean’ Stardust grain spectrum. Spectra were collected from a single millimetre-sized piece of aerogel resting on a quartz-glass slide.

**Mineral grains.** Spectral characteristics were recorded from a range of minerals in addition to particulate olivine standards in an attempt to build a library of spectra that could be used for comparison with Stardust particles. There was little preparation required for the samples. Olivine, (Fe,Mg)$_2$SiO$_4$, was measured as a series of powders sprinkled on a quartz-glass slide, as were samples of the clay minerals saponite and montmorillonite. All other minerals were measured as single crystals, again simply placed on quartz-glass slides.

**Meteorites.** Spectra were acquired from thin sections of two carbonaceous chondrites, Allende (CV3) and Cold Bokkeveld (CM2). Despite a certain amount of aqueous alteration, the former is known for its large, well-delineated chondrules (Krot et al. 1998), whilst the latter is known to have been altered heavily by fluids (Greenwood et al. 1994) and is rich in fine-grained matrix which is intimately mixed with a cross-linked macromolecular organic material. The sections analysed were regular thin sections (30 μm thick) mounted on soda-glass slides in Lakeland™ resin.

**Results**

**Aerogel**

The UV-Vis spectrum of aerogel is flat and featureless, apart from a single broad absorption centred at around 220 nm (Fig. 2(a)). Aerogel is an extended Si—O lattice and, like quartz (an extended SiO$_2$ lattice), might have been assumed to be transparent to UV radiation, i.e. to have a completely featureless spectrum. However, aerogel is manufactured by chemical precipitation, and so can contain impurities from the manufacturing process. The feature at 220 nm is possibly from such impurities and, given its position in the spectrum, could be from organic species.

**Mineral grains**

Spectra from different mineral grains have been obtained, in order that they can be used as a reference material for UV-Vis spectroscopy. In order to verify that our experiments produced results that could be compared directly with those from other analysts, we measured the spectra of a suite of synthetic olivines of known specific forsterite composition (Fo$_{0.0}$, Fo$_{0.20}$, Fo$_{0.50}$ and Fo$_{0.70}$). The olivines are crystalline, not glassy, and were produced by a method similar to that described by Redfern et al. (2000). They were powdered to a homogeneous grain size of at most 1 μm, and the results are shown in Fig. 2(b). Four of the five olivine powders have similar spectra, with a single very broad and weak absorption at ~650 nm. The most magnesian of the series, Fo$_{0.9}$, has a spectrum that turns over and drops off rapidly at wavelengths below ~330 nm. The cause of this feature is not known; it might be an artefact.

Figure 2(a) is a compilation of spectra acquired from several mineral species other than olivine. The minerals were selected on the grounds of relevance to interpretation of meteoritic (asteroid) and Stardust (comet) spectra. The enstatite grain (MgSiO$_3$) is the only one of the minerals that was coloured – it is a grain, about 50 μm across, and bright...
green in colour. All the other grains were either colourless or grey (saponite and montmorillonite). With the exception of the enstatite, it seems that there are few specific features at wavelengths longer than $\approx 300 \text{ nm}$. The spectrum for orthoclase ($\text{KAISi}_3\text{O}_8$), an alkali feldspar, is dominated by a deep absorption centred at $\approx 240 \text{ nm}$. Its extent and reproducibility will be checked by analysis of the plagioclase feldspars (albite and anorthite) with which it has a close structural relationship.

**Meteorites**

Reflectance spectra were acquired of components in thin sections from two different primitive meteorites.

**Allende.** Allende is a type CV3 carbonaceous chondrite. It has well-defined chondrules (near-spherical, sub-millimetre assemblages of olivine, pyroxene and feldspar), plus sulphide and metal grains in a matrix dominated by olivine. Millimetre-sized Calcium- and Aluminium-rich Inclusions (CAI) are abundant. Allende was selected for analysis because the clearly delineated chondrules are composed of readily identifiable mineral grains, and the effects of secondary, parent-body processing are minimal. Figure 3 shows part of a barred olivine chondrule, where grains of olivine are set in a feldspathic groundmass. Spectra were acquired from both the olivine and the groundmass.

**Cold Bokkeveld.** Cold Bokkeveld is a CM2 meteorite. It is very fine grained with abundant opaque matrix and isolated grains of olivine. Like Allende, it contains chondrules; however, they are much smaller in Cold Bokkeveld and show...
evidence of having been altered by fluid. Cold Bokkeveld is a fairly typical CM2 meteorite; it has a higher matrix-to-chondrule ratio than Allende, and the matrix is rich in secondary components (clay minerals, carbonates) produced by fluid flow on its parent. Figure 4 shows a matrix-rich area of Cold Bokkeveld from which a UV-Vis spectrum was acquired.

Discussion

The results that we have obtained so far show that UV-Vis spectra can be acquired on micrometre-sized grains or areas of material. We can take spectra from single crystals, powders or thin sections. This shows that the technique is a useful and non-destructive method that can be employed as a tool for preliminary examination of tiny or very fine-grained materials. Our system is suitable for acquisition of UV-Vis spectra from Stardust grains.

We can see from the results from meteorites that UV-Vis spectroscopy picks out features that might be characteristic (if not completely diagnostic) of different phases. In the chondrule from Allende, the two spectra are very similar, with no strong features other than a weak and broad absorption centred around $\sim 310$ nm. In the spectrum from Cold Bokkeveld matrix, we can see features at 300, 640 and 740 nm. The first of these is not the same feature seen in the silicates from the Allende chondrule – it is not only displaced 740 nm. The first of these is not the same feature seen in the Cold Bokkeveld matrix, we can see features at 300, 640 and 6740 nm. In the spectrum from Cold Bokkeveld matrix, we can see features at 300, 640 and 740 nm. The first of these is not the same feature seen in the silicates from the Allende chondrule – it is not only displaced from that feature by $\sim 10$ nm (a spectral resolution easily achievable in the microspectrophotometer system), but is narrower and sharper. This region of the spectrum is where organic compounds containing multiple conjugate bonds (i.e. single, double and triple bonds) exhibit absorption features, and in Cold Bokkeveld might therefore be indicative of the highly cross-linked macromolecular material known to occur in CM2 chondrites. The features at longer wavelengths are more likely to be associated with the silicate component of the matrix.

Although UV-Vis spectroscopy is a common tool for compositional measurements by remote techniques, there is little that has been published in terms of laboratory measurements of extraterrestrial materials. There is only one study of the visible spectra of IDPs (Bradley et al., 1996), and their data were taken from $\sim 380$ nm upwards. Figure 5 shows data the authors obtained from an anhydrous cluster IDP. As can be seen, the spectra all drop off rapidly at the shortest wavelengths and, in their paper, the authors suggested that this might be an analytical artefact. Data in Fig. 5 can be compared with results from Allende and Cold Bokkeveld (Figs 3 and 4). The meteorites do not show a similar effect, implying that Bradley et al. were correct in their inference that the drop off was not real.

Summary

UV-Vis spectroscopy is a non-destructive technique that can be used to identify a range of minerals within micrometre-sized sample areas. UV-Vis spectroscopy is of equal importance in both the telescopic and microscopic context. A large amount of spectral data from planets, satellites and comets have been collected via remote telescopic observations and space missions. These data have been applied successfully as a method of classifying asteroid types. Owing to their high spatial and spectral resolutions, microspectrophotometer systems are an ideal method for the analysis of small samples. Particles and grains extracted from meteorites will be used for comparison with spectra from Stardust grains, and they will also act as a useful diagnostic of spectral features within the astronomical environment.

This paper is a report of the first, and most preliminary, measurements that we have obtained from planetary materials in preparation for analysis of Stardust grains. It is clear from our preliminary results that we still have much work to do in terms of the calibration of UV-Vis spectra. Nevertheless, we are encouraged that we are able to acquire spectra at such high spatial resolution, and we have shown that we have a system that is capable of analysing Stardust grains. Future work will include analysis of organic compounds, as well as an increased number of inorganic, mineral and meteorite species.

Acknowledgements

Gratitude is extended to the Natural History Museum, London for provision of mineral and meteorite samples for analysis, and to Lindsay Keller, NASA-JSC (National Aeronautics and Space Administration (Johnson Space Center)) for the aerogel. The research was supported by the PPARC (Particle Physics and Astronomy Research Council) through a rolling grant to the PSSRI (Planetary and Space Sciences Research Institute). We also thank Dr Mark Burchell (University of Kent at Canterbury) for the opportunity to present this work as a poster at the Second UK Astrobiology Society meeting held in Kent in April 2006.

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