The term “dust grain” is understood here to extend down to molecules containing tens of atoms, as there is no discontinuity in the physics as the particle size decreases from microns to Angstroms.

The Beginning: Dark Regions in Space

“Hier ist wahrhaftig ein Loch im Himmel”

Observed for the first time by Wilhelm Herschel in 1784

Wilhelm Herschel (1738-1822)
“I have swept well over Scorpio and have many entries in my sweeping books of the kind you describe viz: blank spaces in the heavens without the smallest star.” (22 February 1835)
The First “Dark Matter”

Early observations showed “Holes in the sky”

- Interstellar voids?
- absorption of light in space by “ether”?

“The space absorption of light is thus immediately related to the question of the presence, distributions, and constitution of dark matter in the universe.”

R.J. Trumpler, PASP 1930
“Unless we are willing to admit that the dimension of open clusters depend on their distance from the sun, we are led to the conclusion that the inverse square law on which the photometric distances are based does not hold and that a general absorption is taking place within our stellar system.”

R.J. Trumpler, PASP 1930
Dust

No Dust

Atomic Hydrogen ($H_\alpha$)

Extinction by Dust $\rightarrow$

Dust

Optically Excited Dust $\rightarrow$
The Perception of Dust has changed

Initially, interstellar dust was regarded as an obstacle that obscures and contaminates the signature of objects that were considered more interesting.

In the meantime, interstellar dust has evolved in an exciting and active field of research.

Dust is important because:

- It weakens the light and thus limits our view of the universe,
- It converts UV and visible radiation into the infrared, in some galaxies up to 99%,
- It determines the spectral appearance of stars during their formation,
- It strongly influences the physical and chemical conditions of the interstellar medium,
- It provides reactive surfaces to catalyze reactions (H₂ formation!)
- It is the basis for the formation of planets,
- Man is made of interstellar dust!
Outline

- The interstellar extinction curve and its features
  a) General shape, IR lines
  b) The 2175 Å bump and the history of C60
  c) Unidentified Infrared Emission Bands and PAHs
  d) A few words about DIBS
  e) Signature of Ices

- Interstellar Dust
  a) Surface Reactions
  b) H₂ formation, etc ...

- Interplanetary Dust
  Dust collectors (example: Cassini CDA)
Interstellar Extinction
Interstellar Extinction Curve

- General trend: more extinction at shorter wavelength → Reddening
- The shape of the curve is well-represented by a 7-parameter fit (Cardelli 1989):
  \[ \frac{A_\lambda}{A_1} = f(\lambda, R_V, C_1, C_2, C_3, C_4, \lambda_0, \gamma) \]
- It is possible to estimate all parameters, if $R_V$ is known.

- Grain absorption and scattering processes at a certain wavelength $\lambda$ are correlated with the size of the particle
- Rise towards the UV means that there are a lot more small particles
**Magnitude Scale**

The optical depth through a medium is defined by the fraction of the flux that remains in the beam:

\[
I(\lambda, \tau) = I_0(\lambda) e^{-\tau_{ext}}
\]

The extinction can be caused by absorption at the dust grain or by scattering out of the beam:

\[
\tau_{ext} = \tau_{abs} + \tau_{sca}
\]

Now in magnitudes: apparent magnitude

\[
m_x = -2.5 \log_{10} \left( \frac{F_x}{F_{x0}} \right)
\]

Extinction in magnitudes:

\[
A(\lambda) \sim 1.086 \tau_{ext}
\]

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<tr>
<th>Visible to typical human eye</th>
<th>Apparent magnitude</th>
<th>Brightness relative to Vega</th>
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<td>340 000</td>
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Elemental Abundances

Prime candidates for solid particles:

C, Si, Mg, Fe
Interstellar Dust: Soot and Sand

Dust grains are produced in the outflows of Stars and stellar envelopes
- Carbon-rich stars produce carbonaceous grains (soot)
- Oxygen-rich stars make metallic oxides and silicates

Nature of Interstellar Dust:
- Ranges in size from 1nm to 10μm
- Many more small grains than large
- The larger grains are likely to be non-spherical, perhaps porous, fluffy, even fractal
- Composition is likely to contain metallic silicates, carbonaceous material, and GEMS (glasses with embedded metal and sulfites)
- Mantles of ices (H2O, CO, CO2, CH3OH) are found in dense regions

Gas-phase condensation of silicate particles
Cornelia Jäger MPIA / Friedrich Schiller Universität Jena

Pulsed Nd:YAG laser, 532nm
30-240 mJ per pulse, 5ns

- Laser ablation of Mg/Fe/Si, Mg/Si, Fe/Si mixed targets (olivine and pyroxene stoichiometry) and of an olivine crystal
- Beam extraction, deposition on CaF2 substr.

Quenching gas: He or He/O₂ mixtures

Olivine: magnesium iron silicate (Mg, Fe)₂SiO₄
Pyroxene: silicate crystals SiO₄ substructure
Gas-phase condensation by Laser Pyrolysis
Cornelia Jäger MPIA / Friedrich Schiller Universität Jena

High-temperature condensation: **Laser pyrolysis or laser ablation** with a pulsed laser ($T \geq 3500$ K); **Fullerene-like carbon grains**

Low-temperature condensation: Laserpyrolysis with cw-laser ($T \leq 1700$ K) soot and PAHs
The 220 nm Bump and The History of C\textsubscript{60}
220 nm hump caused by Graphite?

Particle ($\ll \lambda$) composed of oscillators

(1) Single free oscillator

\[ \ddot{\delta} + \omega_0^2 \delta = \frac{Q}{\mu} E_{ex}(t) \]

(2) Many oscillators

\[ E_p = S \delta \quad S = \text{shape factor} \]
\[ E_{in} = E_{ex} - S \delta \]
\[ \ddot{\delta} + \omega_0^2 \delta = \frac{Q}{\mu} E_{in} = \frac{Q}{\mu} (E_{ex} - S \delta) \]

\[ \ddot{\delta} + (\omega_0^2 + \frac{Q}{\mu} S) \delta = \frac{Q}{\mu} E_{ex}(t) \]
\[ D = \varepsilon E \]

\[ \varepsilon = \varepsilon(\omega, k) \]

\[ \varepsilon = m^2 \]

\( \omega \) frequency

\[ \varepsilon = \varepsilon_1 + i\varepsilon_2 \] complex dielectric function

\( k \) wave vector

\[ m = n + ik \] complex refraction index

Rayleigh particle: size \( \ll \) wavelength
Carbon dust particles collected on quartz substrates quenching gas: He

Large Mismatch in Width
Small Mismatch in Position
Carbon dust particles
collected on Ge substrates
quenching gas: He
Eiji Osawa
HÜCKEL MOLECULAR ORBITALS

EXCITED STATES

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<td>-1.00β</td>
<td>(hu)^9 (t_{1g})^1 T_{1u}, T_{2u}, G_u, H_u</td>
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</table>

ENERGY (β)

VIBRATIONS

2a_g + 3t_{1g} + 4t_{2g} + 6g_g + 8h_g
+ 4a_u + 4t_{1u} + 5t_{2u} + 6g_u + 7h_u
C₆₀: Buckminsterfullerene


Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells, graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedral structure, a polyhedron with 60 vertices and 32 faces, of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The C₆₀ molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.

The technique used to produce and detect this unusual molecule involves the vaporization of carbon from the surface of a solid disk of graphite into a high-density helium flow, using a focused pulsed laser. The vaporization laser was the second harmonic of Q-switched Nd:YAG producing pulse energies of ~10 mJ. The resulting carbon clusters were expanded in a supersonic molecular beam, photometric using an excimer laser, and detected by time-of-flight mass spectrometry. The vaporization chamber is shown in Fig. 2. In the experiment the pulsed valve was opened first and then the vaporization laser was fired after a precisely controlled delay. Carbon species were vaporized into the helium stream, cooled and partially equilibrated in the expansion, and traveled in the resulting molecular beam to the ionization region. The clusters were ionized by direct one-photon excitation with a carefully synchronized excimer laser pulse. The apparatus has been fully described previously.*

The vaporization of carbon has been studied previously in a very similar apparatus. In that work clusters of up to 190 carbon atoms were observed and it was noted that for clusters of more than 40 atoms, only those containing an even number of atoms were observed. In the mass spectra displayed in ref. 6, the C₆₀ peak is the largest for cluster sizes of >40 atoms, but it is not completely dominant. We have recently re-examined this system and found that under certain clustering conditions the C₆₀ peak can be made about 40 times larger than neighbouring clusters.

Figure 3 shows a series of cluster distributions resulting from various vaporization conditions evolving from a cluster distribution similar to that observed in ref. 3, to one in which C₆₀ is totally dominant. In Fig. 3c, where the firing of the vaporization laser was delayed until most of the He pulse had passed, a roughly gaussian distribution of large, even-numbered clusters with ~30-120 atoms resulted. The C₆₀ peak was largest but not dominant. In Fig. 3b, the vaporization laser was fired at the time of maximum helium density; the C₆₀ peak grew into a feature perhaps five times stronger than its neighbours, with the exception of C₇₄. In Fig. 3a, the conditions were similar to those in Fig. 3b but in addition the integrating cup depicted in Fig. 2 was added to increase the time between vaporization and expansion. The resulting cluster distribution is completely dominated by C₆₀; in fact more than 50% of the total large cluster abundance is accounted for by C₆₀. The C₆₀ peak has diminished in relative intensity compared with C₆₀ but remains rather prominent, accounting for ~5% of the large cluster population.

Our rationalization of these results is that in the laser vaporization, fragments are torn from the surface as pieces of the planar graphite fused six-membered ring structure. We believe that the distribution in Fig. 3c is fairly representative of the nascent distribution of larger fragment clusters. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions towards the most-stable species, which appears to be a unique cluster containing 60 atoms.

When one thinks in terms of the many fused-ring isomers with unsatisfied valences at the edges that would naturally arise from a graphite fragmentation, this result seems impossible: there is not much to choose between such isomers in terms of stability. If one tries to shift to a tetrahedral diamond structure, the entire surface of the cluster will be covered with unsatisfied valences. Thus a search was made for some other plausible structure which would satisfy all sp³ valences. Only a spherical structure appears likely to satisfy this criterion, and this Buckminster Fuller's studies were consulted (see, for example, ref. 7). An unusually beautiful (and probably unique) choice is the truncated icosahedron depicted in Fig. 1. As mentioned above, all valences are satisfied with this structure, and the molecule appears to be aromatic. The structure has the symmetry of the icosahedral group. The inner and outer surfaces are covered with a sea of π electrons. The diameter of this C₆₀ molecule is ~7 Å, providing an inner cavity which appears to be capable of holding a variety of atoms.

Assuming that our somewhat speculative structure is correct, there are a number of important ramifications arising from the existence of such a species. Because of its stability when formed under the most violent conditions, it may be widely distributed in the Universe. For example, it may be a major constituent of circumstellar shells with high carbon content. It is a feasible constituent of interstellar dust and a possible major site for building carbon-based molecules.

*Permanent address: School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK.
R. Buckminster Fuller
Carbon dust particles
quenching gas: He

EI-Mass Spectrum

Relative Intensity

Mass (amu)

$C_{60}^+$

$C_{70}^+$

$C_{60}$

$C_{70}$
Fullerenes finally score as Nobel committee honours chemists

London. The Nobel committee last week gave the answer to a favourite topic of speculation at chemistry conferences for several years: when would the chemistry prize be awarded for the discovery that carbon atoms can assemble into the $C_60$ carbon cages of buckminsterfullerene — and who would win it?

Both questions have now been answered, the second with the decision to award the prize to Sir Harry Kroto of the UK University of Sussex (bottom right), and Robert Curl and Richard Smalley of Rice University in Houston, Texas (right).

The discovery of buckminsterfullerene, named after the American architect Buckminster Fuller, who used similar geodesic domes to construct large-scale structures, was made at Rice University in 1985 during experiments to investigate carbon clusters formed by laser ablation of graphite.

That the discovery of $C_60$ would one day earn Nobel recognition has been widely regarded as inevitable. It is hard to identify any other recent finding in chemistry that has stimulated such intense and diverse activity throughout the physical sciences.

Organic chemists have literally found a new dimension for synthesis in $C_60$’s spherical topology. Solid-state physicists have scaled new heights in molecular superconductivity. Films of solid $C_60$ doped with alkali metals are superconducting at up to 33 degrees kelvin, 20 K above the previous record for a molecular superconductor.

$C_60$ exhibits novel tribological effects and promising nonlinear optical properties, and is a candidate for the carrier of unexplained features in astronomical spectra. It “has completely changed our perspective on carbon chemistry,” says Kroto.

The question was never so much whether $C_60$ would win a Nobel prize as when, and — most of all — for whom, David Jones, a chemist at the University of Nottingham, says he had expected that the award might be given “only when $C_60$ turned out to be of some use”.

But commercial applications remain remote, and Jones considers that $C_60$ and the related carbon-cage clusters collected so far do not have little of practical value “other than providing entertainment” (Jones’s speculations about a curved form of graphite in his Dagdaus column in New Scientist in 1966 are commonly regarded as the conceptual beginning of fullerene science).

In contrast, Robert Haddon, one of the team at Bell Laboratories in New Jersey who discovered superconducting $C_60$ compounds in 1991, feels that the prize “could have been awarded by the end of 1991, when it was clear that fullerenes would change organic chemistry and materials science”.

The question of who was the hardest, as the route from discovery to worldwide impact has involved many significant contributions. But no award would have made sense that omitted Kroto, Smalley or Curl.

$C_60$ might well have stayed the curiosity it remained for the next five years if physicists Wolfgang Krätschmer, Don Huffman and their respective students Kosta Postioropoulos and Lowell Lamb had not found a way to make the compound in gram quantities in 1990. It was this discovery that allowed fullerene science to blossom.

There is no question that fullerenes have provided entertainment for scientists and non-scientists alike. But how important are they? Kroto feels that the Nobel committee have taken “a gamble that fullerenes will be one of the biggest things in the 21st century”. In Haddon’s view, the significance is in fundamental, not applied, science: “It’s the kind of fundamental breakthrough in chemistry of the kind we don’t really see any more,” he says.

Curl is confident that technological uses will come in the next few decades. But he suggests that the most telling factor now is that fullerenes illustrate “the interplay of [molecular] topology and structures”. Fullerenes science has led to the discovery of a host of materials, carbon-based and otherwise, whose atomic-scale structure dictates particular nanoscale shapes and forms.

Carbon nanotubes, discovered in 1991, are the most celebrated example: tubes of graphite-like carbon a few nanometres in diameter whose closed end caps are curved by the same five-membered-ring defects that induce the curvature of the $C_60$ cage.

Smalley agrees that “the utility of $C_60$ is in what it has taught us about nanoscale carbon structures” — namely that the graphite sheet is “a pretty cool thing”. Fullerenes may turn out to be not so much an end in themselves as the beginning of a new view of materials science at the interface of the molecular and the bulk scale.
A NEW FORM OF CARBON

UNDERSTANDING ANTARCTIC OZONE DEPLETION

The cellular defect behind cystic fibrosis
Pure $C_{60}$ crystal
Polycyclic Aromatic Hydrocarbon (PAH) molecules

Simple aromatic molecule: \( \text{C}_6\text{H}_6 \)
Fullerene Production in Interstellar Space

UV photons de-hydrogenate and fragment the molecules

PAH: Polycyclic Aromatic Hydrocarbon

Berne and Tielens, “Formation of buckminsterfullerene (C60) in interstellar space”, PNAS 2011
PAHs as carriers of the interstellar UV bump

Spectroscopy of PAHs in Ne-ice matrix, and as cold PAH films resembling the cluster formation

Steglich, M., Jäger, C., Rouillé, G. et al. 2010
Detection of $C_{60}$ and $C_{70}$ in a Young Planetary Nebula

Jan Cami, Jeronimo Bernard-Salas, Els Peeters, Sarah Elizabeth Malek

Another feature: the Diffuse Interstellar Bands
The Diffuse Interstellar Bands

- DIBS 5780, 5797 seen as unidentified bands by Mary Lea Heger (Lick Observatory, 1919)
- Broad (“diffuse”)
- “Possibly Stationary” (interstellar)
About 300 absorption lines between the UV and IR
- Seen for the first time in 1919
- Some correlation with dust extinction
  - For a long time solid state carriers were suspected

- Today several facts seem to speak against solid state carriers
  a) peaks don’t shift
  b) no emission!

Longest standing mystery in Astronomy!
Disqualified DIB Candidates

Solid Particles:

- Cr$^{3+}$ ion in MgO crystals (Duley 1979)
- Fe$^{3+}$ in minerals,
- Ca, Ca$_2$ in benzene or in dust grains (Duley, Graham 1969)

Gas Phase Molecules:

- CO$_2$ (Swings 1937)
- Na$_2$, NaK (Saha 1937)
- (O$_2$)$_2$ (McKellar 1960)
- NH$_4$ (Herzberg 1955)
- O$^-$, C$^-$ (Herzberg 1955)
- CH$_4^+$ (Herzberg 1955)
- H$^-$ (Rudkjobing 1969)
- HCOOH$^+$ (Herzberg, 1988)

The “interesting” ones: Alien bacteria an Panspermia theories

ON THE NATURE OF INTERSTELLAR GRAINS

F. HOYLE* and C. WICKRAMASINGHE

Dept of Applied Mathematics and Astronomy, University College, Cardiff, Wales

(Received 30 March, 1979)

Spectroscopic Evidence of Cosmic Life

N. Chandra Wickramasinghe, Ph.D.

Cardiff Centre for Astrobiology, 24 Llwynypia Road, Lisvane, Cardiff CF14 0SY

Abstract

A wide range of spectroscopic data from the far infrared to the far ultraviolet points to the conclusion that life is a cosmic phenomenon. Although there is a lingering reluctance to accept this position, alternative explanations for the total data set are beginning to appear contrived.
Matrix Isolation Spectroscopy

Laboratory of Prof. John Maier
University of Basel

Matrix induces Shift in the spectral Features

Cavity Ringdown Spectroscopy
(record the gas phase spectrum)
A promising DIB candidate (for a while): $\text{C}_7^-$

Laboratory Spectrum of $\text{C}_7^-$: 

DIB catalogue

Another one bites the dust: $\text{C}_7^-$

6270 DIB observed with High-resolution echelle spectrograph at the Apache Point Observatory

Simulations of $\text{C}_7^-$ line with 10 km s$^{-1}$ (derived from observation)

Neither Position nor width fit!

Hot candidate: \( I{-}\text{C}_3\text{H}_2 \)

See also: Oka & McCall, Science (Perspectives) 331, 294 (2010)
Trying to find correlations: the APO DIB Survey

- Apache Point Observatory 3.5-meter
- 3,600–10,200 Å ; $\lambda/\Delta\lambda \sim 37,500$
- 119 nights, from Jan 1999 to Jan 2003
- $S/N$ (@ 5780Å) $> 500$ for 160 stars (114 reddened)

Benjamin J. McCall (UIUC), Meredith M. Drosback (Virginia), Julie Thorburn Dahlstrom (Carthage College), Don York (Chicago), Scott Friedman (STScI), Lew Hobbs (Yerkes), Brian Rachford (Embry Riddle), Ted Snow (Colorado), Paule Sonnentrucker (STScI), Dan Welty (Illinois)
Very good Correlation between 6196 and 6613

$\text{Common carrier?}$

- $r=0.55$
- $r=0.986$
DIBS have Structure!

Present DIB Consensus
- Gas phase molecules,
- Probably large,
- Carbon based,
- PAH ions?
- Carbon chains?

Recorded with the Ultra-High-Resolution Facility (UHRF) on the Anglo-Australian Telescope

Features in the Mid-IR: Unidentified Infrared Emission Bands (UIR)
PAH molecules

**PAH Structures**

### Pericondensed
- Pyrene \(C_{16}H_{10}\)
- Perylene \(C_{20}H_{12}\)
- Anthanthrene \(C_{22}H_{12}\)

### Catacondensed
- Coronene \(C_{24}H_{12}\)
- Benzo[ghi]perylene \(C_{22}H_{12}\)
- ovalene \(C_{32}H_{14}\)
- Naphthalene \(C_{10}H_{8}\)
- Tetraphene \(C_{18}H_{12}\)
- Pentaphene \(C_{22}H_{14}\)
- Phenanthrene \(C_{14}H_{10}\)
- Chrysene \(C_{18}H_{12}\)
- Pentacene \(C_{22}H_{14}\)
Non-thermal emission
    → emission from gas phase rather than dust particles,

Intensity correlated with Carbon abundance
    → carbonaceous molecules,

Carriers must survive under harsh conditions
    → PAHs very stable molecules,

The line positions are stable while intensities vary
    → indication that the carriers come from a certain class of molecules.
Figure 1.4 — A simplified illustration of the main vibrational modes in a PAH molecule. Possible vibrational modes can involve a change in the C-C and C-H bond length (C-C stretch and C-H stretch respectively) or bending of the C-H bond in the plane of the PAH molecule and out of the plane of the PAH molecule.
Figure 1.5 — The IR spectrum of a massive star forming regions. The UIR bands are clearly present (the atomic emission lines are removed).
Detection of individual 0.4–28 $\mu$m wavelength photons via impurity-impact ionization in a solid-state photomultiplier

M. D. Petroff, M. G. Stapelbroek, and W. A. Kleinhaus

Rockwell International Science Center, 3370 Miraloma Avenue, Anaheim, California 92803

(Received 16 March 1987; accepted for publication 8 June 1987)

A solid-state device capable of continuous detection of individual photons in the wavelength range from 0.4 to 28 $\mu$m is described. Operated with a dc applied bias, its response to the absorption of incident photons consists of submicrosecond rise time pulses with amplitudes well above the electronic readout noise level. A counting quantum efficiency of over 30% has been demonstrated at a wavelength of 20 $\mu$m, and over 50% was observed in the visible-light region. Optimum photon-counting performance occurs for temperatures between 6 and 10 K and for count rates less than $10^{10}$ counts/s per cm$^2$ of detector area. The operating principle of the device is outlined and its performance characteristics as a photon detector are presented.
Some Neutral Spectra
neutrals don’t fit: maybe ions?

Infrared emission spectra of candidate interstellar aromatic molecules

D. J. Cook, S. Schlemmer, N. Balucani, D. R. Wagner, B. Steiner & R. J. Saykally*

Department of Chemistry, University of California, Berkeley, California 94720-1460, USA
* To whom correspondence should be addressed.

Interstellar dust is responsible, through surface reactions, for the creation of molecular hydrogen, the main component of the interstellar clouds in which new stars form. Intermediate between small, gas-phase molecules and dust are the polycyclic aromatic hydrocarbons (PAHs). Such molecules could account for 2–30% of the carbon in the Galaxy1, and may provide nucleation sites for the formation of carbonaceous dust2. Although PAHs have been proposed3 as the sources of the unidentified infrared emission bands that are observed in the spectra of a variety of interstellar sources4–11, the emission characteristics of such molecules are still poorly understood. Here we report laboratory emission spectra of several representative PAHs, obtained in conditions approximating those of the interstellar medium, and measured over the entire spectral region spanned by the unidentified infrared bands. We find that neutral PAHs of small and moderate size can at best make only a minor contribution to these emission bands. Cations of these molecules, as well as much larger PAHs and their cations, remain viable candidates for the sources of these bands.

FIG. 1 Chemical structures representing the PAH molecules studied by SPIRES in this work. These include: four unsubstituted PAHs, phenanthrene (a, C_{14}H_{10}), pyrene (b, C_{16}H_{10}), perylene (c, C_{20}H_{12}) and coronene (d, C_{24}H_{12}); two methyl substituted PAHs, 2-methylnaphthalene (e, C_{11}H_{10}), and 2-methylphenanthrene (f, C_{16}H_{12}); and two hetero-substituted PAHs, phenanthridine, (g, C_{14}N_{2}H) and dibenzofuran (h, C_{13}H_{2}O). Molecules the size of coronene have recently been postulated to account for the 3.3-μm UIR band10.

coverage of the infrared spectral regions spanned by the UIRs. To obtain such extensive spectral coverage, we use ultraviolet-laser-induced desorption to introduce highly excited gas phase PAHs into a low-infrared-background cryogenic high vacuum chamber. A cryogenic monochromator disperses the infrared emission, and a blocked impurity band solid-state photomultiplier13 is used to count single infrared photons. Our initial results15, in which this single-photon infrared emission spectroscopy (SPIRES) appar-
Ionized PAHs as carrier of UIRs
A PAH Emission Experiment with Ions

Saykally Group / Berkeley

FIG. 6. SIMION ion beam simulations (Top: Ion beam trajectory during signal measurement. Bottom: Beam trajectory during background measurement). The trajectories are based on the observation of the ion current using a homemade Faraday cup. The xy deflectors is switched to +500 V, steering the beam away from the sample Dewar aperture. The measured ion currents shown were collected at 1 keV energy.
Problems

- Thermal background
- No mass separation

UIRs remain “Unidentified”
More features: Ices


Flux (Jy) vs. λ (μm) for NGC7538 IRS9

Absorption features include:

- H₂O
- CO
- CO₂
- CH₃OH
- (3.47) μm band
- (6.85) μm band
- (‘XCN’) band
- H₂O, (HCOOH)

Silicate feature at 9 μm

Gas mixture: H₂O, CO, NH₃, CH₄, ...

Infrared Detector

Vacuum

Cold Finger

Ultraviolet Source

Laboratory

Interstellar

Typical Ice experiments

Elemental Depletion

\[
D_x = \log \left[ \frac{N(x)}{N(H)} \right] - \log \left[ \frac{N(x)}{N(H)} \right]_\odot
\]

Timescale for depletion:

\[
\tau_d = \frac{1}{\varepsilon f(X)v(X) n}
\]

- \varepsilon \quad \text{Grain surface per H atom cm}^{-3}
- f(X) \quad \text{Sticking probability for species } X
- v(X) \quad \text{velocity of species } X
- n \quad \text{cloud density}

---

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<th>Relative solar abundance</th>
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<td>1.0</td>
<td>0.43</td>
</tr>
<tr>
<td>Li, Li(^+)</td>
<td>(5.2 \times 10^{-11})</td>
<td>(1.55 \times 10^{-9})</td>
<td>1.47</td>
</tr>
<tr>
<td>C, C(^+)</td>
<td>(1.6 \times 10^{-4})</td>
<td>(3.72 \times 10^{-4})</td>
<td>0.37</td>
</tr>
<tr>
<td>N</td>
<td>(7.2 \times 10^{-5})</td>
<td>(1.15 \times 10^{-4})</td>
<td>0.2</td>
</tr>
<tr>
<td>O</td>
<td>(5.0 \times 10^{-4})</td>
<td>(6.76 \times 10^{-4})</td>
<td>0.1</td>
</tr>
<tr>
<td>Na, Na(^+)</td>
<td>(2.1 \times 10^{-7})</td>
<td>(1.74 \times 10^{-6})</td>
<td>0.9</td>
</tr>
<tr>
<td>Mg, Mg(^+)</td>
<td>(1.0 \times 10^{-6})</td>
<td>(3.50 \times 10^{-5})</td>
<td>1.5</td>
</tr>
<tr>
<td>Al, Al(^+)</td>
<td>(1.3 \times 10^{-9})</td>
<td>(2.5 \times 10^{-6})</td>
<td>3.3</td>
</tr>
<tr>
<td>Si, Si(^+)</td>
<td>(8.2 \times 10^{-7})</td>
<td>(3.5 \times 10^{-5})</td>
<td>1.6</td>
</tr>
<tr>
<td>P(^+)</td>
<td>(2.1 \times 10^{-8})</td>
<td>(2.7 \times 10^{-7})</td>
<td>1.1</td>
</tr>
<tr>
<td>S, S(^+)</td>
<td>(8.2 \times 10^{-6})</td>
<td>(1.6 \times 10^{-5})</td>
<td>0.3</td>
</tr>
<tr>
<td>Cl, Cl(^+)</td>
<td>(9.9 \times 10^{-8})</td>
<td>(4.4 \times 10^{-7})</td>
<td>0.65</td>
</tr>
<tr>
<td>Ar</td>
<td>(8.4 \times 10^{-7})</td>
<td>(4.4 \times 10^{-6})</td>
<td>0.72</td>
</tr>
<tr>
<td>K, K(^+)</td>
<td>(1.0 \times 10^{-8})</td>
<td>(1.1 \times 10^{-7})</td>
<td>1.0</td>
</tr>
<tr>
<td>Ca, Ca(^+), Ca(^{2+})</td>
<td>(4.5 \times 10^{-10})</td>
<td>(2.0 \times 10^{-6})</td>
<td>3.65</td>
</tr>
<tr>
<td>Ti, Ti(^+)</td>
<td>(2.2 \times 10^{-10})</td>
<td>(5.5 \times 10^{-8})</td>
<td>2.4</td>
</tr>
<tr>
<td>Mn, Mn(^+)</td>
<td>(1.5 \times 10^{-8})</td>
<td>(2.6 \times 10^{-7})</td>
<td>1.24</td>
</tr>
<tr>
<td>Fe, Fe(^+)</td>
<td>(2.7 \times 10^{-7})</td>
<td>(2.5 \times 10^{-5})</td>
<td>1.97</td>
</tr>
<tr>
<td>Ni, Ni(^+)</td>
<td>(9.5 \times 10^{-9})</td>
<td>(1.9 \times 10^{-6})</td>
<td>2.3</td>
</tr>
<tr>
<td>Cu, Cu(^+)</td>
<td>(6.3 \times 10^{-10})</td>
<td>(2.8 \times 10^{-8})</td>
<td>1.65</td>
</tr>
<tr>
<td>Zn(^+)</td>
<td>(1.4 \times 10^{-8})</td>
<td>(2.5 \times 10^{-8})</td>
<td>0.27</td>
</tr>
<tr>
<td>H(_2)</td>
<td>0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HD</td>
<td>(1.1 \times 10^{-7})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^{12})CO</td>
<td>(9.1 \times 10^{-7})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^{13})CO</td>
<td>(&lt;1.8 \times 10^{-8})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH</td>
<td>(2.4 \times 10^{-8})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(^+)</td>
<td>(6.6 \times 10^{-9})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN</td>
<td>(6.2 \times 10^{-9})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>(3.6 \times 10^{-8})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_2)</td>
<td>(2.3 \times 10^{-9})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

Diffuse cloud \((n=10^3 \text{ cm}^{-3}; T=100 \text{ K})\) | Dark cloud \((n=2 \times 10^4 \text{ cm}^{-3}; T=30 \text{ K})\)

\[
M = 10 \text{ a.m.u.} \quad \tau_d = 1.0 \times 10^{14} \text{s} \quad \tau_d = 9.4 \times 10^{11} \text{s}
\]

\[
50 \quad 2.3 \times 10^{14} \quad 2.1 \times 10^{12}
\]

\[
100 \quad 3.3 \times 10^{14} \quad 3.0 \times 10^{12}
\]

Typical cloud lifetime: \(3 \times 10^{14} \text{ s}\)

Duley & Williams, “Interstellar Chemistry”
**H\(_2\) formation on grains**

1. H collides with grain
2. H explores grain until either
   - encounter with another H
   - immobilized at enhanced binding site
3. Second H atom collides with grain: explores surface and encounters first H atom
4. **H\(_2\) formation on surface**
5. H\(_2\) ejected from surface
Gas grain processes: diffuse and direct
Gas grain processes: diffuse and direct

- **Diffusive mechanism** (Langmuir-Hinshelwood)
  - $X + g:Y \rightarrow X:g:Y \rightarrow X-Y:g \rightarrow XY + g$
  - \[ \text{sticking} \quad \text{diffusion} + \quad \text{desorption} \]
  - \[ \text{molecule formation} \]

- **Direct mechanism** (Eley-Rideal)
  - $X + Y:g \rightarrow X-Y:g \rightarrow XY + g$
  - \[ \text{direct reaction} \quad \text{desorption} \]

- Surface can be silicates, carbonaceous, ice, ...
Adsorption time

- Classical expression: \( t_a = \frac{1}{v} \exp\left(\frac{E_d}{kT}\right) \)

- With \( E_d = \) binding energy; \( v = E_d/k \sim 10^{12} \text{ s}^{-1} \)

- Physical adsorption: \( E_d \sim 400 \text{ K} \) =>
  - \( t_a = 3 \times 10^5 \text{ s at } T = 10 \text{ K} \)
  - \( t_a = 2 \times 10^{-8} \text{ s at } T = 40 \text{ K} \)

- Chemisorption: \( E_d \sim 20000 \text{ K} \) =>
  - \( t_a = \infty \text{ at } 100 \text{ K} \)

=> H atoms will evaporate above 40 K before forming \( \text{H}_2 \), unless the grain has strong binding sites
Sequence of bond breaking and recombination occurring in ultraviolet irradiated ice mantles
Examples of Surface Reactions

1. Atom-atom reactions, e.g.,
   \[ N + O \rightarrow NO \]

2. Radical-atom reactions, e.g.,
   \[ H + NO \rightarrow HNO \]

3. Radical-radical reactions, e.g.,
   \[ CH_3 + OH \rightarrow CH_3OH \]

4. Radical-H\(_2\) reactions, e.g.,
   \[ OH + H_2 \rightarrow H_2O + H \]

5. Molecule – atom reactions, e.g.,
   \[ CO + O \rightarrow CO_2 \]

6. Hydrogen abstraction reactions, e.g.,
   \[ H_2CO + H \rightarrow HCO + H_2 \]

Type 1,2,3: No activation barrier (typically)
Type 4,5,6: Activation barrier
Dust Collectors (provided by V. Sterken MPI-K Dust group)

Ballistic rockets in Kiruna (Sweden)

HEOS-2 @ Earth (apo 38 R_E)

HELIOS @ Sun-Earth (apo 0.3 AU, peri 0.88 AU)

Galileo @ Jupiter (5 AU)

Cassini @ Saturn (10 AU)

Ulysses - around the Sun, out of the ecliptic plane! @ 1.3-5.4 AU (almost Jupiter)

Rosetta mission to comet Landing in 2014

Giotto encounter with comet Halley 1986

Trajectory sensor for future missions: JUICE, SARIM+, DUNE,...
The Heidelberg Dust Accelerator

Testing & Calibration with the dust accelerator

Impacts on foils, aerogel, dust instruments, ...
Calibration of dust instruments
Using different dust “analogues”
Dust Source
The Stardust Mission Returns Interstellar Dust to Earth

- Launch: 1996
- 2 ISD capture periods in 2000 & 2002
- Aerogel collector (2 sides)
- 2006: Earth return
- 4 ISD candidates found (Westphal, LPIC conf.)

- Why did they ‘only’ find 4 (candidate) ISD grains?
- What is their impact velocity?
Impact speeds and directions of interstellar grains on the Stardust dust collector


Stardust@home: You can become a “duster” too!
Salt Water Geysers on Enceladus

Saturn's Ring Structure

Credit: Cassini Imaging Team, SSI, JPL, ESA, NASA
The Cassini Cosmic Dust Analyzer
The Cassini Cosmic Dust Analyzer
Salt Water Ocean on Enceladus

Cassini Dust Detector (Enceladus Plume)

Laser dispersion of salt water in the laboratory

Postberg et. al, Nature 459, 1098 (2009)
Literature

J. M. Greenberg: “Cosmic dust and our origins”
Surface Science 500, 793-822 (2002)

B.T. Draine: “Interstellar Dust Grains”

D.A. Williams D.A. Williams E. Herbst
“It’s a dusty Universe: surface science in space”
Surface Science 500, 823-837 (2002)