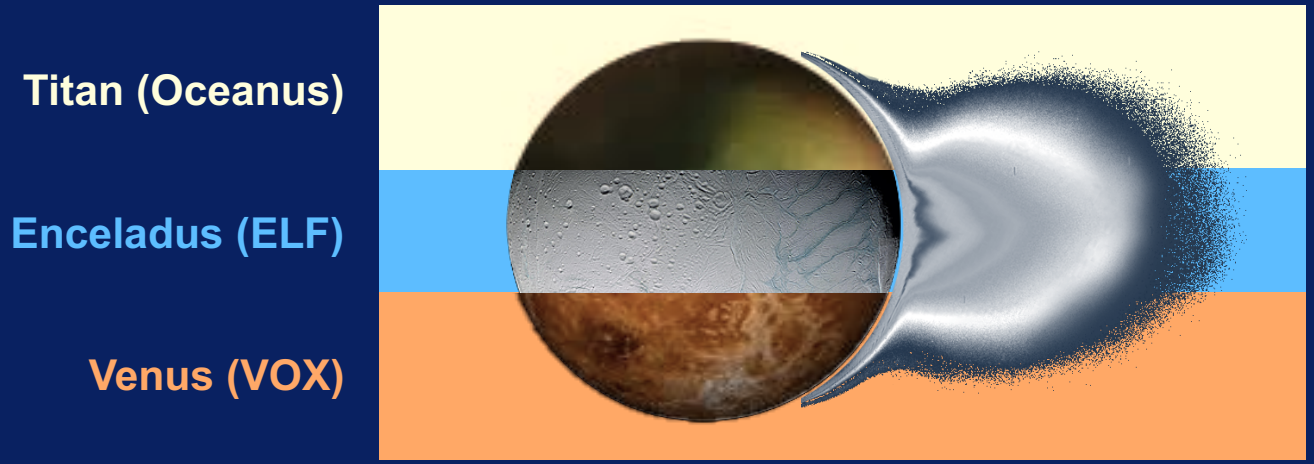
Hypervelocity Sampling Across the Solar System: Retiring Risks for Titan, Enceladus, and Venus New Frontiers Proposals



Virtual Research Presentation Conference

Hypervelocity Sampling Across the Solar System: Retiring Risks for Enceladus, Europa, Titan, and Venus — Task 2: Titan

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Program: Strategic Initiative

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Jet Propulsion Laboratory
California Institute of Technology

Tutorial Introduction

Abstract

The *Cassini* spacecraft flew through the enceladean plume at velocities of 6.2–17.8 km/s, depending on individual flyby. At this range, the spacecraft was passing through the plume at hypervelocity (i.e., velocities greater than ~2 km/s).

The overarching goal of this work was to determine whether current hypervelocity sampling strategies, such as those implemented by *Cassini*, are able to collect samples from Titan's atmosphere during fast flyby/flythrough encounters **without** resulting in such complete impact-induced molecular fragmentation that the original molecules cannot be identified.

To address this goal, we developed a two-pronged action plan that involved both experimental and theoretical research projects that both complemented and supplemented one another. **Figure 1** shows a snapshot from a molecular dynamics simulation investigating the hypervelocity impact of an organic molecule with a multi-layered graphene surface.

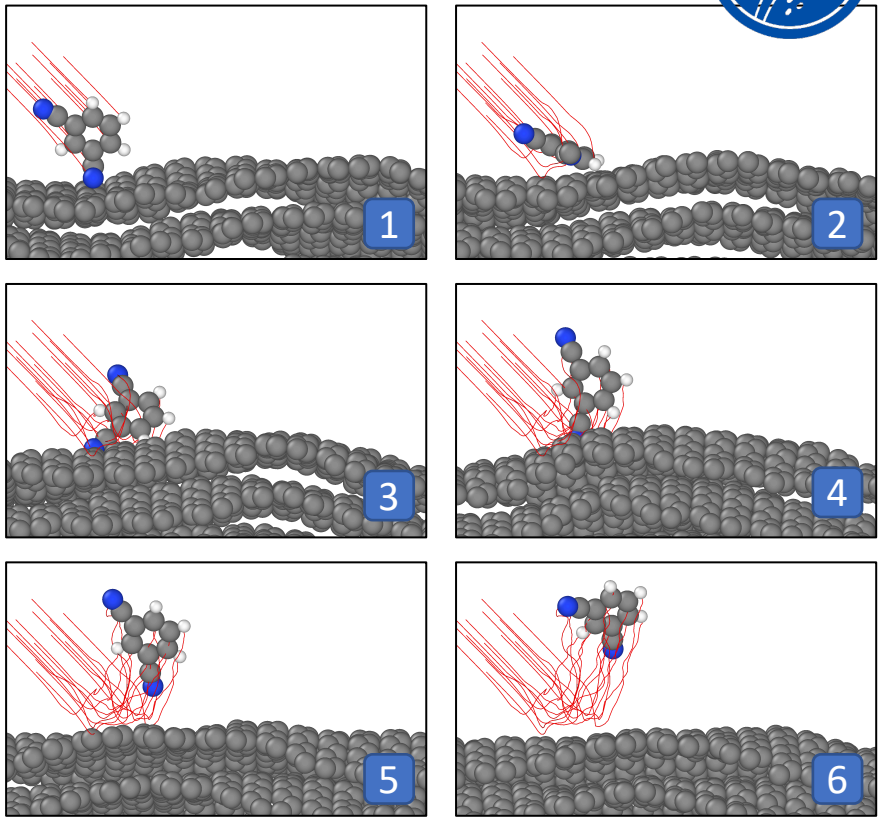


Figure 1. Six snapshots in time from a model simulating 1,3-dicyanobenzene impacting and scattering off a multi-layered graphene surface at hypervelocity.

Provided by A. Jaramillo-Botero

Problem Description

Why this problem? Why now?

Our specific objectives were tailored to address (and retire) a major weakness from the JPL-led *Oceanus* New Frontiers 4 proposal that involved hypervelocity sampling in the Titan atmosphere. The results of this work were to support a resubmission of *Oceanus*—or a similar mission—to the NF5 call.

Comparison to State-of-the-Art

The proposed work is, for the first time, linking experimental data to theoretical modeling to address that question. By partnering with Co-I Minton, JPL had access to unique instrumentation and expertise capable of performing these critical experiments and analyzing the data. The strategic partnership with Caltech (Co-I Jaramillo-Botero) allowed us to put these experimental results into context by fully bounding the impact velocities and angles in the theoretical modeling regime.

Relevance to NASA and JPL

The proposed work would retire a key weakness in the JPL-led *Oceanus* New Frontiers proposal.

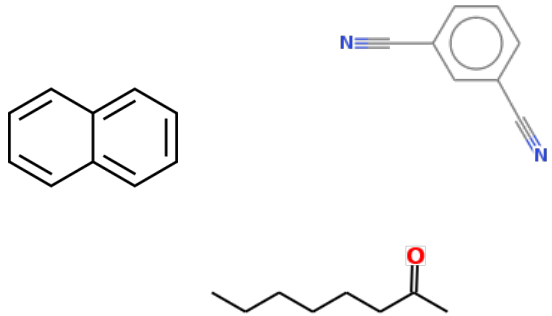


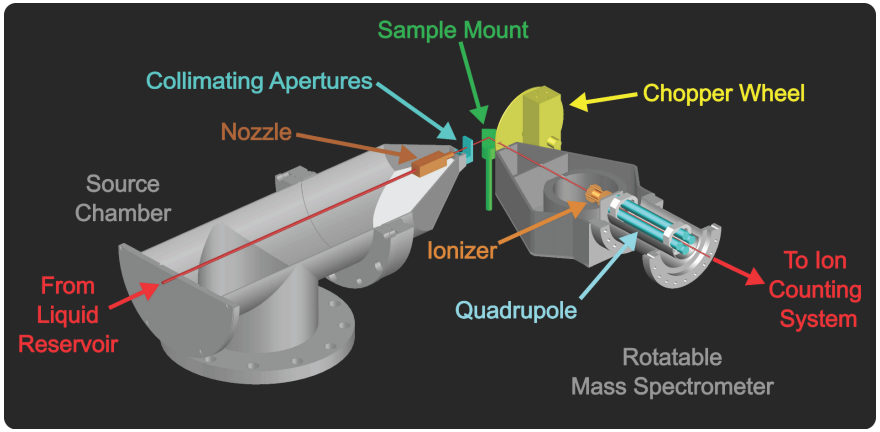
Figure 2. The collection of isobaric (same mass, 128.2 Da) organic molecules chosen for this study. From left to right: naphthalene, 2-octanone, 1,3-dicyanobenzene. Choices explained further in the audio voice-over.

Methodology: Experiments

The experiments make use of the unique Beam Surface Scattering Machine of Co-I Minton at Montana State University, a schematic of which is shown in **Figure 3**.

Molecules of interest are lofted in a carrier gas and accelerated towards an inert target. The configuration of the BSSM allows the angle at which the incident beam impacts the target to be modified.

Upon impact, molecules may interact with, skitter along, or bounce off the surface. Scattered molecules are detected (and identified) via mass spectrometry, the detector for which can be rotated such that products can be associated with the angle at which they scattered from the surface.



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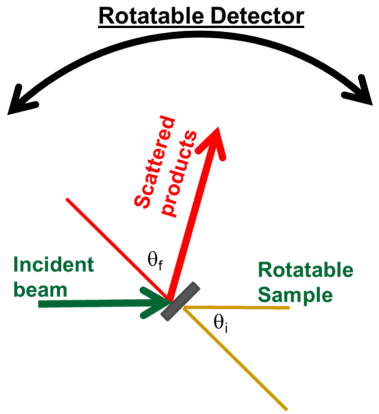

Figure 3. Left: Simplified CAD schematic of the molecular beam surface scattering machine in the laboratory of Co-I Minton at Montana State University. **Right:** Simplified diagram illustrating how the scattered products' mass spectra are collected as a function of the angle at which they scatter off the surface post-impact.

Methodology: Theory

The theoretical work (performed by Co-I Jaramillo-Botero at Caltech) was designed to evaluate the effects of hypervelocity impacts—including angle of impact, molecular orientation upon impact, and energy transfer both intramolecularly and between the impacting molecule and the impacted surface—on the mass spectra of our three representative molecules.

To achieve that overarching objective, the work was subdivided into three tasks:

1) Use first-principles based Reactive Molecular Dynamics (RMD) simulations to predict energy gain/loss after hypervelocity impact.

2) Corroborate scattering dynamics and extend simulations above 2.5 km/s (up to 12 km/s).

3) Use quantum mechanics (QM) based simulations to predict the mass spectra of excited, isobaric species at different velocities and compare to experimental results.

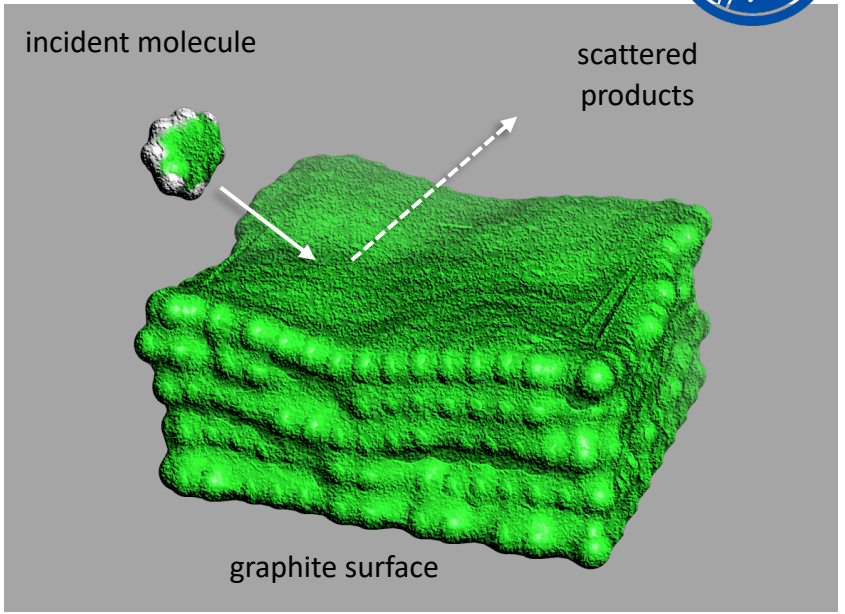

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Figure 4. Snapshot of a 'graphite' surface (modeled as layers of graphene sheets) showing thermal fluctuations that lead to surface topography. Trajectories of incident molecules (such as naphthalene, as shown here) are calculated, following the molecule pre- to post-impact. Molecular interactions with the surface as well as their orientation upon impact are calculated, as are all associated energies.

Results: Experiments

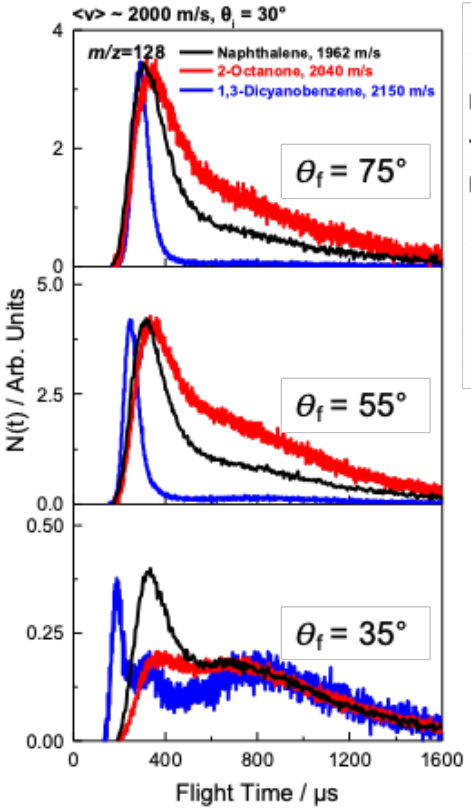
Experimental results for all three molecular species—accelerated to velocities between 2 and 3 km/s—indicated that molecule-impact surface interactions contribute to changes in the internal energy of the molecules upon impact.

This 'redistribution' of internal energy ultimately manifests itself as changes in the fragmentation patterns of those molecules as observed in their mass spectra.

Significance:

Beam surface scattering experiments involving massive and more complex organic molecules—such as those explored in this study—are novel.

The experiments performed under this task represent a new state-of-the-art for testing mass spectrometry of isobaric species relevant for hypervelocity sampling of Titan and other atmospheres containing organic molecules.



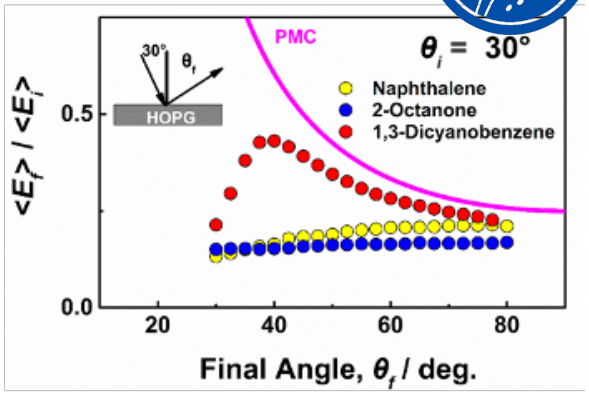


Figure 5. Left: Time-of-flight distributions illustrating molecule + surface interactions that delayed the molecules' arrival at the mass spectrometer. **Top:** Experimental data showing energy loss (ratio of final energy to initial energy) as a function of the scattering products' exit angle following hypervelocity impact with the surface. A more detailed description of both figures is provided in the audio-over.

All provided by T. Minton

Results: Theory

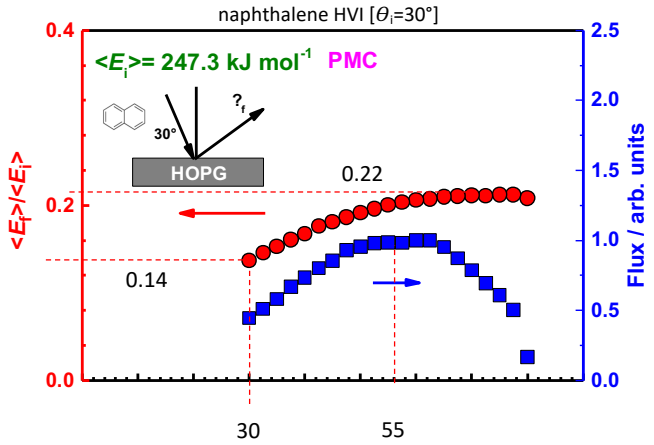
The simulation results constitute new breakthroughs in our understanding of:

1) The fundamental energetics and thermodynamics of molecular fragmentation at hypervelocity, and

2) How non-ionizing electronic excitations are converted into vibrational modes that affect the mass spectra.

Significance:

Understanding the fundamental underlying physical chemistry governing the observed changes in mass spectra will enable us to make predictions regarding an array of other molecules at a range of velocities, as appropriate for individual planetary bodies and mission concepts.



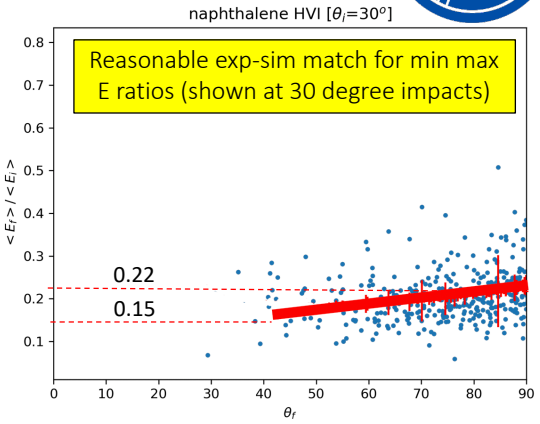


Figure 6 (top). Comparison of experimental (left) and theoretical (right) results in terms of theory being capable of predicting the full range of final-to-initial energy ratios in scattered naphthalene molecules. A more detailed explanation is provided in the audio-over.

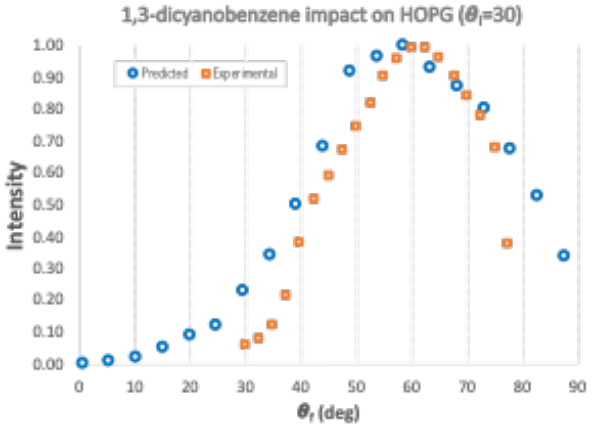


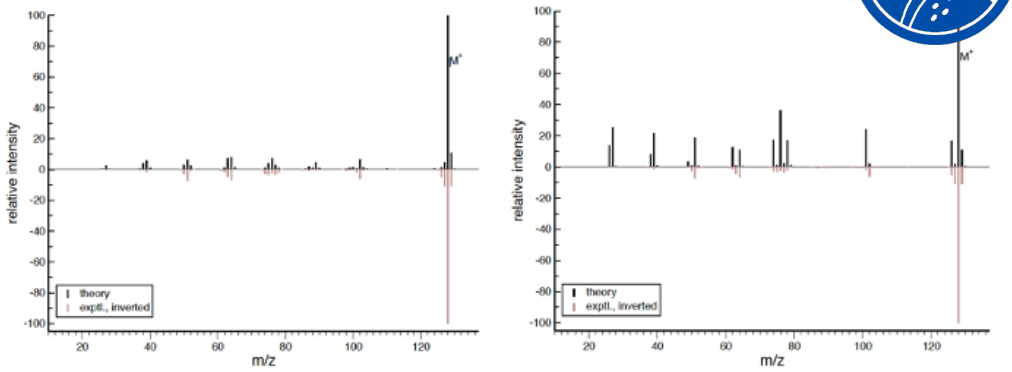
Figure 7 (right). An example of model validation against experimental results, showing the distribution (effectively a histogram) of the number of scattered products per exit angle.

All provided by A. Jaramillo-Botero

Results: Mass Spectra

The most significant discovery from this work was learning that, even at velocities less than those required for impact-induced molecular fragmentation, hypervelocity impacts can repartition molecular internal energy in such a way as to non-trivially alter the mass spectrum of a scattered product such that it bears little resemblance to the canonical ambient condition reference mass spectrum of the same material that the majority of researchers use in identification of unknown species.

These results have significant implications for overall mission design as well as for instrumentation, sample collection, and data processing and analysis.



Provided by A. Jaramillo-Botero

Figure 8 (top). Sample mass spectra for naphthalene as calculated from first principles (black) and as provided by NIST. A more detailed explanation is provided in the audio-over.

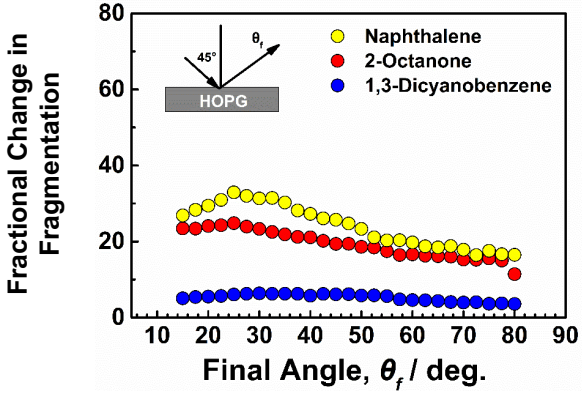


Figure 9 (right). Experimental results illustrating that fragmentation patterns in mass spectra of post-impact scattered products change due to interactions with the impacted surface.

Provided by T. Minton

Publications

[A] Chenbiao Xu, Cal M. Treadway, Vanessa J. Murray, Timothy K. Minton, Michael J. Malaska, Morgan L. Cable, & Amy E Hofmann, “Inelastic scattering dynamics of naphthalene and 2-octanone on highly-oriented pyrolytic graphite”, *The Journal of Chemical Physics* 152: 244709, 2020. doi: 10.1063/5.0011958 — **Selected as an Editor’s Pick!**

[B] Andres Jaramillo-Botero, Morgan L. Cable, Amy E. Hofmann, Michael Malaska, Rob Hodyss, & Jonathan Lunine, “Understanding hypervelocity sampling of biosignatures in space missions,” *In revision for Astrobiology.*

[C] Chenbiao Xu, Cal M. Treadway, Vanessa J. Murray, Timothy K. Minton, Michael J. Malaska, Morgan L. Cable, Amy E. Hofmann, & Andres Jaramillo-Botero, “Inelastic scattering dynamics of 1,3-dicyanobenzene on highly-oriented pyrolytic graphite”, *In preparation for submission to The Journal of Chemical Physics*.

[D] Andres Jaramillo-Botero, Amy E. Hofmann, Michael J. Malaska, Robert Hodyss, & Morgan L. Cable, “Structural scattering dynamics of naphthalene, 2-octanone, and 1,3-dicyanobenzene on HOPG”, *In preparation for submission to the Journal of Physical Chemistry C*.