



## Hypervelocity Impact Effect of Molecules from Enceladus' Plume and Titan's Upper Atmosphere on NASA's Cassini Spectrometer from Reactive Dynamics Simulation

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The NASA/ESA Cassini probe of Saturn analyzed the molecular composition of plumes emanating from one of its moons, Enceladus, and the upper atmosphere of another, Titan. However, interpretation of this data is complicated by the hypervelocity (HV) flybys of up to  $\sim 18$  km/sec that cause substantial molecular fragmentation. To interpret this data we use quantum mechanical based reactive force fields to simulate the HV impact of various molecular species and ice clathrates on oxidized titanium surfaces mimicking those in Cassini's neutral and ion mass spectrometer (INMS). The predicted velocity dependent fragmentation patterns and composition mixing ratios agree with INMS data providing the means for identifying the molecules in the plume. We used our simulations to predict the surface damage from the HV impacts on the INMS interior walls, which we suggest acts as a titanium sublimation pump that could alter the instrument's readings. These results show how the theory can identify chemical events from hypervelocity impacts in space plumes and atmospheres, providing in turn clues to the internal structure of the corresponding sources (e.g., Enceladus). This may be valuable in steering modifications in future missions.

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The Cassini Saturn orbiter has returned a wealth of data from its Ion and Neutral Mass Spectrometer (INMS) [1] on the composition of Titan's upper atmosphere and the plumes of Enceladus. Enceladus' plume has been sampled during five fly-bys (*E1-E5*) and found to be composed predominantly of  $\text{H}_2\text{O}$ , with  $\text{CO}_2$  as the second most abundant species. The latest encounters have yielded data with high signal-to-noise ratios, enabling the identification of trace species, including complex organics such as benzene, that were not distinguishable in INMS data from the earlier fly-bys [2]. Cassini's INMS is a quadrupole mass spectrometer equipped with two separate ion sources, a closed source and an open source. The composition of the Enceladus plumes and the upper atmosphere of Titan have been obtained primarily with the closed source, which is made up of a spherical titanium (Ti) antechamber connected to a hot filament electron impact ionizer by means of a transfer tube [1]. The 70 eV ionizer fragments and ionizes the incident molecules before they are focused in the quadrupole for mass analysis. Atmospheric gas molecules enter the antechamber through an entrance aperture, and are thermalized through collisions with the antechamber walls before entering the ionizer. This arrangement achieves a direction-dependent ram enhancement of the gas pressure in the antechamber above that of the ambient gas due to the high velocity of the spacecraft [3].

Interpretation of the INMS spectra requires careful deconvolution of a complex pattern of mass peaks that

represent the parent species and dissociative ionization products resulting from the ionizer and from hypervelocity (HV) impacts with the INMS chamber walls. The fundamental physical and chemical properties of HV molecular collisions are largely unknown for the species of relevance to Cassini's INMS data. Here, we focus on predicting the influence of specific factors on the interpretation of INMS data: namely, the effect of encounter velocity (energy) on molecular fragmentation processes, the molecular topology effects from different isomers on fragmentation patterns, the INMS  $\text{TiO}_2$  surface reactivity or composition changes from HV impact of ice clusters or cosmic dust, and the probability of physisorbed or chemisorbed species on the  $\text{TiO}_2$  INMS surfaces. The results are analyzed using INMS data at the encounter velocities *E2* (8 km/s), *E3* (14.41 km/s), and *E5* (17.73 km/s) [2] with Enceladus' plume, and the October 26 2004 Titan fly-by at  $\sim 6$  km/s [4].

*Computational methods and models.*—These factors are addressed using the first-principles-based reactive molecular dynamics (RMD) ReaxFF method [5,6], for simulating general chemical reaction processes, and the electron force field method (eFF) [7,8], for simulating electronically excited states from an approximate nonadiabatic solution to Schrödinger's equation. ReaxFF provides nearly the accuracy of ground state quantum mechanics (QM) for describing reactive processes at the expense of conventional force fields. It enables the simulation of reactivity,

diffusion, material decohesion and fragmentation, and phase transitions, which are essential to capturing the gas or surface chemistry and transport of molecular species during HV impact events across the INMS surfaces. eFF on the other hand, is a mixed quantum-classical nonadiabatic solution to the time-dependent Schrödinger's equation that enables an accurate description of large-scale nonadiabatic electronic processes, such as those expected from ionizing and excited electrons at high energy. From our preliminary eFF HVI simulation results for various materials, including organic molecules [9] and metal clusters or slabs [10], we established that excitation effects (e.g., ionization) become non-negligible above impact velocities of 15 km/s, which consequently led us to expect homolytic ground-state reactions dominate (i.e., no ionization products) in the reported range of velocities experienced during the Cassini fly-bys. ReaxFF is ideally suited to model the dynamics of such ground-state reaction processes. The ReaxFF force field, see the Supplemental Material (SM) for details [11], was prepared from QM (DFT-B3LYP) for compressive, equilibrium and dissociative Ti/O/H/C/N interactions, using the Ti/O/H force field from Ref. [12] as a starting point. It is used here in RMD to explore the relationship between velocity of impact and energetic fractionation in HV collisions between different gas phase molecules and clathrates on a TiO<sub>2</sub> rutile (110) surface in the range of 6 km/s, *E2*, *E3*, and *E5*. A TiO<sub>2</sub> molecular slab model with dimensions  $67.1 \times 56.8 \times 66.3$  Å and a total of 24 000 atoms was prepared along with molecular models for impactors, which included H<sub>2</sub>O ice clusters of radius 10.5–13.0 Å (219–416 water molecules), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), benzene (C<sub>6</sub>H<sub>6</sub>), serial and branched hexane (C<sub>6</sub>H<sub>14</sub>), cyclohexane (C<sub>6</sub>H<sub>12</sub>), and ammonia (NH<sub>3</sub>) gas phase molecules, and CO<sub>2</sub> and NH<sub>3</sub> clathrates of 20H<sub>2</sub>O. The target slab and individual impactor models were combined into a unit cell with a depth of 300 Å in the impact direction and an initial separation of  $\sim 20$  Å. In addition, all electron eFF RMD simulations of ethane (C<sub>2</sub>H<sub>6</sub>) impacts on a hydrogen-capped diamondoid surface were performed to gage the role of ionization in the dissociation of molecular species during the HV collisions at 20 km/s (i.e., equivalent to the  $\sim 70$  eV energy from the INMS ionizing gun). eFF is currently accurate up to  $Z = 14$  (silicon); thus, we use the simpler hydrocarbon on diamond impact model to explore the underlying electronic phenomena that occur during HVI. All model systems were optimized using the corresponding ReaxFF or eFF force field to an energy tolerance of  $1 \times 10^{-5}$  and an RMS force tolerance of  $1 \times 10^{-6}$ , and equilibrated to 150 K [3] using canonical ensemble molecular dynamics with a Nosé-Hoover thermostat, i.e., a constant number of particles, volume, and temperature. Instantaneous impactor velocities were applied and the collision dynamics modeled with a microcanonical ensemble (constant number of particles, volume, and energy) with 0.1 fs time steps for

ReaxFF and 0.001 fs in eFF. CRYSTAL09 [13] was used for the required QM calculations and the reaxFF/C and eFF packages in LAMMPS [14] for RMD.

**Results.**—Figure 1 summarizes the fragment evolution from ReaxFF RMD of the ice clusters (averaged over 4 sizes) and CO<sub>2</sub> molecules and ice clathrate as a function of impact encounters with the TiO<sub>2</sub> surface. Each case corresponds to an average over 100 independent impact trajectories. We assume infrequent gas-phase collisions between original species after impact, consistent with low plume or atmospheric densities observed at Enceladus and Titan [3]. The fractions for H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, CO, and CO<sub>2</sub> production as a function of impact energy are consistent with INMS data reported by Waite and colleagues [2], with two exceptions: (i) larger release of O<sub>2</sub> as a function of impact energy from our simulations (all impactors), and (ii) CO<sub>2</sub> fraction is larger and remains inversely proportional to the impact velocity through *E5* (i.e., no inflection point between *E3* and *E5*). Both cases are influenced by a underpredicted Ti-O surface bond energy in the ReaxFF description. Softer Ti-O surface bond takes energy away from C-O bond breaking.

Table I shows that the mixing ratios for H<sub>2</sub>/H<sub>2</sub>O from CO<sub>2</sub>-ice clathrate impact simulations accurately corresponds with INMS data. A comparison with molecular impacts indicates a relatively higher fraction of ice-born species. The CO/CO<sub>2</sub> mixing has the correct qualitative trend between *E3* and *E5*, but its magnitude is underpredicted by our reaxFF dynamics.

Figure 2 shows the extent of reaction processes occurring after impact with the TiO<sub>2</sub> surface for methane,

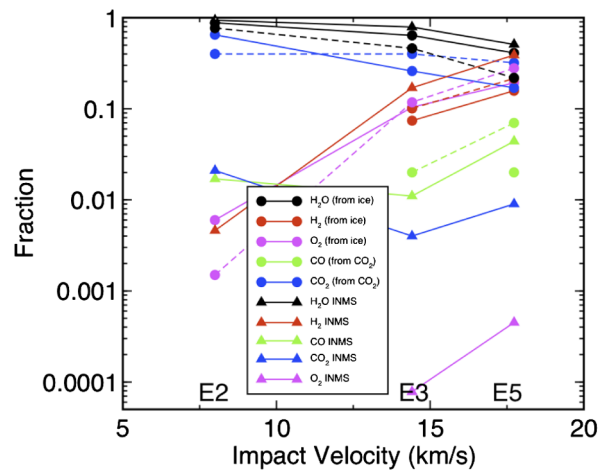


FIG. 1 (color online). Predicted and INMS fragment data from H<sub>2</sub>O ice clusters of radius 10.5 to 13.0 Å in increments of 0.5 Å, CO<sub>2</sub> molecules and CO<sub>2</sub>[20H<sub>2</sub>O] ice water clathrate (dotted lines) impacts as a function of encounter velocity. Accurate fractions and rates of change predicted for H<sub>2</sub>O, H<sub>2</sub>, and CO production, compared to INMS data from Ref. [2]. Correct trend for CO<sub>2</sub> and O<sub>2</sub> production, except for a decrease in CO<sub>2</sub> between *E3*-*E5* and albeit overpredicted magnitudes.

TABLE I. Mixing ratios from INMS/ReaxFF at *E3* and *E5*. Magnitude and velocity dependence of  $H_2/H_2O$  ratio, and velocity dependence of  $CO/CO_2$  ratio agree with INMS data.

Source (encounter)	$H_2/H_2O$	$CO/CO_2$
INMS ( <i>E3</i> ) [2]	0.22	2.75
INMS ( <i>E5</i> ) [2]	0.77	4.89
ReaxFF 20 $H_2O$ [ice]- $CO_2$ clathrate ( <i>E3</i> )	0.22	0.05
ReaxFF 20 $H_2O$ [ice]- $CO_2$ clathrate ( <i>E5</i> )	0.98	0.22

ethylene, and benzene impacts. For increasing impact velocities fewer impactor molecules remain intact after collision. We highlight an almost constant ( $\sim 10\%$ ) production of formaldehyde ( $CH_2O$ ) for ethylene impacts at all encounter velocities, as well as  $H_2$  and water beyond the *E3* velocity for all molecules. Formaldehyde formation was also constant for *E3* and *E5* after methane ( $\sim 10\%$ ) and benzene ( $\sim 4\%$ ) impacts, which may serve as a scaling factor for INMS data. A significant production of  $CO_2$  occurred in ethylene ( $\sim 25\%$ ) and benzene ( $> 50\%$ ) impacts at *E3*, and a lower number of CO molecules. No CO was produced from methane and only a few (4)  $CO_2$ 's. Other events not evident from this graph include radical formation for all cases, oxidation or chemisorption of the original molecules on the  $TiO_2$  surface (frequent for benzene even by *E2*). C-O formation is via oxidation.

Preliminary calculations using eFF simulated collisions of ethane ( $C_2H_6$ ) and methane on a partially H-capped diamondoid surface show negligible ionization up to *E2* velocities, yet a significant increase in fractions between *E3* and *E5*. This would lead to increased chemisorption of products in the INMS due to image attraction of the ions to the metallic surface. The resulting dissociation patterns offer evidence of topological dependencies, e.g., the stiffer benzene ring tends to be more brittle on impact, and single

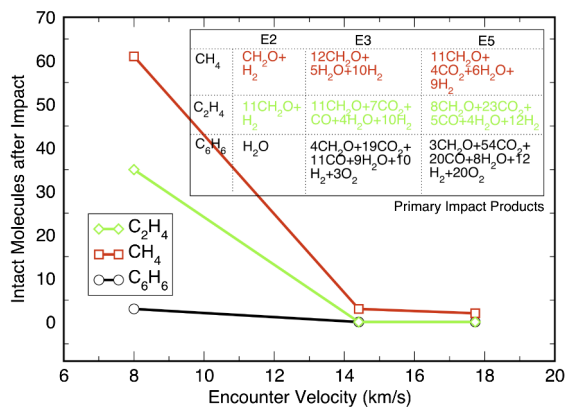


FIG. 2 (color online). Primary predicted fragments for methane, ethylene, and benzene molecular impacts. H, OH,  $CH_2$ , and  $CH_3$  radicals not included. Each case corresponds to one randomly oriented molecule per  $TiO_2$  surface impact over 100 trajectories per impact velocity. Curves correspond to reflected species. Chemisorbed molecules not included.

C-C bond scissions led more often to chemisorption on the  $TiO_2$  surface.

Such topological differences in the incident molecules affect how the translational energy is dissipated during impact. To explore this idea further, we performed RMD collision simulations of different hexane isomers (unbranched, branched (neo), and cyclic) on the  $TiO_2$  surface. We find that molecular dissociation is energetically unfavorable below 5 km/s with most of the energy converted into vibrational and translational energy in the impacting molecule due to the stiffness of the  $TiO_2$  substrate. At  $\sim 5$  km/s, chemisorption, dissociative scattering, and inelastic scattering begin to occur. C-H dissociation commonly occurred before C-C scission because the initial impact kinetic energy is transferred or dissipated into C-H bond degrees of freedom. C-C bond breaking in cyclohexane leads to oxygen bridging chains on the  $TiO_2$  surface, requiring the least effort due little impact energy dissipation. We also find the branching ratio between fragmentation processes to be related to the degree of molecular branchedness. For example, in neohexane (most branched), the C-C bond dissociation energies are lower than those in ordinary hexane or cyclohexane, so demethylation requires less energy. Likewise, highly branched alkyl radicals are more stable than unbranched radicals, so permanent hydrogen loss and dissociation occurs at lower impact energies for branched molecules. Neohexane also had the lowest inelastic scattering probability, which results in low-energy fragmented species more likely to be adsorbed than to scatter, leading to the highest dissociative chemisorption to dissociative scattering ratio of all the hexane isomers up to 10 km/s impacts. Higher velocities (100 eV's) lead to adsorption, implantation and more extensive fragmentation. At 15 km/s oxygen atoms are knocked out of the  $TiO_2$  surface, whereas at 20 km/s Ti atoms are also sputtered. Fragmentation patterns do not differ significantly above 20 km/s. Normalized mass spectra results for the different encounter velocities are shown in Fig. 3. The observed fragmentation processes versus impact energy are consistent with experimental results from Ref. [15].

Since the presence of ammonia ( $NH_3$ ) at Enceladus would provide strong evidence for the existence of liquid water down to temperatures as low as 176 K [2] we performed RMD impact simulations of  $NH_3$  at Cassini's fly-by velocity through Titan ( $\sim 6$  km/s) and Enceladus (8–17.73 km/s). Table II provides evidence that nitrogen compounds (including  $NH_3$ ) are chemisorbed onto the  $TiO_2$  surface at 6 km/s. While ammonia is most likely the primordial source of nitrogen on Titan [16], it is currently not observed in its atmosphere. Nevertheless, carryover of nitrogen containing compounds (possibly as amines) from Titan is likely, since 6 km/s impacts yields a high amount of N adsorption. This strongly suggests that INMS data from Enceladus flybys may contain traces from Titan's atmosphere. We observe that nitrogen species are

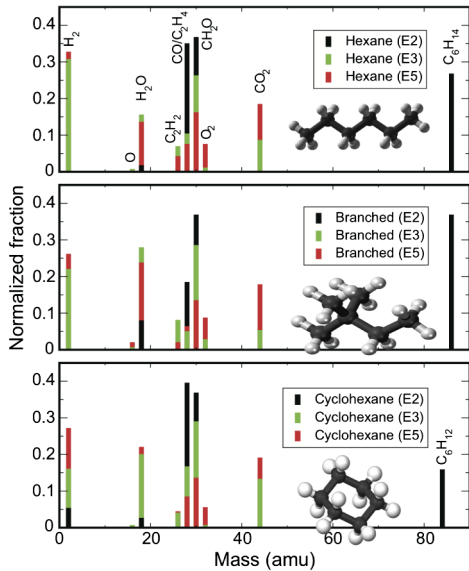


FIG. 3 (color online). Simulated mass spectra for hexane isomers shows topological effects on fragmentation patterns after impact and the possibility of disambiguating overlapping spectral peaks from INMS data (e.g., mass 28, CO, and  $C_2H_4$ ).

more likely to be chemisorbed, even at  $E3$  and  $E5$  velocities, if carried by a clathrate. It is unlikely that pure molecular  $NH_3$  would be chemisorbed at the higher velocity encounters. A significant amount of hydrogen and oxygen gas is also produced from  $NH_3$  impacts at high velocities ( $E3$  and  $E5$ ), while water production is observed to be inversely proportional to the impact velocity (see Fig. 1).

Finally, we characterized the size of impact craters on the  $TiO_2$  surface formed under  $E2$ ,  $E3$ , and  $E5$  conditions by ice-clusters of various sizes (10.5–13.0 Å radius). We focus on ice clusters since a large portion of the species reported from the plume of Enceladus are likely to be ice born, yet cosmic dust could have a similar effect on surface morphology. Figure 4 shows that energetic impact of ice clusters on the  $TiO_2$  surface lead to significant alterations of surface properties, including roughness from crater formation and altered surface reactivity from oxygen and Ti emission and re-plating after impacts. From these results, it follows that Ti replating could create a Ti sublimation

TABLE II. Product yields from 100 ammonia clathrate ( $NH_3[20 H_2O]$ ) impacts on  $TiO_2$  surface. H, OH,  $NH_4O$  radicals are not listed. Absorbed N means different nitrogen compounds are chemisorbed on the  $TiO_2$  surface.

Encounter	$NH_3$	Absorbed N	$H_2$	$H_2O$	$O_2$
Titan (6 km/s)	11	71	0	1731	0
$E2$ (8 km/s)	15	78	0	1692	5
$E3$ (14.41 km/s)	1	91	212	979	216
$E5$ (17.73 km/s)	1	98	503	429	548

pump, which adsorbs active gases such as oxygen, water vapor and some organic molecules. Water dissociates on the Ti surface, releasing  $H_2$  back into the gas phase while oxygen remains bound to the surface. The ejected material mass ( $m_E$ ) for a crater of radius  $r_c$  may be estimated, assuming hemisphericity, as  $m_E = (2\pi/3)r_c^3\rho_t$ , where  $\rho_t$  is the density of  $TiO_2$ .  $r_c/r_p$  scales linearly for hyper-velocity impacts as in Ref. [17].

*Closing remarks*—Our results indicate that molecular fragmentation due to HV impacts must be taken into account even at the relatively modest encounter velocities of 5 km/s and above. Dissociative adsorption and dissociative scattering are likely to appear by 6 km/s impacts remain dominant above 8 km/s and through  $E5$ , inelastic scattering will dominate up to  $\sim 8$  km/s, while adiabatic sputtering and implantation and nonadiabatic fragmentation processes will become increasingly important by 15 km/s. Summarizing, we have (i) related energy of HV impact to fragmentation for different species relevant to INMS data, (ii) obtained molecular species mixing ratios and mass spectra that compare directly to existing INMS data, (iii) described molecular topology factors that affect fragmentation processes and INMS data interpretation, (iv) identified important species that may be a product of HV impact (e.g., formaldehyde from hydrocarbons), (v) confirmed that  $NH_3$  and other organic species may have been chemisorbed on the  $TiO_2$  INMS detector surfaces during Titan’s fly-by, therefore potentially affecting nitrogen-based readouts from Enceladus, and (vi) explored the effect of molecular impact on the chemical and morphological properties of the INMS  $TiO_2$  antechamber walls, which may also affect INMS data interpretation.

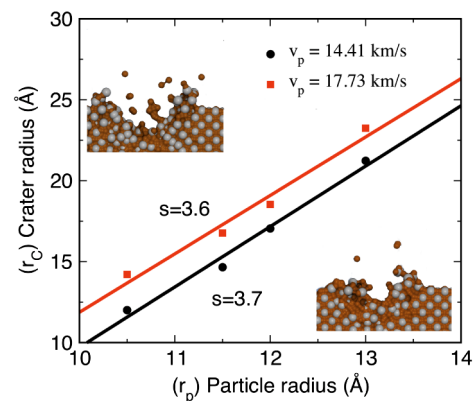


FIG. 4 (color online). RMD simulated  $TiO_2$  (110) crater radius versus ice cluster impactor radius is consistent with experimental data from Kearsley *et al.* [18] associated with NASA’s Stardust mission. Atomistic crater profiles shown as insets. The ratio of crater ( $r_c$ ) to cluster radius ( $r_p$ ) is linear over the range of impact velocities and its slope ( $s$ ) provides an indication of increasing or decreasing damage (i.e., at  $E5$   $s = 3.6$ ; therefore, a larger diameter damage is expected than at  $E3$  with  $s = 3.7$ ). Kearsley *et al.* report an  $s = 2.2$ –4.63.

ReaxFF provides an unprecedented opportunity for describing the dynamics of molecular dissociation resulting from impacts up to  $\sim 14\text{--}15$  km/s velocities, while eFF has the potential to explore higher energy regimes in which electronic excitations play a significant role in fragmentation. Their potential role in improving the development of instruments for future missions is also highlighted (e.g., controlling the spacecraft's velocity may lead to a natural production of ions from impact, thereby avoiding the need for electronic impact guns in spectrometers).

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