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 ~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.

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 H_2O, with 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 impacts with the INMS chamber walls. The fundamental physical and chemical properties of hypervelocity (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 TiO_2 surface reactivity/composition changes from HV impact of ice clusters or cosmic dust, and the probability of physisorbed or chemisorbed species on the 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 flyby at ~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 non-adiabatic 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/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 non-adiabatic solution to the time-dependent Schrödinger's equation that enables an ac-

curate description of large-scale non-adiabatic 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/slabs[10], we established that excitation effects (e.g. ionization) become non-neglible above impact velocities of 15km/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 flybys. ReaxFF is ideally suited to model the dynamics of such ground-state reaction processes. The ReaxFF force field, see supplemental material (SM) for details, 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 [11] 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_2 rutile (110) surface in the range of 6 km/s, E2, E3, and E5. A TiO_2 molecular slab model with dimensions 67.1x56.8x66.3 Å and a total of 24,000 atoms was prepared along with molecular models for impactors, which included: H_2O ice clusters of radius 10.5-13.0 Å(219-416 water molecules); carbon dioxide (CO_2), methane (CH_4), ethylene (C_2H_4), benzene (C_6H_6), serial and branched hexane (C_6H_{14}), cyclohexane (C_6H_{12}), and ammonia (NH_3) gas phase molecules; and CO_2 and NH_3 clathrates of $20H_2O$. 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 ~20 Å. In addition, all electron eFF RMD simulations of ethane (C_2H_6) 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~ 70eV 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 $1e^{-5}$ and an RMS force tolerance of $1.0e^{-6}$, and equilibrated to 150 K [3] using canonical ensemble molecular dynamics with a Nosè-Hoover thermostat, i.e. 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 timesteps for ReaxFF and 0.001 fs in eFF. Crystal09[12] was used for the required QM calculations and the reaxFF/C and eFF packages in LAMMPS [13] for RMD.

Results. Fig. 1 summarizes the fragment evolution from ReaxFF RMD of the ice clusters (averaged over 4 sizes) and CO_2 molecules and ice clathrate as a function of impact encounters with the TiO_2 surface. Each
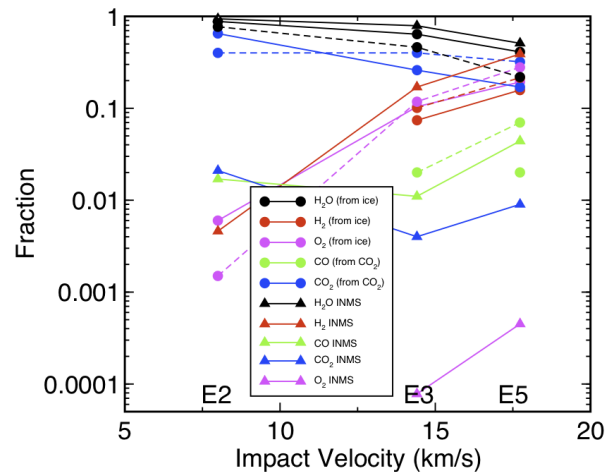

FIG. 1. (Color online). Predicted and INMS fragment data from H_2O ice clusters of radius 10.5 to 13.0Å in increments of 0.5Å, CO_2 molecules and $CO_2[20H_2O]$ ice water clathrate (dotted lines) impacts as a function of encounter velocity. Accurate fractions and rates of change predicted for H_2O, H_2 and CO production, compared to INMS data from [2]. Correct trend for CO_2 and O_2 production, except for a decrease in CO_2 between E3-E5 and albeit overpredicted magnitudes.

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/atmospheric densities observed at Enceladus and Titan [3]. The fractions for H_2, O_2, H_2O, CO and CO_2 production as a function of impact energy are consistent with INMS data reported by Waite and colleagues [2], with two exceptions: 1) larger release of O_2 as a function of impact energy from our simulations (all impactors), and 2) CO_2 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 under-predicted Ti-O surface bond energy in the ReaxFF description. Softer Ti-O surface bond takes energy away from C-O bond breaking.

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 (E3)[2]	0.22	2.75
INMS (E5)[2]	0.77	4.89
ReaxFF $20H_2O$[ice]-CO_2 clathrate (E3)	0.22	0.05
ReaxFF $20H_2O$[ice]-CO_2 clathrate (E5)	0.98	0.22

Table I shows that the mixing ratios for H_2/H_2O from CO_2-ice clathrate impact simulations accurately correspondend with INMS data. A comparison with molecular impacts indicate a relatively higher fraction of ice-bourn

species. The CO/CO_2 mixing has the correct qualitative trend between E3 and E5, but its magnitude is under-predicted by our reaxFF dynamics.
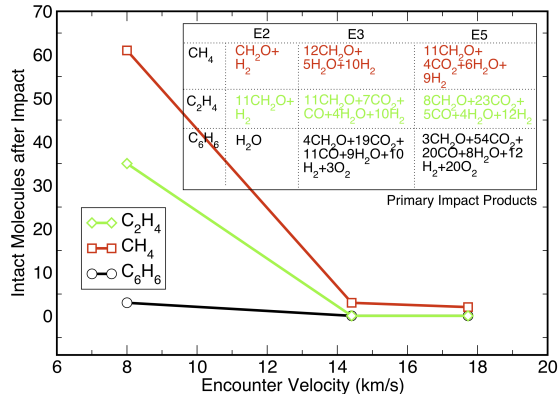

FIG. 2. (Color online). Primary predicted fragments for methane, ethylene, and benzene molecular impacts. H, OH, CH_2, and CH_3 radicals not included. Each case corresponds to one randomly oriented molecule per TiO_2 surface impact over 100 trajectories per impact velocity. Curves correspond to reflected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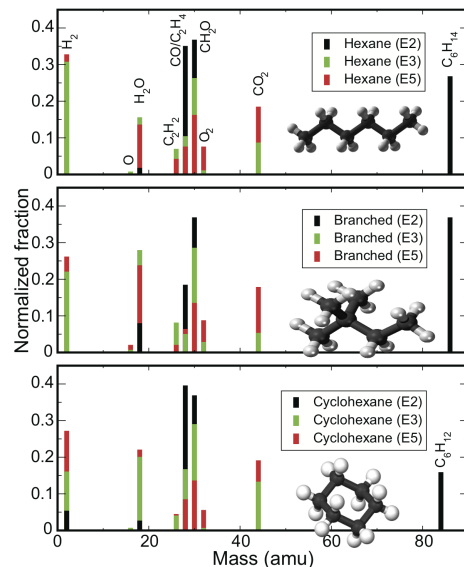

FIG. 3. (Color online). Simulated mass spectra for hexane isomers shows topological effects on fragmentation patterns after impact and the possibility of disambiguating overlapping spectral peaks from INMS data (e.g. mass 28, CO and C_2H_4).

Fig. 2 shows the extent of reaction processes occurring after impact with the TiO_2 surface for methane, 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 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/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 20km/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 [14].

TABLE II. Product yields from 100 ammonia clathrate (NH_3[20 H_2O]) impacts on TiO_2 surface. H, OH, NH_4O radicals 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

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 flyby 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 6km/s. While ammonia is most likely the primordial source of nitrogen on Titan [15], 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 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 (10.5-13.0Å radius). We focus on ice clusters since a large portion of the species reported from the plume of Enceladus are likely to be ice-bourn, yet cosmic dust could have a similar effect on surface morphology. Fig. 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 re-plating could create a Ti sublimation 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 sur-
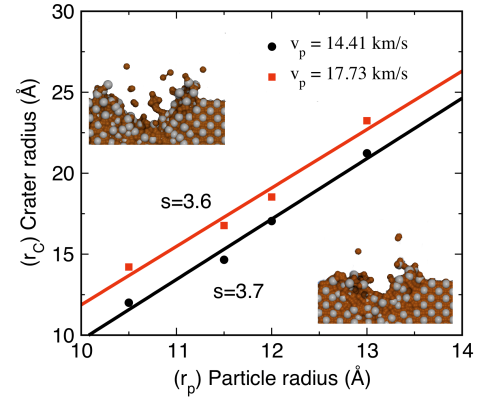

FIG. 4. (Color online). RMD simulated TiO_2 (110) crater radius versus ice cluster impactor radius is consistent with experimental data from Kearsley et al [16] associated with NASA's Stardust mission. Atomistic crater profiles shown as insets. The ratio of crater (r_c) to cluster radius (r_p) is linear over the range of impact velocities and its slope (s) provides an indication of increasing/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.

face. 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 ρ_t is the density of TiO_2. r_c/r_p scales linearly for hypervelocity impacts as in [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 8km/s and through E5, inelastic scattering will dominate up to $\sim$8km/s, while adiabatic sputtering and implantation and non-adiabatic fragmentation processes will become increasingly important by 15km/s. Summarizing, we have: 1) related energy of HV impact to fragmentation for different species relevant to INMS data, 2) obtained molecular species mixing ratios and mass spectra that compare directly to existing INMS data, 3) described molecular topology factors that affect fragmentation processes and INMS data interpretation, 4) identified important species that may be a product of HV impact (e.g. formaldehyde from hydrocarbons), 5) confirmed that NH_3 and other organic species may have been chemisorbed on the TiO_2 INMS detector surfaces during Titan's flyby, therefore potentially affecting nitrogen-based readouts from Enceladus, and 6) 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. ReaxFF provides an unprecedented opportunity for describing the dynamics of molecular dissociation resulting from impacts up to $\sim$14-15km/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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