Amorphous Solid Water: Laser-Induced Eruptions

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Abstract

Molecular transport, morphological change, and heat transfer in thin films of amorphous solid water (ASW) were investigated. The experimental strategy was centered on the introduction of a buried layer of material (N$_2$O$_4$) that efficiently absorbs ultraviolet radiation and converts the absorbed energy to heat. Specifically, a single 10-ns, 266-nm pulse of 1-2 mJ in a diameter of ~0.3 mm turns the N$_2$O$_4$ layer into a hot fluid that heats surrounding material. Resulting temperature and pressure gradients create "vertical" fissures through which material passes from the heated layer to vacuum (UHV). Film thickness up to 2400 ML was examined. In all cases, it was straightforward to eject material from the N$_2$O$_4$ reservoir with just a single laser pulse. The fissures were robust, enabling material transport to vacuum to proceed for many pulses. Material that entered the gas phase was detected using a time-of-flight mass spectrometer that recorded complete spectra every 10 µs. An ASW spacer layer between the MgO substrate and the N$_2$O$_4$ layer provided insulation between the heated layer and the high-thermal-conductivity 100 K MgO substrate. This was verified both experimentally and with heat transfer simulations. Fluid composed of N$_2$O$_4$, its photo-products, and water was heated throughout its trip to vacuum by the 10 ns pulse. This fluid removed water from the fissure walls, as demonstrated using alternate layers of H$_2$O and D$_2$O. Virtually all of the water that entered vacuum did so via this mechanism. Little material enters the gas phase after cessation of the 10 ns pulse because of rapid cooling by the ASW. This ensures that material passing through the fissures to vacuum does so with a speed of at least 100 m/s. Gaseous water undergoes collisions just above the film surface, where high fissure density and the fluid nature of the material passing through the fissures ensures a high density of ejected material. This system has many features in common with the water jets observed on Saturn's moon Enceladus. In both cases, warm fluid is driven through fissures, material is expelled vigorously, and the majority of the released material is not found in jets. Rather, it appears to ooze from the surface. It is believed that liquid water moves through the fissures in Enceladus. In our experiments, the N$_2$O$_4$ reservoir and the fluid that passes through fissures can be heated in a controlled manner. The use of photons to heat material rising through fissures provides a means of exploring, and perhaps controlling, its movement, particularly how it interacts with the icy walls it on the way out. The qualitative model presented herein can provide insight into astrophysical and astro-chemical mechanism.

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I. Introduction

This paper is centered on molecular transport in a form of low-temperature solid water known as amorphous solid water (ASW). This ill-defined material presents intrigue, while at the same time it is enormously important. For example, it accounts for the majority of the water in the Universe [1]. ASW has been the subject of intense research, motivated by both intellectual curiosity and the role it plays in deep space as an incubator and molecular factory in the interstellar medium (ISM) [2]. Space-borne telescopes and spectrometers have probed faraway places [3], and their extensive data acquisition has advanced greatly our understanding of the cosmos. Nonetheless, there is a limit to the kind and amount of information that can be gleaned through images and spectroscopic observations recorded from such large distances. In other words, laboratory experiments are essential insofar as validating models.

The Cassini spacecraft has orbited Saturn since 2004, and remarkable features of Saturn's ice-covered moons, notably Titan and Enceladus, have been discovered using an array of diagnostics. Enceladus has recently provided the greatest excitement because it exhibits cryovolcanic activity in its south polar terrain (SPT), specifically, the four parallel fissures referred to as the "tiger stripes" [4].

Spectacular water jets have been observed that extend hundreds of kilometers above the moon's surface [5,6]. However, the majority of the released water (96%) issues from the tiger stripe fissures without forming robust jets. The water that enters the moon's sparse atmosphere carries with it small molecules such as CO$_2$, H$_2$, NH$_3$, HCN, CH$_2$O, CO, CH$_4$, and a large number of other light hydrocarbons. Twenty-four molecules (plus $^{40}$Ar) have been identified using mass spectrometry [7], complemented by far ultraviolet (110-190 nm) and extreme ultraviolet (55-110 nm) absorption spectroscopy [8]. A subsurface ocean (whose salinity of 0.5-2% is similar to that of earth's oceans) was reported in 2014 [9].

Taking all factors into account, Enceladus is now considered a top candidate for hosting alien microbial life in our solar system [6], which explains part of the excitement about these findings.

How water is transported between Enceladus' subsurface ocean and its sparse atmosphere has been conjectured, but many issues remain open [6,10]. It is accepted that a substantial water ocean, roughly 10 km thick, lies beneath the moon's frozen water mantle, which is estimated to be 30-40 km thick [9]. It is also believed that tidal forces due to Enceladus' gravitational interactions with Saturn and the moon Dione result in hot spots whose temperatures are as high as ~ 200 K. They also result in stresses that modulate the intensity of the jets [11,12]. It is known that the horizontal stresses vary from compressive to shear to tensile, accounting for some of the opening and closing of escape pathways for water exiting the fissures. Comprehensive back-to-back 2014 papers summarize our current understanding of these eruptions and describe models that reconcile some of the experimental data [6,10].

At the same time, experiments have been carried out in which gaseous material spews from thin ASW films doped with atomic and molecular species. Extensive work at Pacific Northwest National Laboratory (PNNL) [13,14], as well as our use of infrared laser radia-
tion to initiate vigorous release of water monomer and small clusters [15], has examined the molecular volcano phenomenon associated with morphological changes in ASW.

Our goals at the outset of the present study were twofold: (1) understand better the phenomena that take place when heat is supplied in controlled amounts at specific distances below the ASW surface; and (2) identify the processes that control material release into vacuum. In the course of these experiments, we discovered surprising parallels between the eruptions observed in ASW thin films and those observed in Enceladus. This enabled us to scrutinize our results in a broader context, as discussed in Section IV.

In the work reported herein, we have examined dynamical processes that involve ASW films doped with a relatively thin N$_2$O$_4$ layer. The N$_2$O$_4$ has been used as a means of introducing heat into a stratum buried within the ASW. The general idea is depicted in Figure 1, and is elaborated in Sections II and III. A 10 ns pulse of 266-nm radiation excites the N$_2$O$_4$ layer, initiating a host of processes in and near the N$_2$O$_4$ layer that evolve rapidly to heat, creating large temperature and pressure gradients. We find that fissures (not indicated in Figure 1) are formed in the upper ASW layer. They tend to be oriented more or less vertically and span the distance from the N$_2$O$_4$ layer to vacuum.Nitrogen oxides (N$_2$O$_4$, NO$_2$, etc.) and water pass into vacuum through the fissures. In these experiments, the N$_2$O$_4$ reservoir and the N$_2$O$_4$-rich fluid that passes through fissures can be heated in a controlled manner. The heated material rising through the fissures interacts with their icy walls on its way out.

Our fissures differ greatly from those on Enceladus. For example, Enceladus' water mantle is 30-40 km thick, whereas our thickest films are ~ 1 µm. Moreover, in our case, heat is introduced using photons, whereas residual heat and gravitational forces are implicated in Enceladus. Despite these and other differences, parallels and insights from our work may prove germane to Enceladus. In both cases warm fluid is driven through fissures, and material is expelled vigorously. In both cases the majority of the released material is not found in jets. Rather, it appears to ooze from the surface.

The preparation of ASW films deserves comment. In the work reported here, films are prepared by vapor deposition near 100 K. There are other ways to prepare ASW, but for our purposes, this is the easiest and most versatile. It is established that the properties of vapor-deposited ASW depend on deposition temperature, rate, and method, and even the substrate upon which it sits. Thus, conditions need to be specified [16]. In the range 130-155 K, what existed as ASW at lower temperatures is often described as a glass or highly viscous liquid, and this regime has engendered interest and controversy [1,17]. This material converts to cubic ice at 155 K [18], and to hexagonal ice at higher temperature.
The order of presentation is as follows. Details of the experimental arrangement and strategy are presented in Section II. Representative data are presented in Section III, with additional data given as Supplementary Material. In Section IV, we discuss and rationalize our results, and then discuss them vis-à-vis the phenomena discovered on Enceladus. The paper ends with a summary and assertions about future work.

II. Experimental Arrangement and Details

Figure 2 is a schematic drawing of the apparatus and arrangement. Experiments with ASW/N₂O₄ films were conducted in a UHV chamber \((3 \times 10^{-10} \text{ Torr})\) using pulsed \((10 \text{ ns}; 1-2 \text{ mJ})\) 266 nm radiation in conjunction with a high repetition rate time-of-flight mass spectrometer (TOFMS; Jordan TOF Products). The UHV chamber uses two of its three tiers, as described in previous papers [19-21]. The top tier accommodates temperature programmed desorption (TPD) and Fourier transform infrared (FTIR) spectroscopy, while the middle tier is configured for TOFMS measurements.

![Figure 2](image)

Figure 2. The UHV chamber is equipped with TOFMS and FTIR diagnostics. 266-nm radiation excites the sample at normal incidence causing material to enter the gas phase. The black rectangle labeled e-beam indicates the portion of the ionized region that is extracted through the mesh aperture that lies below it in the figure. Ions are extracted at a repetition rate of 100 kHz. Samples deposited on the MgO(100) surface can be irradiated in nine areas, indicated on the left, to achieve signal averaging while maintaining single-pulse conditions. For the FTIR studies, the focusing lens is removed and a relatively large area is irradiated. The surface is then translated to the upper tier of the chamber. IR radiation is brought to a focus at the surface using a parabolic mirror. It is then focused onto the InSb detector using a second parabolic mirror.

The MgO (100) substrate was prepared by cleaving a crystal (MTI Corporation) on both sides in dry N₂. The 0.8 mm × 10 mm × 10 mm substrate was then transferred to the UHV chamber. Oxygen vacancies were filled through exposure of the surface to \(10^{-7} \text{ Torr}\) of O₂.
while annealing at 600 K for an hour. This procedure has been shown to produce a high quality MgO(100) surface [19,22].

The substrate was clamped in 0.3 mm thick copper foil (ESPI Metals). A 6 mm × 6 mm aperture in the foil enables radiation to pass through. It was then attached to the arm of one of two electrically isolated copper blocks that were mounted on a copper-capped stainless steel cold finger on a LN₂ reservoir (Kurt Lesker, altered by McAllister Technical Services). Using this configuration, the surface could be cooled to 100 K. Temperature was monitored using a K-type thermocouple (Ceramabond 835-M, Aremco Products) bonded to one side of the MgO surface. A tantalum wire cemented to the back of the copper housing of the surface was used for resistive heating. The cryostat was fitted with bellows, and the sample holder was capable of XYZ translation and 360° rotation.

Samples were grown at 100 K. Layers were deposited after heating the surface to ~ 200 K to remove condensed background gas, and then cooling it to 100 K. All species except NO₂ were introduced to the surface using background dosing. Because NO₂ reacts with metal surfaces, a 0.75 cm ID × 23 cm long glass tube was affixed to a precision leak valve for directed dosing. The surface was rotated from the TOF position such that the end of the tube was ≈ 4 cm from the surface, with the tube oriented normal to the surface. Following deposition, the surface was rotated back to the TOF position.

H₂O(D₂O) layer thicknesses are reported using units of monolayers. Under our deposition conditions 1 L of H₂O formed 1.67 ML on the MgO surface at 100K. This has been previously verified by comparing the integrated intensities of the monolayer peak to the multilayer peak using TPD. For N₂O₄, we expect similar sticking probabilities; however we do not have an experimental verification of the deposition rate, so the thicknesses of those layers are reported in Langmuirs.

The 266-nm radiation was the fourth harmonic of a Nd:YAG laser (Continuum PL9010, 10 Hz). A chopper wheel (ThorLabs MC1000) was used to select every tenth pulse. Beam diameter was reduced from 8 mm to 3 mm using a telescope. This radiation was focused to ~ 0.3 mm diameter at the substrate using a 50 cm focal length CaF₂ lens.

The TOFMS was a Wiley-McLaren design with three electrode plates and an electron beam source ≈ 25 mm from the surface. Triggering at 100 kHz yielded a mass spectrum every 10 µs. Laser irradiation resulted in ablated material passing through the ionizing region (Figure 2). The plume was subjected to 70-eV electron ionization. The plates were usually held at 1800 V, and positive ions were extracted every 10 µs by dropping the potential on the extractor plate to 1550 V for 3 µs. Ions were then accelerated using a grounded third plate, after which they entered the 48 cm field-free drift tube. They were detected at the end of the drift tube using a multi-channel plate (MCP) detector connected to a fast pre-amplifier (SRS D-300 MHz). The amplified current from the MCP was recorded on a computer with an analog-to-digital converter (Gage CS 8500, 8 bit, 512k samples). Spectra were collected using a custom LabView program (National Instruments) and further processed using IGOR Pro (WaveMetrics). The set of 30-120 individual mass spectra collected following a single laser pulse shall be referred to hereafter as a temporal profile.

A species' arrival time at a small volume in the ionization region can reflect its speed when \( v = \frac{d}{t} \) applies, where \( d \) is the distance the species travels prior to its ionization, and the species departs from the surface at \( t = 0 \). The size and shape (12 mm diameter) of the extraction region confounds this, as it limits resolution. Species having a given speed and
departing from the surface at \( t = 0 \) might arrive at different parts of the extraction region. In other words, a given speed contributes to signal at different times. Likewise, different speeds contribute to signal at a given extraction time. Consequently, velocity resolution is low. We accepted this in the present experiments as a trade-off in favor of large signal-to-noise ratio (S/N), which enabled us to obtain high quality spectra following a single laser pulse.

Nine spots in a three-by-three grid could be irradiated per surface to give nine individual temporal profiles. This provided the option of averaging to improve S/N and reduce effects due to laser energy fluctuations and film irregularity. This means of averaging is applied to whichever pulse we are interested in (i.e., first, second, and so on). Because of the limited horizontal diffusion of absorbed laser energy, moving the laser position by 1 mm ensured irradiation of an undisturbed section of the film.

FTIR spectra were collected using a Nicolet Protegé 460 spectrometer equipped with a LN\(_2\)-cooled InSb detector. Spectra were recorded using OMNIC software. The range 1850-7000 cm\(^{-1}\) was covered at 1 cm\(^{-1}\) resolution, averaging 200 scans. The IR beam was trimmed using an iris to 2 mm diameter to ensure that it sampled the part of the surface that was irradiated. To collect an FTIR spectrum, the surface was raised to the top tier to collect a background. The surface was then lowered to the middle tier for the dosing procedure and then raised again to collect a baseline FTIR spectrum. After the surface was lowered again, the 50 cm CaF\(_2\) focusing lens was removed from the 266-nm beam path to give a roughly 3 mm diameter beam centered on the surface. Following 266-nm irradiation, the surface was raised again to take the final spectrum.
III. Results

Time-of-flight mass spectra (70 eV) and temporal profiles were recorded for molecules that enter the gas phase following 266-nm pulsed irradiation using the sandwich arrangement indicated in Figure 1. In order to interpret these mass spectra, it was necessary to obtain individual mass spectra of the stable molecules that arise in the experiments: N$_2$O$_4$, NO$_2$, NO, and H$_2$O. It is noteworthy that N$_2$O$_4$ yields no ions heavier than NO$_2^+$, which complicates distinguishing N$_2$O$_4$ from NO$_2$. In addition, temporal profiles and their individual mass spectra were recorded for material released into vacuum following the 266-nm irradiation of exposed N$_2$O$_4$. These data are presented in Section III.1.

In Section III.2, mass spectra and temporal profiles are presented for the first laser pulse to interact with freshly prepared samples such as the one indicated in Figure 1. The TOFMS diagnostic provides excellent single-shot S/N. Results for the second, third, etc. pulses incident on the same spot are presented in Section III.3. As discussed in Section II, no signal averaging is carried out for TOFMS results from successive pulses that fall incident on the same spot. In other words, effects due to the first, second, third, etc. pulses are isolated from one another. In Section III.4, it is shown that material ejection takes place through fissures that originate at the laser-heated region. At low fluence, the progress of the N$_2$O$_4$-rich material upward toward vacuum stops short of ejecting material into vacuum. A second (or third) pulse invigorates the trapped material in the incipient fissure, enabling it to enter vacuum. Experimental results obtained using layers of D$_2$O and H$_2$O in the upper ASW are presented in Section III.4, demonstrating that the water ejected into vacuum is removed from the fissure walls. Preliminary results obtained using the FTIR probe are presented in Section III.5.

III.1. Mass Spectra of NO$_2$, N$_2$O$_4$, NO, and H$_2$O

Data analyses make use of comparisons between mass spectra, including subtracting contributions from species whose spectra are known with good accuracy. Therefore, mass spectra of NO$_2$, N$_2$O$_4$, NO, and H$_2$O were recorded using our apparatus, as opposed to relying on spectra taken from the literature. This obviates the need to account for differences due to experimental arrangements (e.g., time-of-flight versus quadrupole), thereby enabling the most reliable analyses. The relevant mass spectra obtained using the arrangement shown in Figure 2 are shown in Figure 3. Those for NO$_2$, NO, and H$_2$O of course can be found in the literature. Nonetheless, we find that our cracking patterns differ slightly from those reported in the NIST database [23]. The mass spectrum of gaseous N$_2$O$_4$ was not available in the literature, and its acquisition was more challenging, as discussed below.

N$_2$O$_4$

Mass spectra of gaseous N$_2$O$_4$ were recorded by maintaining solid N$_2$O$_4$ at temperatures such that its sublimation provided adequate density in the ionization region of the TOFMS. Temperatures around 155 K were used. Impurity NO was minimized through the use of freeze-pump-thaw cycles, with the addition of O$_2$ during the warm phase. Lack of light
blue color in the condensed material indicated minimal N₂O₃, which is known to be present when there is an NO impurity [24]. Furthermore, neutral NO yields a signal at \( m/e = 15 \) due to NO²⁺ [23], as seen in Figure 3. This is absent in spectra such as the one shown in Figure 3(d). Finally, the dissociation \( \text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2 \) is endergic by 4440 cm⁻¹ [25], whereas the binding energy of an \( \text{N}_2\text{O}_4 \) molecule to its solid is 3800 cm⁻¹ [26]. For NO₂ to enter the gas phase during sublimation, it would be necessary to break the N-N bond in \( \text{N}_2\text{O}_4 \) and have NO₂ desorb. The difference between the energies required to enter the gas phase for \( \text{N}_2\text{O}_4 \) versus NO₂ augurs for a small percentage of NO₂ leaving the film. To the best of our knowledge, this is the first report of a direct measurement of the cracking pattern of this important gas phase molecule.

Referring to Figure 3(d), the 70 eV electron impact ionization of \( \text{N}_2\text{O}_4 \) yields no ions heavier than NO²⁺, i.e., neither \( \text{N}_2\text{O}_4^+ \) nor \( \text{N}_2\text{O}_3^+ \) is observed. The red arrows indicate where signals would have appeared had \( \text{N}_2\text{O}_4^+ \) and \( \text{N}_2\text{O}_3^+ \) been present. The fact that only \( \text{NO}^+, \text{NO}_2^+, \text{O}^+, \text{O}_2^+, \text{and N}^+ \) are present in sublimation spectra recorded using condensed
N₂O₄ samples (no water) presents a challenge insofar as assigning neutral parentages of ion signals. The amount of NO⁺ relative to NO₂⁺ is denoted by the ratio NO⁺/NO₂⁺, where NO⁺ and NO₂⁺ are the areas of the respective signals; likewise for O⁺/NO₂⁺ and N⁺/NO₂⁺. Ratios for neutral species, e.g., NO₂/N₂O₄, are denoted similarly. These latter ratios take into account the 70 eV ionization cross sections for N₂O₄, NO₂, NO, and O (Table 1), as discussed in Appendix A.

Carrying out this calibration for N₂O₄ [Figure 3(d)] gives NO⁺/NO₂⁺ = 0.9 and O⁺/NO₂⁺ = 0.1. For 300 K NO₂ [Figure 3(a)] these values are 3.1 and 0.6, respectively. The large difference in the NO⁺/NO₂⁺ ratios for the mass spectra of NO₂ and N₂O₄ facilitates data analysis, as described below.

If N₂O₄ molecules that sublime at ≈ 155 K strike a nearby 300 K metal surface, they might stick and dissociate, yielding surface-bound NO₂. In turn, NO₂ might be released into the gas phase. This would yield an N₂O₄ spectrum contaminated by NO₂. This was checked using different electrode configurations in the TOFMS extraction region (Figure 4). When a significant amount of metal was placed opposite the sample, as indicated in Figure 4(a), the NO⁺/NO₂⁺ ratio increased to ≈ 1.0. This indicates the presence of NO₂ brought about through collisions of N₂O₄ with the metal surface facing the plume. However, without this added metal [Figure 4(b)], spectra such as the one shown in Figure 3(d) were recorded, giving NO⁺/NO₂⁺ ≈ 0.9 for N₂O₄ subliming at ≈ 155 K. There may be a modest amount of NO₂ contaminant, but the dominant N₂O₄ features are those shown in Figure 3(d).

| Table 1. 70 eV ionization cross-sections (10⁻¹⁶ cm²)† |
|----------------|------------------|------------------|------------------|------------------|
| Compound       | N₂O₄            | NO₂              | NO               | N₂               |
|                | 7.34            | 3.53             | 2.81             | 2.51             |
|                |                 |                  |                  |                  |
|                | O               | H₂O              | O                |                  |
|                | 1.36            | 2.28             | 1.36             |                  |
| †Values are from the NIST database [23] except N₂O₄, which was computed [44]. |

Next, samples were prepared that were composed of 300 ML of H₂O covered by 48 L of N₂O₄, as shown in Figure 5. Irradiation using a single ~ 1-mJ, 266-nm pulse yielded broad temporal profiles and a large number of individual mass spectra. Figure 5 shows a typical single-shot (9-point average) result that characterizes exposed N₂O₄. The variation of the NO⁺/NO₂⁺ ratio across the temporal profile depends on N₂O₄ and H₂O layer thicknesses, whereas the overall profile shape (roughly exponential decrease) is independent of these details. This will be discussed in a later publication. In the present study, the shape of the temporal profile serves as an indicator of exposed, as opposed to buried, N₂O₄.

N₂O₄ atop H₂O

Figure 4. (a) Molecules passing through the lower right slot into the ionization region strike a large amount of metal on the other side. (b) Most of the metal on the other side has been removed, resulting in significantly fewer molecule-surface collisions.
Referring to the upper left of Figure 5, 300 ML of H₂O provides thermal insulation against the high thermal conductivity of MgO, i.e., ~250 W m⁻¹ K⁻¹ for MgO at 100 K [27] versus < 1 W m⁻¹ K⁻¹ for ASW [28]. By using D₂O in place of H₂O in this layer, we have verified (using both FTIR and TOFMS) that there is no transport whatsoever of water across the N₂O₄ layer. Figure 6 illustrates the important role of the water spacer between MgO and N₂O₄ in increasing signal intensity.
The first reliable mass spectrum in the temporal profile shown in Figure 5(a) is obtained for the 20-µs extraction, which corresponds to a speed of \( \sim 1.2 \times 10^7 \) cm/s. The present arrangement is such that early arrival times yield crude estimates of speed because the transit time across the large ionization region is significant. In addition, the 3-µs extraction pulse that commences 20 µs after the laser firing follows a 7 µs duration ionization pulse, and these durations need to be taken into account. Notwithstanding these caveats, such estimates provide valuable qualitative insight.

The kinetic energy of an NO₂ molecule whose speed is \( 1.2 \times 10^5 \) cm/s is \( 2800 \) cm\(^{-1}\). On the other hand, the speed of a species that leaves the surface at \( t = 0 \) and arrives at a point 2.5 cm from the surface 300 µs later (the last extraction in the temporal profile) is \( 8 \times 10^3 \) cm/s. This estimate is more accurate than that for early times because the uncertainties constitute a smaller percentage of the arrival time at the ionization region. Were NO₂ and N₂O₄ to leave the surface at \( t = 0 \), the 300 µs arrival time would correspond to kinetic energy values of 12.5 and 25 cm\(^{-1}\), respectively. Later we will see that NO₂ most likely arises from photodissociation of N₂O₄ that has entered vacuum. The low energy of 25 cm\(^{-1}\) can be rationalized as being in the tail of a warm distribution. For example, the amount of signal in the 300 µs extraction is of order 1% of the total signal for the interval 0-300 µs.

The NO₂/N₂O₄ ratio of neutral molecules can be expressed in terms of the respective numbers of ions: NO₂⁺, NO⁺, O²⁻, and N⁺, as well as the N₂O₄ and NO₂ ionization cross-sections at 70 eV. An expression is derived in Appendix A that makes use of these quantities. Equation A(6) from there is given here as eqn (1):

\[
\frac{\text{NO}_2}{\text{N}_2\text{O}_4} = 2.08 \left( \frac{\text{NO}^+ / \text{NO}_2^+}{F_{\text{NO}_2^+}^{\text{NO}^+} - \left( \frac{\text{NO}^+ / \text{NO}_2^+}{F_{\text{NO}_2^+}^{\text{NO}^+}} \right)} \right),
\]

where \( F_{\text{Y}^+}^{\text{X}^+} \) is the percentage of ion X⁺ that derives from parent ion Y⁺. The number 2.08 is the ratio of the ionization cross sections for N₂O₄ and NO₂ (see Table 1).

The data given in Figures 3(a) and 3(d) were used to obtain values for the four F-factors in eqn (1). Values of NO⁺/NO₂⁺ vary slightly at late times from one extraction to the next. Their average value is 0.95. When these numbers are used with eqn (1), it is found that late times in the temporal profiles are dominated by N₂O₄. The NO₂/N₂O₄ ratios obtained using eqn (1) fluctuate around 0.2. This result is robust from one temporal profile to the next including later extraction times than the longest times in Fig. 5(a). This trend is also evident from simple visual inspection of the temporal profiles.

**III.2. Sandwiches: Single-Pulse Results**

Samples such as those shown in Figure 1 are composed of a lower ASW layer of H₂O or D₂O, an N₂O₄ layer (typically 48 L), and a range of ASW (H₂O and D₂O, either separately or in adjacent layers) upper layer thickness. Deposition is carried out near 100 K. It is possible that some reaction takes place at interfaces between N₂O₄ and ASW yielding, for example, HNO₂ and HNO₃ [29,30]. The extent of such reactions is not known. In addition, the porous nature of ASW accommodates penetration. These caveats notwithstanding, N₂O₄ is contained in a reasonably well-defined layer. Figure 7 shows typical temporal pro-
files and individual mass spectra. Unless otherwise stated, ~ 1 mJ pulses were used under the conditions described in Section II.

Figure 7. Temporal profiles and mass spectra for upper H$_2$O layer thickness: (1) 600 ML, (2) 1200 ML, and (3) 2400 ML. Each profile is the average of nine individual first-pulse profiles (1 mJ, 266 nm). Red corresponds to NO$^+$ and NO$_2^+$. Black corresponds to H$_2$O$^+$, OH$^+$, and H$^+$. The temporal profiles in rows (1)–(3) are on the same ordinate scale. The lower ASW layer is 300 ML of D$_2$O, and the N$_2$O$_4$ layer is 48 L. Note that ASW is given in ML and N$_2$O$_4$ is given in L (see text). Mass spectra are shown in each row for the respective extractions in the temporal profiles indicated with vertical arrows. The sample composition is shown at the bottom.
Rows (1) – (3) in Figure 7 correspond to ASW (H$_2$O) upper layers of 600, 1200, and 2400 ML. The ordinate scales are the same in rows (1) – (3). The temporal profile in row (1) shows that H$_2$O monomer arrives at the ionization region in two groups. On the other hand, NO$_2^+$ and NO$^+$ have temporal profiles that differ significantly from those of H$_2$O. The NO$_2^+$ peak arises from NO$_2$ and N$_2$O$_4$, whereas the NO$^+$ peak arises from NO, NO$_2$, and N$_2$O$_4$. The NO contribution is modest, most likely arising from NO$_2$ photolysis. Hereafter, we shall refer to the combination of NO, NO$_2$, and N$_2$O$_4$ as N$_x$O$_y$, and we shall refer to the NO$^+/NO_2^+$ ratio as $R_N$. Detailed shape and timing features of the lumpy features in the water temporal profiles vary from one first-shot temporal profile to the next. What is robust, however, is that lumpy features are always present, as seen also (vide infra) in Figure 10 and in the Supplementary Material.

$R_N$ values for the Figure 7 mass spectra differ slightly from one another, but none is close to the value of 3.1 obtained for the NO$_2$ mass spectrum [Figure 3(a)]. Each is significantly smaller. The largest $R_N$ value is for row (1), spectrum (a), which has $R_N = 1.34$ (Table 2). Many spectra have been examined, both within the temporal profiles given in Figure 7, and in numerous other first-pulse temporal profiles recorded over roughly a year. $R_N$ is close to unity in essentially all of them, except at the shortest extraction times. Figure 8 shows $R_N$ values for each of the extractions in the Figure 7 temporal profiles.

Referring to Figure 3(d), $R_N$ for 70 eV electron impact ionization of N$_2$O$_4$ is 0.9. This is only slightly lower than the ratios associated with Figure 7, which are summarized in Table 2 and Figure 8. On the other hand, the $R_N$ value of 3.1 for NO$_2$ is much greater that the observed first-pulse $R_N$ values in Figure 8, except for the first extraction or two, which incidentally have low S/N. Thus, we conclude that N$_2$O$_4$ is the dominant N$_x$O$_y$ constituent under the first-pulse conditions used to obtain the data presented in Figures 7 and 8.

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<td></td>
<td>$R_N$</td>
<td>$R_N$</td>
</tr>
<tr>
<td>(a)</td>
<td>1.92 1.27 0.95</td>
<td>0.18 5.35 1.97</td>
</tr>
<tr>
<td>(b)</td>
<td>1.86 0.40 0.40</td>
<td>2.12 1.18 0.72</td>
</tr>
<tr>
<td>(c)</td>
<td>1.86 1.14 1.01</td>
<td>0.42 5.30 1.70</td>
</tr>
<tr>
<td>(d)</td>
<td>2.82 0.49 0.44</td>
<td>2.39 2.46 1.38</td>
</tr>
<tr>
<td>(e)</td>
<td>2.64 0.89 0.95</td>
<td>0.00 5.51 1.80</td>
</tr>
<tr>
<td>(f)</td>
<td>2.75 0.38 0.45</td>
<td>3.45 1.14 0.91</td>
</tr>
</tbody>
</table>

Table 2. Peak areas and $R_N$ values for the spectra shown in Figs. 7 and 11.
Figure 7, row (2) shows data for an upper ASW layer of 1200 ML. The temporal profile has a different shape than that of row (1). Aside from that, there is not a remarkable difference, despite a factor of two increase in upper ASW thickness relative to that of row (1). The upper ASW layer used for row (3) is 2400 ML, which is a factor of four thicker than for row (1). A clear propensity toward longer times is evident. The amount of H$_2$O that arrives at the ionization region is larger for row (3) than for row (1) or (2), despite the greater upper ASW thickness. One might have expected additional thickness to lessen the release of material into vacuum, e.g., because the increased heat capacity of the larger ASW volume would result in more efficient colling. In fact, the opposite trend is observed.

In principle, paths between the N$_2$O$_4$ layer and vacuum could have complicated circuits and shapes and still function as conduits, e.g., were the ejected species small and non-condensible. With a fluid comprising N$_2$O$_4$, NO$_2$, and H$_2$O, however, such paths would result in condensation and blockage. Note that the upper ASW layers used in Figure 7 are too thick for their temperature to rise to the point of significant H$_2$O sublimation. In Section IV we propose that the H$_2$O that enters vacuum must do so via more-or-less vertical fissures that connect the N$_2$O$_4$ heated layer to the vacuum.

Figure 8. $R_N$ for a large number of extractions, starting at the earliest extraction: First-pulse $R_N$ values (black) settle down after the first few extractions to values of order unity. Second-pulse $R_N$ values (red) reflect the fact that a significant amount of N$_2$O$_4$ is present in the surface region.
Temporal Profiles

A simple calculation indicates that most of the H$_2$O signal in Figure 7 does not arise from molecules that travel from the surface to the detector along a straight line path. The distance between the surface and the center of the ionization region is 2.5 cm, and transit times of hundreds of µs over a 2.5 cm distance correspond to very small kinetic energy values. Figure 9 illustrates this by showing a plot of $\frac{1}{2}mv^2$ versus $\tau$, where $v = d / \tau$, with $d = 2.5$ cm. The $\tau$ values are those of the temporal profile horizontal axis. Clearly, the kinetic energies of H$_2$O molecules that leave the surface at $t = 0$ and arrive at the ionization region without collisions are unreasonably small for most of the $\tau$ values in the temporal profiles.

Thus, there is no possibility that the majority of the H$_2$O detected mass spectrometrically leaves the film at $t = 0$ and travels without collision to the ionization region. For example, were this the case, the H$_2$O signal beyond 200 µs would correspond to H$_2$O molecules whose kinetic energy is $< 10$ cm$^{-1}$. Figure 10 shows significant signal at times of
many hundreds of µs, indeed, in excess of 1 ms, underscoring this incompatibility. In Section IV it is shown that this phenomenon is in accord with a model in which water molecules undergo collisions shortly after they emerge from the fissures on their way to the ionization region.

### III.3. Subsequent Laser Pulses Incident on the Same Spot

Application of the first laser pulse alters a doped ASW sample significantly. Consequently, we studied effects brought about by subsequent pulses (second, third, etc., albeit one at a time) incident on the same spot.

![Figure 11. Temporal profiles are shown for a second 1-mJ laser pulse at the same locations as in Figure 7: Each profile is the sum of profiles from 9 spots. Red corresponds to NO$^+$ and NO$_2^+$, black to H$_2$O. The ordinate scale is the same as in Figure 7. Mass spectra are shown on the right for the respective extractions in the temporal profiles indicated with vertical arrows on the left.](image-url)
Figure 11 shows temporal profiles for second pulses incident on the same spots as were the first. Results from all nine spots are summed. A striking effect is seen in the N\textsubscript{x}O\textsubscript{y} profiles: the R\textsubscript{N} values obtained for each of them (summarized in Table 2) resemble those of an exposed N\textsubscript{2}O\textsubscript{4} surface (Figure 5). This supports a model in which robust channels or fissures are formed with the first pulse, through which N\textsubscript{2}O\textsubscript{4} can be transported to the surface region. The R\textsubscript{N} values for the earliest extractions in each temporal profile indicate that NO\textsubscript{2} reaches the mass spectrometer, confirming that N\textsubscript{2}O\textsubscript{4} has already been transported to the surface region. In light of the role played by 266-nm photodissociation of N\textsubscript{2}O\textsubscript{4}, it is not feasible to determine quantitatively the respective amounts of gas phase N\textsubscript{2}O\textsubscript{4} and NO\textsubscript{2}.

III.4. Fissure Growth in Stages

The results described in Sections III.2 and III.3 indicate the formation of fissures (due to 266-nm laser irradiation) through which material passes on its way to vacuum. This process depends on laser fluence. Indeed, results obtained with the laser fluence lowered by an order of magnitude (with the laser energy kept constant) are consistent with the fissure model. In this case, the first pulse yielded no signal. However, a second (or sometimes third) pulse yielded respectable signal. Likewise, subsequent pulses continued to yield significant signal, and the N\textsubscript{x}O\textsubscript{y} temporal profiles displayed the characteristic shape and mass spectra of exposed N\textsubscript{2}O\textsubscript{4}, i.e., similar to those shown in Figure 5. Apparently the first pulse pushes fluid toward vacuum, but with insufficient thrust for it to exit the film. Namely, competition between moving toward vacuum versus freezing onto the fissure walls favors the latter to the extent that nothing exits the film.

The next pulse heats the N\textsubscript{2}O\textsubscript{4} reservoir plus the N\textsubscript{2}O\textsubscript{4}-rich material trapped in incipient fissures. The additional thrust results in material entering vacuum. Sometimes a third pulse is required. This behavior is in accord with the model discussed in Section IV.

III.5. Isotope Scrambling: Scraping the Walls

H/D isotope exchange (scrambling) sheds light on the mechanism of material transport. Figure 12 shows an example of facile H/D exchange that takes place when layers of D\textsubscript{2}O and H\textsubscript{2}O are placed atop N\textsubscript{2}O\textsubscript{4} and the sample is irradiated. The samples were prepared at 100 K, at which temperature there is no exchange [31]. This was verified in our experiments using FTIR.

The mass spectra shown in Figure 12(a) and (b) indicate that extensive exchange has occurred during the heated fluid’s brief transit through the fissures. The upper ASW is composed of 200 ML each of D\textsubscript{2}O and H\textsubscript{2}O: (a) D\textsubscript{2}O over H\textsubscript{2}O, and (b) H\textsubscript{2}O over D\textsubscript{2}O. This corresponds to an upper ASW thickness of roughly 140 nm, and exchange can only occur in the top half. This facile exchange underscores the heated nature of the fluid passing through the fissures and efficient mixing of H\textsubscript{2}O and D\textsubscript{2}O. The extent to which traces (a) and (b) resemble one another is striking. These data indicate that water is removed by the heated fluid from the fissure walls throughout the length of the fissure. Trace (c) is a check. It shows that there is very little isotope scrambling due to impurity H\textsubscript{2}O when 300 K gaseous D\textsubscript{2}O is introduced into the chamber.
III.6. FTIR: A Preliminary Result

It would be desirable to monitor the removal of material from the solid sample by using FTIR following a single laser pulse. This has not yet been achieved because of insufficient laser fluence and our inability to detect infrared radiation at the low frequencies needed to monitor species such as N$_2$O$_4$. However, we have recorded FTIR spectra (as described in Figure 12. (a) and (b) show mass spectra recorded for extractions at 50-60 µs, following first-pulse 266-nm irradiation (1.5 mJ) for samples that have 48 L of N$_2$O$_4$ atop a 300 ML H$_2$O spacer and alternating H$_2$O and D$_2$O upper layers. In (a), the upper ASW layer has 200 ML of D$_2$O atop 200 ML of H$_2$O, and in (b) this is reversed. In (c), a D$_2$O spectrum of a 300 K gaseous sample that was recorded the same day shows only modest HDO contamination; there is almost no H$_2$O$^+$. Figure 13. (a) Before and after FTIR spectra starting with sandwich comprising 300 ML D$_2$O, 48 L N$_2$O$_4$, and 2400 ML H$_2$O, deposited at 100 K and irradiated with 70 pulses (6 mJ). The OD peak is unchanged, whereas the OH peak has decreased by 14%. (b) FTIR spectra of 2400 ML of H$_2$O deposited at 100 K and annealed to 165 K for 10 minutes to induce crystallization. The spectrum in (a) does not appear more crystalline in character after irradiation.

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Section II) that demonstrate removal of water from the upper ASW layer. As mentioned earlier, the ASW spacer between the MgO and the N$_2$O$_4$ is robust. We have never seen evidence of it crossing the N$_2$O$_4$ barrier, even with repeated pulses incident on the same spot.

Figure 13 shows that 14% of the upper ASW layer is removed when irradiating a sample with 70 laser pulses. The fluence in this experiment is low compared to the fluence used in the TOFMS studies, i.e., an order of magnitude lower than achieved with 1 mJ in a 0.3 mm diameter spot. The amorphous nature of the water is unchanged by the irradiation, as evidenced by the spectra in Figure 13(a) and (b).

IV. Discussion

The data presented in Section III, together with a few straightforward estimates, led us to propose a model for material transport from the N$_2$O$_4$ layer to vacuum, including fluid-wall interactions. This model differs greatly from our original expectations. For example, we expected that an ASW upper layer several tens of ML thick would result in a modest amount of material entering the gas phase, and several hundred ML would result in (for all practical purposes) nothing entering the gas phase. In contrast, the data presented in Section III demonstrate that the thickest ASW layer that was used, 2400 ML, yielded the largest amount of released material, not the smallest. Clearly, our initial thinking was naïve. Reconsideration led to the qualitative model described below.

In Sections IV.1–IV.4, we discuss the experimental results presented in Section III in terms of our qualitative model. In Section IV.5 we address a number of compelling parallels between the results presented herein and discoveries made within the last decade regarding the south polar terrain (SPT) of Enceladus, a moon of Saturn.

IV.1. Observables

Before discussing individual aspects of the proposed model, it is useful to summarize the experimental observations that are central to its formulation. First, it needs to be recognized that the ejection of material into vacuum initiated by pulsed laser photolysis of buried layers differs qualitatively from that of pulsed laser irradiation of samples of uniform composition. For example, small protonated water clusters have not been observed in the mass spectra recorded in the present study, whereas they are readily observed under other conditions, e.g., when exciting ASW/CO$_2$ mixtures using focused infrared radiation in the OH-stretch region [15]. This underscores the fact that the mechanism for the ejection of material into the gas phase differs for these two cases. Our experimental strategy enables heat to be implanted in spatially confined regions – in the present case, layers.

In the experiments under consideration here, a thin layer of N$_2$O$_4$ absorbs the 266-nm radiation and converts it to heat. Without going into detail, we know that the photodissociation of N$_2$O$_4$ yields NO$_2$ with substantial kinetic and internal energies. However, the dense fluid environment facilitates recombination, and the net effect is that nascent excitations degrade to heat on a time scale much shorter than the laser pulse duration. Thus, irradiation heats the N$_2$O$_4$ layer and its immediate surroundings. When the heated mixture
cools following cessation of the laser pulse, different binding energies work to segregate H$_2$O and N$_2$O$_4$. This facilitates continued laser-initiated transport of material from the reservoir to vacuum.

Shortly after irradiation, molecules detected by the TOFMS include N$_2$O$_4$, NO$_2$, NO, and H$_2$O, as well as a modest amount of O$_2$. When the upper ASW layer is composed of layers of H$_2$O and D$_2$O, there is also HDO and D$_2$O. We found it convenient to use D$_2$O as the spacer material between the MgO substrate and the N$_2$O$_4$ layer in order to distinguish this layer (spectrally) from H$_2$O atop the N$_2$O$_4$. As mentioned earlier, this D$_2$O never crosses the N$_2$O$_4$ layer and enters fissures. We also note that the amount of NO is modest and it is mostly a secondary NO$_2$ photolysis product. It shall not be considered further.

Comparisons of temporal profiles and mass spectra obtained with the N$_2$O$_4$ layer exposed versus covered by ASW layers of different thickness are revealing. In cases where the N$_2$O$_4$ layer is covered by ASW, the gas phase N$_x$O$_y$ that derives from the first laser pulse is mainly N$_2$O$_4$. This conclusion is based on the fact that R$_N$ is roughly 1.0 [Figure 3(d)], which is much smaller than the corresponding value for NO$_2$. As shown in Section III, the signature of exposed N$_2$O$_4$ is that larger amounts of NO$_2$ enter vacuum, resulting in larger R$_N$ values (Figure 5). These larger R$_N$ values are encountered when a spot is irradiated by second, third, etc., pulses. This indicates that under our experimental conditions, N$_2$O$_4$ arrives at the surface already with the first pulse. Subsequent pulses show signatures of exposed N$_2$O$_4$.

These observations led us to conclude that heated N$_2$O$_4$ reaches vacuum via more or less vertical fissures. This is supported by experiments carried out at lower fluence, which show that under low-fluence conditions additional pulses are required to bring N$_2$O$_4$ to vacuum. In addition, facile H/D exchange occurs when the upper ASW is composed of alternating layers of H$_2$O and D$_2$O. These experiments showed that most of the water that reaches the mass spectrometer derives from a process in which heated material moving through fissures entrains water that it removes from the fissure walls.

Other data presented in Section III reveal additional phenomena that can be explained by our model, e.g., temporal profiles having lumpy character at long-times due to colliding jets. Several aspects of the model are analyzed below, starting with a phenomenon that caught our attention from the start and was initially puzzling: exceptionally long time scales for material that arrives at the ionization region of the mass spectrometer.

### IV.2. Time Scales: Origins and Implications

Information gleaned from temporal profiles plays a central role insofar as evaluating the likely participation of different ASW fracture and material transport mechanisms. Temporal profiles obtained using samples such as the one depicted in Figure 1 span time scales of at least several hundred µs, and in many cases the time scales exceed 1 ms. For example, in Figure 10 signals at 1200 µs are substantial and cannot be neglected. This surprised us at first, as it could not be explained by straightforward interpretation of time-of-flight data. We had not expected molecules to be present in the ionization region of the mass spectrometer at such long times. The lumpy character of the signals at long times also took us by surprise.
After repeating and scrutinizing the experiments over many months, while also exploring a broad range of parameter values, we concluded that the main character of the temporal profiles such as the ones shown in Figure 10 is robust. The lumps differ from one single-shot profile to the next, but the profiles always display lumpy character at long times. This lumpy character is a signature of the dynamical processes whereby material is ejected into vacuum.

There is no possibility that any reasonable amount of H$_2$O leaves the sample at $t = 0$, and arrives 1200 µs later at the center of the ionization region, which is 2.5 cm away, without undergoing collisions. Were collision-free transit to commence at $t = 0$, the H$_2$O kinetic energy for a 1200 µs arrival time would be a minuscule 0.33 cm$^{-1}$ (Figure 9). For an arrival time of 150 µs, the H$_2$O kinetic energy would be 21 cm$^{-1}$, also too small to accommodate a mechanism in which H$_2$O leaves the surface at $t = 0$. These low kinetic energies cannot be dismissed as belonging to the tail of a distribution. For example, in the profile shown in Figure 10(a), which is typical, only ~ 4% of the H$_2$O is contained within the first 150 µs, and this does not take into account times exceeding 1200 µs.

These observations can be explained only if we assume that the majority of the water molecules that leave the film at $t = 0$ and arrive at the ionization region at long times do so after undergoing collisions. In principle they could have departed from the film at times later than $t = 0$. However, this would require delayed departures of at least hundreds of µs, in which case the region emitting the molecules would have to have lost thermal contact with the rest of the film, and to an extraordinary extent. We deem this highly unlikely, because heat transfer to the substrate is much faster, as described later. The key to understanding the long-time signals lies with the fissures and their effluents.

IV.3. Fissures

As discussed above, our experimental conditions differ greatly from those of conventional surface ablation [32]. In our case, material enters vacuum via fissures. The data are consistent with a fracture mechanism in which porous ASW grown by vapor deposition from background gas [33,34] contracts toward a more stable form when subjected to increased temperature and pressure from below. For a laser beam diameter of 0.3 mm and a film thickness of 300 nm, the diameter-to-thickness ratio is $10^3$. Contraction is free to occur in the vertical direction, whereas in the horizontal direction fissures are expected to develop because the ASW must maintain its overall two-dimensional density, while at the same time accommodating its transition toward more stable bonding. In other words, there is a propensity to develop vertical fissures between the heated layer and vacuum. Analogous changes have been examined by Smith and Kay [13,14].

The dense fluid in the vicinity of the heated zone is composed of N$_2$O$_y$ and water, and its upward movement promotes fissure development. Though a great deal of activity transpires over the duration of the 10-ns laser pulse, we believe that the larger fissures, once established, are robust from pulse to pulse. This is supported by the second, third, etc. pulse data (Figure 11).

A key feature is the proximity of fissures to one another, as our experiments involve a high fissure density. We currently have no quantitative knowledge regarding their shapes.
or density. We believe that the fissures that yield signal are "vertical" in the sense that there is a more or less direct path connecting the N$_2$O$_4$ layer to vacuum. Material coming from the N$_2$O$_4$ reservoir layer cannot follow a complicated trajectory that twists and turns on the way out without freezing. Were an ASW density of 0.8 g cm$^{-3}$ to convert completely to crystalline ice and vertical fissures, the fissures would account for about 13% of the surface area. This limit is not achieved, as evidenced by the large number of laser pulses needed to deplete the N$_2$O$_4$ reservoir. Nonetheless, the density must be significant.

As material flows out of the fissures, collisions take place between the effluent of a given fissure and effluents from nearby fissures. Figure 14 illustrates the general idea. No matter what the angular spread of a given effluent, direction of its main flow, or its fissure shape, there are simply too much fissure opening per unit area to not have collisions just above the film surface, where the density of ejected material is high. It is not possible that any reasonable amount of low-density gas travels through the fissures to vacuum, because such a gas would freeze onto the fissure walls. The material that makes its way to the top of the fissures is a fluid (liquid and/or high-density gas). Though we do not know the shapes and sizes of the fissure openings, it is unlikely they are only several molecular diameters wide, as this would not be conducive to expelling significant amounts of water.

Collisions between effluents from different fissures will deflect species in many directions, giving rise also to collisions with metal surfaces and bouncing around within the region bounded by metal surfaces (Figures 2 and 4). The net effect is a spatially inhomogeneous water density in the extraction region. We propose that this spatial inhomogeneity gives rise to the lumpy character of long-time spectra. Simple hydrodynamic flow emanating from the surface would display qualitatively different temporal profiles. Likewise, molecular flow could not account for the observations.

The picture that emerges is that following pulsed laser heating, local pressure and temperature increase, resulting in a complex assortment of fissures that connect the reservoir to vacuum. Horizontal contraction of the ASW encourages more or less vertical fractures that serve as conduits for transport to vacuum. Heated N$_2$O$_4$ leaving its reservoir layer removes water from the walls and carries it along.

The 10-ns laser pulse duration is long enough to photolyze N$_2$O$_4$ as it passes through fissures, thereby maintaining a warm fluid. The radiation also photodissociates N$_2$O$_4$ that has entered the gas phase prior to the termination of the laser pulse. For example, if a fluid moves through a 1000 nm fissure at 200 m/s, only 5 ns is required for its passage, as discussed later.
IV.4. Fracture Mechanisms and Material Transport

It is well established that background dosing at 100 K creates porous ASW [34]. In our experiments the N₂O₄ layer is subjected to 266-nm radiation. This radiation dissociates the N₂O₄, acts further on the NO₂ produced through N₂O₄ photolysis, and almost certainly causes other changes. It is important that the high-density environment promotes recombination and degradation of specific excitations into heat. The net effect is that laser heating of N₂O₄ – both in the reservoir layer and the fissures – raises the fluid temperature significantly.

The temperature and pressure gradients that manifest in the upper ASW layer initiate morphological change. The column densities of the film's ingredients cannot change over large horizontal length scales (say, of several microns or more), whereas over smaller horizontal length scales (say, tens of nanometers) the water will tend to form regions of lower porosity. As discussed above, this yields fissures, many of which are wide enough to enable heated N₂O₄ fluid to pass into vacuum upon application of the first laser pulse. Such fissures are expected to be robust in the sense that subsequent laser pulses also heat N₂O₄, but without destroying such fissures.

Heat transfer to the substrate is much more efficient than to the upper ASW, particularly as the surface-vacuum interface is approached. We have carried out calculations of heat flow in layered films using the program COMSOL Multiphysics©. The goal was to judge, at a qualitative level, the degree to which films cool following pulsed excitation. Thermal contact between layers was assumed, and phase changes and thermal desorption were neglected in these preliminary calculations.

Physical properties of the materials are known to varying degrees. Densities [27,33,35] and thermal conductivities [27,36,37] for MgO, porous ASW, and N₂O₄(s) at 100 K were held constant (3.591, 0.82, and 1.964 g cm⁻³; and 250, 0.025, and 0.2 W m⁻¹ K⁻¹, respectively), whereas heat capacities were allowed to vary with temperature – primarily because their temperature dependence is known [38-40]. The heat capacities for ASW and N₂O₄ vary linearly with temperature above 90 K, and they were extrapolated to higher temperatures, as phase change was not allowed. **Though thermal conductivity values of ASW and N₂O₄ are not known, reasonable lower bounds were chosen**. A range of thermal conductivity values was explored and the results were in qualitative accord with those presented in Figure 15.

In spite of the uncertainty regarding thermal conductivity values, the calculations indicate convincingly that, as long as thermal contact is maintained, the system recovers to < 120 K in at most a few µs. Thus, for heated material to reach the surface in 10 ns through a 1000 nm fissure, it must travel with a speed of at least 100 m/s. If it moves more slowly, it will freeze rather than enter vacuum.
This picture reconciles our observations. For example, even with thick ASW upper layers, a large amount of N\textsubscript{2}O\textsubscript{4} enters vacuum with the first laser pulse. Referring to Figure 10, it is impressive that heated fluid passes through 2400 ML of ASW with a single pulse. There is no way this could happen without its journey to vacuum proceeding via fissures.

As mentioned above, material that enters vacuum has been pushed through fissures as a fluid. Near the vacuum interface, the fissures may give way to cracks, smaller fissures, and irregularities. In any event, the first pulse deposits N\textsubscript{2}O\textsubscript{4} near and sometimes on the surface. Referring to Figure 11, there is strong similarity between the N\textsubscript{x}O\textsubscript{y} signals observed for the second pulses and those associated with exposed N\textsubscript{2}O\textsubscript{4}. Though not shown in Figure 11, this correspondence persists for third, fourth, etc. pulses. Indeed, this correspondence persists up to the largest number of pulses used (~ 70). This behavior is consistent with the proposed model, in which repeated photoexcitation pumps N\textsubscript{2}O\textsubscript{4} from its reservoir to the surface region though existing fissures.

Another result that is consistent with the model is that when the laser fluence is lowered to below the threshold for material release into vacuum, it takes two or more laser pulses to observe N\textsubscript{x}O\textsubscript{y} signals. When the heated fluid lacks the thrust necessary to enter vacuum, efficient cooling traps material and its release to vacuum awaits the next pulse.

The model also explains the facile isotope exchange (H/D scrambling) that takes place in water that travels through fissures and enters vacuum (Figure 12). Such exchange does not occur to any measurable extent in freshly prepared samples at 100 K. Isotope exchange was found to be efficient regardless of whether the D\textsubscript{2}O layer is above the H\textsubscript{2}O layer or below it. These data demonstrate that water is stripped from the fissure walls throughout the escape path. It will be informative to examine such exchange by using laser pulses of, say, 20 ps duration, as this separates (temporally) photoexcitation from transport through

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**Figure 15.** Computed maximum temperature of a 5.6 nm film of N\textsubscript{2}O\textsubscript{4} sandwiched between 115 nm of ASW on a 1 mm MgO substrate, all initially at 100 K. The N\textsubscript{2}O\textsubscript{4} layer is heated for 10 ns (not shown) by a 0.24 \(\mu\)W/nm\textsuperscript{3} square pulse (roughly the energy absorbed by the N\textsubscript{2}O\textsubscript{4} layer), then allowed to cool via thermal conduction. The maximum temperature of the system drops from 435 to 130 K within 1 \(\mu\)s, even though phase changes and thermal desorption are neglected.
fissures. It restricts photoexcitation to the N$_2$O$_4$ layer, not N$_2$O$_4$ that is traveling through fissures.

IV.5. Relationship to Astrophysics and Astrochemistry

The present paper reports an experimental study of a microcosm that bears a degree of resemblance to Enceladus' cryovolcanism. Of course it differs vastly in many respects, even beyond the enormous scale difference, i.e., 30-40 km for the Enceladus solid water mantle versus $\sim 10^{-6}$ m for 2400 ML of ASW in the present study. Still, one cannot help but notice parallels such as the following.

- **Enceladus**: A subsurface ocean of liquid water estimated to be 8-10 km thick lies between the moon's rocky core and its solid water mantle, whose thickness is 30-40 km. The surface temperature of the solid water mantle during the warmest time of the day is 75 K [41], except near hot spots, which can be as warm as 200 K [42].

  **Present study**: Vacuum deposited films are prepared at 100 K with an N$_2$O$_4$ layer between a MgO substrate (usually topped with a 300 ML ASW spacer for thermal insulation) and an ASW upper layer. The N$_2$O$_4$ layer is turned into a dense fluid using pulsed laser heating.

- **Enceladus**: Stresses due to gravitational interactions cause fissures to expand and contract, releasing water (plus small molecules) and creating jets. The openings are robust enough to survive long periods of cycling. Liquid water makes its way from the subsurface ocean to the moon's surface, where it is released into the moon's sparse atmosphere, creating solid particles of salty water in addition to water vapor. Jets are formed, but they account for only 4% of the total water output.

  **Present study**: Laser-heating of the N$_2$O$_4$ layer produces temperature and pressure gradients. Fluid passes through fissures from the N$_2$O$_4$ layer to the film surface, where it enters the gas phase. Fissures are sufficiently robust that repeated irradiation continues to transfer N$_2$O$_4$ from its reservoir layer to the film surface. Material that enters the gas phase is a mixture of N$_x$O$_y$ and water. That the latter is removed from the fissure walls over the full lengths of the fissures is demonstrated by the facile isotope exchange observed between layers of H$_2$O and D$_2$O.

- **Enceladus**: Water emanating from the south polar terrain (SPT) has been characterized by: (1) the respective amounts of solid versus vapor constituents in overall released water; solid/total $\approx 0.3$, (2) the ratio of the mass flux contained only in the jets versus the total mass; jet flux/total flux $\approx 0.04$; and (3) for the jets alone, the respective amounts of solid versus vapor constituents; solid/vapor $\approx 6$.

  **Present study**: Fissure formation commences near the heated layer. The fissures extend to vacuum, accommodating fluid that is heated by the 266-nm radiation. Near the film's surface, the fissures might have a filamentary structure, (as in hydraulic fracking [43]), resulting in high fissure density. Material that exits fissures does so at sufficiently high density to avoid being frozen out on the fissure walls, and effluents from fissures near one another undergo collisions before reaching the ionization region of the detector.
V. Summary

A versatile experimental approach has been developed for studying laser-initiated material transport and removal in layered films of ASW and N₂O₄. In the present study, a MgO substrate cooled to 100 K is covered with an ASW layer to insulate the heated N₂O₄ from MgO, which has high thermal conductivity. The N₂O₄ layer is covered, in turn, with ASW layers of varying thickness, up to 2400 ML. Pulsed 266-nm irradiation (10 ns; 1 mJ, focused with a 50 cm lens to a diameter of ~ 0.3 mm) heats the N₂O₄ layer, and upward material flow takes place through vertical fissures that extend from the N₂O₄ layer to vacuum. A single pulse can result in transport of heated N₄Oₓ fluid, together with water from the film, into vacuum. Temporal profiles and TOF mass spectra following a single laser pulse provide information on timescales and transport mechanisms.

The microcosm created in these studies is challenging insofar as developing a quantitative, predictive model. Nonetheless, qualitative understanding, with trends and phenomena in line with predictions, has been achieved. Advancing to a quantitative model will require significantly more effort, but should be possible with additional laboratory studies. The main features of the current model are summarized below.

Laser-initiated heating of the N₂O₄ layer results in fissures that connect the heated layer to vacuum. The elevated pressure of the heated fluid provides the thrust that launches material upward toward the surface. The fissures must be nearly vertical to allow transport of heated material to vacuum without freezing on the fissure walls. Many of the fissures are robust, in that they persist even after many laser pulses. It is possible to halt the upward flow of heated fluid prior to it entering vacuum by reducing the laser fluence. Subsequent irradiation causes fluid to enter vacuum, and this fracking-like pumping continues with consecutive laser pulses. H/D scrambling experiments using alternating H₂O and D₂O layers demonstrate that water is removed from the fissure walls and entrained in the upward flow of fluid over the length of the fissures. In fact, there is complex interplay between the upward-moving fluid freezing onto fissure walls versus entrainment of water from the fissure walls by the heated fluid.

Under our experimental conditions, heated material can reach vacuum following a single laser pulse, and we find that as the thickness of the upper ASW layer increases, the fractional amount of water that enters vacuum increases. This is because the warm fluid passes over more fissure area, increasing the fractional amount of water. This is evident when comparing results for 600 and 2400 ML of ASW (Figures 7 and 10).

The N₄Oₓ-rich fluid that moves through the fissures continues to be heated as long as the laser pulse remains on. Figure 15 shows that cooling is efficient, enough so that fluid present in a fissure quickly freezes upon termination of the laser pulse. This rapid freezing can be used to obtain a crude estimate (order of magnitude lower bound) of the speed with which the heated fluid must pass through fissures to reach vacuum.

Such a simple calculation for a 1000-nm thick ASW layer demonstrates that the material that travels through the fissures must do so at least as fast as 100 m/s for the laser fluence used to generate the data presented in Figure 10 and in the Supplementary Material. Had the speed been lower, material that commenced travel at the N₂O₄ layer with the onset of the laser pulse would freeze before it reached vacuum. In other words, as the material
moves toward the surface, it cools rapidly, and may freeze on the fissure wall before exiting. With thinner samples, it follows that a significant amount of effluent enters the gas phase within the duration of the laser pulse. This is consistent with our observation of early N$_3$O$_5$ arrival times at the ionization region, as well as the presence of NO$_2$, presumably due to N$_2$O$_4$ 266-nm photodissociation.

The density of fissures must be high to allow for collisions between effluents ejected from adjacent fissure openings. This is the only way to explain the long arrival times of gaseous molecules to the ionization region, which can exceed 1 ms, and the lumpy appearance of the water temporal profiles presented in Figures 7 and 10. We propose that the ejected material undergoes collisions with other molecules, as well as with metal surfaces, and takes a circuitous path before reaching the ionization region of the detector.

The present results display uncanny parallels with those obtained through observations of Enceladus carried out by the Cassini spacecraft, which has been orbiting Saturn since 2004. A great deal of Cassini's attention has been focused on the water that is released into the moon's sparse atmosphere from fissures in the SPT, which has four fissures referred to as the "tiger stripes." These fissures enable the release of water containing other molecules, including CH$_4$ and other light hydrocarbons [7]. Liquid water rising from a submerged ocean travels tens of km on its way out, and increased heat and pressure are required to drive its transport upward through fissures.

We end this article with two assertions relevant to future work. (1) Modeling well-controlled systems such as the one described herein might serve well the Cassini Mission's goals. Cassini will soon crash into Saturn and it will be a long time before another spacecraft reaches Saturn. Therefore, it is imperative that supportive laboratory experiments complement the data generated by Cassini. (2) An improved laboratory experimental strategy should include creating fissures that are well characterized, rather than trying to simulate the behavior of existing fissures. The fissures should have known (vertical) length, roughly azimuthal symmetry, and well-defined volume. Experiments can then be carried out under well-defined conditions and with better control over parameters. We plan to commence such experiments in the near future.

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Appendix A

Expressions are derived for the concentration ratio of the neutral molecules NO₂ and N₂O₄, namely, NO₂/N₂O₄. In general each is present in the part of the plume that passes through the ionization region of the mass spectrometer. Other ratios of neutral species can be derived in a like manner. The ratio NO₂/N₂O₄ is the most relevant ratio of neutral species in the present context.

Ratios are expressed in terms of ionization cross-sections, parent ion fragmentation patterns (see Figure 3), and relative ion signals. For example, use is made of easily measured quantities such as NO⁺/NO₂⁺ and O⁺/NO₂⁺, where NO⁺, O⁺, and NO₂⁺ are the areas of the respective ion signals. It is assumed that the micro-channel plate detector has equal sensitivity for each ion. To begin, expressions for the amounts (concentrations) of NO₂⁺, NO⁺, and O⁺ are written:

\[
NO₂^+ = \sigma_{N₂O₄}^{\text{ion}} F_{N₂O₄}^{NO₂^+} N₂O₄ + \sigma_{NO₂}^{\text{ion}} F_{NO₂}^{NO₂^+} NO₂ \tag{A1}
\]

\[
NO^+ = \sigma_{N₂O₄}^{\text{ion}} F_{N₂O₄}^{NO^+} N₂O₄ + \sigma_{NO₂}^{\text{ion}} F_{NO₂}^{NO^+} NO₂ + \sigma_{NO}^{\text{ion}} F_{NO}^{NO^+} NO \tag{A2}
\]

\[
O^+ = \sigma_{N₂O₄}^{\text{ion}} F_{N₂O₄}^{O^+} N₂O₄ + \sigma_{NO₂}^{\text{ion}} F_{NO₂}^{O^+} NO₂ + \sigma_{NO}^{\text{ion}} F_{NO}^{O^+} NO + \sigma_{O₂}^{\text{ion}} O + \sigma_{H₂O}^{\text{ion}} F_{H₂O}^{O^+} \tag{A3}
\]

where \( \sigma_X^{\text{ion}} \) is the 70 eV ionization cross section for the neutral species \( X \), and \( F_Y^+ \) is the fraction of the daughter ion \( Y^+ \) that arises from fragmentation of the parent ion \( X^+ \).

The use of equal signs, rather than proportionality constants, in eqns (A1) – (A3) is in anticipation of the fact that the proportionality constants would inevitably cancel were they carried along. The relatively small amounts of \( O₂^+ \) that appear in spectra shall be ignored. The latter comes directly from \( O₂ \), which is produced either through recombination, or from an O-atom abstracting an O-atom from either NO₂ or N₂O₄. Abstraction is presumably more important than recombination under the present experimental conditions.

Let us make the assumption that the number of NO molecules and O-atoms present is negligible. This is a good assumption for long arrival times at the ionization region, but it is not necessarily a good approximation for short arrival times. However, it is easy to obtain a mathematical expression using this assumption, so we shall do this first, and then proceed to the inclusion of NO and O.

To proceed, the last term in eqn (A2) and the last two terms in eqn (A3) are dropped, in which case eqn (A3) is decoupled from eqns (A1) and (A2). Referring to eqn (A2), \( NO^+ = (NO^+/NO₂^+) NO₂^+ \) is introduced. Combining eqns (A1) and (A2) then yields:

\[
\left( NO^+/NO₂^+ \right) \left( \sigma_{N₂O₄}^{\text{ion}} F_{N₂O₄}^{NO₂^+} N₂O₄ + \sigma_{NO₂}^{\text{ion}} F_{NO₂}^{NO₂^+} NO₂ \right) = \sigma_{N₂O₄}^{\text{ion}} F_{N₂O₄}^{NO^+} N₂O₄ + \sigma_{NO₂}^{\text{ion}} F_{NO₂}^{NO^+} NO₂ . \tag{A4}
\]

Separating this into separate terms for NO₂ and N₂O₄ gives

\[
NO₂ \sigma_{NO₂}^{\text{ion}} \left( \left( NO^+/NO₂^+ \right) F_{NO₂}^{NO₂^+} - F_{NO₂}^{NO^+} \right) = N₂O₄ \left( \sigma_{N₂O₄}^{\text{ion}} F_{N₂O₄}^{NO^+} - \left( NO^+/NO₂^+ \right) F_{NO₂}^{NO₂^+} \right). \tag{A5}
\]
Further rearrangement yields the desired ratio:

\[
\frac{\text{NO}_2}{\text{N}_2\text{O}_4} = \frac{\sigma_{\text{NO}_2}^{\text{ion}}}{\sigma_{\text{N}_2\text{O}_4}^{\text{ion}}} \left( \frac{\text{NO}^+}{\text{NO}_2^+} \right) F_{\text{NO}_2^+}^{\text{NO}_2} - F_{\text{NO}_2^+}^{\text{N}_2\text{O}_4}. \tag{A6}
\]

\[
\frac{\text{NO}_2}{\text{N}_2\text{O}_4} = \frac{2.08}{\sigma_{\text{N}_2\text{O}_4}^{\text{ion}}} \left( \frac{\text{NO}^+}{\text{NO}_2^+} \right) F_{\text{NO}_2^+}^{\text{NO}_2} - F_{\text{NO}_2^+}^{\text{N}_2\text{O}_4}. \tag{A7}
\]

The known values of parameters have been included in going from eqn (A6) to eqn (A7). This expression can be used to obtain relative NO\(_2\) and N\(_2\)O\(_4\) concentrations when NO and O are each in sufficiently low concentration to justify ignoring them.

Continuing in the same vein, if there are no NO molecules present, there can be no O-atoms present. In this case, the only route to O\(^+\) is through parent ion fragmentation. This provides a means of checking the reliability of eqn (A6). Equations (A1) and (A3) (without its last two terms) are solved in exactly the same way as eqns (A1) and (A2) were solved. This time, however, we use O\(^+\) = (O\(^+\)/NO\(_2^+\))NO\(_2^+\), and eqn (A8) replaces eqn (A2):

\[
O^+ = \sigma_{\text{N}_2\text{O}_4}^{\text{ion}} F_{\text{N}_2\text{O}_4}^{\text{O}^+} \cdot \text{N}_2\text{O}_4 + \sigma_{\text{NO}_2}^{\text{ion}} F_{\text{NO}_2^+}^{\text{O}^+} \cdot \text{NO}_2. \tag{A8}
\]

The ratio obtained via this route is

\[
\frac{\text{NO}_2}{\text{N}_2\text{O}_4} = \frac{\sigma_{\text{N}_2\text{O}_4}^{\text{ion}}}{\sigma_{\text{NO}_2}^{\text{ion}}} \left( \frac{\text{O}^+}{\text{NO}_2^+} \right) F_{\text{NO}_2^+}^{\text{NO}_2} - F_{\text{NO}_2^+}^{\text{N}_2\text{O}_4}. \tag{A9}
\]

\[
\frac{\text{NO}_2}{\text{N}_2\text{O}_4} = \frac{2.0}{\sigma_{\text{N}_2\text{O}_4}^{\text{ion}}} \left( \frac{\text{O}^+}{\text{NO}_2^+} \right) F_{\text{NO}_2^+}^{\text{NO}_2} - F_{\text{NO}_2^+}^{\text{N}_2\text{O}_4}. \tag{A10}
\]

For a given data set that satisfies the requirement of sufficiently modest NO and O-atom contributions to justify ignoring them, application of eqns (A7) and (A10) should yield the same number, or at least numbers that are close to one another.

Let us now switch to cases in which NO and O-atoms are each present. In other words, it is necessary to deal with the last two terms in eqn (A3). It is now assumed that the NO and O-atom concentrations are comparable to one another, in which case:

\[
\sigma_{\text{NO}}^{\text{ion}} F_{\text{NO}^+}^{\text{O}^+} \cdot \text{NO} + \sigma_{\text{O}}^{\text{ion}} F_{\text{O}^+}^{\text{O}^+} \sim \left( \sigma_{\text{NO}}^{\text{ion}} F_{\text{NO}^+}^{\text{O}^+} + \sigma_{\text{O}}^{\text{ion}} \right) \text{NO}. \tag{A11}
\]

When this is introduced into eqn (A3), it is a straightforward, albeit tedious, matter to eliminate NO from the equations, again yielding an expression for the ratio NO\(_2\)/N\(_2\)O\(_4\).
References


Temporal profiles of desorbed material for eight different spots (see Figure 2) on a sandwich consisting of 300 ML H₂O / 48 L N₂O₄ / 2400 ML H₂O ASW: Each panel represents a single, 1-mJ, 266-nm pulse. Red corresponds to nitrogen oxides, black to H₂O.