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Key Points:

- We describe the development of a comprehensive spectral database containing laboratory analogue data for spaceborne mass spectrometers
- The database is based on a Relational Database Management System with a web interface and accessible for community use
- Filtering the laboratory data using a wide range of experimental parameters allows a straightforward analysis of returned flight data

Supporting Information:

Supporting Information may be found in the online version of this article.

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Developing a Laser Induced Liquid Beam Ion Desorption Spectral Database as Reference for Spaceborne Mass Spectrometers

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Abstract Spaceborne impact ionization mass spectrometers, such as the Cosmic Dust Analyzer on board the past Cassini spacecraft or the SURface Dust Analyzer being built for NASA's upcoming Europa Clipper mission, are of crucial importance for the exploration of icy moons in the Solar System, such as Saturn's moon Enceladus or Jupiter's moon Europa. For the interpretation of data produced by these instruments, analogue experiments on Earth are essential. To date, thousands of laboratory mass spectra have been recorded with an analogue experiment for impact ionization mass spectrometers. Simulation of mass spectra of ice grains in space is achieved by a Laser Induced Liquid Beam Ion Desorption (LILBID) approach. The desorbed cations or anions are analyzed in a time-of-flight mass spectrometer. The amount of unstructured raw data is increasingly challenging to sort, process, interpret and compare with data from space. Thus far this has been achieved manually for individual mass spectra because no database containing the recorded reference spectra was available. Here we describe the development of a comprehensive, extendable database containing cation and anion mass spectra from the laboratory LILBID facility. The database is based on a Relational Database Management System with a web server interface and enables filtering of the laboratory data using a wide range of parameters. The mass spectra can be compared not only with data from past and future space missions but also mass spectral data generated by other, terrestrial, techniques. The validated and approved subset of the database is available for general public (<https://lilbid-db.planet.fu-berlin.de>).

Plain Language Summary Thousands of laboratory mass spectra, each with an individual set of experimental parameters, have been recorded so far using a facility situated at Freie Universität Berlin, Germany. The mass spectra help analyze and interpret data returned from spacecraft in the vicinity of icy moons in the Solar System. The unstructured laboratory data is increasingly challenging to sort and compare to the data from space. We developed an extendable database containing the laboratory data. The database is available for general public and allows filtering the stored data for a wide range of experimental parameters and, in turn, significantly improves analysis of data not only from past space missions but also future missions in particular.

1. Introduction

Impact ionization mass spectrometers on spacecraft perform in situ analysis of dust grains made of refractory material as well as ice grains, thereby providing important information about the grains' compositions and their sources (e.g., Hillier et al., 2007; Hsu et al., 2015; Kempf et al., 2008; Khawaja et al., 2019; Kissel et al., 1986; Postberg et al., 2008, 2009, 2011, 2018). In such a mass spectrometer, grains impinge onto the detector's target plate at hypervelocities (>1 km/s) and form impact clouds of cations, anions, electrons and neutral fragments. The cations or anions, depending on the instrument's polarity, are accelerated through an electric field toward a multiplier, which measures the flux of ions as a function of arrival time and subsequently result in time-of-flight (ToF) mass spectra.

Measurements by one such mass spectrometer, the Cosmic Dust Analyzer (CDA; Srama et al., 2004) on board the past Cassini spacecraft, showed that a large number of the ice grains, ejected into space in the Saturnian

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system from Enceladus, were formed from liquid subsurface ocean water from within the icy moon (Postberg et al., 2009, 2011). Analysis of the ice grain spectra provides insights into the chemical and physical properties of the subsurface ocean and the interactions between the ocean and the moon's rocky core (Hsu et al., 2015; Khawaja et al., 2019; Postberg et al., 2009, 2011, 2018; Sekine et al., 2015). Other impact ionization mass spectrometers are currently being built, such as the SURface Dust Analyzer (SUDA; Kempf et al., 2014) or proposed, for example, the ENceladus Ice Analyzer (ENIA; Srama et al., 2015) for future space missions to icy moons in the outer Solar System (e.g., Howell & Pappalardo, 2020; Reh et al., 2016). Another impact ionization mass spectrometer, selected for JAXA's future Destiny+ mission (Ozaki et al., 2022) to the asteroid 3200 Phaethon, is the Destiny Dust Analyzer (DDA; Srama et al., 2019). For instrument calibration and data interpretation, laboratory analogue experiments are crucial (e.g., Klenner et al., 2019; Taubner et al., 2020). Accelerating nm- or μm -sized ice grains to relevant speeds in the laboratory is technically challenging (e.g., Belousov et al., 2021; Miller et al., 2022), and the Laser Induced Liquid Beam Ion Desorption (LILBID) approach (Kleinekofort, Avdiev, & Brutschy, 1996; Kleinekofort, Pfenninger, et al., 1996) has therefore been adapted to simulate mass spectra analogous to those generated by impacts of ice grains onto metal targets in space (e.g., Klenner et al., 2019). By using LILBID analogue experiments for instrument calibration, compositional and non-compositional variations in mass spectra from space can be reproduced, and the compounds mixed with the water matrix and their concentrations are known. This makes the LILBID simulation facility an essential tool for the interpretation of past and future space mission data (e.g., Klenner, Postberg, Hillier, Khawaja, Cable, et al., 2020; Klenner, Postberg, Hillier, Khawaja, Reviol, et al., 2020). In addition to applications in space, LILBID mass spectrometry is commonly used for the analyses of organic molecules (Charvat et al., 2002; Mager et al., 2010; Morgner et al., 2006, 2007, 2008; Peetz et al., 2018). Further applications also include the medical field, such as the diagnoses of diseases (Patel, 2015; Sim et al., 2015) and pancreatic cancer research (Grüner et al., 2012; Padoan et al., 2013; Zhong et al., 2015).

In LILBID, a pulsed and focused infrared laser irradiates a μm -sized liquid water beam with substances at known concentrations dissolved therein. The transferred laser energy mechanically disrupts the liquid beam, producing charged and uncharged fragments (Charvat & Abel, 2007; Wiederschein et al., 2015). The created cations or anions are analyzed in a commercial ToF mass spectrometer. Collisional impacts onto space detectors and LILBID create almost exclusively singly charged species (e.g., Karas et al., 2000) and the ions' flight times therefore only dependent on their masses.

Much of the data collected by mass spectrometers on board spacecraft (e.g., CDA on board Cassini) remains uninvestigated because manual evaluation of the large datasets is required. Laboratory LILBID datasets have also been manually investigated thus far. A complete comparison of for example, CDA spectra with laboratory LILBID spectra is extremely time consuming, and still in progress. Only about 15% of all CDA mass spectra obtained from July 2004 to September 2017 have so far (2022) been investigated and compared with laboratory analogue data. It is therefore evident that an easily accessible and well organized database containing all laboratory LILBID mass spectra will facilitate the more rapid evaluation of flight data not only from CDA but particularly future spaceborne instruments, such as SUDA (Kempf et al., 2014) or ENIA (Srama et al., 2015). In contrast to CDA data, the prospective data can then be investigated without any further delay.

Existing databases containing mass spectrometric data created through diverse ionization methods include the NIST Chemistry WebBook (<https://webbook.nist.gov/>), the mzCloud Advanced Mass Spectral Database (<https://www.mzcloud.org/>), the MassBank of North America (MoNA; <https://mona.fiehnlab.ucdavis.edu/>) and a database for oligosaccharides in human milk (Remoroza et al., 2018). However, to the best of our knowledge, no such openly accessible spectral database for LILBID data exists.

We here describe the development and functionality of our new extendable database containing LILBID mass spectra based on a Relational Database Management System (RDBMS) and SQL (Structured Query Language). The frontend of the RDBMS enables the sorting and filtering of laboratory LILBID data via a range of adjustable parameters specific to the used experimental setup (e.g., laser energy) as well as parameters that depend on the measured substances (e.g., compositions). These parameters are important for the analysis and subsequent interpretation of data from space as, for example, the combination of delay time and laser energy in the LILBID system can be correlated to the impact speeds of the ice grains onto the spaceborne mass spectrometer (Klenner et al., 2019). A Python-based peak detection routine applied to all stored data enables queries for certain spectral signals, that is, single mass lines as well as combinations of mass lines.

The ease and rapidity of interrogating this large library of spectral calibration data significantly improves and accelerates analyses of mass spectra from space and thereby aids planning for future space missions. The LILBID data can also be compared rapidly and reliably with other kinds of available mass spectrometric data. The developed database system is available for community use and will continuously be extended and improved in the future.

2. Methods

The experimental LILBID setup, the data pre-processing, the development of the database, and the manual data post-processing are described below.

2.1. The LILBID Facility

The experimental setup used to generate the LILBID mass spectra is described in detail in Klenner et al. (2019). We therefore only provide a brief overview here.

A liquid water beam (radius of 7–12 μm) containing dissolved, or suspended, substances is injected into a high vacuum (5×10^{-5} mbar) at an adjustable flow rate of typically 0.15–0.30 mL/min. The liquid beam is irradiated by a pulsed and focused infrared laser (20 Hz, 7 ns pulse length, wavelength = 2840 nm) with adjustable pulse energies of up to 4 mJ, heats up due to the energy transferred from the laser, and explosively disperses into atomic, molecular and macroscopic fragments. The created cations or anions, depending on the instrument's polarity, are analyzed in a commercial reflectron-type (Mamyrin, 1994) ToF mass spectrometer at $\sim 10^{-7}$ mbar. In addition to pure water, mixtures of water with organic solvents can be used as matrix solutions and therefore all water soluble and many water insoluble substances can be measured and investigated with the LILBID setup. The mass spectrometer uses the principle of delayed extraction, in which the created ions are extracted as a function of their initial velocities (Klenner et al., 2019). The generated mass spectral signals (sampling interval: 1 ns) are amplified, digitized using an 12-bit Analogue to Digital Converter (ADC; Acqiris) and recorded with a LabVIEW®-controlled computer that calibrates the ions' flight times onto a mass scale by using a second order equation (Christian et al., 2000). Typically 300–500 mass spectra are averaged to improve the signal-to-noise ratio. The recorded mass spectra have a mass resolution of between 600 and 800 $m/\Delta m$ (Full Width at Half Maximum, FWHM).

2.2. Data Pre-Processing

At the time of implementing the data acquisition process using LabVIEW, use of a database to store the spectra was not foreseen. Instead, a major focus was on the quick and easy manual location of different measurements stored on the hard drive of the analyzing scientist's computer. Therefore it was originally decided to have one line (the “solution” line; Figure S1 in Supporting Information S1) in the header of the recorded raw data files (level-0), which includes numerous significant parameters, such as the names of the used analyte substances and their concentrations, separated by the “underscore” special character. This line, combined with other significant experimental parameters that are provided in other header lines, is then used as the filename for the raw data files. This enabled easy manual location of the measurements relevant to certain substances, their concentrations and significant experimental parameters. However, combining different parameters in the same header line of the data files (Figure S1 in Supporting Information S1) turned out to be a major challenge with regards to automatic processing of the data files and this information could not simply be ingested into a RDBMS. Additionally, there were inconsistencies in the naming of the files depending on the respective person performing the measurement. For these reasons, we apply a validation script which checks for the correct number of seven underscores in the solution name. If the data file does not pass this first validation script, it has to be manually examined and edited to conform to the right format. The other values from the headers of the mass spectra text files are extracted and re-arranged (data cleaning). The data files are automatically reformatted such that each header line contains information about a single experimental parameter. An example header from such a level-1 data file can be found in Figure S2 of Supporting Information S1.

The level-1 mass spectra files are reorganized text files (Figure S2 in Supporting Information S1) with a header that contains a unique spectral identifier (date and time) and information about experimental parameters

(examined substances, solution, delay time, number of averaged spectra etc.). Below the header, the text files contain two columns with the x - and y - values (floats) of the mass spectra, with x representing mass (in u) and y representing intensity (in V). The time interval between two consecutive lines of the columns corresponds to the sampling interval (1 ns) of the measurement computer (see Section 2.1).

After the file format check and any required manual editing, a peak detection routine is applied to the spectra. The peak detection routine is implemented in Python using the `find_peaks_cwt` algorithm within the SciPy scientific library. Its general approach is to smooth the data by convolving it using a wavelet transformation and then find relative maxima which appear over sufficient length scales and with suitably high signal-to-noise ratios (<https://docs.scipy.org/doc/scipy/reference/signal.html>). The peak detection routine calculates a local baseline for a variable number of data points and uses a local percentile rank for the peak detection threshold. The resulting peak tables are stored in separate text files on the internal server.

The complete data pre-processing, including data validation and peak detection is implemented via a combination of several Python scripts called from a Bash shell script. After copying the raw data from the laboratory computer this script is manually executed on the database server and creates new text files which are then ready for ingestion into the internally accessible version of the database.

2.3. The Database System

We use a client-server infrastructure as the general system design, with the web browser representing the frontend and an RDBMS together with a web server acting as the backend. The spectrum parameters and extracted peaks are stored in relational tables in a MariaDB (<https://mariadb.org/>) database instance. The frontend's web pages are composed using HTML (Hypertext Markup Language), PHP (Hypertext Preprocessor), CSS (Cascading Style Sheets), and JavaScript. An Apache™ (<https://apache.org/>) web server serves a query form with entry fields for several possible parameter filters as the start page. After the user enters none, one or several filter parameters and submits the query, the server connects to the database (via the PHP module) and retrieves the relevant entries. When no values for filtering are entered and submitted, the server lists all available entries. As the peak identities are stored in the database, the data can be filtered not only for the experimental parameters used during the measurements but also for the peaks present in the mass spectra. The layout of the user interface allows for adjustable block-wise (10, 25, 50, or all entries per block) browsing of the results.

The automatic workflow of the steps from data acquisition in the laboratory, data pre-processing, data ingestion and finally the data query is shown in Figure 1. As new laboratory data is acquired, the database is regularly updated using the combined Bash/Python script (see Section 2.2).

2.4. Data Post-Processing

Software on the measurement computer converts the ions' flight times into their masses by use of a second order calibration equation. The applied delayed extraction method (Klenner et al., 2019) and variable initial ion velocities result in unavoidable mass shifts (deviances up to $>1 u$) of the converted masses compared to the real ion masses in level-1 spectra during conversion of the ions' flight times into their masses (Christian et al., 2000), with increasing mass shifts for increasing ion masses.

For a reliable analysis of the mass spectra, it is critical to recalibrate the mass spectra to minimize the mass shifts. Recalibrated level-2 mass spectra are produced by applying a Python script developed in-house. The script calculates a polynomial function based on real peak masses (x -values) for previously detected (shifted) peaks and fits the corresponding data file with this function.

The resulting level-2 spectra often possess an uneven baseline due to instrumental, chemical and random background noise during the measurements (Urban & Štys, 2015). The noise can either produce false positive signals or hide small peaks in the mass spectra. To fully interpret the mass spectra and further improve the spectral analysis, the background noise needs to be smoothed. Several methods and programs that are capable of subtracting the baselines from mass spectra exist (e.g., Urban & Štys, 2015; Xu et al., 2011). We here apply an in-house developed Python script based on the Penalized Least Squares Method (Zhang et al., 2020) to create baseline subtracted data (level-3).

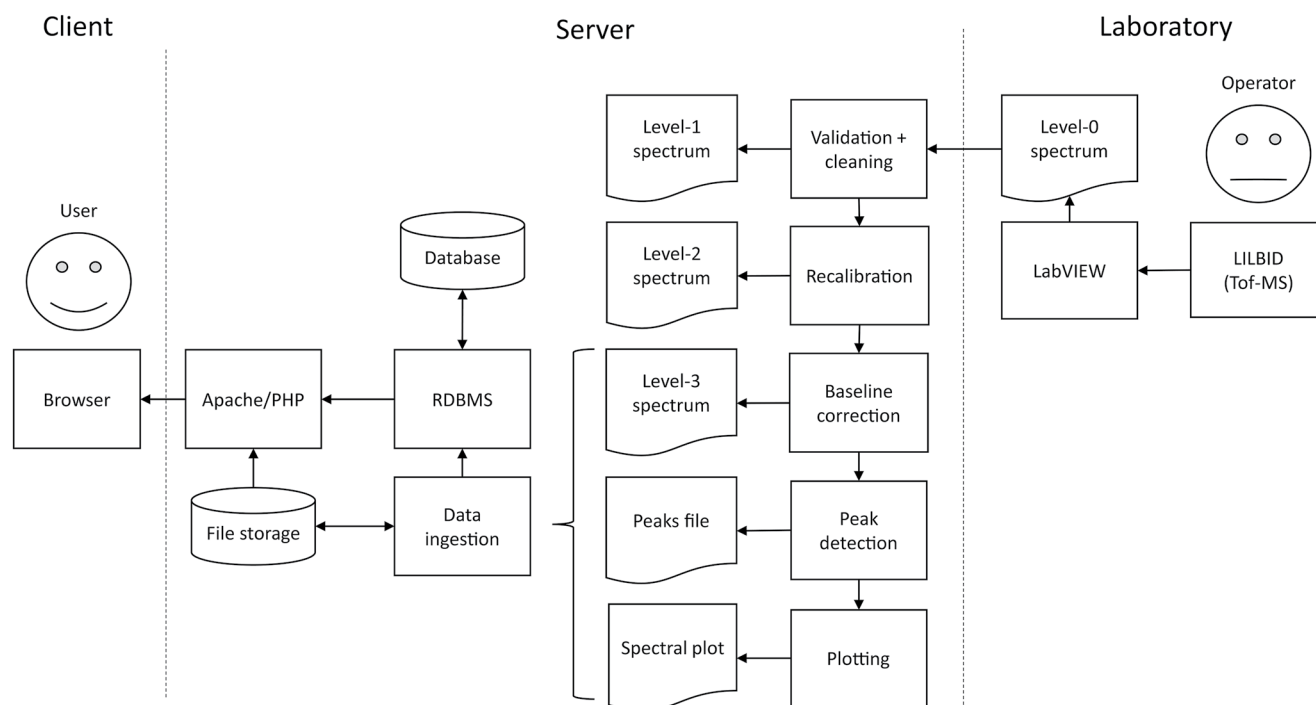


Figure 1. Flowchart of the extendable, publicly accessible database system including (from right to left) data acquisition, data pre-processing, data ingestion and post-processing. Processes shown to the right, with exception of the laser induced Liquid Beam Ion Desorption (LILBID) technique itself, are performed on the laboratory computer (sampling). Processes shown to the left are performed on the server (pre-processing, ingestion and data retrieval) and on the user computer (information selection and output).

The peaks in the level-3 mass spectra are then labeled with their corresponding masses (x -values). The peak labeling can be done either manually, or automatically using a software. Automatic peak detection routines can reliably detect peaks with significantly high amplitudes (y -values) but might overlook smaller peaks and detect false positives. For the reliable detection of small peaks, manual peak identification is indispensable. After peak detection, graphical plots of level-3 mass spectra are created using Python Matplotlib and stored on the server (Figure 1).

The validated subset of the data (exclusively level-3) is accessible via the public database web server interface (see Section 3.1).

3. Results and Discussion

3.1. The LILBID Spectral Database

The in-house version of the spectral database currently contains more than 12,000 LILBID mass spectra recorded using a wide range of experimental parameters. The publicly available version contains a selection of validated and published reference spectra (level-3) and is accessible via the following link: <https://lilbid-db.planet.fu-berlin.de>.

Figure 2 shows the search interface of the publicly available database. The spectra in the database can be searched using numerous experimental parameters, as described below, in order from upper left to lower right in the search interface. Moving the cursor over one of the parameters in the search interface shows a popup window (hover) with more descriptive information about this parameter.

Substance: The name of the analyte.

Matrix: The name of the solvent.

Peaks: The peaks in the mass spectra (x -values with significantly high y -values) created by the analyte, the solvent and physico-chemical interactions between both. The peaks are detected by a peak detection routine (see

Figure 2. Search interface of the Laser Induced Liquid Beam Ion Desorption (LILBID) mass spectral database. It is possible to filter the database output via parameters that depend on the measuring solution (e.g., substance name and apparent peaks in the mass spectra) as well as adjustable setup parameters (e.g., laser intensity and delay time). Here, as an example, given input parameters are I. Substance = sodium chloride, II. Ion Mode = positive, III. Delay Time = 4.8–6.0 μs . Filtering for these input parameters results in the interface shown in Figure 3.

Section 2.2 and Section 2.4). An error (+/–) can be applied because of the potential peak shifts in level-1 mass spectra (see Section 2.4).

Ion Mode: Ion mode of the mass spectrometer, that is, positive (cations) or negative (anions).

Numerical abundances of the most common elements in the used analytes' molecular structures. The most common elements are carbon (C), hydrogen (H), nitrogen (N), oxygen (O), sodium (Na), potassium (K), chlorine (Cl), phosphorus (P), and sulfur (S).

Laser intensity: The intensity of the laser (typically varying from 85% to 100%).

Delay Time: The time between laser shot and ion acceleration (typically between 4 and 8 μs). A combination of delay time and laser energy can be correlated to impact speeds of ice grains onto mass spectrometers in space (Klenner et al., 2019).

The data can be filtered using either a single experimental parameter or a combination of multiple experimental parameters. When applying the filter, all matches will be shown in the results interface (Figure 3) and can be sorted by individual parameters. Clicking on the name of the substance redirects to the corresponding Wikipedia article to provide additional information about the measured substances (solubility in water, toxicity, etc.) without adding new columns to the Database Management System to maintain the database as small and efficient as possible. Graphical plots of the mass spectra can be retrieved via the “Images” column. The “Files” column allows to download the spectral text files. A search function on the top right of the results interface lets one search for individual spectra within the results interface (Figure 3).

Other available databases (see Section 1) can provide structural information or thermodynamic data about an analyzed single substance. In contrast, the LILBID spectral database contains mass spectra of single substances and mixtures of substances in variable background matrices recorded with individual sets of experimental

The screenshot shows the LILBID spectral reference library interface. At the top, it says 'LILBID spectral reference library'. Below that, there is a search bar and a 'Show 10 entries' dropdown. The main part of the interface is a table with the following columns: Substance, Formula, Concentration, Matrix, Laser Intensity (%), Ion Mode, Delay Time (μs), Images, and Files. The table contains three entries for Sodium chloride. Below the table, it says 'Showing 1 to 3 of 3 entries' and has 'Previous', '1', and 'Next' navigation buttons.

Substance	Formula	Concentration	Matrix	Laser Intensity (%)	Ion Mode	Delay Time (μs)	Images	Files
Sodium chloride	NaCl	0.1M	H2O	94.3	pos	5.1	Image	Download
Sodium chloride	NaCl	1e-07M	H2O	93.2	pos	4.9	Image	Download
Sodium chloride	NaCl	1e-07M	H2O	90.3	pos	5.7	Image	Download

Figure 3. Results interface of the Laser Induced Liquid Beam Ion Desorption (LILBID) mass spectral database after filtering for example, input parameters (see Figure 2). Formula: Chemical formula of the analyte. Concentration: Concentration of the analyte. Images: Graphical plot of the level-3 file. Files: Download of the spectral text file.

parameters that are important for the comparison with and interpretation of impact ionization mass spectra recorded in space.

The data in the LILBID spectral database can be searched for particular peaks in the mass spectra after processing with the peak detection routine (see Section 2.2 and Section 2.4). In rare cases, if the baseline is extremely uneven and varies by at least half an order of magnitude (caused by e.g., very salty measuring solutions or high detector voltages) or if the dynamic range (ratio of the largest to smallest detected signal) of the recorded mass spectrum is clearly below 10^1 , tiny peaks are potentially not detected and the routine detects a sparse number of false positives instead. This algorithm will be further improved in the future.

3.2. Science Case: Data Post-Processing of a LILBID Mass Spectrum and Comparison With a CDA Mass Spectrum

Graphical plots of an example LILBID mass spectrum at different data processing levels are shown in Figure 4. The mass spectrum was recorded in the positive ion mode using water containing about 10^{-7} M NaCl. The applied experimental parameters correspond to intermediate impact speeds (8–10 km/s) of ice grains onto spaceborne mass spectrometers (Klenner et al., 2019). Peaks in the mass spectrum represent cationic water species of the form $[\text{H}_2\text{O}]_{0-3}\text{H}_3\text{O}^+$ and cationic sodium-water species of the form $[\text{H}_2\text{O}]_{0-2}\text{Na}^+$.

The level-1 mass spectrum has a slightly uneven baseline and peak shifts of about 0.1 u from the correct isotopic masses. Uneven baselines and peak shifts can hinder analysis, especially of more complex mass spectra (e.g., spectra of organic mixtures or high salinity solutions). In level-2 mass spectra, peak shifts are reduced and level-3 mass spectra are additionally baseline corrected, which aids peak detection and subsequent spectral analyses (Figure 4). After processing to level-3, and with the current mass resolution of the laboratory ToF-MS (600–800 m/Δm), it is often possible to resolve interfering species at the same integer mass with a mass difference of about 0.15–0.25 u (Klenner, Postberg, Hillier, Khawaja, Cable, et al., 2020).

So-called Type-1 mass spectra of ice grains recorded by the CDA in the Saturnian system show peaks that are almost exclusively related to cationic water species of the form $[\text{H}_2\text{O}]_n\text{H}_3\text{O}^+$ with n ranging from 0 to >10 (Postberg et al., 2008, 2009). In addition to cationic water species, occasional traces of sodium can be observed in Type-1 spectra. One such spectrum is shown in Figure 5. The much lower mass resolution of the CDA instrument (20–50 m/Δm; Srama et al., 2004) compared to the LILBID setup (600–800 m/Δm) is apparent. The spectrum shows the same water and sodium-water species as the laboratory LILBID spectrum at similar relative abundances (Figure 4), with $[\text{H}_3\text{O}]^+$ at m/z 19 being slightly more abundant in the CDA spectrum and $[\text{H}_2\text{O}]_3\text{H}_3\text{O}^+$ at m/z 73 being slightly more abundant in the LILBID spectrum. For an even better quantitative match with flight mass spectra, laboratory spectra generated using different experimental parameters can be co-added (Klenner et al., 2019).

As well as water dominated LILBID mass spectra, more complex spectra, such as those from organic mixtures, salty solutions or even both together, can be compared to impact ionization mass spectra from space (e.g.,

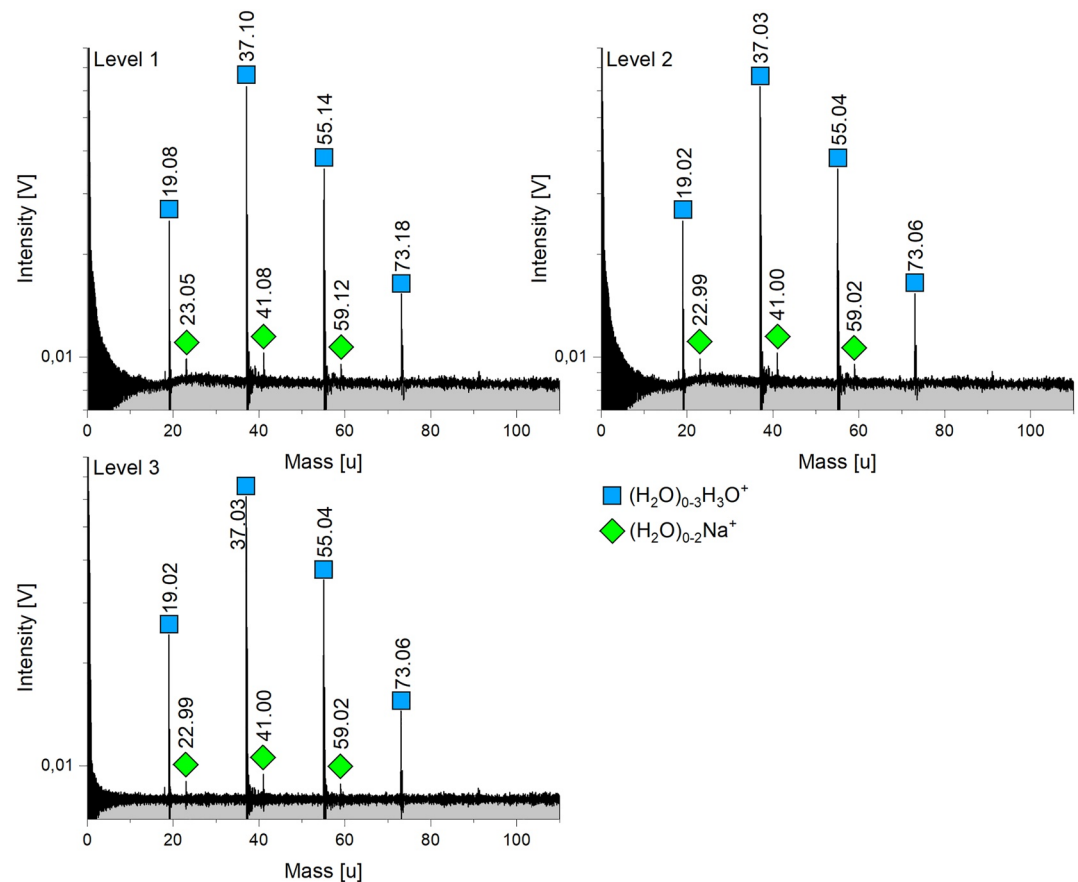


Figure 4. Graphical plots (created using the commercial software OriginPro) of the same Laser Induced Liquid Beam Ion Desorption mass spectrum at different data processing levels. The plots show a cation mass spectrum of water with a NaCl concentration of approximately 10^{-7} M generated using a delay time of $5.5 \mu\text{s}$ and a laser intensity of 98.5%. The peaks are labeled with corresponding masses (x -values). Top left: The pre-processed data (level-1) shows a slightly bumpy baseline and peaks shifted from their real isotopic masses. The text file's header can be found in Figure S2 of Supporting Information S1. Top right: The recalibrated data (level-2) shows corrected isotopic masses but still a slightly bumpy baseline. Bottom left: The recalibrated and baseline corrected data (level-3) exhibits an even baseline and corrected isotopic masses.

Khawaja et al., 2019; Postberg et al., 2009, 2018). The LILBID mass spectra can also be used to forecast the potential mass spectral appearance of all water soluble and many water insoluble substances that might appear in ice grains emitted by extraterrestrial active ocean worlds (e.g., as demonstrated in Klenner, Postberg, Hillier, Khawaja, Cable, et al., 2020; Klenner, Postberg, Hillier, Khawaja, Reviol, et al., 2020).

4. Conclusions and Outlook

The laboratory LILBID facility has been proven to simulate mass spectra produced by ice grain impacts onto spaceborne mass spectrometers. Variations in spectra due to the ice grains' compositions and impact speeds can be accurately reproduced by adjusting appropriate experimental parameters (Khawaja et al., 2019; Klenner et al., 2019; Klenner, Postberg, Hillier, Khawaja, Cable, et al., 2020; Klenner, Postberg, Hillier, Khawaja, Reviol, et al., 2020; Postberg et al., 2009, 2018). Over 12,000 LILBID mass spectra of more than 200 substances, each with their associated experimental parameters, have been uploaded to the internal version of the LILBID mass spectral database and are available to group members at Freie Universität Berlin and cooperation partners only. A subset of validated and approved data is available for the general public (<https://lilbid-db.planet.fu-berlin.de>). The database, containing cation and anion mass spectra, can filter the stored spectra for the used experimental parameters that can be correlated with different properties of the encountered ice grains in space. Processing by a peak detection routine allows the mass spectra to be selected based on the appearance of particular peaks. Besides the spectral data, the database contains all compositional and experimental setup information, as well as

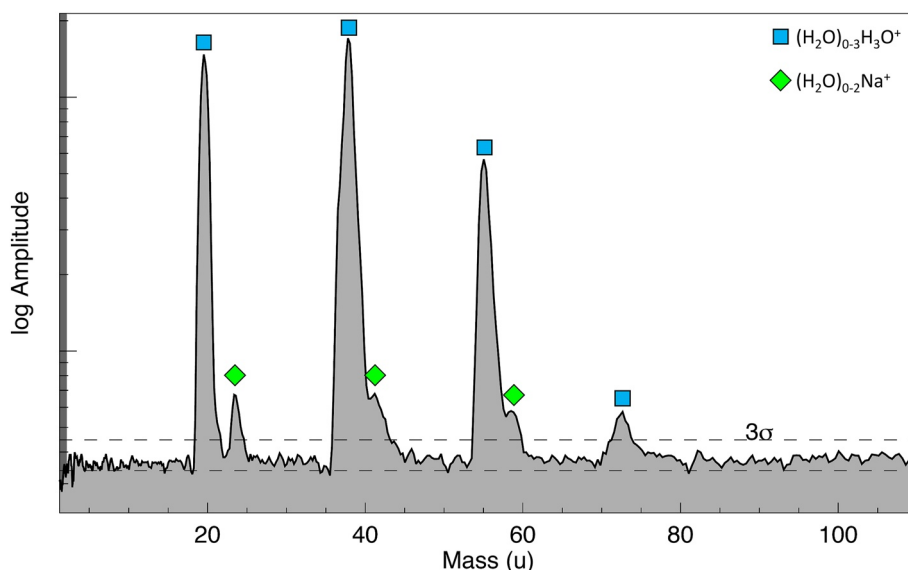


Figure 5. Baseline corrected Cosmic Dust Analyzer mass spectrum of a nearly pure water ice grain containing traces of sodium (Type-1; Postberg et al., 2008, 2009) recorded in the Saturnian system. The ice grain hit the mass spectrometer on board the Cassini spacecraft at a relative speed of approximately 9 km/s. The spectrum shows the same water species, at similar relative abundances, as the Laser Induced Liquid Beam Ion Desorption mass spectrum in Figure 4.

the location of the peaks detected by a peak detection routine. By filtering for experimental parameters and peaks, characteristic mass spectra can be selected for further analysis.

LILBID data processing, mass spectral analysis and comparison of LILBID data with data from space follow a predictable, repetitive pattern. This pattern can be executed more rapidly and efficiently, with reducing risk of user error, by use of the automated processing steps and database storage described above. The database therefore improves the analysis of mass spectra of ice grains recorded in space, from not only past missions (e.g., Cassini) but also future missions with higher resolution mass spectrometers, such as in particular NASA's Europa Clipper (Howell & Pappalardo, 2020). Future data from space can straightforwardly be investigated without any delay. The database can also be used to compare LILBID data with many other types of mass spectrometric data, for example, with electron ionization mass spectra from the NIST Chemistry WebBook (<https://webbook.nist.gov/>).

Newly recorded spectra will be regularly uploaded to the database, and the database system will be continuously improved. The peak detection algorithm will be modified to detect very small peaks and exclude false positive signals even more reliably. We will add a function to filter the measured substances for chemical families (alcohols, ketones, salts, etc.). The LabView component will be adapted to improve the header definition, so that manual data cleaning is no longer necessary.

LILBID data recorded with an Orbitrap™-based mass spectrometer, having significantly improved mass resolution, will complement the Time-of-Flight spectrometer data in the near future. We plan to enhance the capabilities of the LILBID setup to also analyze neutral atoms created by the infrared laser hitting the water beam, which are suspected to be more abundant than ions in the impact cloud of ice grains. The database will then also contain LILBID analogue mass spectra applicable to neutral gas mass spectrometers, such as the Particle Environment Package–Neutral Ion Mass Spectrometer (PEP-NIM; Barabash et al., 2013) or the MAss Spectrometer for Planetary EXploration (MASPEX; Brockwell et al., 2016) on board ESA's JUICE (Grasset et al., 2013) and NASA's upcoming Europa Clipper (Howell & Pappalardo, 2020) missions to the Jovian System, respectively. The neutral atom data will be stored separately from the cationic and anionic desorption data within the database.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Data—The LILBID mass spectrum raw data used in this paper (see Figure 4) can be retrieved from <https://doi.org/10.5281/zenodo.6863855> (Klenner, 2022). Data—The CDA mass spectrum raw data used in this paper (see Figure 5) can be retrieved from NASA's Planetary Data System (PDS) Small Bodies Node via https://sbnarchive.psi.edu/pds3/cassini/cda/COCCA_0007.tar.gz (Planetary Science Institute, 2022).

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References

- Barabash, S., Wurz, P., Brandt, P., Wieser, M., Holmström, M., Futaana, Y., et al. (2013). Particle environment package (PEP). *8th European planetary science congress*.
- Belousov, A., Miller, M., Continetti, R., Madzunkov, S., Simic, J., Nikolic, D., et al. (2021). Sampling accelerated micron scale ice particles with a quadrupole ion trap mass spectrometer. *Journal of the American Society for Mass Spectrometry*, 32(5), 1162–1168. <https://doi.org/10.1021/jasms.0c00442>
- Brockwell, T. G., Meech, K. J., Pickens, K., Waite, J. H., Miller, G., Roberts, J., et al. (2016). The mass spectrometer for planetary exploration (MASPEX). Big Sky. Paper presented at *IEEE aerospace conference*. <https://doi.org/10.1109/AERO.2016.7500777>
- Charvat, A., & Abel, B. (2007). How to make big molecules fly out of liquid water: Applications, features and physics of laser assisted liquid phase dispersion mass spectrometry. *Physical Chemistry Chemical Physics*, 9(26), 3335–3360. <https://doi.org/10.1039/B615114K>
- Charvat, A., Lugovoj, E., Faubel, M., & Abel, B. (2002). Analytical laser induced liquid beam desorption mass spectrometry of protonated amino acids and their non-covalently bound aggregates. *The European Physical Journal D*, 20(3), 573–582. <https://doi.org/10.1140/epjd/e2002-00169-0>
- Christian, N. P., Arnold, R. J., & Reilly, J. P. (2000). Improved calibration of time-of-flight mass spectra by simplex optimization of electrostatic ion calculations. *Analytical Chemistry*, 72(14), 3327–3337. <https://doi.org/10.1021/ac991500h>
- Grasset, O., Dougherty, M. K., Coustenis, A., Bunce, E. J., Erd, C., Titov, D., et al. (2013). JUPITER ICY moons Explorer (JUICE): An ESA mission to orbit Ganymede and to characterise the Jupiter system. *Planetary and Space Science*, 78, 1–21. <https://doi.org/10.1016/j.pss.2012.12.002>
- Grüner, B. M., Hahne, H., Mazur, P. K., Trajkovic-Arsic, M., Maier, S., Esposito, I., et al. (2012). MALDI imaging mass spectrometry for in situ proteomic analysis of preneoplastic lesions in pancreatic cancer. *PLoS One*, 7(6), e39424. <https://doi.org/10.1371/journal.pone.0039424>
- Hillier, J. K., Green, S. F., McBride, N., Schwannethal, J. P., Postberg, F., Srama, R., et al. (2007). The composition of Saturn's E ring. *Monthly Notices of the Royal Astronomical Society*, 377(4), 1588–1596. <https://doi.org/10.1111/j.1365-2966.2007.11710.x>
- Howell, S. M., & Pappalardo, R. T. (2020). NASA's Europa Clipper—A mission to a potentially habitable ocean world. *Nature Communications*, 11(1), 1–4. <https://doi.org/10.1038/s41467-020-15160-9>
- Hsu, H. W., Postberg, F., Sekine, Y., Shibuya, T., Kempf, S., Horányi, M., et al. (2015). Ongoing hydrothermal activities within Enceladus. *Nature*, 519(7542), 207–210. <https://doi.org/10.1038/nature14262>
- Karas, M., Glückmann, M., & Schäfer, J. (2000). Ionization in matrix-assisted laser desorption/ionization: Singly charged molecular ions are the lucky survivors. *Journal of Mass Spectrometry*, 35(1), 1–12. [https://doi.org/10.1002/\(SICI\)1096-9888\(200001\)35:1<1::AID-JMS904>3.0.CO;2-0](https://doi.org/10.1002/(SICI)1096-9888(200001)35:1<1::AID-JMS904>3.0.CO;2-0)
- Kempf, S., Altobelli, N., Briosis, C., Grün, E., Horányi, M., Postberg, F., et al. (2014). SUDA: A dust mass spectrometer for compositional surface mapping for a mission to Europa. Paper presented at *9th European planetary science congress*.
- Kempf, S., Beckmann, U., Moragas-Klostermeyer, G., Postberg, F., Srama, R., Economou, T., et al. (2008). The E ring in the vicinity of Enceladus: I. Spatial distribution and properties of the ring particles. *Icarus*, 193(2), 420–437. <https://doi.org/10.1016/j.icarus.2007.06.027>
- Khawaja, N., Postberg, F., Hillier, J., Klenner, F., Kempf, S., Nölle, L., et al. (2019). Low-mass nitrogen-oxygen-bearing, and aromatic compounds in Enceladean ice grains. *Monthly Notices of the Royal Astronomical Society*, 489(4), 5231–5243. <https://doi.org/10.1093/mnras/stz2280>
- Kissel, J., Sagdeev, R. Z., Bertaux, J. L., Angarov, V. N., Audouze, J., Blamont, J. E., et al. (1986). Composition of comet Halley dust particles from Vega observations. *Nature*, 321(6067), 280–282. <https://doi.org/10.1038/321280a0>
- Kleinkofort, W., Avdiev, J., & Brutschy, B. (1996). A new method of laser desorption mass spectrometry for the study of biological macromolecules. *International Journal of Mass Spectrometry and Ion Processes*, 152(2–3), 135–142. [https://doi.org/10.1016/0168-1176\(95\)04330-6](https://doi.org/10.1016/0168-1176(95)04330-6)
- Kleinkofort, W., Pfenninger, A., Plomer, T., Griesinger, C., & Brutschy, B. (1996). Observation of noncovalent complexes using laser-induced liquid beam ionization/desorption. *International Journal of Mass Spectrometry and Ion Processes*, 156(3), 195–202. [https://doi.org/10.1016/S0168-1176\(96\)04507-7](https://doi.org/10.1016/S0168-1176(96)04507-7)
- Klenner, F. (2022). LILBID mass spectrum of water [Dataset]. Zenodo. <https://doi.org/10.5281/zenodo.6863855>
- Klenner, F., Postberg, F., Hillier, J., Khawaja, N., Cable, M. L., Abel, B., et al. (2020). Discriminating abiotic and biotic fingerprints of amino acids and fatty acids in ice grains relevant to ocean worlds. *Astrobiology*, 20(10), 1168–1184. <https://doi.org/10.1089/ast.2019.2188>
- Klenner, F., Postberg, F., Hillier, J., Khawaja, N., Reviol, R., Srama, R., et al. (2019). Analogue spectra for impact ionization mass spectra of water ice grains obtained at different impact speeds in space. *Rapid Communications in Mass Spectrometry*, 33(22), 1751–1760. <https://doi.org/10.1002/rcm.8518>
- Klenner, F., Postberg, F., Hillier, J., Khawaja, N., Reviol, R., Stolz, F., et al. (2020). Analog experiments for the identification of trace biosignatures in ice grains from extraterrestrial ocean worlds. *Astrobiology*, 20(2), 179–189. <https://doi.org/10.1089/ast.2019.2065>
- Mager, F., Sokolova, L., Lintzel, J., Brutschy, B., & Nussberger, S. (2010). LILBID-mass spectrometry of the mitochondrial preprotein translocase TOM. *Journal of Physics: Condensed Matter*, 22(45), 454132. <https://doi.org/10.1088/0953-8984/22/45/454132>
- Mamyrin, B. A. (1994). Laser assisted reflectron time-of-flight mass spectrometry. *International Journal of Mass Spectrometry and Ion Processes*, 131, 1–19. [https://doi.org/10.1016/0168-1176\(93\)03891-O](https://doi.org/10.1016/0168-1176(93)03891-O)
- Miller, M. E. C., Burke, S. E., & Continetti, R. E. (2022). Production and impact characterization of Enceladus ice grain analogues. *ACS Earth and Space Chemistry*, 6(7), 1813–1822. <https://doi.org/10.1021/acsearthspacechem.2c00087>
- Morgner, N., Barth, H. D., & Brutschy, B. (2006). A new way to detect noncovalently bonded complexes of biomolecules from liquid microdroplets by laser mass spectrometry. *Australian Journal of Chemistry*, 59(2), 109–114. <https://doi.org/10.1071/CH05285>
- Morgner, N., Hoffmann, J., Barth, H. D., Meier, T., & Brutschy, B. (2008). LILBID-mass spectrometry applied to the mass analysis of RNA polymerase II and an F1Fo-ATP synthase. *International Journal of Mass Spectrometry*, 277(1–3), 309–313. <https://doi.org/10.1016/j.ijms.2008.08.001>
- Morgner, N., Kleinschroth, T., Barth, H. D., Ludwig, B., & Brutschy, B. (2007). A novel approach to analyze membrane proteins by laser mass spectrometry: From protein subunits to the integral complex. *Journal of the American Society for Mass Spectrometry*, 18(8), 1429–1438. <https://doi.org/10.1016/j.jasms.2007.04.013>

- Ozaki, N., Yamamoto, T., Gonzales-Franquesa, F., Gutierrez-Ramon, R., Pushparaj, N., Chikazawa, T., et al. (2022). Mission Design of DESTINY+: Toward active asteroid (3200) phaeton and multiple small bodies. arXiv:2201.01933v1.
- Padoan, A., Seraglia, R., Basso, D., Fogar, P., Sperti, C., Moz, S., et al. (2013). Usefulness of MALDI-TOF/MS identification of low-MW fragments in sera for the differential diagnosis of pancreatic cancer. *Pancreas*, *42*(4), 622–632. <https://doi.org/10.1097/MPA.0b013e318273096c>
- Patel, R. (2015). MALDI-TOF MS for the diagnosis of infectious diseases. *Clinical Chemistry*, *61*(1), 100–111. <https://doi.org/10.1373/clinchem.2014.221770>
- Peetz, O., Hellwig, N., Henrich, E., Mezhyrova, J., Dötsch, V., Bernhard, F., & Morgner, N. (2018). LILBID and nESI: Different native mass spectrometry techniques as tools in structural biology. *Journal of the American Society for Mass Spectrometry*, *30*(1), 181–191. <https://doi.org/10.1007/s13361-018-2061-4>
- Planetary Science Institute. (2022). COCDA_0007. Sbnarchive, [Dataset]. Retrieved from https://sbnarchive.psi.edu/pds3/cassini/cda/COCDA_0007.tar.gz
- Postberg, F., Kempf, S., Hillier, J. K., Srama, R., Green, S. F., McBride, N., & Grün, E. (2008). The E-ring in the vicinity of Enceladus: II. Probing the moon's interior—The composition of E-ring particles. *Icarus*, *193*(2), 438–454. <https://doi.org/10.1016/j.icarus.2007.09.001>
- Postberg, F., Kempf, S., Schmidt, J., Brilliantov, N., Beinsen, A., Abel, B., et al. (2009). Sodium salts in E-ring ice grains from an ocean below the surface of Enceladus. *Nature*, *459*(7250), 1098–1101. <https://doi.org/10.1038/nature08046>
- Postberg, F., Khawaja, N., Abel, B., Choblet, G., Glein, C. R., Gudipati, M. S., et al. (2018). Macromolecular organic compounds from the depths of Enceladus. *Nature*, *558*(7711), 564–568. <https://doi.org/10.1038/s41586-018-0246-4>
- Postberg, F., Schmidt, J., Hillier, J., Kempf, S., & Srama, R. (2011). A salt-water reservoir as the source of a compositionally stratified plume on Enceladus. *Nature*, *474*(7353), 620–622. <https://doi.org/10.1038/nature10175>
- Reh, K., Cable, M. L., Clark, K., Lunine, J. I., Postberg, F., Spilker, L., & Waite, J. H. (2016). Enceladus life finder: The search for life in a habitable moon. In *IEEE aerospace conference*. Big Sky. <https://doi.org/10.1109/AERO.2016.7500813>
- Remoroza, C. A., Mak, T. D., De Leoz, M. L. A., Mirokhin, Y. A., & Stein, S. E. (2018). Creating a mass spectral reference library for oligosaccharides in human milk. *Analytical Chemistry*, *90*(15), 8977–8988. <https://doi.org/10.1021/acs.analchem.8b01176>
- Sekine, Y., Shibuya, T., Postberg, F., Hsu, H. W., Suzuki, K., Masaki, Y., et al. (2015). High-temperature water–rock interactions and hydrothermal environments in the chondrite-like core of Enceladus. *Nature Communications*, *6*(1), 1–8. <https://doi.org/10.1038/ncomms9604>
- Sim, K., Shaw, A. G., Randell, P., Cox, M. J., McClure, Z. E., Li, M. S., et al. (2015). Dysbiosis anticipating necrotizing enterocolitis in very premature infants. *Clinical Infectious Diseases*, *60*(3), 389–397. <https://doi.org/10.1093/cid/ciu822>
- Srama, R., Ahrens, T. J., Altobelli, N., Auer, S., Bradley, J. G., Burton, M., et al. (2004). The Cassini cosmic dust analyzer. *Space Science Reviews*, *114*(1–4), 465–518. <https://doi.org/10.1007/s11214-004-1435-z>
- Srama, R., Kobayashi, M., Krüger, H., Arai, T., Kimura, H., Trieloff, M., et al. (2019). Dust astronomy with DESTINY PLUS at 1 AU. *21st European geosciences union general assembly*.
- Srama, R., Postberg, F., Henkel, H., Klopfer, T., Li, Y., Reviol, R., et al. (2015). Enija: Search for life with a high-resolution TOF-MS for in situ compositional analysis of nano- and micron-sized dust particles. Paper presented at *15th European geosciences union general assembly*.
- Taubner, R. S., Olsson-Francis, K., Vance, S. D., Ramkissoon, N. K., Postberg, F., de Vera, J. P., et al. (2020). Experimental and simulation efforts in the astrobiological exploration of exoceans. *Space Science Reviews*, *216*(1), 1–41. <https://doi.org/10.1007/s11214-020-0635-5>
- Urban, J., & Štys, D. (2015). Noise and baseline filtration in mass spectrometry. In F. Ortúño & I. Rojas (Eds.), *Bioinformatics and biomedical engineering* (pp. 418–425). Springer. https://doi.org/10.1007/978-3-319-16480-9_41
- Wiederschein, F., Vöhringer-Martinez, E., Beinsen, A., Postberg, F., Schmidt, J., Srama, R., et al. (2015). Charge separation and isolation in strong water droplet impacts. *Physical Chemistry Chemical Physics*, *17*(10), 6858–6864. <https://doi.org/10.1039/C4CP05618C>
- Xu, Z., Sun, X., & Harrington, P. D. B. (2011). Baseline correction method using an orthogonal basis for gas chromatography/mass spectrometry data. *Analytical Chemistry*, *83*(19), 7464–7471. <https://doi.org/10.1021/ac2016745>
- Zhang, F., Tang, X., Tong, A., Wang, B., & Wang, J. (2020). An automatic baseline correction method based on the penalized least squares method. *Sensors*, *20*(7), 2015. <https://doi.org/10.3390/s20072015>
- Zhong, N., Cui, Y., Zhou, X., Li, T., & Han, J. (2015). Identification of prohibitin 1 as a potential prognostic biomarker in human pancreatic carcinoma using modified aqueous two-phase partition system combined with 2D-MALDI-TOF-TOF-MS/MS. *Tumor Biology*, *36*(2), 1221–1231. <https://doi.org/10.1007/s13277-014-2742-y>