

Laboratory spectroscopy techniques to enable observations of interstellar ion chemistry

Brett A. McGuire^{1,2,3}✉, Oskar Asvany⁴, Sandra Brünken⁵ and Stephan Schlemmer⁴✉

Abstract | Molecular ions have long been considered key intermediates in the evolution of molecular complexity in the interstellar medium. However, owing to their reactivity and transient nature, ions have historically proved challenging to study in terrestrial laboratory experiments. In turn, their detection and characterization in space is often contingent upon advances in the laboratory spectroscopic techniques used to measure their spectra. In this Review, we discuss the advances over the past 50 years in laboratory methodologies for producing molecular ions and probing their rotational, vibrational and electronic spectra. We largely focus this discussion around the widespread H_3^+ cation and the ionic products originating from its reaction with carbon atoms. Finally, we discuss the current frontiers in this research and the technical advances required to address the spectroscopic challenges that they represent.

More than 200 molecular species are now known to be present in the interstellar medium (ISM), but only slightly more than 15% of these are ionic: either positively or negatively charged¹. Yet these charged species have a substantial role in driving chemical evolution in space, where low densities and temperatures present considerable obstacles to reactivity. In a relatively diffuse gas, the time between collisions for two species in space can often be measured in days or months, and even then, only if one of them is hydrogen (H or H_2). When these species do find each other, they typically only react if there is no energetic barrier to do so. Ions help to solve both of these problems.

Because ions are charged, their long-range interactions induce dipole moments in nearby neutral species. Thus, an attractive potential forms between the charged and uncharged species, substantially increasing the frequency of collisions. Reactions with ions are also often barrierless and exothermic, requiring no input of energy to proceed. As a result, much of the initial build-up of chemistry in the ISM is initiated through ion–molecule reactions, which are often faster by orders of magnitude than those between neutral collision partners². FIGURE 1 shows a portion of this early reaction chemistry, demonstrating the role of ion–molecule reactions in generating small hydrocarbons, water and more complex species such as protonated methanol (CH_3OH_2^+). The latter is thought to be an important intermediate in the formation of still more complex species³ but has not yet been detected in the ISM¹.

The primary initiator in this network is the simple polyatomic cation H_3^+ . The importance of H_3^+ in initiating ion–molecule chemistry has long been recognized, and H_3^+ has been invoked as a key intermediate in reaction networks for decades^{3,4,5}. Although laboratory knowledge of its spectrum dates back to 1980 (REF.⁶), it was not detected in the ISM, where it is now widely observed, until 1996 (REF.⁷). The reaction of H_3^+ with heteroatoms ($\text{X} = \text{O}$, C or halogens, among others) is generally exothermic and barrierless, resulting in a protonated species XH^+ :



A cascade of reactions can proceed from the formation of XH^+ , building up larger and more complex species, often through subsequent reaction with H_2 . Alternative initial reaction steps can occur, depending on the astrophysical environment (FIG. 1). There is substantial discussion in the literature as to the extent of complexity that can be built solely through ion–molecule reactions and the competition of these reactions with grain-surface and neutral–neutral reactions^{8–10}. There is little debate, however, about the importance of molecular ions in kick-starting chemical complexity in the ISM.

In this Review, we examine many of the laboratory techniques that have enabled the observation of molecular ion spectra, the current status of the field and the impact of recent advances in the laboratory on the

¹Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA.

²National Radio Astronomy Observatory, Charlottesville, VA, USA.

³Center for Astrophysics, Harvard and Smithsonian, Cambridge, MA, USA.

⁴1. Physikalisches Institut, Universität zu Köln, Köln, Germany.

⁵Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Nijmegen, Netherlands.

✉e-mail: brettmc@mit.edu; schlemmer@ph1.uni-koeln.de
<https://doi.org/10.1038/s42254-020-0198-0>

Key points

- Molecular ions have a key role in driving chemistry in the interstellar medium because their reactions are usually exothermic and the attractive potentials that they induce increase reaction rates.
- The laboratory spectra needed to study ions in space are challenging to collect, as ions are both difficult to produce in large quantities and highly reactive.
- A boom in ion studies was aided by the combination of spectroscopy techniques that greatly increased the optical path length with others that modulated the signal at known frequencies while leaving noise unmodulated.
- Action spectroscopy in cryogenic ion traps indirectly measures absorption by observing changes in counts of the mass-selected, stored ions.
- Action spectroscopy is by far the most sensitive technique and has developed into a versatile tool in the full spectral range of molecular spectroscopy, covering rotational, vibrational and electronic motion.

future observation of ionic species in the ISM. The discussion centres on a few selected ions that we believe exemplify not only the main spectroscopic techniques and advances, but also the close connections between laboratory spectroscopy and observational astronomy: H_3^+ , CH_3^+ , CH^+ , C_3H^+ and C_{60}^+ . The selection of ions also determines the techniques that we highlight herein. As a consequence, many important experimental methods, such as cavity-enhanced Fourier-transform microwave (FTMW) spectroscopy and velocity-modulation infrared absorption spectroscopy, are outside our scope here and are only referenced or discussed briefly.

 H_3^+ as the cornerstone of ion chemistry

The infrared (IR) spectrum of H_3^+ was measured by Oka⁶ in 1980 using a sophisticated direct-absorption spectrometer outfitted with a multi-pass set-up and a frequency-modulated detection system. The discharge cell was liquid-nitrogen cooled in a manner similar to earlier work on HCO^+ (REF.¹¹). In direct-absorption techniques, the strength of the observed absorption signal

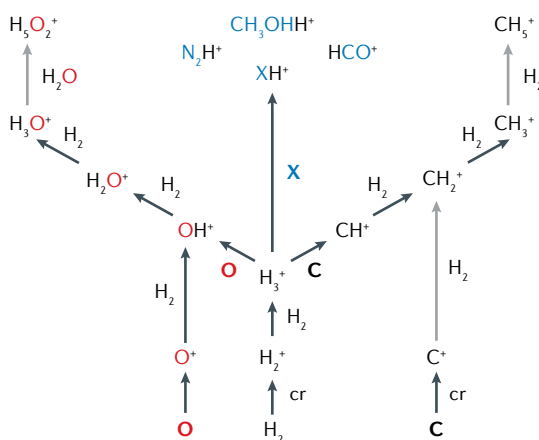


Fig. 1 | Astrochemical ion–molecule reactions. An astrochemical reaction tree depicting several pathways in which ion–molecule reactions build molecular complexity in the interstellar medium¹⁰⁹. The H_3^+ cation has a fundamental role in initiating this network. H_3^+ forms upon ionization of molecular hydrogen (H_2) by cosmic rays (cr) and then consecutive collisions with H_2 . The colours and thicknesses of the arrows depict different reaction mechanisms that occur depending on the astrophysical environment.

(and thus the sensitivity) is directly proportional to the path length. A common technique for increasing the path length, without increasing the physical size of the cell beyond what can reasonably be housed in a laboratory, is to use a system of mirrors to ensure that the light reflects through the absorbing material many times before it is detected. Indeed, in Oka's set-up, the effective path length was 32 m from a 2-m-long cell. There are several variations of this optical set-up; the most common are White-type¹³ and Herriott-type¹³ arrangements, as well as simpler double-pass set-ups that use a polarizing grid and a polarization-rotating rooftop reflector¹⁴. Oka also implemented a phase-locked detection scheme using frequency modulation, which is widely used in spectroscopy.

Two more recent techniques, cavity ring-down spectroscopy (CRDS) and noise-immune cavity-enhanced heterodyne velocity-modulation spectroscopy (NICE-OHVMS), further exploit multi-pass geometries and noise-rejection methods. CRDS uses a pair of high-reflectivity ($R \geq 99.99\%$) supermirrors to create an optical cavity with path lengths of many kilometres¹⁵. With each pass within the cavity, a fraction of the light leaks out of the back of one mirror and is detected as a decay signal. A molecular absorber within the cavity increases this decay rate. Because the change in rate is directly proportional to the molecular absorption, an absorption spectrum can thus be determined. In the case of H_3^+ , CRDS techniques have been used to measure, for example, the electron recombination rate of H_3^+ by monitoring the decay rate of the H_3^+ signal in the cavity^{16,17}.

In addition to cavity enhancement, NICE-OHVMS (FIG. 2) incorporates two modes of modulation¹⁸. Its predecessor, NICE-OHMS (noise-immune cavity-enhanced optical heterodyne molecular spectroscopy), uses a laser locked to the cavity resonant frequency¹⁹. A pair of frequency-modulated sidebands, 180° out of phase with one another, is then added to the laser at a spacing equal to an integer of the cavity free spectral range, allowing the sidebands and laser to be simultaneously coupled into or out of the cavity. When no absorber is present, the beat signals of the two sidebands exactly cancel each other out, eliminating all noise from the system and creating a background-free scenario. An absorption signal is detected when one of the sidebands is absorbed by a molecular carrier. Compared with NICE-OHMS, NICE-OHVMS adds an extra modulation component by varying the velocity of molecular ions within the sample. This further increases the sensitivity of the experiment, as was pioneered by Saykally and co-workers, who applied velocity modulation in standard absorption experiments to a large class of molecular ions^{20–22}. NICE-OHVMS has been used to measure transitions of many molecular cations^{23–25}, in particular H_3^+ (REFS^{26–30}), to sub-Doppler accuracy, enabling measurements made in the IR region to approach microwave-level accuracies on rotationally resolved transitions. The sensitivity of NICE-OHVMS is routinely more than two orders of magnitude higher than that of state-of-the-art multi-pass direct-absorption spectrometers^{26,31}.

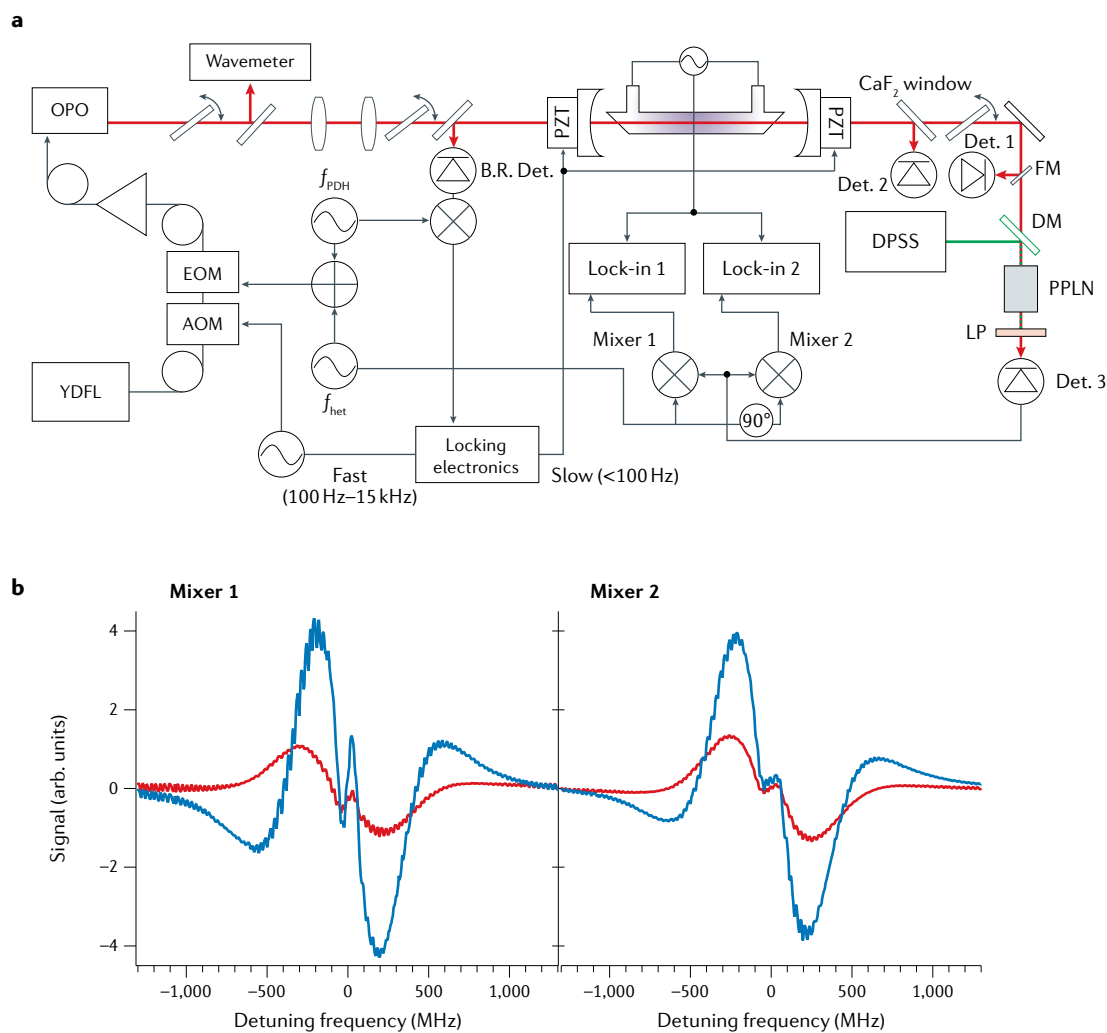


Fig. 2 | **NICE-OHVMS.** **a** | Schematic of an instrument for noise-immune cavity-enhanced heterodyne velocity-modulation spectroscopy (NICE-OHVMS). An ytterbium-doped fibre laser (YDFL) drives an optical parametric oscillator (OPO) and is phase modulated by an electro-optic modulator (EOM) that produces the required sidebands for locking and heterodyne detection²⁶. **b** | Example NICE-OHVMS spectra of the R(1,0) transition of H_3^+ at $2,725.8984\text{ cm}^{-1}$ from the two mixers, showing the in-phase (red) and quadrature (blue) components of the velocity-modulation signal. The transition frequency is determined to megahertz precision by a least-squares fit to the Lamb dip at the centre of each spectrum, as described in REF.²⁷. AOM, acousto-optic modulator; B.R. Det., back reflection detector; Det. 1, mid-infrared transmission detector; Det. 2, mid-IR transmission detector; Det. 3, silicon detector; DM, dichroic mirror; DPSS: diode-pumped solid-state laser; f_{het} , heterodyne frequency; FM, flipper mirror; f_{PDH} , Pound–Drever–Hall frequency; LP, longpass filter; PPLN, periodically poled lithium niobate crystal; PZT, piezoelectric transducer. Adapted with permission from REF.²⁶, OSA Publishing.

Laser-induced reactions

H_3^+ isotopologues. Many of the ions that were first detected using Oka-type discharge absorption experiments have been subsequently investigated in cryogenic ion traps using action spectroscopy, owing to the technique's high selectivity and unprecedented sensitivity. In these experiments, ions of interest are mass-selected and isolated in an ion trap, where they can be investigated over long time periods. This approach therefore offers notable advantages over discharge techniques and the (largely uncontrolled) production of many different short-lived ions. Moreover, buffer-gas cooling of the ions in a cryogenic trap prepares the ensemble in only a few quantum states and thus simplifies the spectra. Within the trap, the interaction of the ions with light leads to a change in the mass composition of the

stored ion ensemble that is detected with near-100% efficiency in an external mass analyser. As the product ions are produced only upon excitation of the parent ion, the method is intrinsically background-free, offering unprecedented gains in sensitivity. In the most popular version of this action spectroscopy, the ion of interest dissociates upon absorption of one^{32–34} or more photons^{35–37}, and thus unimolecular decay is used to detect the photon absorption. Many variations of this method have been added to the toolbox of action spectroscopy, and several associated with ions in the astrophysical context are highlighted below.

Laser-induced reaction (LIR) is an action spectroscopic technique pioneered by Schlemmer and Gerlich^{38,39}, and uses the products of a bimolecular chemical reaction to record high-resolution spectra of stable molecular

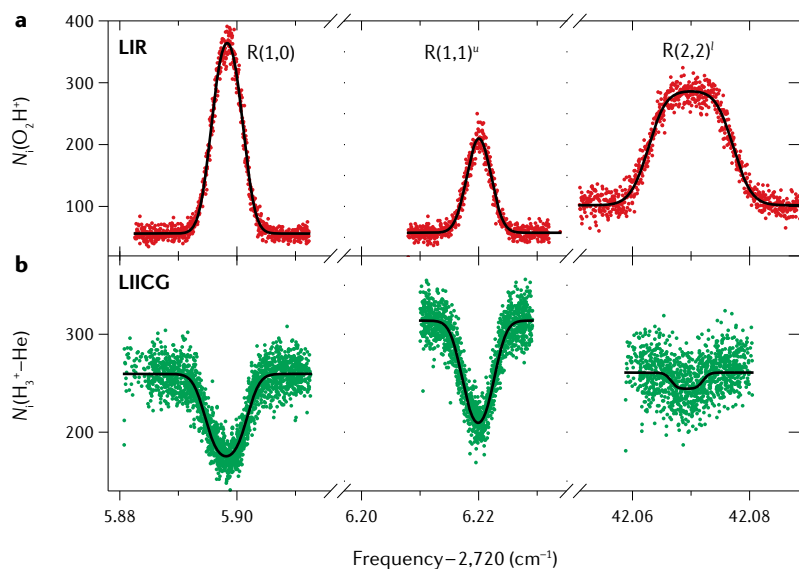
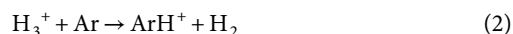


Fig. 3 | Action spectroscopy of H_3^+ . **a** | Rovibrational transitions of H_3^+ measured with the laser-induced reaction (LIR) method. The frequency position for each data point has been accurately determined with a frequency comb⁴². The trap temperature was 4 K, except for the R(2, 2)^l line, for which the trap was heated to ~ 45 K. This line is partly power-saturated. **b** | The same rovibrational transitions of H_3^+ as shown in panel **a**, measured with the laser-induced inhibition of complex growth (LIICG) method. N_i , number of ions detected. Adapted with permission from REF.⁴³, Elsevier.

ions. The first application of this technique to H_3^+ involved proton transfer to an Ar atom:



This reaction is endothermic by 0.57 eV ($\sim 4,600 \text{ cm}^{-1}$), which was overcome by exciting overtones of H_3^+

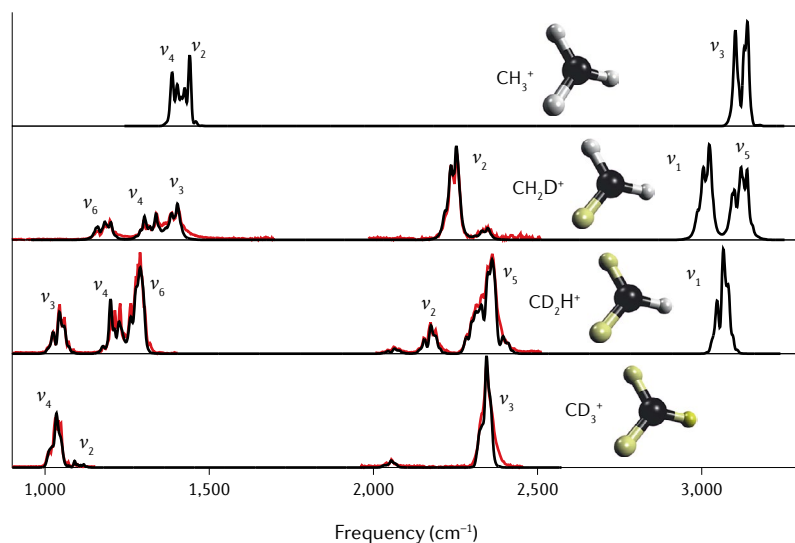


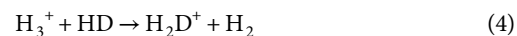
Fig. 4 | LIR measurements of CH_3^+ isotopologues. Measured and simulated low-resolution vibrational spectra of isotopologues of CH_3^+ (REF.⁶⁰). The measured spectra (red) were recorded by using the laser-induced reaction (LIR) method with the free-electron laser FELIX¹¹⁰. The spectroscopic simulations (black) were run by using the PGOPHER programme¹¹¹ and, in the case of CH_3^+ , also drawing on prior work^{61,62}. The infrared-active fundamental vibrational modes are numbered (ν_n , $n=1-6$). All features in the $3\text{-}\mu\text{m}$ ($3,000\text{-cm}^{-1}$) region have also been recorded in high resolution^{49,59,61,62}. As an example, the high-resolution spectrum of the ν_1 mode of CD_2H^+ is shown in FIG. 5. Data (measured) from REF.⁶⁰.

vibrations⁴⁰. For the spectroscopy of the fundamental vibrational bands, proton transfer to molecular oxygen was more suitable, owing to its smaller endothermicity of 78 cm^{-1} (REF.⁴¹):



The rovibrational lines of H_3^+ are measured by counting the number of product O_2H^+ ions as a function of the laser frequency, which results in only three lines for these low-temperature experiments (FIG. 3a). The cryogenic operation in combination with a highly accurate frequency-comb system⁴² enabled measurements of transition frequencies for H_3^+ to sub-megahertz accuracy⁴³. Together with measurements obtained by NICE-OVHMS^{28,29}, among other techniques⁴⁴, a very accurate picture of this fundamental molecular ion is now available.

As H_3^+ is a key molecule for understanding astrochemistry, so too are its deuterated variants H_2D^+ , D_2H^+ and D_3^+ , which are heavily enriched in the ISM owing to isotopic fractionation effects^{45,46}. Differences in the zero-point energies of hydrogen species and their deuterated counterparts make exchange reactions that favour deuterated ionic products slightly exothermic:



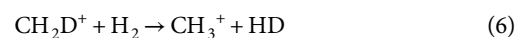
Owing to the low cosmic $[\text{HD}]/[\text{H}_2]$ ratio, this reaction (Eq. 4) produces considerable amounts of H_2D^+ only at very low temperatures (below ~ 20 K). A high $[\text{H}_2\text{D}^+]/[\text{H}_3^+]$ ratio can thus be invoked as an observational tracer of extremely cold conditions, that is, of times in cold molecular clouds shortly before a new star forms, which then destroys the H_2D^+ witness of this event.

The endothermicity of the reverse reaction,



can then be exploited in LIR experiments, in which the appearance of H_3^+ products indicates excitation of the parent H_2D^+ ions. In this way, the rovibrational^{43,47}, and even rotational^{48,49}, spectra of H_2D^+ and D_2H^+ were determined. The knowledge gained from these experiments, together with that from other pioneering laboratory investigations over the past four decades⁵⁰⁻⁵³, enabled the detection of these isotopologues in the ISM⁵⁴⁻⁵⁷ and, in particular, the measurement of the *ortho-para* ratio of their spin isomers. Owing to its sensitivity to the thermal history of an interstellar region, this ratio is an important probe of the age of interstellar sources undergoing star formation^{57,58}.

CH_3^+ isotopologues. Deuterium exchange reactions similar to those mentioned above can be applied for the high-resolution spectroscopy of isotopologues of CH_3^+ , as first demonstrated for CH_2D^+ (REF.⁵⁹):



By using such LIR schemes, all IR-active vibrational modes of CH_2D^+ , CD_2H^+ and CD_3^+ were recorded in low

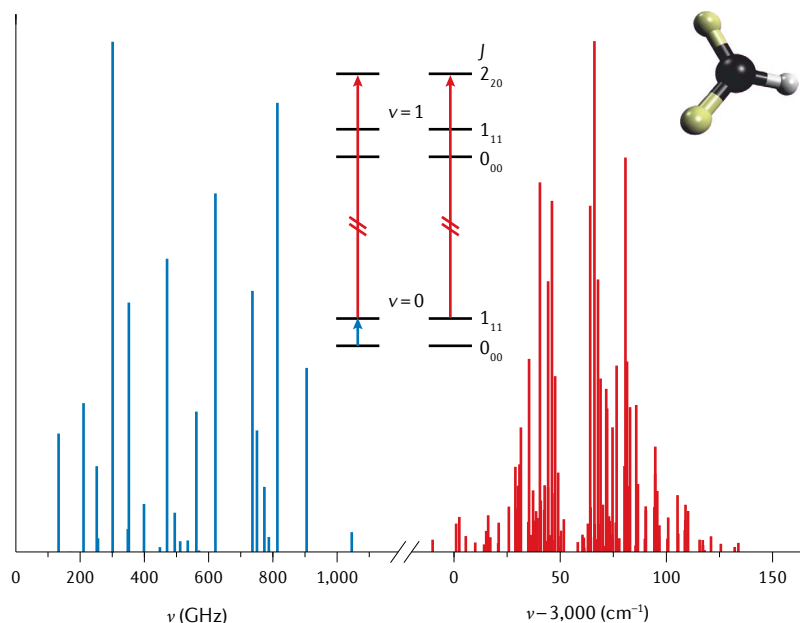


Fig. 5 | High-resolution spectra of CD_2H^+ . Stick spectra summarizing the 108 rovibrational (red, right) and 25 pure rotational (blue, left) lines recorded for CD_2H^+ (top right) in an ion-trap experiment⁴⁹. Note the different frequency (ν) units (cm^{-1} versus GHz) on the abscissa. The rovibrational lines belong to the ν_1 mode whose envelope is depicted in FIG. 4. The insets (where J and ν are the rotational angular momentum and vibrational quantum numbers, respectively) illustrate the applied spectroscopic methods: the rovibrational lines were measured using laser-induced reaction (LIR) (right), whereas the rotational lines were detected with a double-resonance scheme based on LIR (left). Adapted with permission from REF.⁴⁹, Elsevier.

resolution⁶⁰ and are shown in FIG. 4, together with a simulated CH_3^+ spectrum, based on the seminal work of the Oka group^{61,62}. Owing to the limited resolution in this experiment, only the contours of the vibrational bands could be resolved, but the availability of high-resolution lasers in the 3- μm region allows for the investigation of all C–H stretches in rovibrational detail^{49,59,61–63}. For example, the ν_1 stretch of CD_2H^+ was measured by using this approach⁴⁹ (FIG. 5). In this case, high resolution was obtained by applying an optical parametric oscillator as the light source and by cooling the investigated ions in a cryogenic ion trap.

More than 80% of known interstellar molecules were detected for the first time in the ISM by their pure rotational spectra¹, making their laboratory measurement a high priority. When a rovibrational action scheme such as LIR is feasible for a molecule, this can be extended by rotational excitation to a rotational–rovibrational double-resonance scheme to record pure rotational spectra. Such a double-resonance scheme was first demonstrated for H_2D^+ (REF.⁵⁹) and OH^- (REF.⁶⁴). Later, guided by the pioneering work of Amano in measuring the first rotational transitions for CH_2D^+ (REF.⁶⁵), the double-resonance method was exploited to obtain a complete set of high-resolution transitions for CH_2D^+ (REF.⁶⁶) and, subsequently, CD_2H^+ (REF.⁴⁹). For CD_2H^+ , the double-resonance measurement scheme can be explained using the example given in FIG. 5. As shown in the inset, a rovibrational transition (red arrow) was used to create a spectroscopic LIR signal. By scanning

the millimetre-wave frequency of a connected pure rotational transition (blue arrow), the signal was modulated and the rotational transition thus detected with a high signal-to-noise ratio. In this way, 25 rotational transitions of CD_2H^+ were detected in the range up to 1.1 THz (blue sticks in FIG. 5).

Similar to H_3^+ , the deuterium exchange processes of CH_3^+ and its isotopologues are thought to be responsible for the deuteration observed in the ISM. Owing to the relatively high exothermicity of the exchange reactions (for example, the reverse of Eq. 6 has an exothermicity of $>400\text{ K}$)⁶⁷, deuteration can occur even at elevated ISM temperatures ($20\text{ K} < T < 80\text{ K}$). Although a complete and high-resolution data set now exists for the rotational transitions of the CH_3^+ family of molecules, the hypothesized interstellar deuteration via CH_3^+ , unfortunately, rests on weak grounds, as attempts to detect the cationic species involved have so far failed^{67,68}.

Laser-induced inhibition of complex growth

One limitation of the LIR method is the need for an endothermic chemical reaction with a neutral reaction partner that does not condense at the temperature of the cryogenic trap (normally H_2). An alternative, and more generally applicable, action technique is laser-induced inhibition of complex growth (LIICG). This technique emerged with the advent of ion traps cooled to 4 K and exploits the fact that excitation of a stored cation inhibits attachment of He in a cryogenic He bath, as pioneered by Maier, Gerlich and co-workers⁶⁹. The main challenge of this technique lies in the cooling of the parent ions, such that a considerable fraction forms weakly bound complexes with He. As an example, the transitions of the H_3^+ ion measured using LIICG are shown in FIG. 3b. The LIICG lines are measured by counting the number of H_3^+ –He complexes as a function of the excitation frequency. When the excitation frequency is on-resonance with a H_3^+ transition, the molecules do not undergo complexation, and the number of H_3^+ –He complexes in the trap is reduced. The LIICG signals then appear as narrow Gaussian dips in the number of H_3^+ –He counts. As this is not a background-free method, the LIICG lines exhibit a signal-to-noise ratio inferior to those of the LIR method. Nevertheless, LIICG is an indispensable alternative for molecular ions for which no suitable LIR scheme has been found. Beyond H_3^+ (REFS^{43,70}), LIICG has been applied to measure the rovibrational spectrum of the enigmatic CH_5^+ molecule^{71,72}, and has since been applied to many additional cations^{49,73–75}.

Among these additional species is CH^+ (REF.⁷³), which was among the first molecules, and the first molecular ion, detected in the ISM (through its electronic transitions)^{76,77}. Since then, it has been recognized to be widespread in the ISM and has also been observed by its rotational fingerprints^{78–80}. Only recently has CH^+ been detected by its vibrational transitions in the IR region, and indeed in the same source in which the first high- J rotational emission (where J is the rotational angular momentum quantum number) was detected⁷⁸. By serendipity, CH^+ was observed through its IR emission lines in the hot expanding shell of the planetary nebula NGC 7027 in a search that was originally designed to target

the IR signatures of the HeH^+ ion^{81,82}. The detected R(0) line of CH^+ is shown in FIG. 6, and compared with the laboratory LIICG measurement of this same transition, which is the only IR laboratory detection as yet.

Rotational-state-dependent complex formation

In 2012, a series of regularly spaced, unidentified rotational emission lines was detected in astronomical observations of the Horsehead Nebula photodissociation region with the IRAM 30-m telescope⁸³. The spectral pattern could be well described by a linear molecule with a rotational constant of $B = 11,244$ MHz. On the basis of the chemical and physical conditions of the region, and comparison with quantum chemical calculations, it was speculated that the carrier was C_3H^+ . Subsequent astronomical and quantum chemical studies have either supported the assignment through chemical arguments^{84–86} or suggested as an alternative the molecular anion C_3H^- (REFS^{87,88}).

Laboratory efforts to precisely measure the frequencies of the rotational emission lines and confirm the carrier were challenging in terms of producing the molecule and in detecting its rotational transitions, which proved to be extremely weak. The first tentative laboratory detection and assignment (to C_3H^+) was reported as a personal communication (K. N. Crabtree, 2013) in REF.⁸⁵ and published in full 2 years later⁸⁹. Rather than producing the molecule in a discharge cell, as Oka did for H_3^+ , a type of high-voltage discharge coupled to a supersonic expansion source, as pioneered by McCarthy

et al.⁹⁰, was used. These latter sources provide rotationally cold (a few Kelvin) molecules by adiabatically expanding a short pulse of high-pressure gas through a pinhole nozzle (1 mm in diameter) into a high-vacuum chamber. By attaching a narrow nozzle immediately after the pinhole, and coupling with high-voltage electrodes, a plasma discharge strikes during the pulse that ionizes the sample, generating ions directly from neutral gases and also permitting the generation of new species, both ions and neutral molecules, by dissociation in the discharge and subsequent reactions in the supersonic expansion. Rather than a direct-absorption technique, the rotationally cold product species were then probed using cavity-enhanced FTMW spectroscopy⁹¹. This well-established experimental method has enabled the rotational spectroscopic characterization of a multitude of protonated^{92,93} and anionic species^{94,95}.

Another variant of action spectroscopy was used to definitively identify C_3H^+ as the carrier of the astronomical lines. This method relies on the rotational-state-dependent attachment of rare gas atoms (ROSAA) to cold molecular ions, as outlined in detail in REFS^{96,97}. Briefly, hydrocarbon ions were produced by electron impact ionization of allene (C_3H_4) in a storage-ion source, then mass-selected, injected into the cryogenic ion trap, and cooled to the ambient temperature of 4.1 K through collisions with He gas. Under these conditions, the ions form weakly bound complexes with the He atoms through ternary collision processes. These complexes are also destroyed in binary collisions with He, quickly reaching a steady-state concentration of parent and cluster ions.

Unlike in LIICG, in which cluster formation is inhibited for the vibrationally excited ions, in ROSAA the He attachment rate, and thus the steady-state concentration, depends on the rotational state of the ion. As a consequence, the number of cluster ions is modified when the parent ion is rotationally excited by irradiation with microwave or terahertz radiation on-resonance with a rotational transition. The spectrum is then read out as a fractional change in the number of ion–He complexes versus frequency (see, for example, the spectra for C_3H^+ in FIG. 7). The relative change in the number of ion–He complexes formed depends not only on the photon absorption cross section, but also on the relative population of a specific targeted rotational level, the achievable population change between rotational levels and the change in the attachment rate for these levels. In the case of C_3H^+ , the observed relative change was only a few per cent (FIG. 7).

Despite these challenges and limitations, ROSAA has proved to be a versatile tool for rotational spectroscopy of molecular ions and, in particular, for reactive ions that are extremely difficult to produce in high enough number densities for conventional absorption or FTMW spectroscopy. Several more recent examples include the deuterated ammonium^{98,99} and methylum ions⁴⁹, isotopes of CH^+ (REFS^{73,97}), HCO^+ (REFS^{97,100}) and CN^+ (REF.¹⁰¹), as well as SiH^+ (REF.¹⁰²), CO^+ (REF.⁹⁷) and CF^+ (REF.⁹⁸). The technique has also recently been further developed by implementing a double-resonance scheme for the rotational (and rovibrational) characterization of

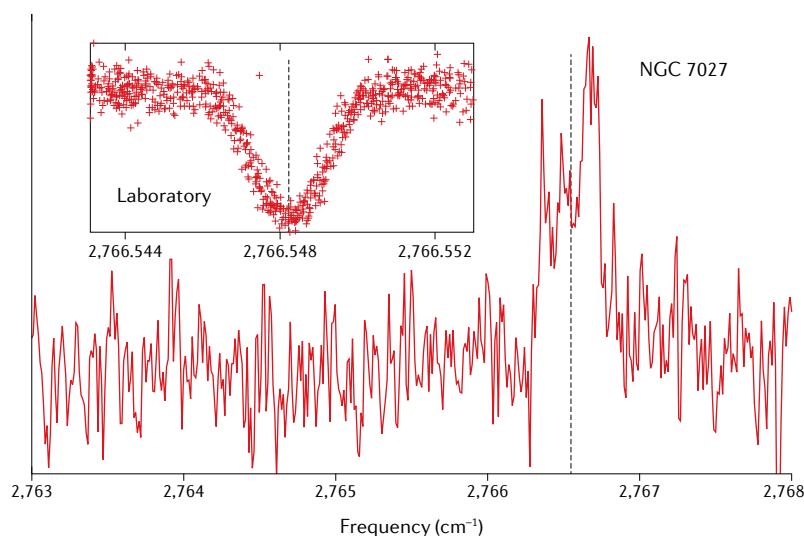


Fig. 6 | **Laboratory and space detection of CH^+ in the infrared.** Spectra showing the laboratory (inset) and space detection of the R(0) transition of CH^+ (REFS^{73,81}). For the laboratory measurement, CH^+ –He complexes were counted as a function of the irradiating frequency, using the laser-induced inhibition of complex growth (LIICG) method. The interstellar emission spectrum was acquired with the iSHELL spectrograph at the NASA Infrared Telescope Facility towards the NGC 7027 planetary nebula. The laboratory spectral profile is a very narrow Gaussian owing to the 4-K cold trapped ion ensemble, whereas the astronomical signal is broadened (note the difference in wavenumber scale) because of the Doppler shift caused by the fast motion of the CH^+ ions in the hot expanding shell of NGC 7027. The rest frequency as measured in the laboratory is shown as a vertical black dashed line in both traces. Although the detail of a single transition is shown here, the identification of CH^+ and other molecules in interstellar spectra is typically supported by many such lines. Data (space) from REF.⁸¹.

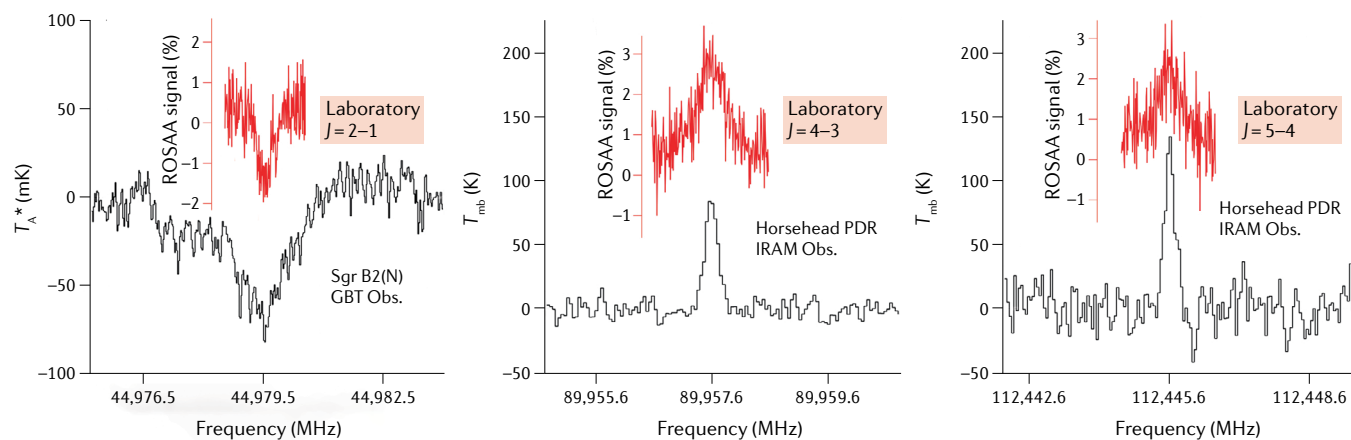


Fig. 7 | Laboratory and space detection of C_3H^+ . Green Bank Telescope (GBT) observations of the high-mass star-forming region Sagittarius (Sgr) B2(N) (left, black) from the PRIMOS Project¹¹², showing the absorption signal attributed to the $J = 2-1$ transition (where J is the rotational angular momentum quantum number) of C_3H^+ (REF.⁸⁴). Observations of the Horsehead photodissociation region (PDR) using the IRAM telescope⁸³ (centre and right, black) attributed to the $J = 4-3$ and $J = 5-4$ transitions (in emission). The laboratory measurements of the corresponding C_3H^+ transitions made using the rotational-state-dependent attachment of

rare gas atoms (ROSAA) technique are overplotted in red⁹⁶. The ROSAA signals are vertically offset and inverted for clarity. The laboratory linewidths are dominated by power-broadening effects. By contrast, the observed line profile towards Sgr B2(N) is due to absorbing foreground gas with different velocity components, and the narrow linewidths in the Horsehead PDR are caused mainly by the turbulent motion of the emitting gas. T_A^* , intensity as antenna temperature; T_{mb} , intensity as main beam brightness temperature. Data from REFS^{83,84} (observational) and REF.⁹⁶ (laboratory).

the $CH_2NH_2^+$ ion⁷⁵, allowing its application to an even wider class of molecular ions.

Future perspectives

The development of ion spectroscopy and associated laboratory techniques has led to the detection of numerous molecular ions in the ISM. Indeed, several species that have long been speculated to be key reaction intermediates (FIG. 1) have since been identified on the basis of laboratory spectra acquired through techniques outlined in this Review. These identifications now allow not only the detection of these species, but also the determination of their abundances and physical conditions. This information can then be compared to astrochemical models designed to simulate our understanding of the reaction pathways in the ISM. The agreement, or lack thereof, with the models in turn reveals which reaction pathways warrant further study. Ions are often one of the most crucial intermediates, making their chemistry particularly impactful on the wider chemical network.

FIGURE 1 shows a bottom-up version of interstellar chemistry, in which species are formed from the most abundant, primary ions, such as H_3^+ . Despite the tremendous success of this approach and the recent detection of many molecular ions, numerous important ions remain to be detected. Among these, are the deuterated isotopologues of CH_3^+ , for which detailed laboratory spectra are now available but are hard to find in observations owing to detection limits, even in the age of the ALMA and NOEMA observatories.

The spectra of many more ions have yet to be recorded in the laboratory. The end products of chemical evolution are key species in the reaction scheme in FIG. 1 and form when, for example, an ion is completely hydrogenated, as in the case of CH_5^+ . Through action spectroscopy, considerable progress has been made in deciphering the rich spectrum of CH_5^+ . Owing to

the equivalence of the five protons in this very floppy molecule, the spectrum contains contributions from three nuclear spin isomers, which have begun to be untangled⁷². However, even at low temperatures, the spectrum remains complex, in part owing to the interplay between the end-over-end rotation of the almost spherical molecule and the fluxional nature of its internal rotation. Despite these difficulties, the methods described here, in particular the double-resonance method in action spectroscopy, may finally enable the determination of the lowest energy transitions, and thus perhaps the best candidates for interstellar detection, in this elusive molecule.

Perhaps more crucially, the end products in FIG. 1 are thought to be precursors to a host of yet more complex molecules. For example, the protonation of possibly the most widespread complex species, methanol (CH_3OH), to form $CH_3OH_2^+$ is thought to be central to understanding how molecules of even greater complexity, such as precursors of amino acids, could be formed in abundances that would enable their detection⁹. In the laboratory, chemical reactions to establish a LIR scheme would involve condensable gases and thus would require modifications of the trap instrument to allow overlap of the trap volume with a molecular beam carrying the neutral reaction partner to prevent its freezing to the cold trap wall. Such a development would provide access to the spectroscopy of many more molecular ions, even beyond the scope of astrochemistry. Indeed, preliminary results in recording low-resolution spectra of $CH_3OH_2^+$ with the approach used for CH_3^+ and its isotopologues appear promising¹⁰³. Therefore, the next important step is to record the high-resolution rovibrational spectrum of $CH_3OH_2^+$.

It should also be noted that FIG. 1 is only one way of looking at astrochemistry. Although bottom-up pathways are certain to be efficient for the formation of

relatively small molecules from more abundant elements, a top-down route to molecular complexity involves the destruction of large molecules or (very) small grains. After the detection of interstellar C_{60} (REF.¹⁰⁴), the logical next step was to search for the C_{60}^+ ion. C_{60}^+ has long been considered as a possible carrier of the diffuse interstellar bands (DIBs), a widespread forest of unidentified absorption features first discovered by Mary Lea Heger in 1919 and seen in diffuse gas within the galaxy¹⁰⁵. Nearly eight decades later, two of the strongest DIB features were assigned¹⁰⁶ to an electronic absorption in C_{60}^+ on the basis of early matrix measurements¹⁰⁷. Almost a century after the discovery of the DIBs, this assignment was confirmed through the measurement of the electronic spectrum of C_{60}^+ in an ion-trap experiment involving the pre-dissociation of a

complex of C_{60}^+ with He atoms¹⁰⁸, employing yet another method of action spectroscopy in ion traps.

In addition to its being the first definitively identified DIB, the discovery of C_{60}^+ in sizable amounts raises questions regarding the chemical routes for its production and whether such a large species may be the top-down source for chemically enriching the ISM. Regardless, this detection and many other recent successes highlight the continuing need to develop more sensitive and more accurate laboratory methods for the spectroscopic characterization of molecular ions. Although challenging to study both in the laboratory and observationally, they undoubtedly have key roles in the chemical evolution of the Universe, and are thus crucial species to observe and understand.

Published online 7 July 2020

- McGuire, B. A. 2018 census of interstellar, circumstellar, extragalactic, protoplanetary disk, and exoplanetary molecules. *Astrophys. J. Suppl. Ser.* **239**, 17 (2018).
This work presents an overview of all known interstellar molecules, providing statistics on ions in relation to other types of species.
- Watson, W. D. The rate of formation of interstellar molecules by ion–molecule reactions. *Astrophys. J.* **183**, L17–L20 (1973).
This paper describes ion–molecule reactions in space.
- Geppert, W. D. et al. Dissociative recombination of protonated methanol. *Faraday Discuss.* **133**, 177–190 (2006).
- Martin, D. W., McDaniel, E. W. & Meeks, M. L. On the possible occurrence of H_3^+ in interstellar space. *Astrophys. J.* **134**, 1012–1013 (1961).
- Herbst, E. & Klemperer, W. The formation and depletion of molecules in dense interstellar clouds. *Astrophys. J.* **185**, 505–533 (1973).
- Oka, T. Observation of the infrared spectrum of H_3^+ . *Phys. Rev. Lett.* **45**, 531–534 (1980).
This study reports the laboratory measurement of H_3^+ spectra using several techniques in tandem.
- Geballe, T. R. & Oka, T. Detection of H_3^+ in interstellar space. *Nature* **384**, 334–335 (1996).
- Herbst, E. & van Dishoeck, E. F. Complex organic interstellar molecules. *Annu. Rev. Astron. Astrophys.* **47**, 427–480 (2009).
- Garrod, R. T. A three-phase chemical model of hot cores: the formation of glycine. *Astrophys. J.* **765**, 60 (2013).
- Balucani, N. et al. A theoretical investigation of the reaction between the amidogen, NH, and the ethyl, C_2H_5 , radicals: a possible gas-phase formation route of interstellar and planetary ethanimine. *Mol. Astrophys. J.* **13**, 30–37 (2018).
- Woods, R. C., Dixon, T. A., Saykally, R. J. & Szanto, P. G. Laboratory microwave spectrum of HCO^+ . *Phys. Rev. Lett.* **35**, 1269–1272 (1975).
- White, J. U. Long optical paths of large aperture. *J. Opt. Soc. Am.* **32**, 285–288 (1942).
- Herrriott, D., Kogelnik, H. & Kompfner, R. Off-axis paths in spherical mirror interferometers. *Appl. Opt.* **3**, 523–526 (1964).
- Drouin, B. J., Fischer, J. & Gamache, R. R. Temperature dependent pressure induced lineshape of O_3 rotational transitions in air. *J. Quant. Spectrosc. Radiat. Transf.* **83**, 63–81 (2004).
- Kotterer, M., Conceicao, J. & Maier, J. P. Cavity ringdown spectroscopy of molecular ions: $A^2\Pi_u \leftarrow X^2\Sigma_g^+$ (6–0) transition of N_2^+ . *Chem. Phys. Lett.* **259**, 233–236 (1996).
- Macko, P. et al. Afterglow studies of H_3^+ ($v=0$) recombination using time resolved cw-diode laser cavity ring-down spectroscopy. *Int. J. Mass. Spectrom.* **233**, 299–304 (2004).
- Dohnal, P. et al. Towards state selective recombination of H_3^+ under astrophysically relevant conditions. *Faraday Discuss.* **217**, 220–234 (2019).
- Siller, B. M., Porambo, M. W., Mills, A. A. & McCall, B. J. Noise immune cavity enhanced optical heterodyne velocity modulation spectroscopy. *Opt. Express* **19**, 24822–24827 (2011).
- Ye, J., Ma, L.-S. & Hall, J. L. Ultrasensitive detections in atomic and molecular physics: demonstration in molecular overtone spectroscopy. *J. Opt. Soc. Am. B* **15**, 6–15 (1998).
This paper provides a detailed description of the NICE-OHMS technique.
- Gudeman, C. S., Begemann, M. H., Pfaff, J. & Saykally, R. J. Velocity-modulated infrared laser spectroscopy of molecular ions: the ν_1 band of HCO^+ . *Phys. Rev. Lett.* **50**, 727–731 (1983).
- Owrutsky, J. C., Rosenbaum, N. H., Tack, L. M. & Saykally, R. J. The vibration–rotation spectrum of the hydroxide anion (OH^-). *J. Chem. Phys.* **83**, 5338–5339 (1985).
- Stephenson, S. K. & Saykally, R. J. Velocity modulation spectroscopy of ions. *Chem. Rev.* **105**, 3220–3234 (2005).
This paper provides a detailed description of velocity modulation techniques.
- Markus, C. R. et al. High precision rovibrational spectroscopy of OH^+ . *Astrophys. J.* **817**, 138 (2016).
- Perry, A. J., Hodges, J. N., Markus, C. R., Kocheril, G. D. & McCall, B. J. Communication: high precision sub-Doppler infrared spectroscopy of the HeH^+ ion. *J. Chem. Phys.* **141**, 101101 (2014).
- Markus, C. R., Kocheril, P. A. & McCall, B. J. Sub-Doppler rovibrational spectroscopy of the ν_1 fundamental band of D_2H^+ . *J. Mol. Spectrosc.* **355**, 8–13 (2019).
- Markus, C. R., Perry, A. J., Hodges, J. N. & McCall, B. J. Improving cavity-enhanced spectroscopy of molecular ions in the mid-infrared with up-conversion detection and Brewster-plate spoilers. *Opt. Express* **25**, 3709–3721 (2017).
- Crabtree, K. N. et al. Sub-Doppler mid-infrared spectroscopy of molecular ions. *Chem. Phys. Lett.* **551**, 1–6 (2012).
- Hodges, J. N., Perry, A. J., Jenkins II, P. A., Siller, B. M. & McCall, B. J. High-precision and high-accuracy rovibrational spectroscopy of molecular ions. *J. Chem. Phys.* **139**, 164201 (2013).
- Markus, C. R. & McCall, B. J. Highly accurate experimentally determined energy levels of H_3^+ . *J. Chem. Phys.* **150**, 214303 (2019).
- Perry, A. J., Hodges, J. N., Markus, C. R., Kocheril, G. S. & McCall, B. J. High-precision R-branch transition frequencies in the ν_2 fundamental band of H_3^+ . *J. Mol. Spectrosc.* **317**, 71–73 (2015).
- Laas, J. C., Hays, B. M. & Widicus Weaver, S. L. Multipass millimeter/submillimeter spectrometer to probe dissociative reaction dynamics. *J. Phys. Chem. A* **117**, 9548–9554 (2013).
- Okumura, M., Yeh, L. I. & Lee, Y. T. The vibrational predissociation spectroscopy of hydrogen cluster ions. *J. Chem. Phys.* **83**, 3705–3706 (1985).
This study demonstrates action spectroscopy using predissociation in an ion trap.
- Dopfer, O., Olkhov, R. & Maier, J. Microsolvation of the methyl cation in neon: infrared spectra and ab initio calculations of CH_3^+-Ne and $CH_3^+-Ne_2$. *J. Chem. Phys.* **112**, 2176–2186 (2000).
- Brümmer, M., Kaposta, C., Santambrogio, G. & Asmis, K. R. Formation and photodepletion of cluster ionmessenger atom complexes in a cold ion trap: infrared spectroscopy of VO^+ , VO_2^+ , and VO_3^+ . *J. Chem. Phys.* **119**, 12700 (2003).
This study reports the tagging of cations with He in an ion trap.
- Oomens, J., van Roij, A., Meijer, G. & von Helden, G. Gas phase infrared photodissociation spectroscopy of cationic polyaromatic hydrocarbons. *Astrophys. J.* **542**, 404–410 (2000).
- Asmis, K. R. et al. Gas-phase infrared spectrum of the protonated water dimer. *Science* **299**, 1375–1377 (2003).
- Boyarkin, O. V., Mercier, S. R., Kamariotis, A. & Rizzo, T. R. Electronic spectroscopy of cold, protonated tryptophan and tyrosine. *J. Am. Chem. Soc.* **128**, 2816–2817 (2006).
- Schlemmer, S., Kuhn, T., Lescop, E. & Gerlich, D. Laser excited N_2^+ in a 22-pole ion trap: experimental studies of rotational relaxation processes. *Int. J. Mass. Spectrom.* **185–187**, 589–602 (1999).
This is the proof-of-principle of LIR in a cryogenic ion trap.
- Schlemmer, S., Lescop, E., von Richthofen, J. & Gerlich, D. Laser induced reactions in a 22-pole ion trap: $C_2H_3^+ + hv_2 + H_2 \rightarrow C_2H_5^+ + H$. *J. Chem. Phys.* **117**, 2068–2075 (2002).
- Mikosch, J. et al. Action spectroscopy and temperature diagnostics of H_3^+ by chemical probing. *J. Chem. Phys.* **121**, 11030–11037 (2004).
- Kluge, L. et al. Transfer of a proton between H_2 and O_2 . *Phil. Trans. R. Soc. A* **370**, 5041–5054 (2012).
- Asvany, O., Krieg, J. & Schlemmer, S. Frequency comb assisted mid-infrared spectroscopy of cold molecular ions. *Rev. Sci. Instrum.* **83**, 093110 (2012).
- Jusko, P., Konietzko, C., Schlemmer, S. & Asvany, O. Frequency comb assisted measurement of fundamental transitions of cold H_3^+ , H_2D^+ and D_2H^+ . *J. Mol. Spectrosc.* **319**, 55–58 (2016).
- Guan, Y.-C. et al. Precision saturated absorption spectroscopy of H_3^+ . *J. Chem. Phys.* **148**, 124310 (2018).
- Millar, T. J. Deuterium fractionation in interstellar clouds. *Space Sci. Rev.* **106**, 73–86 (2003).
- Caselli, P., Sipilä, O. & Harju, J. Deuterated forms of H_3^+ and their importance in astrochemistry. *Phil. Trans. R. Soc. A* **377**, 20180401 (2019).
- Asvany, O. et al. Overtone spectroscopy of H_2D^+ and D_2H^+ using laser induced reactions. *J. Chem. Phys.* **127**, 154517 (2007).
- Asvany, O. et al. High-resolution rotational spectroscopy in a cold ion trap: H_2D^+ and D_2H^+ . *Phys. Rev. Lett.* **100**, 233004 (2008).
Demonstration of rotational action spectroscopy.
- Jusko, P. et al. High-resolution vibrational and rotational spectroscopy of CD_3H^+ in a cryogenic ion trap. *J. Mol. Spectrosc.* **332**, 59–66 (2017).
- Bogey, M., Demuynck, C., Denis, M., Destombes, J. L. & Lemoine, B. Laboratory measurement of the $1_{01}-1_{11}$ submillimeter line of H_2D^+ . *Astron. Astrophys.* **137**, L15–L16 (1984).
- Amano, T. & Hirao, T. Accurate rest frequencies of submillimeter-wave lines of H_2D^+ and D_2H^+ . *J. Mol. Spectrosc.* **233**, 7–14 (2005).
- Hirao, T. & Amano, T. Laboratory submillimeter-wave detection of D_2H^+ : a new probe into multiple deuteration? *Astrophys. J.* **597**, L85–L87 (2003).

53. Yonezu, T., Matsushima, F., Moriawaki, Y., Takagi, K. & Amano, T. THz spectroscopy of H_2D^+ . *J. Mol. Spectrosc.* **256**, 238–241 (2009).
54. Stark, R., van der Tak, F. F. & van Dishoeck, E. F. Detection of interstellar H_2D^+ emission. *Astrophys. J.* **521**, L67–L70 (1999).
55. Vastel, C., Phillips, T. G. & Yoshida, H. Detection of D_3H^+ in the dense interstellar medium. *Astrophys. J.* **606**, L127–L130 (2004).
56. Parise, B., Belloche, A., Du, F., Güsten, R. & Menten, K. M. Extended emission of D_3H^+ in a prestellar core. *Astron. Astrophys.* **526**, A31 (2011).
57. Brünken, S. et al. H_2D^+ observations give an age of at least one million years for a cloud core forming Sun-like stars. *Nature* **516**, 219–221 (2014).
This paper highlights the importance of combining laboratory, modelling and observational efforts.
58. Harju, J. et al. Detection of interstellar ortho- D_3H^+ with SOFIA. *Astrophys. J.* **840**, 63 (2017).
59. Gärtner, S. et al. High-resolution spectroscopy of CH_2D^+ in a cold 22-pole ion trap. *J. Phys. Chem. A* **117**, 9975–9984 (2013).
60. Asvany, O., Thorwirth, S., Redlich, B. & Schlemmer, S. Spectroscopy of the low-frequency vibrational modes of CH_2^+ isotopologues. *J. Mol. Spectrosc.* **347**, 1–6 (2018).
61. Crofton, M. W., Jagod, M., Rehfuss, B. D., Kreiner, W. A. & Oka, T. Infrared spectroscopy of carbo-ions. III. ν_3 band of methyl cation CH_3^+ . *J. Chem. Phys.* **88**, 666 (1988).
62. Jagod, M.-F., Rösslein, M., Gabrys, C. M. & Oka, T. Infrared spectroscopy of carbo-ions: the ν_1 and ν_2 bands of CH_2D^+ , and the ν_1 band of CHD_2^+ . *J. Mol. Spectrosc.* **153**, 666–679 (1992).
63. Roesslein, M., Jagod, M. F., Gabrys, G. M. & Oka, T. Laboratory infrared spectra of CH_2D^+ and HCCD^+ and predicted microwave transitions. *Astrophys. J.* **382**, L51–L53 (1991).
64. Jusko, P., Asvany, O., Wallerstein, A.-C., Brünken, B. & Schlemmer, S. Two photon rotational action spectroscopy of cold OH^- at 1 ppb accuracy. *Phys. Rev. Lett.* **112**, 253005 (2014).
65. Amano, T. Submillimetre-wave spectrum of CH_2D^+ . *Astron. Astrophys.* **516**, L4 (2010).
66. Töpfer, M., Jusko, P., Schlemmer, S. & Asvany, O. Double resonance rotational spectroscopy of CH_2D^+ . *Astron. Astrophys.* **593**, L11 (2016).
67. Roueff, E. et al. CH_2D^+ , the search for the holy grail. *J. Phys. Chem. A* **117**, 9959–9967 (2013).
68. Indriolo, N., Oka, T., Geballe, T. R. & McCall, B. J. Constraining the environment of CH^+ formation with CH_2^+ observations. *Astrophys. J.* **711**, 1338–1342 (2010).
69. Chakrabarty, S. et al. A novel method to measure electronic spectra of cold molecular ions. *J. Phys. Chem. Lett.* **4**, 4051–4054 (2013).
70. Savić, I., Gerlich, D., Asvany, O., Jusko, P. & Schlemmer, S. Controlled synthesis and analysis of HeH_3^+ in a 3.7 K ion trap. *Mol. Phys.* **113**, 2320–2332 (2015).
71. Asvany, O., Brünken, S., Kluge, L. & Schlemmer, S. COLTRAP: a 22-pole ion trapping machine for spectroscopy at 4 K. *Appl. Phys. B* **114**, 203–211 (2014).
This paper reports vibrational LIICG, demonstrated for protonated methane.
72. Asvany, O., Yamada, K. M. T., Brünken, S., Potapov, A. & Schlemmer, S. Experimental ground-state combination differences of CH_3^+ . *Science* **347**, 1346–1349 (2015).
73. Doménech, J. L., Jusko, P., Schlemmer, S. & Asvany, O. The first laboratory detection of vibration-rotation transitions of $^{12}\text{CH}^+$ and $^{13}\text{CH}^+$ and improved measurement of their rotational transition frequencies. *Astrophys. J.* **857**, 61 (2018).
74. Kohguchi, H., Jusko, P., Yamada, K. M. T., Schlemmer, S. & Asvany, O. High-resolution infrared spectroscopy of O_3H^+ in a cryogenic ion trap. *J. Chem. Phys.* **148**, 144303 (2018).
75. Markus, C. R., Thorwirth, S., Asvany, O. & Schlemmer, S. High-resolution double resonance action spectroscopy in ion traps: vibrational and rotational fingerprints of CH_2NH_2^+ . *Phys. Chem. Chem. Phys.* **21**, 26406–26412 (2019).
76. Dunham, T. J. Interstellar neutral potassium and neutral calcium. *Publ. Astron. Soc. Pac.* **49**, 26–28 (1937).
77. Douglas, A. E. & Herzberg, G. Note on CH^+ in interstellar space and in the laboratory. *Astrophys. J.* **94**, 381 (1941).
78. Cernicharo, J. et al. Discovery of far-infrared pure rotational transitions of CH^+ in NGC 7027. *Astrophys. J. Lett.* **483**, L65–L68 (1997).
79. Falgarone, E., Phillips, T. G. & Pearson, J. C. First detection of $^{13}\text{CH}^+$ ($J=1-0$). *Astrophys. J. Lett.* **634**, L149–L152 (2005).
80. Amano, T. The $J=1-0$ transitions of $^{12}\text{CH}^+$, $^{13}\text{CH}^+$, and $^{12}\text{CD}^+$. *Astrophys. J. Lett.* **716**, L1–L3 (2010).
81. Neufeld, D. A. et al. Detection of vibrational emissions from the helium hydride ion (HeH^+) in the planetary nebula NGC 7027. *Astrophys. J.* **894**, 37 (2020).
82. Güsten, R. et al. Astrophysical detection of the helium hydride ion HeH^+ . *Nature* **568**, 357–359 (2019).
83. Pety, J. et al. The IRAM-30 m line survey of the Horsehead PDR. *Astron. Astrophys.* **548**, A68 (2012).
84. McGuire, B. A. et al. A search for $I\text{-C}_3\text{H}^+$ and $I\text{-C}_3\text{H}$ in Sgr B2(OH), and the dark cloud TMC-1. *Astrophys. J.* **774**, 56 (2013).
85. McGuire, B. A. et al. An observational investigation of the identity of B11244 ($I\text{-C}_3\text{H}^+/\text{C}_3\text{H}^+$). *Astrophys. J.* **783**, 36 (2014).
86. McGuire, B. A. et al. A CSO search for $I\text{-C}_3\text{H}^+$: detection in the Orion bar PDR. *Mon. Not. R. Astron. Soc.* **442**, 2901–2908 (2014).
87. Huang, X., Fortenberry, R. C. & Lee, T. J. Spectroscopic constants and vibrational frequencies for $I\text{-C}_3\text{H}^+$ and isotopologues from highly accurate quartic force fields: the detection of $I\text{-C}_3\text{H}^+$ in the Horsehead Nebula PDR questioned. *Astrophys. J.* **768**, L25 (2013).
88. Fortenberry, R. C., Huang, X., Crawford, T. D. & Lee, T. J. High-accuracy quartic force field calculations for the spectroscopic constants and vibrational frequencies of $1^1\text{A}'\text{-C}_3\text{H}^+$: a possible link to lines observed in the Horsehead Nebula photodissociation region. *Astrophys. J.* **772**, 39 (2013).
89. McCarthy, M. C. et al. A laboratory study of C_3H^+ and the C_3H radical in three new vibrationally excited $^2\Sigma$ states using a pin-hole nozzle discharge source. *Astrophys. J. Suppl. Ser.* **217**, 10 (2015).
90. McCarthy, M. C., Chen, W., Travers, M. J. & Thaddeus, P. Microwave spectra of 11 polyyne carbon chains. *Astrophys. J. Suppl. Ser.* **129**, 611–623 (2000).
91. Balle, T. J. & Flygare, W. H. Fabry–Perot cavity pulsed Fourier transform microwave spectrometer with a pulsed nozzle particle source. *Rev. Sci. Instrum.* **52**, 33–45 (1981).
92. Ohshima, Y. & Endo, Y. Rotational spectroscopy of jet-cooled molecular ions and ion complexes. *Chem. Phys. Lett.* **256**, 635–640 (1996).
93. Lattanzi, V., Thorwirth, S., Gottlieb, C. A. & McCarthy, M. C. Two isomers of protonated isocyanic acid: evidence for an ion–molecule pathway for $\text{HNCO} \leftrightarrow \text{HOCN}$ isomerization. *J. Phys. Chem. Lett.* **3**, 3420–3424 (2012).
94. McCarthy, M. C., Gottlieb, C. A., Gupta, H. & Thaddeus, P. Laboratory and astronomical identification of the negative molecular ion C_6H^- . *Astrophys. J.* **652**, L141–L144 (2006).
95. Gupta, H. et al. Rotational spectra of the carbon chain negative ions C_4H^- and C_6H^- . *Astrophys. J.* **655**, L57–L60 (2007).
96. Brünken, S., Kluge, L., Stoffels, A., Asvany, O. & Schlemmer, S. Laboratory rotational spectrum of $I\text{-C}_3\text{H}^+$ and confirmation of its astronomical detection. *Astrophys. J.* **783**, L4 (2014).
Application of the ROSAA method, confirming the presence of a key ionic intermediate in the ISM.
97. Brünken, S., Kluge, L., Stoffels, A., Pérez-Ríos, J. & Schlemmer, S. Rotational state-dependent attachment of He atoms to cold molecular ions: an action spectroscopic scheme for rotational spectroscopy. *J. Mol. Spectrosc.* **332**, 67–78 (2017).
98. Stoffels, A., Kluge, L., Schlemmer, S. & Brünken, S. Laboratory rotational ground state transitions of NH_2D^+ and CF^+ . *Astron. Astrophys.* **593**, A56 (2016).
99. Doménech, J. L., Schlemmer, S. & Asvany, O. Accurate rotational rest frequencies for ammonium ion isotopologues. *Astrophys. J.* **866**, 158 (2018).
100. Salomon, T. et al. Double resonance rotational spectroscopy of He-HCO^+ . *Phys. Chem. Chem. Phys.* **21**, 3440–3445 (2019).
101. Thorwirth, S., Schreier, P., Salomon, T., Schlemmer, S. & Asvany, O. Pure rotational spectrum of CN^+ . *Astrophys. J. Lett.* **882**, L6 (2019).
102. Doménech, J. L., Schlemmer, S. & Asvany, O. Accurate frequency determination of vibration-rotation and rotational transitions of SiH^+ . *Astrophys. J.* **849**, 60 (2017).
103. Jusko, P. et al. The FELIX cryogenic ion trap beam line at the FELIX free-electron laser facility: infrared signatures of primary alcohol cations. *Faraday Discuss.* **217**, 172–202 (2019).
104. Cami, J., Bernard-Salas, J., Peeters, E. & Malek, S. E. Detection of C_{60} and C_{60}^+ in a young planetary nebula. *Science* **329**, 1180–1182 (2010).
105. McCall, B. J. & Griffin, R. E. On the discovery of the diffuse interstellar bands. *Proc. R. Soc. A* **469**, 20120604 (2013).
106. Foing, B. H. & Ehrenfreund, P. Detection of two interstellar absorption bands coincident with spectral features of C_{60}^+ . *Nature* **369**, 296–298 (1994).
107. Fulara, J., Jakobi, M. & Maier, J. P. Electronic and infrared spectra of C_{60}^+ and C_{60} in neon and argon matrices. *Chem. Phys. Lett.* **211**, 227–234 (1993).
108. Campbell, E. K., Holz, M., Gerlich, D. & Maier, J. P. Laboratory confirmation of C_{60}^+ as the carrier of two diffuse interstellar bands. *Nature* **523**, 322–323 (2015).
109. McCall, B. J. *Spectroscopy of H_2^+ in Laboratory and Astrophysical Plasmas*. PhD thesis, Univ. Chicago (2001).
110. Oepts, D., van der Meer, A. & van Amersfoort, P. The free-electron-laser user facility FELIX. *Infrared Phys. Technol.* **36**, 297–308 (1995).
111. Western, C. M. PGOPHER: a program for simulating rotational, vibration and electronic spectra. *J. Quant. Spectrosc. Radiat. Transf.* **186**, 221–242 (2017).
112. Neill, J. L. et al. Segmented chirped-pulse Fourier transform submillimeter spectroscopy for broadband gas analysis. *Opt. Express* **21**, 19743–19749 (2013).

Acknowledgements

The authors thank J. Pety for providing access to observational data towards the Horsehead PDR, and J. L. Doménech and D. Neufeld for help in producing Fig. 6. Support for B.A.M. for the initial portions of this work was provided by NASA through a Hubble Fellowship (grant no. HST-HF2-51396) awarded by the Space Telescope Science Institute, which is operated by the Association of Universities for Research in Astronomy for NASA, under contract NAS5-26555. The National Radio Astronomy Observatory is a facility of the US National Science Foundation operated under cooperative agreement by Associated Universities, Inc. S.S., O.A. and S.B. thank the Deutsche Forschungsgemeinschaft for long-term support of the development of the action spectroscopy techniques in the Cologne laboratory through numerous projects.

Author contributions

The authors contributed equally to all aspects of the article.

Competing interests

The authors declare no competing interests.

Peer review information

Nature Reviews Physics thanks Satoshi Yamamoto and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

Publisher's note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© Springer Nature Limited 2020