

Chapter 13

Infrared Spectroscopy of Ions of Astrophysical Interest

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Abstract Molecular ions are key species in the chemistry of the interstellar medium (ISM). Given the low temperatures and number densities typically occurring in the ISM, one of the few available mechanisms to form more complex molecules is through barrierless exothermic reactions, as it is the case for many ion-molecule reactions. Ions are highly reactive species but they can be formed efficiently in the ISM by cosmic-ray or ultraviolet ionization and can survive for relatively long times due to the few collisions they suffer. On earth, molecular ions are “exotic” species much more difficult to produce in appreciable quantities. Electrical discharges in low pressure gases form cold plasmas which can be used to produce molecular ions in abundances high enough to enable their spectroscopic study.

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13.1 Introduction: Spectroscopy, Astrophysics, Chemistry and Plasmas All Stirred

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The light coming from space, whether it reaches our eyes or the detectors in the most sophisticated telescopes, is the only way to gather knowledge about the “vastly, hugely, mind-bogglingly big” (Adams 1979) space surrounding our solar system. Just the closest planets or asteroids can be reached by probes capable of performing in situ analysis. The rest of the Universe can only be investigated analyzing the quantity and distribution of the light emitted, scattered or absorbed by the zoo of astronomical environments in our galaxy and beyond. Surpassing imaging and photometry, spectroscopy at all wavelengths is the most powerful tool to gain insight about the chemical composition and the physical conditions out there, and it is not surprising that astronomy and spectroscopy have walked hand in hand since the development of the latter in the early nineteenth century.

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For more than one hundred years astronomical spectroscopy was mostly devoted to the analysis of stars, comets, nebulae and galaxies, all of them bright sources in the visible region of the spectrum, and atomic spectroscopy was the tool to gather information about the composing elements and their excitation or ionization state. It was not until (roughly) the beginning of the twentieth century that it became increasingly evident that the interstellar medium was not empty, and that, furthermore, that harsh environment did not contain only atoms and their ions, but also chemically bonded species. Until then, it was generally assumed that any molecule would be dissociated, the constituent atoms would lose their valence electrons and the formation of a new bond would be impossible. Eddington (1926) suggested that the opacity of interstellar clouds could be explained by the presence of molecules shielded from the radiation field, and the discovery of absorption lines of CH, CN and CH⁺ against bright visible stars in the period 1937–1941 proved the existence of molecules in interstellar space (see e.g. Herzberg 1980 for a recollection of these early discoveries). Twenty years later a new diatomic molecule, the radical OH, was identified by its radio emission (Weinreb et al. 1963), and a few years afterwards the first polyatomic, ammonia (NH₃, by Cheung et al. 1968), also by its microwave emission.

To make a really long story short, the development of astronomical spectroscopy techniques, most notably, radioastronomy, brought up the science of molecular astrophysics, a.k.a astrochemistry. Up to today, around 200 molecules (including closed-shell neutrals, radicals, cations and anions), with up to 60 atoms, have been identified in space, revealing that there is a rich chemistry up there that has to be understood. Updated lists of identified molecules in the interstellar and circumstellar medium, together with bibliographic references, can be found in the web page maintained by D. E. Woon (www.astrochimist.org) or in the Cologne Database for Molecular Spectroscopy (Müller et al. 2001, 2005) at www.astro.uni-koeln.de/cdms/molecules. More descriptive accounts have been written over the years, e.g. Menten and Wyrowski (2011) and Kroto (1981).

The classification or description of the different environments of the ISM is well beyond the scope of this chapter and of the abilities of the author, and readers are referred to the reviews by Snow and McCall (2006) and Snow and Bierbaum (2008) or to many books on molecular astrophysics.

There is no single model of chemistry in space. Different processes prevail in different environments, and, moreover, astronomical observations are not always able to resolve a “pure” environment. Rather, the same line of sight intercepts different regions. The ISM is heterogeneous, with more diffuse regions permeated by UV radiation, and cold dusty regions shaded from UV but exposed to cosmic rays, with globular or filamentary structures with different densities, temperatures and dust content. However, most models for chemical reactions in the ISM, share two common basic premises: (1) given the low densities in the ISM, collisions are binary, and (2) dust grain surfaces are key elements by providing an energy release path for binary encounters (recall that a binary collision cannot result in a bond between the colliders unless there is a way to release part of the kinetic energy of the colliding pair, either a third body or the emission of a photon). The first

attempts to model gas phase chemistry in dark clouds (e.g. Watson 1973; Herbst and Klemperer 1973; Black et al. 1978) already relied on ion-molecule reactions as an important mechanism to form new molecules, as these reactions are typically exothermic and barrierless. The role of dust grains in the formation of the most abundant molecule, H_2 , was discussed by Hollenbach and Salpeter (1971) and for a variety of other molecules by Tielens and Hagen (1982).

Most of the molecules identified in space have been found in dense clouds, where the central role in initiating the chemistry is played by the ion H_3^+ , which, in turn, is formed upon ionization of H_2 by cosmic rays followed by a collision with another H_2 molecule:



The proton affinity of H_2 is rather low, and H_3^+ acts as a proton donor to almost any other molecule or atom upon collision, in a reaction of the type



(Only the proton affinities of He, Ne, Ar, N, and O_2 are smaller than that of the abundant H_2 , and then the previous reaction does not proceed.) In general, the species XH^+ is much more reactive than X, initiating a chain of reactions forming more complex molecules. In particular the reaction $\text{H}_3^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{H}_2$ produces the most abundant ion in dense clouds, HCO^+ , which was the second molecular ion to be detected in space and the first to be detected by its rotational emission. In fact it took several years before it was detected in the laboratory, definitely sanctioning the ion-molecule mechanism. Since then, many other cations have been detected: N_2H^+ , HCS^+ , HOCO^+ , HOC^+ , NO^+ , HCNH^+ , H_3O^+ , SO^+ , CO^+ , HC_3NH^+ , H_3^+ , H_2COH^+ , CF^+ , H_2O^+ , OH^+ , H_2Cl^+ , HCl^+ , SH^+ , C_3H^+ , C_{60}^+ , NH_4^+ , ArH^+ , H_2NCO^+ , NO^+ , NCCNH^+ and NS^+ . As it can be seen, many of them can be considered protonated forms of neutral molecules. It is worth noting that, although astronomers had considered some processes through which anions might form in interstellar clouds and circumstellar envelopes, it was not until the detection in 2006 of a rotational line emission from C_6H^- that their role in astrochemistry was vindicated (Millar et al. 2017). Anions identified up to now are C_nN^- ($n = 1, 3, 5$) and C_nH^- ($n = 4, 6, 8$).

In order to assign any spectral feature in an astronomical observation to a particular spectroscopic transition of a particular molecule, the frequency of that transitions must be accurately known. In other words, laboratory spectroscopy has to provide the transition frequencies, and, if possible also the Einstein coefficients, in order to interpret astronomical spectra. It is quite safe to state that no identification of any species in space is secure if there is not reliable laboratory support for it.

The infrared study of ions in the laboratory requires to have a column density of ions in the observation volume high enough to allow for their detection. This is not an easy task. In the ISM the densities are so low ($\sim 10^4 \text{ cm}^{-3}$ in a typical dense

cloud, or 10^2 cm^{-3} in a diffuse cloud) that collisions take place very rarely and the reactive molecular ions can survive for a long time. Under the best laboratory conditions, it is exceedingly difficult to achieve a vacuum of $\sim 10^{-12}$ mbar (roughly 10^4 cm^{-3}) and obviously the optical path is negligible, compared to that in an interstellar cloud, forcing us to devise ways to generate molecular ions in much more abundant quantities to produce detectable absorptions or emissions. Cold plasmas formed in low pressure electrical discharges (“glow discharges”) are one of those environments.

A very general definition of a plasma is *an electrically quasi-neutral gas formed by neutral and charged particles that exhibits a collective behaviour*. Usually, the negative charged particles are mostly electrons, and cations maintain the electrical neutrality of the system. In a simple scheme, plasmas can be classified into *thermal* plasmas and *cold* plasmas. Thermal plasmas usually happen at high pressure (~ 1 bar) and they exhibit local thermal equilibrium (LTE) between the different types of particles (electrons, ions and neutrals), all possessing quite a high energy content (10^2 – 10^4 eV). Examples are flames, arcing, lightning or fusion plasmas. Cold plasmas lack LTE, with electrons having a much higher temperature (1–10 eV or 10^4 – 10^5 K) than the positive ions, that are at nearly the same temperature than the neutrals (or the bulk of the system). Examples are the ionosphere, the aurorae, or glow discharges. The *degree of ionization* (the ratio of the number density of ions to the sum of the number densities of ions and neutrals) in a glow discharge is rather low, 10^{-4} – 10^{-6} , meaning that only a small fraction of the neutral species becomes ionized.

Glow discharges are luminous electrical discharges which glow due to the emission from electronically excited states. Very succinctly, the very few free electrons in a low pressure gas (produced by natural radioactivity or cosmic rays) are accelerated by the electric field between the electrodes and gain kinetic energy. Upon collision with neutral particles, owing to the huge mass difference, little kinetic energy is transferred, but the neutrals can be ionized releasing new electrons that start a sort of chain reaction, called *Townsend's avalanche*. The heavier ions and the neutrals accelerated by collisions with the ions, can strike the surface of the cathode releasing *secondary electrons*, and it is actually this secondary electrons emission that sustains the discharge. For the purposes of this introduction, lets suffice to say that this type of glowing plasma is a highly reactive medium with translationally cold ions and molecules. Depending on the geometry of the discharge, and the type and position of the electrodes, the plasma can exhibit a complex pattern of bright and dark regions determined by electron-gas interactions (see Fig. 13.1). Also for the purposes of this description, two luminous regions are the most relevant, the *negative glow* and the *positive column* (see e.g. Piel 2010 or Fridman 2008 for detailed descriptions of the anatomy of a glow discharge). The negative glow resides close to the cathode, the electric field is close to zero and it is the region with the highest ion density. The positive column occupies a region near the anode and has a weak axial field. In a typical Crookes-type discharge, by increasing the distance between electrodes, the positive column can occupy most of

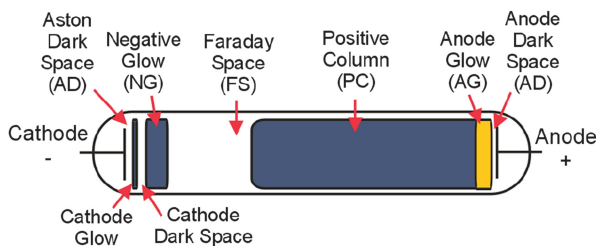


Fig. 13.1 A diagram showing the different glowing regions in the gas that appear when a high DC voltage is applied between the electrodes of a Crookes tube. <http://en.wikipedia.org/wiki/User:Iantresman> (https://commons.wikimedia.org/wiki/File:Electric_glow_discharge_schematic.png), “Electric glow discharge schematic”, <https://creativecommons.org/licenses/by/2.5/legalcode>

the volume, while the reverse can make it disappear. Other important types of glow discharges, besides the DC discussed above, are radio frequency discharges and microwave discharges. Energy is coupled into the system capacitively or inductively at frequencies of 13.56 or 2450 MHz typically.¹ Although they have some useful properties in the formation of ions and radicals, they have been less widely used than DC discharges for the study of astrophysical ions.

It has already been stated that rotational spectroscopy has been instrumental in our knowledge about the molecular universe, but, of course, it is not the only tool. In particular, high resolution IR spectroscopy, accessing transitions among vibration-rotation levels, has some unique characteristics that are of benefit in this field. First, all polyatomic molecules, regardless of their permanent electric dipole moment, have IR absorption spectra. Only homonuclear diatomics escape, and not all of them, since, e.g. H_2 can be detected by its quadrupole transitions. Some very important interstellar molecules have no permanent dipole moment, and have been detected by its IR spectrum: H_3^+ , CH_4 , SiH_4 , C_2H_2 , C_3 , to name a few. For the particular case of ions, some of them, like H_3^+ do not have bound electronic states, and no vis-UV spectrum. Second, for the same reflector size, the higher frequency of the radiation allows for higher spatial resolution. Also, different sources and objects can be studied: the infrared region of the spectrum is particularly valuable for investigating cool thermal sources (i.e. temperatures less than a few thousand K) as well as any astronomical sources that are highly extinguished by foreground dust. Finally, the analysis of vibration-rotation bands provide the energy levels of the upper and lower vibrational states, which, indirectly, allows us to compute the frequencies of the rotational transitions (see Sects. 13.3.2 and 13.3.3). Because of their large rotational constants, many light protonated ions have widely spaced rotational lines, and, often, only one or two can be measured with the same

¹There is nothing magical about these particular frequencies. They are within bands assigned by the International Telecommunication Union for Industrial, Scientific and Medical (ISM!) purposes, other than radiocommunications.

instrument, both in the lab and in radiotelescopes. In the IR domain, the same setup can cover wide spectral regions. Although, generally speaking, instrumental resolution and frequency accuracy are higher in the radiofrequency domain, both laboratory and astronomical instrumentation in the IR are becoming more and more refined, and the rotational frequencies derived from IR spectra are accurate enough to efficiently guide both astronomical and laboratory searches.

13.2 Experimental Techniques

In this section I intend to cover some practical aspects of laboratory astrochemistry experiments related to the IR spectroscopy of molecular ions. It is not possible to make a unique classification of experimental methods, since the ion production techniques, the infrared sources available, and the methods used to increase the sensitivity can mingle in almost any possible combination. Therefore I will try to give a broad overview that serves to illustrate all significant aspects of the experiments.

As far as the production of ions goes, glow discharges have played a prominent role, using both the positive column and the negative glow regions of the discharge. The field of IR spectroscopy of molecular ions was born when Takeshi Oka at the University of Chicago recorded the vibration-rotation spectrum of the very fundamental H_3^+ . The ion was produced in the positive column of a discharge in pure hydrogen, cooled by liquid nitrogen, and he employed direct laser absorption spectroscopy to detect the spectrum (Oka 1980).² He estimated a density of H_3^+ ions $n \simeq 3 \times 10^{10} \text{ cm}^{-3}$, or equivalently, 1 μbar partial pressure in a 1 mbar H_2 buffer. Note that this is probably one of the cleanest (i.e. with less interfering species) discharges that can be made in the laboratory with molecular ions present, so it illustrates the sensitivity and selectivity that are necessary to detect ions by IR absorption in more complex mixtures. Since the blooming of IR spectroscopy of ions in the 1980s a variety of techniques have been developed in order to increase the sensitivity for these weak signals and also the selectivity to discriminate them from those coming from the much more abundant neutral precursor and/or reaction products.

²Other authors had made significant contributions before and should also be mentioned: Wing et al. (1976) and Carrington and Softley (1983) developed the Doppler-tuned ion-beam infrared spectroscopy technique, in which the transitions of the ions were brought into resonance with a fixed-frequency laser using electric fields and the Doppler effect. Saykally and Evenson (1979) used the Laser Magnetic Resonance technique (LMR), in which far-IR transitions of paramagnetic species (such as HBr^+ in that work) were brought into resonance by tuning the transitions with an electric field using the Zeeman effect. In both types of experiments CO_2 and CO lasers were used. These are fixed frequency lasers, emitting in the IR, that can only be tuned line-by-line, thus making the techniques applicable only to a few molecules with resonances close to the laser lines. The success of Oka in recording the IR spectrum of the ν_2 band of H_3^+ was partly due to a high resolution broadly tunable IR source, a difference frequency spectrometer (Pine 1974, 1976) continuously tunable from 2400 to 4500 cm^{-1} .

A known hurdle of direct absorption (more properly, transmission) measurements of weak transitions is the fact that the detector receives a large background of IR radiation (produced by the source and also coming from the environment), and the signal is a tiny decrease in the photon flux that has to be detected against this strong background. Modulation techniques have been extensively used to increase both selectivity and sensitivity, shifting the detection band to higher frequencies, where the signal can be effectively filtered out from the unwanted background or from absorption signals of other neutral species. *Phase-sensitive detection* (a.k.a. *lock-in detection*) is profusely used to retrieve the signal at the modulation frequency (or some multiple).

13.2.1 Velocity Modulation

The experiment by Oka on H_3^+ used a DC discharge, and only frequency modulation of the IR radiation was used to increase the sensitivity. This got rid of the IR environmental radiation and of that of the discharge itself in the detection, but any species absorbing in the frequency scan would have been detected as well. Fortunately, the dominant species in this discharge is H_2 , that has very few populated rotational levels and no vibration dipole absorption, so it did not cause major interferences, but this discharge is certainly the exception and not the rule.

Gudeman et al. (1983) used the Doppler shift of the transitions of ions due to the drift velocity induced by the electric field of the positive column to develop the technique of *velocity modulation*, and detected the ν_1 band of HCO^+ . By applying an AC discharge current, rather than a DC one, the ions are accelerated towards one of the electrodes in one half period of the discharge, and to the other one in the next half period. Neutral particles are not affected. In this way, when the IR source is tuned across a transition of the ion, the transmitted intensity is modulated at the frequency of the discharge (typically in the tens of kHz regime), since the symmetric oscillating electric field Doppler-shifts the absorption frequency of the ionic vibration-rotation transition in and out of resonance with the infrared radiation. The suppression of signals from the much more abundant neutral species was 20–30 dB. The technique of velocity modulation was extensively used by numerous groups in combination with different tunable IR sources: difference frequency spectrometers, color-center lasers, lead-salt diode lasers and, more recently, quantum-cascade lasers and optical parametric oscillators (OPO). The review by Stephenson and Saykally (2005) provides a good overview of the technique and of many significant achievements. Let's mention here only two caveats: (1) In principle, light should travel in only one direction for the method to work, thus making a multipass arrangement difficult (there are tricks to overcome this limitation, and some will be shown below), and (2) any asymmetry between the electric field in the two halves of the discharge plasma translates into an offset of the measured frequency. In any case, together with the availability of narrow-linewidth broadly-tunable IR lasers, velocity modulation was a cornerstone in the

spectroscopy of molecular ions. Probably the most notable contributions were those from the groups of R. Saykally (Berkeley, USA), T. Oka (Chicago, USA) and P.B. Davies (Cambridge, UK).

13.2.2 Concentration Modulation

An alternative approach to identifying absorptions due to molecular ions makes use of their rather short lifetimes compared to neutral species. Typically, a large hollow cathode electrode arrangement with the anode external and perpendicular to the tube at its midpoint is used. When the discharge is established (through a hole cut in the cathode wall), a negative glow region fills most of the space inside the cathode, thus taking advantage of the fact that ion production is enhanced in the negative glow as compared to the positive column. By pulsing a DC discharge (again at rates of some kHz) the ion production is also modulated, following the discharge cycle. This type of discharge cell works as a rectifier, i.e. only when the copper tube is at negative potential respect to the outer electrode the plasma can ignite (Foster and McKellar 1984). The ion concentration follows that of the electrons in the discharge, swinging from zero to whatever small value it reaches. Precursor gases and stable products do not follow the discharge current so rapidly, and produce a signal with much smaller “contrast”. Nevertheless, the discrimination between ion signals and that of stable molecules is poorer than that in the velocity modulation scheme. That said, some advantages must also be noted: rotational and translational temperatures are generally lower than in positive column discharges (very close to that of the cathode wall), ion production is enhanced, a multipass arrangement is easily implemented and the electric field in the axial direction is negligible. This is particularly relevant for the precise measurement of transition frequencies, as mentioned in the previous subsection. Also, from the astrophysical point of view, hollow cathode discharges are more effective in producing protonated ions, such as many of those mentioned in the preceding section, through the mechanism of Eq. (13.2). Positive column discharges are more effective in producing radicals and excited states. The work of T. Amano at NRC (Ottawa, Canada) and the group of Hirota at the IMS (Okazaki, Japan) is particularly relevant in this context, the former using a difference frequency laser, and the latter using lead-salt diode lasers as IR sources.

13.2.3 Magnetic Field Modulation

While developing techniques for the study of molecular ions in the mm and sub-mm wave regions, De Lucia and Herbst (1983) observed a dramatic 10 to 100-fold increase in the signal coming from ions when a longitudinal magnetic field was applied to a glow discharge. Building upon those observations, Kawaguchi

et al. (1985) found that the signal intensity of ions was decreased by an order
of magnitude by applying a magnetic field of about 100 G to a hollow cathode
discharge. In this way they devised another way to discriminate absorptions
produced by ions from those produced by closed-shell neutrals, that would not
be affected by the magnetic field. Actually the magnetic field effect in the hollow
cathode discharge is different than in the common (two opposite electrodes) glow
discharge. In the former, it seems that the loss of energy by the electrons in the
magnetic field decreases the yield of impact ionization, while in the latter it is the
confinement of the electrons and the decrease of electron-wall collisions the cause
of the higher ion production rate (together with an enlargement of the negative
glow region). Magnetic field modulation is another powerful method to imprint a
modulation on only the absorption signal due to ions. However, it has been more
widely used together with discharge current modulation to tag the lines as coming
from ions or neutrals by observing their different behaviour under a static magnetic
field (which is typically 50–200 G).

13.2.4 *Supersonic Expansions*

Supersonic expansions are a well-known method to obtain rotationally cold
molecules, facilitating the interpretation of complex spectra thanks to concentration
of population in fewer levels and the intensity of the spectrum in fewer lines. An
electric discharge in the nozzle extends these benefits to the study of ions and
other transient molecules. Several groups have developed this type of systems,
again, in conjunction with a tunable IR laser source. The spectrometer developed
by the group of D. Nesbitt at JILA (Boulder, USA) used a difference frequency
spectrometer (Davis et al. 2001), while that developed at NRC (Ottawa, Canada)
used also a diode laser, depending on the frequency region (Yunjie et al. 1995).
In both of them, the discharge across the nozzle was pulsed, so the concentration
modulation technique was used to further increase the sensitivity. More recently,
the group of H. Linnartz (Leiden, The Netherlands) has set up a slit discharge
expansion using a cw OPO as the IR source and with *Cavity Ring-Down* detection
(Zhao et al. 2013; Verbraak et al. 2007). The B. McCall group (Urbana, USA) has
setup a similar system, but with a pinhole nozzle in this case (Crabtree et al. 2010;
Talicska et al. 2016).

Cavity Ring-Down (CRD) Spectroscopy

As this technique is possibly not so well-known to some readers, I will take a
short detour just to highlight its most relevant aspects. A much better treatment
can be found in e.g. Berden and Engeln (2009). A ring-down cavity is basically an
optical resonator formed by two highly reflective mirrors. When a pulse of laser
light is coupled into the cavity, at each round-trip, a small fraction escapes, and the
envelope of the outgoing pulses intensity follows an exponential decay. If a cw laser

is coupled into the cavity, and is suddenly switched off, the light leak-out intensity follows an exponential decay. It can be shown that the time constant τ of those decays can be expressed as

$$\tau = \frac{L}{c(1 - R - \alpha l)} \quad (13.3)$$

where L is the optical length of the cavity, c the speed of light, R the averaged reflectivity of the two mirrors and αl the absorbance for a sample present in the cavity with absorption coefficient α and length l . As it is immediately seen from Eq. (13.3) the absorption coefficient can be determined independently of the laser power, since it only depends on the decay time constant, and not on its amplitude. This immunity to source noise is one of the beauties of CRD, the other one being the high optical absorption paths achieved because of the high reflectivity mirrors. Effective pathlengths 10^4 – 10^5 times larger than the separation between mirrors can easily be achieved. These characteristics have made CRD a very sensitive detection technique for weakly absorbing species such as ions formed in discharges.

13.2.5 NICE-OHVMS

Noise Immune Cavity Enhanced Optical Heterodyne Velocity Modulation Spectroscopy (NICE-OHVMS) is one a sensitive spectroscopic technique specific to molecular ions that is being developed at the University of Illinois. NICE-OHVMS combines three separate techniques, each of them being a powerful tool. The *noise immunity* comes from the locking scheme of the laser frequency to an optical cavity, which was originally developed for metrology purposes (Drever et al. 1983). Two sidebands are imposed on the laser central frequency by frequency modulation (i.e. *heterodyning*), with the spacing between them set to an integer multiple of the free spectral range of the cavity. In this way the carrier and the two sidebands are coupled in and out of the cavity simultaneously and a fast photodiode measures the beat signals among them. Because the two sidebands have the same intensity when no absorbers are present within the cavity and are 180° out of phase with one another, the positive and negative RF beat signals created by the sideband frequencies beating against the carrier frequency cancel each other out, giving a zero-background. As the laser is scanned across a resonance of a molecule in the cavity, one of the sidebands is absorbed more than the other one, giving an imbalance between the two beats that can be used to derive a spectroscopic signature. *Cavity enhancement* extends the interaction pathlength of the light through the absorber, while frequency modulation encodes the detected signal at radio frequencies to minimize the $1/f$ noise. If the centre frequency of the laser and the two sidebands match exactly the cavity modes, any noise in the laser-cavity lock is the same for the carrier and both sidebands, so the demodulated signal is unaffected. The optical cavity also results in a large power enhancement through the absorber which can saturate molecular transitions.

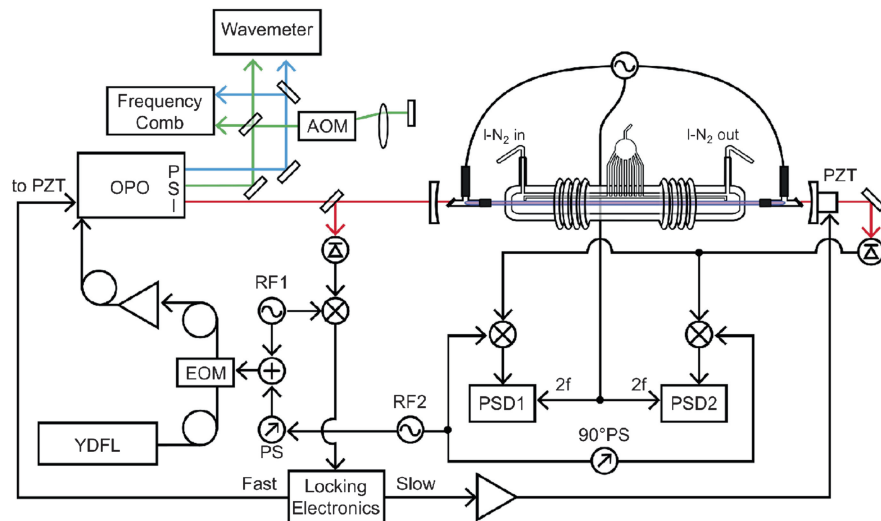


Fig. 13.2 A diagram of the NICE-OHVMS instrument. PZT: Piezo Transducer, EOM: Electro-Optic Modulator, PS: Phase Shifter, PSD: Phase Sensitive Detector, RF: Radio Frequency Oscillator, OPO: Optical Parametric Oscillator, P: Pump, S: Signal, I: Idler, YDFL: Ytterbium Doped Fiber Laser. A YDFL is fiber coupled to an EOM where locking and heterodyne sidebands are placed on the laser. The laser is then amplified in a fiber amplifier and sent to an OPO. The OPO creates the signal and idler beams. The pump and signal are used for frequency measurements, and the idler in the mid-IR is used for spectroscopy. The back reflection detector is used for Pound-Drever-Hall locking, and the signal from the transmission detector is sent to rf mixers for heterodyne processing. The output of the mixers is sent to PSDs to process the velocity modulation signal. The output is then recorded as the spectrum. Reprinted from Hodges et al. (2013), with the permission of AIP Publishing

The Lamb dips in the spectra, due to saturation, are free from Doppler broadening, and can be fit with high precision. The use of an optical frequency comb as an accurate frequency reference allows transitions to be recorded with MHz/sub-MHz uncertainty. In many cases, these represent a two order of magnitude improvement on the transition frequency measurement. Finally *velocity modulation* makes the detection specific to ions. This is not a simple setup! I refer the readers to the papers of the group for a rigorous description (e.g. Hodges et al. 2013 and references therein). Figure 13.2 shows a schematic of this experiment.

13.2.6 Action Spectroscopy in Cryogenic Ion Traps

By action spectroscopy I mean techniques in which the spectroscopic signal does not come from the observation of the light, but of some chemical change, like the rate of production of a given species, which is altered by the interaction of light

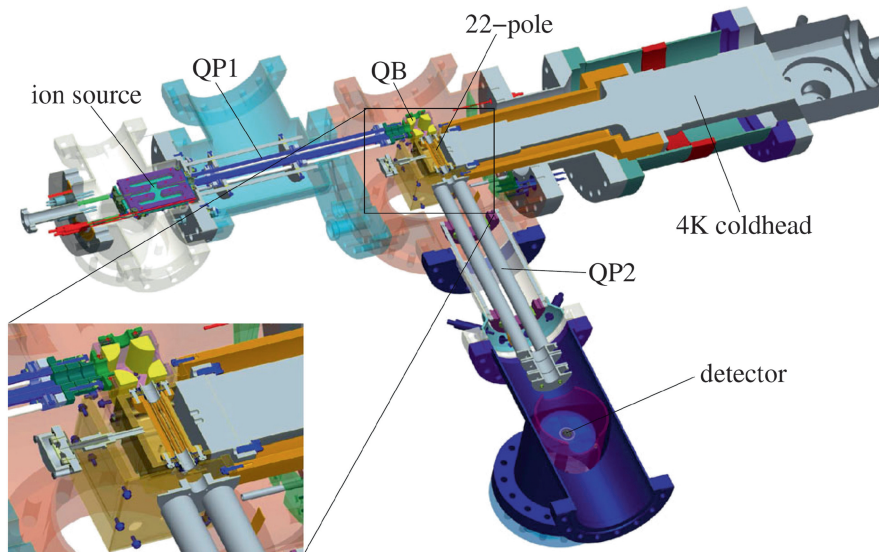


Fig. 13.3 Setup of the Cologne-built 4 K ion trap machine COLTRAP. It comprises an ion storage source, a first quadrupole mass selector (QP1), an electrostatic quadrupole bender (QB), the 22-pole ion trap mounted on a 4 K coldhead, the second quadrupole mass selector (QP2) and finally a Daly-type ion detector. While both end flanges (close to QB and detector) can be used for laser access, the flange closer to the 22-pole trap is especially suited for attaching a THz radiation source or a molecular beam which can traverse the trap. Reprinted by permission from Springer Nature, Applied Physics B: Lasers and Optics, COLTRAP: a 22-pole ion trapping machine for spectroscopy at 4 K, Asvany et al. ©2013

with the parent ion.³ Ion traps are multipolar arrangements (four poles being the simplest, and 22-pole being a common one) in which a rapid change (at MHz rate, hence the term *rf-trap*) of the potential applied to the electrodes, maintains ions trapped in an effective radial potential well from which it cannot escape (Gerlich 1995). Electrostatic potentials “open” or “close” the longitudinal ports of the trap. In the frame of IR and rotational spectroscopy of ions these experiments are led by S. Schlemmer’s group at the University of Cologne. Only a couple of techniques will be briefly described here: the laser induced reaction method (LIR) and the state-dependent attachment of He atoms to ions.

The experiment is depicted in Fig. 13.3. It begins with the electron impact ionization of the precursors in a storage chamber, followed by the production of other ions and products by collisions. The target ions are mass-filtered and

³I have already mentioned the problem of detecting small fluctuations in the photon flux received by a detector, especially if the background is strong. Moreover, the quantum efficiency of detectors for low energy photons (like those in the IR or microwave energy range) is rather low. On the contrary, ion-counting techniques are extremely well developed, and even a single ion can be counted.

extracted from the mixture of other products formed in the ion source, and are directed to the trap, where they are kept for times ~ 1 s. Inside the trap, held at cryogenic temperatures, the ions thermalize with a buffer gas and can interact with the radiation and with some carefully chosen “reactant”. In the LIR method, one seeks a reaction which has an activation barrier lower than the energy of the photons from radiation source. The reaction product (a different ion) is only formed if the parent ion has absorbed a photon and has gained enough energy to overcome the barrier. By mass selecting again the trap products, it is possible to count the number of product ions as a function of the frequency of the source, and, in so doing, obtain an absorption spectrum of the parent ion (e.g. Asvany 2005; Schlemmer et al. 2002). This method can be applied not only to IR transitions, but also to purely rotational transitions, although the higher energy of IR photons favours the first. However, if combined with a THz source in a double resonance experiment rotational spectroscopy can also be performed. The second method uses the state selective attachment of helium to the cold stored molecular ions as action spectroscopic probe [*Light Induced Inhibition of Complex Growth, or LIICG* (Asvany et al. 2014)]. When the ions are admitted to the trap, a pulse of He is injected, and He_nX^+ complexes form (X^+ is the parent ion). The rate of attachment of He atoms to X^+ depends on the internal excitation state of the latter, so, if X^+ has absorbed a photon, less He_nX^+ form in a given time. By mass selecting one of these complexes and counting them after each trapping cycle as a function of the source frequency, the absorption spectrum of X^+ can be obtained. This method is of more general applicability, working for rotational, ro-vibrational and even electronic spectroscopy. One recent example is the accurate measurement of rotational and vibrational transitions of the fundamental CH^+ ion (Doménech et al. 2018). The power of these methods resides mainly in their high selectivity. Ions can be selectively admitted to and extracted from the trap, so, in principle, the signals are free from interference from the potpourri of species present in the ion source or the trap. The infrared source in the laboratories at Cologne is an OPO, whose frequency is accurately measured by using a frequency comb. This is similar to the setup at Urbana, and a new small detour will be taken here to briefly describe its workings.

OPO's and Frequency Combs

An Optical Parametric Oscillator (OPO) is a non-linear optical device that splits an input laser wave (the *pump* beam) with frequency ω_p into two different output waves: the *signal beam* with frequency ω_s and the *idler* beam, with frequency ω_i . Conservation of energy holds ($\omega_p = \omega_s + \omega_i$), as well as that of momentum ($\mathbf{k}_p = \mathbf{k}_s + \mathbf{k}_i$, where the \mathbf{k} 's are the corresponding wavevectors). The OPO's used for IR generation usually contain a LiNbO_3 crystal inside a cavity which is resonant for one of the signal or idler waves. Tuning is achieved by either changing the pump frequency or the phase matching condition (the momentum conservation relation above) by changing the refraction indexes of the waves (usually by temperature

tuning of the crystal) or a combination of both. IR powers of ~ 1 W can be achieved, with very narrow linewidth (below 100 kHz) in the 2.2–4.6 μm mid-IR region. As with any narrowband radiation source, it is necessary to measure its frequency with an accuracy as high as required for the experiment. Optical frequency combs have become one of the best standards for optical metrology. A modelocked femtosecond laser puts out a train of short pulses at a very well defined repetition rate. The frequency spectrum corresponding to this time behaviour is a “frequency comb”, i.e., a set of very narrow lines precisely spaced by the inverse of the repetition rate. Since this frequency is in the ~ 100 MHz range, very accurate time references (traceable to the Cs-clock standard) can be used to control the frequency spacing of the comb teeth. The principle behind using a frequency comb to measure an unknown laser frequency is the measurement of the beat frequency between the unknown laser and that of a comb tooth which is a multiple of the comb spacing. (There is a potential issue due to the so called “carrier envelope offset” that has to be addressed, but I will not get into that.) As already mentioned, accurate frequency measurement in the MHz domain is a nearly trivial task, so the frequency of the unknown laser can be determined with sub-MHz precision just by knowing the frequency of the comb tooth, and the beat-note frequency. Of course there is a load of subtleties and nuances that I have overlooked in this short description. The point of this paragraph is to stress that IR frequencies can now be measured with accuracies approaching those of microwave rotational spectroscopies (see e.g. Asvany et al. 2012).

13.3 Case Studies

In this section I show two examples of the interplay between laboratory spectroscopy of ions and astrophysics, that illustrate and emphasize the role of high resolution infrared spectroscopy in the growing field of Laboratory Astrophysics. I have chosen two studies where the spectroscopic experiments have been performed in the laboratory of IR laser spectroscopy at the Molecular Physics Department of IEM-CSIC, in close collaboration with astronomers and other Molecular-Physics groups.

13.3.1 *The Experimental Setup at IEM*

The setup consists of a difference frequency laser spectrometer, coupled to a hollow cathode discharge with concentration modulation. The difference frequency spectrometer follows the design by Pine (1976), with some improvements. Briefly, frequency-tunable IR radiation is generated by mixing the output of an Ar^+ laser with that of a tunable ring dye laser in a periodically poled LiNbO_3 crystal contained in a temperature-controlled oven (30–200 $^\circ\text{C}$). The Ar^+ laser is locked to the $^{127}\text{I}_2$

a_3 hyperfine component of the $B - X$ P(13) 43–0 transition⁴ with an in-house built polarization spectroscopy setup. The laser frequency has a residual frequency jitter <1 MHz and similar long-term stability. The tunable single mode ring dye laser is also frequency stabilized, with commercial stabilization electronics (residual jitter <2 MHz). Its wavelength is measured with a high accuracy commercial wavemeter (High Finesse WSU10, with stated accuracy of 10 MHz (3σ)), calibrated with the stabilized Ar⁺ laser. The IR frequency is calculated at each data point as the difference in frequency between that of the precisely known Ar⁺ laser frequency and the instantaneous wavemeter reading, and is therefore limited by the wavemeter accuracy. The wavelength coverage is ~ 2.2 – 5.3 μm , with ~ 2 MHz linewidth and ~ 1 mW power. The IR beam is amplitude modulated at ~ 15 kHz, and is split into two fractions, one directed towards the discharge reactor and an InSb detector and the other directly to a reference detector. A home-made autobalanced amplifier (designed after Lindsay 2002) is used to subtract the laser amplitude noise from the signal.

The hollow cathode reactor follows the design of Foster and McKellar (1984) (actually the blueprints were graciously given to us by Bob McKellar), albeit some modifications have also been introduced along the development of our experiments. The cathode is an 80 cm long copper tube, 50 mm diameter, surrounded with copper tubing coils for cooling. The anode is a stainless steel piece placed external and perpendicular to the cathode at its midpoint, and the discharge is established through a hole cut in the cathode wall. A piece of quartz tubing helps to prevent the discharge from spilling over to the outside of the cathode. Typical discharge conditions are 500 V between electrodes and 300 mA current. The reactor is enclosed in a glass tube with a vacuum insulation jacket, with the sides closed by flanges that hold the windows for coupling the IR radiation, and gold coated spherical mirrors in a White-type multipass arrangement (White 1942). It is possible to achieve ~ 32 m optical absorption path inside the discharge. The discharge is modulated at ~ 10 kHz by passing the driving current through a rectifier bridge, therefore it is a DC-pulsed discharge. The system is evacuated down to $\sim 10^{-3}$ mbar prior to the introduction of the precursors, whose flows are adjusted by mass flow controllers. Typical discharge pressures are 1–0.1 mbar.

The detection is made with a lock-in amplifier referenced to the sum of the modulation frequencies of the IR beam amplitude and of the discharge current, the input to the lock-in being the output of the autobalanced amplifier. The goal of the double-modulation scheme is to detect only changes of the IR intensity that are due to changes in the transmission of the reactor. With this arrangement, neither the emission from the discharge, nor IR background fluctuations in the laboratory introduce drifts in the baseline. IR scans are typically made at a 0.01 cm^{-1}/s speed, and the use of the wavemeter eases the task of averaging many scans, in order to increase the signal to noise ratio.

A schematic of the setup is depicted in Fig. 13.4.

⁴Known to ~ 0.1 MHz accuracy (Quinn 2003).

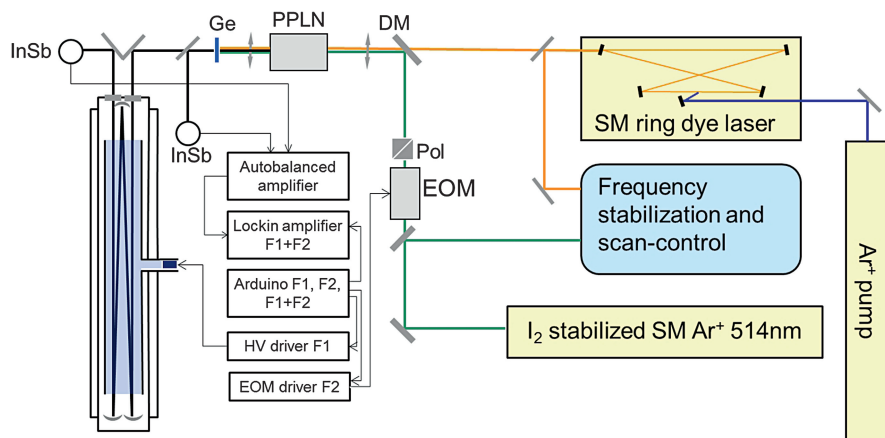


Fig. 13.4 Schematic of the main components of the high resolution infrared spectrometer coupled to a hollow cathode reactor at IEM-CSIC. SM means single-mode. EOM: electrooptic modulator. Pol: polarizing beam-splitter. DM: dichroic mirror. PPLN: periodically poled LiNbO₃ crystal. Ge: Germanium filter. InSb: liquid nitrogen cooled indium antimonide detectors. The frequency stabilization and scan control box comprises the optics and electronics for the SM Ar⁺ laser frequency lock, the stabilization of the ring dye laser, and the wavemeter. The main components of the double modulation rig are also shown

13.3.2 A New Molecule Identified in Space: NH₃D⁺

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Two of the most abundant nitrogen-bearing molecules in the ISM are N₂ and NH₃, which models predict to be present in many different astrophysical media. Diazenylium (N₂H⁺) and ammonium (NH₄⁺), the protonated ions of N₂ and NH₃, can provide crucial information for the understanding of interstellar chemistry involving nitrogen. Since N₂ is nonpolar it cannot be detected by radioastronomy, but N₂H⁺, usually taken as a tracer of N₂, has been detected in numerous sources. NH₄⁺ is a key precursor of NH₃ and other nitrogen bearing molecules, potentially pre-biotic. Indeed, NH₃ and its deuterated isotopologues have also been detected in numerous sources. Chemical models predict rather high abundances of NH₄⁺, since the proton affinity of NH₃ is very high, and once it is formed, it remains stable against further collisions with the abundant H₂. Unfortunately, NH₄⁺ has tetrahedral symmetry, hence no permanent electric dipole moment and no rotational spectrum, making it unsuitable for astronomical searches. Its deuterated variants (*d*₁ to *d*₃), on the contrary, do possess small permanent dipole moments, and could be candidates for an astronomical identification. The only laboratory spectroscopic information on NH₃D⁺, until recently, was an IR spectrum taken by Nakanaga and Amano (1986) of the ν₄ band with a difference frequency laser spectrometer and a hollow cathode discharge. From the analysis of that spectrum they could provide an estimation of the lower rotational transitions of this molecule, namely the 1₀–0₀ transition, at 262,807 MHz with a standard deviation σ = 3 MHz. It turns out

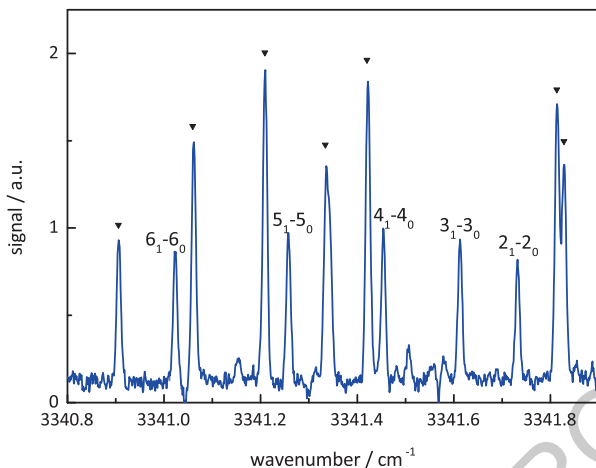


Fig. 13.5 Portion of the ν_4 band of NH_3D^+ near the band center. The labeled lines belong to the $(J, K' = 1) \leftarrow (J, K'' = 0)$ progression. Lines marked with a triangle belong to NH_4^+ . Adapted from Doménech et al. (2013), ©American Astronomical Society

that one of the strongest unidentified lines in a line survey of Orion-IRc2 (Tercero 527
 et al. 2010, 2011) lies at 262816.7 MHz, slightly above the 3σ confidence interval 528
 derived from the IR spectrum. Since the linewidth of this line was similar to that of 529
 NH_2D also observed in the same survey, there were chemical arguments to support 530
 the presence of NH_4^+ and, given the proximity of the frequency to the one derived 531
 from the laboratory measurement, the possibility of the unknown line being a 532
 rotational transition of NH_3D^+ was quite promising, so a more specific investigation 533
 was initiated. Astronomers made new observations towards the cold prestellar core 534
 B1-bS, where almost all isotopologues of ammonia and diazenylium had already 535
 been identified, and, as a result, a narrow feature was detected at the expected 536
 frequency. However, in order to claim a detection, more accurate laboratory data 537
 were also necessary. At that time, no laboratory rotational spectrum of NH_3D^+ was 538
 available, and even some concurrent dedicated efforts at JPL were unsuccessful, 539
 so the ν_4 band of deuterated ammonium was measured again at IEM, with better 540
 absolute frequency calibration and more lines than those reported previously. An 541
 example of some of the measured lines is shown in Fig. 13.5. The derived rotational 542
 frequency was 262,817 MHz with a standard deviation $\sigma = 2$ MHz, in excellent 543
 agreement with the astronomical observations, therefore securing the assignment of 544
 the observed features in Orion IRC2 and B1-bS to the 1_0-0_0 rotational transition of 545
 NH_3D^+ (Cernicharo et al. 2013; Doménech et al. 2013).⁵ 546

This study beautifully illustrates the interplay between laboratory spectroscopy 547
 and astrophysics and the benefit that can be obtained from the development of 548

⁵Some years later, the rotational transition was accurately measured in Cologne, obtaining a value 262816.904 with $\sigma = 15$ kHz (Stoffels et al. 2016).

Laboratory Astrophysics. It also demonstrates the capability of high resolution 549
infrared spectroscopy to provide pure rotation frequencies with accuracies high 550
enough to guide both laboratory and radioastronomical searches. 551

13.3.3 The High Resolution Spectrum of SiH⁺ 552

Only about twelve out of the nearly 200 molecules identified in the ISM contain 553
silicon. Surprisingly, only in three of them Si is bound to the most abundant 554
element, hydrogen (these are silane SiH₄, methyl-silane CH₃SiH₃ and silyl-cyanide 555
SiH₃CN.) The hydrides SiH (silyldiyne) and SiH⁺ (silyldinium) have only been 556
identified in the photosphere of the sun (SiH also in the envelopes of some cold 557
stars). Although these simple hydrides should be among the first species to form out 558
of the bare atoms or ions, the models do not predict a high abundance: in cold clouds 559
most Si is supposed to be depleted onto dust grains and SiO is the most abundant 560
gas phase Si-containing species, therefore the reaction H₃⁺+Si → SiH⁺+H₂, although 561
exothermic, would not be very efficient. In diffuse environments where Si could be 562
ionized, the reaction Si⁺+H₂ → SiH⁺ is quite slow, since it is highly endothermic 563
(by ~14,200 K). However, it is worth noting that the chemically similar CH⁺ is 564
much more abundant in the diffuse medium than it is predicted by models, and 565
the same is true for SH⁺. In both cases there is a formation barrier, albeit smaller 566
than that for SiH⁺, and a warm chemistry with vibrationally excited H₂, shocks 567
and turbulence is invoked to overcome the energy barrier and interpret the observed 568
abundances. Furthermore, the spectroscopic information on SiH⁺ was surprisingly 569
scarce, with no accurate measurements or predictions of its rotational frequencies. In 570
view of all the above considerations, the effort of undertaking a careful measurement 571
of those frequencies seemed advantageous. 572

The $v = 1 - 0$ fundamental vibration of SiH⁺ was recorded at IEM with the 573
difference-frequency laser spectrometer coupled to the hollow cathode discharge 574
system. A mixture of SiH₄ in He was used as precursor. Finally, a total of 23 575
lines were measured, from P(11) to R(11), spanning the range 1902–2236 cm⁻¹ 576
(see Fig. 13.6 for two examples). Besides providing a much more accurate and 577
complete set of infrared frequencies than previously available, it allowed for an 578
accurate prediction of the $J = 1-0$ rotational transition. The predicted value was 579
453057.7 MHz with $\sigma = 0.5$ MHz. The fundamental rotational transition of SiH⁺ 580
was then measured in the Cologne laboratories using the rotational state dependence 581
of the attachment of He atoms to cations obtaining a value of 453056.3632 MHz, 582
 $\sigma = 0.4$ kHz, within just 1.3 MHz of the IR prediction. A more detailed account of 583
this work is given in Doménech et al. (2017). 584

The Herschel Space Observatory (Pilbratt et al. 2010) produced huge amounts 585
of information on interstellar hydrides in its lifetime (2009–2013). Unfortunately, 586
the frequency of the $J = 1 - 0$ transition of SiH⁺ was outside its frequency 587
coverage. Since there are no other current far-IR satellite missions, observations 588
with radiotelescopes from ground could be an alternative: ALMA (Atacama Large 589

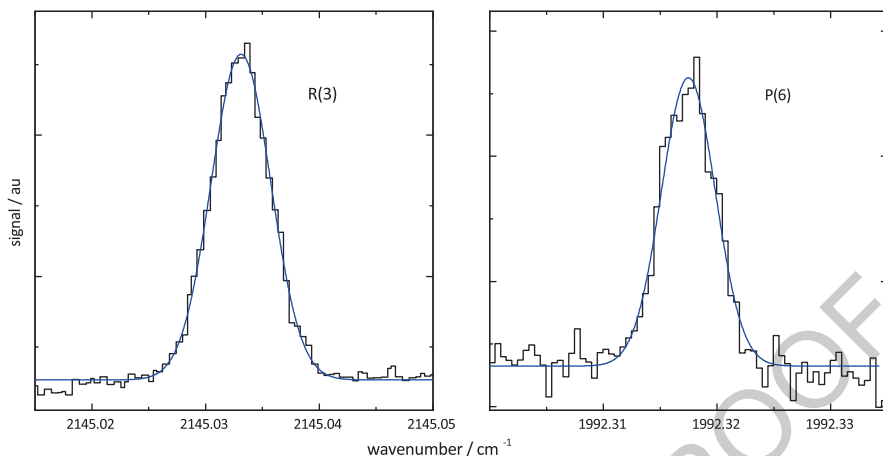


Fig. 13.6 Two examples of detected lines of SiH^+ and their Gaussian fits. Both lines are the result of averaging 100 scans (total 1000 s integration time). Adapted from Doménech et al. (2017), ©American Astronomical Society

Millimeter Array) or APEX (Atacama Pathfinder EXperiment), are both in very dry 590 sites and above 5000m altitude, and both cover that frequency. Unfortunately a 591 telluric water vapor line lies very close by, and atmospheric transmission under 592 average weather conditions (1 mm precipitable water vapor) drops to $\sim 15\%$. Yet 593 another alternative is to use high resolution infrared telescopes from ground: 594 iSHELL (an IR spectrograph for NASA Infrared Telescope Facility on Maunakea) 595 or CRIRES+⁶ (at the Very Large Telescope facilities of Cerro Paranal) have high 596 resolution and cover the vibration rotation band. 597

The accurate frequencies determined in this work enable the search for this 598 fundamental ion in space. The lines of sight would be those of the diffuse medium, 599 shock regions, or supernova ejecta against bright IR sources. 600

13.4 Final Remarks 601

Infrared astronomy is a very active field, more so with the excitement aroused by the 602 almost daily discovery of new exoplanets. The James Webb Space Telescope carries 603 two infrared spectrometers onboard, and several ground-based facilities offer (or 604 will offer soon) high sensitivities and spectral resolutions of $R \simeq 100,000$. Accurate 605 laboratory measurements in the IR regions will help maximize the scientific return 606 of these efforts. Furthermore, since the end of the successful Herschel mission, 607 infrared astronomy from the ground is one of the few alternatives to continue the 608 study of light hydrides, as it is the case of many protonated ions. Infrared laboratory 609

⁶Expected to be in operation in 2018.

spectroscopy is an enabling tool not only for those direct IR observations but also for observations in the radio or mm-wave domains. The new interferometric facilities such as ALMA, or NOEMA as well as laboratory rotational spectroscopy will also benefit from accurate IR data, since good predictions can spare very long searching times, both at the telescopes and in the lab.

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