Article 25fa pilot End User Agreement

This publication is distributed under the terms of Article 25fa of the Dutch Copyright Act (Auteurswet) with explicit consent by the author. Dutch law entitles the maker of a short scientific work funded either wholly or partially by Dutch public funds to make that work publicly available for no consideration following a reasonable period of time after the work was first published, provided that clear reference is made to the source of the first publication of the work.

This publication is distributed under The Association of Universities in the Netherlands (VSNU) ‘Article 25fa implementation’ pilot project. In this pilot research outputs of researchers employed by Dutch Universities that comply with the legal requirements of Article 25fa of the Dutch Copyright Act are distributed online and free of cost or other barriers in institutional repositories. Research outputs are distributed six months after their first online publication in the original published version and with proper attribution to the source of the original publication.

You are permitted to download and use the publication for personal purposes. Please note that you are not allowed to share this article on other platforms, but can link to it. All rights remain with the author(s) and/or copyrights owner(s) of this work. Any use of the publication or parts of it other than authorised under this licence or copyright law is prohibited. Neither Radboud University nor the authors of this publication are liable for any damage resulting from your (re)use of this publication.

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please contact the Library through email: copyright@ubn.ru.nl, or send a letter to:

University Library
Radboud University
Copyright Information Point
PO Box 9100
6500 HA Nijmegen

You will be contacted as soon as possible.
The FELion cryogenic ion trap beam line at the FELIX free-electron laser laboratory: infrared signatures of primary alcohol cations†

Pavol Jusko,*‡ Sandra Brünken,‡ Oskar Asvany,‡ Sven Thorwirth,‡ Alexander Stoffels,§ Lex van der Meer,b Giel Berden,‡ Britta Redlich,b Jos Oomensb and Stephan Schlemmer*‡

Received 3rd December 2018, Accepted 22nd January 2019
DOI: 10.1039/c8fd00225h

The combination of a 4 K 22-pole ion trap instrument, FELion, with the widely tunable free electron lasers at the FELIX Laboratory is described in detail. It allows for wide-range infrared vibrational spectroscopy of molecular ions. In this study, the apparatus is used for infrared vibrational predissociation (IR-PD) measurements of the simple alcohol cations of methanol and ethanol as well as their protonated forms. Spectra are taken by tagging the cold molecular ions with He atoms. The infrared spectrum of protonated methanol is recorded for the first time, and the wavelength coverage for all other species is substantially extended. The bands of all spectra are analysed by comparison to ab initio calculation results at different levels of theory. Vibrational bands of different isomers and conformers (rotamers) are discussed and identified in the experimental spectra. Besides the measurement of IR-PD spectra, the method of infrared multiple photon dissociation IR-MPD is applied for some cases. Spectral narrowing due to the cold environment is observed and rotational band contours are simulated. This will help in identifying more complex species using the IR-MPD method in future measurements. Overall the IR-PD spectra reveal more bands than are observed for the IR-MPD spectra. In particular, many new bands are observed in the fingerprint region. Depletion saturation of the finite number of trapped ions is observed for the IR-PD spectra of the ethanol cation and the presence of only one isomeric species is concluded. This special feature of ion trapping spectroscopy may be used in future studies for addressing specific isomers or cleaning

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8fd00225h
‡ Present address: Institut de Recherche en Astrophysique et Planétologie (IRAP), Université de Toulouse (UPS), CNRS, CNES, 9 Av. du Colonel Roche, 31028 Toulouse Cedex 4, France.
§ The completion of this work is dedicated to Alexander Stoffels (29 July 1985 to 13 December 2016).
the ion cloud from specific isomers or conformers. In addition, the results of this study can be used as a basis to obtain high-resolution infrared vibrational and THz rotational spectra of alcohol ions in order to detect them in space.

1 Introduction

Since the pioneering work of Y. T. Lee and collaborators on the infrared predissoiation (IR-PD) of hydrogen cluster ions performed some 30 years ago\(^1\) infrared action spectroscopy of molecular ions has been developing into a rather mature technique to determine the spectra and structures of many molecular ions. In contrast to ordinary absorption spectroscopy, action spectroscopy uses changes of the mass-to-charge ratio of the investigated ions as a result of photon absorption. For the study of vibrational spectra, in the infrared, the use of widely tunable IR OPO systems allows us to cover not only the X–H stretching (X = C, N, O) regime around 3 microns but to access the fingerprint region where characteristic modes can be addressed.\(^2\)–\(^6\) These capabilities are exceeded by free electron lasers, like the Free Electron Laser for Infrared eXperiments (FELIX) in the Netherlands\(^7\) and the Centre Laser Infrarouge Orsay (CLIO) in France,\(^8\) which cover even wider spectral ranges at once and with much higher intensities than available in table top laser experiments. The use of these highly intense pulsed FEL sources allowed for the establishment of infrared multiple photon dissociation (IR-MPD), which by now is one of the standard techniques to unravel the structures of molecular ions by the analysis of their vibrational bands.\(^9\)–\(^13\)

Many groups use radio frequency guides and ion traps to mass select and store the ions of interest, thus becoming molecule specific and allowing for long exposure times, which increases the sensitivity tremendously compared to the beam methods of earlier years. Even commercial trap apparatus are modified to turn them into action spectroscopy instruments.\(^14\)–\(^17\)

Buffer gas cooling is a standard way to simplify the spectra by narrowing the Doppler widths and most importantly by lowering the partitioning of the internal energy of the stored ion. This feature is particularly interesting for larger molecules where the number of different isomers and conformers (rotamers) as well as the number of hot bands should be reduced to unravel the vibrational structure of the ion of interest. Cooling the ions to the extent that these species can be tagged with atoms or molecules which in a second step can be pre-dissociated by just one infrared photon made action spectroscopy even more attractive. However, substantial band shifts had to be taken into consideration when interpreting the observed spectra to obtain information about the bare molecule. This limitation was largely overcome when it became possible to attach He atoms to the stored ion ensemble because the spectral shifts are often negligible compared to the spectral resolution. In trap experiments this was first demonstrated by Asmis and coworkers\(^18\) and later adapted by other groups.\(^15,19\) The development of these techniques is summarized in a recent review by Dieter Gerlich.\(^20\)

In this work, we describe a unique 22-pole ion trap experiment, named FELion, which is coupled to the high intensity IR free electron laser beam line at the FELIX Laboratory\(^\dagger\). The capability to reach low enough temperatures to attach He is now

\(^\dagger\) http://www.ru.nl/felix/
of the respective trap instrument, and predissociation of He-complexes of simple ions derived from primary alcohols formed in the FELion cryogenic ion trap is used in the work presented here to infer the vibrational bands for these ions which are also relevant in an astrophysical context.

Of the 200+ molecules now identified to occur in interstellar environments, methanol (CH$_3$OH) was among the first, detected at an early stage of astrochemical research. In 1970, just a few years after the discovery of astrophysical maser emission from OH, maser emission from methanol was observed at a large number of pure rotational transitions.$^{21}$ This emission is even observed from galaxies at high redshift and has for instance recently been used to investigate possible drifts in the proton-to-electron mass ratio over time.$^{22-24}$ Also, methanol plays a key role in many interstellar reaction networks modeling the abundances of small organic molecules in astrophysical environments. Although the radical cation of methanol also occurs in these networks, it has thus far not been detected in the ISM, because microwave spectra are missing. Further laboratory characterization of the microwave and IR spectra of CH$_3$OH$^+$ is therefore of interest.

Of particular interest in the study of cationic methanol is its existence as two isomeric forms, being the canonical CH$_3$OH$^+$ form and the alternative methylene-oxonium CH$_2$OH$_2^+$ form. Interestingly, methylene-oxonium is significantly lower in energy than the methanol cation. Duncan and coworkers reported vibrational IR spectra of the two isomeric forms of the cation in the hydrogen stretching frequency range.$^{25}$ In their ion source, the canonical form of the cation was exclusively formed when methanol was used as the precursor and the methylene-oxonium ion was formed when using ethylene glycol (ethane-1,2-diol).

As mentioned above, the Ar tag used in the messenger spectroscopy method from Duncan and coworkers$^{25}$ causes significant frequency shifts of specific IR bands; in particular, binding of the Ar tag to the hydroxyl proton induces a redshift of the OH stretch of several hundreds of wavenumbers. Fujii and coworkers reported IR spectra for the radical cations of the series of alcohols from ethanol to butanol using a VUV-IR scheme.$^{26}$ The OH stretch band in these untagged systems is observed as a strong feature in their spectra between 3500 and 3600 cm$^{-1}$. Here we present the first experimental vibrational spectrum of the methanol radical cation tagged with a He atom over the entire IR frequency range from 400 to 4000 cm$^{-1}$. The vibrational bands will be compared to results of ab initio calculations. In the same series of experiments spectra of the ethanol cation as well as the protonated forms of methanol and ethanol are studied.

Once the vibrational bands are obtained, ro-vibrational and even rotational lines can be recorded at high resolution, as has been demonstrated in previous studies.$^{27-32}$ Recording the vibrational bands of the simple alcohol molecules described here will be the first step in also identifying the alcohol cations or their protonated versions in space via their rotational transitions using the most sensitive radio telescopes available.

In this paper we first give a detailed description of the cryogenic 22-pole ion trap instrument FELion interfaced to the free electron lasers (FELs) at the FELIX Laboratory (Section 2), and the action spectroscopic methods that can be employed (Section 3). The instrument has been developed and built in Cologne in collaboration with the FELIX team and is by now available as a user station at FELIX. To demonstrate the capabilities of this unique combination of a cryogenic ion trap with the ultrabright and widely tunable radiation of the FELIX FELs, we
recorded IR spectra of the primary alcohols methanol and ethanol, and their protonated variants, and interpreted the results with the help of quantum-chemical calculations (Section 4). Several aspects of the employed methodology are discussed in Section 5 before conclusions are drawn (Section 6).

2 Experimental setup: FELion beam line at the FELIX Laboratory

2.1 Cryogenic radio-frequency 22-pole ion trap machine FELion

A schematic view of the cryogenic radio-frequency (RF) linear 22-pole ion trap instrument FELion can be seen in Fig. 1. This instrument is similar to the COLTRAP instrument described in detail by Asvany et al. It offers the key advantages of storing and cooling mass-selected molecular ions and good optical access for their characterisation using action spectroscopic techniques. The instrument has been used in the past for rotational studies of cold molecular ions, and since its installation at the FELIX Laboratory in 2014 for several vibrational spectroscopic studies on a variety of ionic systems.

In the following we will describe the FELion instrument in more detail, focusing on its three main operational units: ion preparation, storage, and analysis.

2.1.1 Ion preparation. The ion source used for the experiments presented in this work is an RF storage ion source, described in detail by Gerlich. This type of source employs RF trapping fields in the region where ions are produced via electron impact ionisation of a suitable precursor gas (electron energy on the order of tens of eV, typical source pressures of $10^{-6}$–$10^{-5}$ mbar). In this way, ions can be thermalised and accumulated in the source for the duration of an
experimental cycle (typically 1 s). At the beginning of each cycle the ions are pulse-extracted from the source (typically 1–100 ms long pulses) and the mass of interest is selected by a custom-made quadrupole mass filter with an inscribed radius of \( r_0 = 4.3 \text{ mm} \) driven by a home-built push–pull type RF generator operating at \( \sim 1.5 \text{ MHz} \).\(^{41}\) The source region of the setup has an independent pumping system in order to prevent precursor gases leaking into the main UHV chamber containing the 22-pole trap.

**2.1.2 Cryogenic 22-pole trap.** After passing a quadrupole bender, several thousand mass-selected ions are guided to the heart of the instrument, a 22-pole ion trap, described in detail by Asvany et al.\(^{42}\) The copper housing of the trap is mounted directly onto a cold head (Sumitomo RDK-408E2) allowing it to cool to a minimum temperature of slightly below 4 K. The temperature is monitored using an attached Si diode (Lakeshore DT-470-CU-13). The ions are kinetically and internally cooled by collisions with He buffer gas, which is admitted directly into the trap region at high number densities \( \sim 10^{14}–10^{15} \text{ cm}^{-3} \) via a pulsed piezo valve. Apart from the short (a few \( \mu \text{s} \)) pulse operation described by Asvany et al.,\(^{33}\) the valve can also be used for gated longer pulses (typically around 10–100 ms) by driving it with a sinusoidal excitation voltage (a few tens of Volts in amplitude) at its resonance frequency (1.8 kHz) provided by a home-built FPGA-based signal generator. The temperature of the trap can be varied between 4 and 30 K through a resistively heated kapton thermostrip (providing up to 40 W heating power) mounted on the cold head. In the following text, temperature refers to the nominal temperature of the trap housing, although previous studies\(^{43}–\!^{46}\) have shown that the actual ion temperature (internal and kinetic) in 22-pole traps is generally higher than the nominal trap temperature, and possible heating mechanisms have been discussed in the literature.\(^{47,48}\)

A second pulsed piezo valve and a gas line for a continuous gas supply are connected to the trap housing such that the temperature of the injected gas is close to the wall temperature. The 22-pole trap RF is generated using the amplified (10 W amplifier) output from a commercial DDS (direct digital synthesizer) and is operated at the trap resonance frequency of around 17 MHz with typical amplitudes of only a few tens of Volts to keep the RF heating effects at a minimum.

**2.1.3 Ion analysis.** After a certain storage time (typically 1–5 s), during which radiation can be coupled axially into the trap region for action spectroscopic measurements, the ions are extracted from the trap and either the parent or possible product ions are mass-selected with a second quadrupole mass-filter. This quadrupole has a rod diameter of 18 mm (inscribed diameter of \( 2r_0 = 15.678 \text{ mm} \)), driven by a Pfeiffer QMH 410-3 (1.44 MHz) RF power supply, allowing analysis of ions up to a mass of 130 u.\(\|^\) The ions are detected with either a Daly detector\(^{49}\) for positive ions, or a multi-channel-plate (MCP) detector for negative ions. The pulses generated by the detector are amplified and discriminated (Phillips Scientific model 6906, 300 MHz), and counted with a gated 100 MHz counter (Ortec model 996).

\(\|^\) In the meantime the second quadrupole mass-filter has been exchanged for a system with an 8 mm rod diameter (\( r_0 = 3.5 \text{ mm} \) inscribed radius) driven by a Pfeiffer QMH 410-2 (1.3 MHz) RF power supply, extending the mass range to \( \sim 2000 \text{ u} \).
2.2 Radiation sources

The ion trap machine FELion is interfaced to the FELIX-1 and FELIX-2 free electron lasers of the FELIX Laboratory via an evacuated beamline. Free-electron lasers operating in the MIR and FIR region of the electromagnetic spectrum offer the advantage of a very wide tunability and high pulse power, enabling the recording of unbiased vibrational overview spectra for molecular science. Therefore, cryogenic ion trap machines have been applied for many years in combination with free electron lasers, in particular with FELIX.7

2.2.1 FELIX. FELIX delivers pulsed infrared radiation continuously tunable from 100–2000 cm$^{-1}$, and in the 3rd harmonic operation mode even beyond 2000 cm$^{-1}$. Tuning of the laser wavelength can be controlled by the user through adjusting the undulator gap. The wavelength setting can be calibrated online using a spectrum analyzer contained in the FELIX beamline. The repetition rate of the macropulses is maximum 10 Hz, and the pulses have a typical length of 7 μs, with a 1 GHz microstructure originating from electron-bunching in the linear accelerator. The macropulses have an energy content of up to 50 mJ as measured at the user station, giving a cw power on the order of 500 mW. The bandwidth of the radiation is Fourier-transform limited and on the order of 0.5% FWHM, i.e. the typical bandwidth in our experiment is $\Delta \nu = 5$ cm$^{-1}$ (FWHM) at 1000 cm$^{-1}$.

At the user station, the IR radiation is coupled and focused into FELion via two mirrors and a vacuum window. The region between the two evacuated systems (FELIX beamline and FELion) is flushed with nitrogen to avoid absorption of IR radiation. At the moment, we use a KRS-5 vacuum window (75% transmission), which permits experiments down to about 250 cm$^{-1}$. The laser pulses of FELIX and the ion pulses of FELion are synchronized (by synchronizing the FELion cycle to the mains power), guaranteeing a constant phase of the FELIX pulses in relation to the trapping period. The number $N$ of laser pulses typically used is between 6 and 36 for spectroscopic scans, and can be extended up to several hundred for saturation depletion measurements (see Section 5.2).

2.2.2 Infrared parametric oscillator/amplifier. For accessing the important C–H and O–H stretching regions in the range 2900–3700 cm$^{-1}$, a table-top LaserVision pulsed optical parametric oscillator/amplifier (OPO/OPA) system has been used, provided by the FELIX facility.53 The OPO/OPA system is pumped with a 1064 nm Nd:YAG laser operating at 10 Hz. This system has a bandwidth of $\sim$3.5 cm$^{-1}$ (unseeded) and pulse energies of up to 17 mJ. The IR laser wavelength is calibrated with a wavemeter.

3 Methods

3.1 Experimental: action spectroscopy techniques

As the number density of ions in the trap ($\ll 10^5$ cm$^{-3}$) is too low for traditional absorption or emission spectroscopy, action spectroscopic techniques are applied to record the vibrational spectra. These methods rely on a change of the chemical composition of ions (and thus the change of mass composition) upon the absorption of a photon, and spectra can be recorded by counting the number of parent or product ions as a function of excitation frequency. In the experiments presented here, the methods of infrared pre-dissociation (IR-PD or “rare-gas...
tagging”) and multiple-photon dissociation (IR-MPD) were used and will be described in more detail in the following.

3.1.1 Infrared pre-dissociation spectroscopy IR-PD (“rare-gas tagging”). The absorption of a single IR photon (on a vibrational resonance) is not sufficient to break covalent bonds in a molecule. However, the situation changes in the case of weak bonds, e.g. in van der Waals complexes with typical binding energies on the order of only a few 100 cm\(^{-1}\), where even a far IR photon possesses sufficient energy to dissociate the complex. Attaching rare gas atoms or small molecules, i.e. tags, to the ion of interest is thus usable as an action spectroscopic scheme, as first demonstrated by Lee and coworkers,\(^1\) and adopted and further developed by many groups worldwide.\(^2,3,54\) One of the most recent developments is the use of cryogenic ion traps operating at close to or below 4 K, allowing \textit{in situ} tagging of molecular ions with He via ternary association reactions.\(^4,18,33,55,56\) Using He as a tagging agent has the advantage of inducing only a small shift of the vibrational band positions compared to the bare ion, due to its low polarizability and, therefore, influence on the structure and bond strengths of the tagged ion.

The typical experimental time sequence used in the FELion instrument in the present experiments is depicted in Fig. 2 (upper panel). The injection of the mass-selected primary ions into the 22-pole ion trap is always accompanied by an intense He gas pulse through the piezo valve in order to increase the trapping efficiency. Since high numbers of He-ion clusters are required for pre-dissociation experiments, the He pulse is deliberately prolonged to tens of ms, leading to efficient \textit{in situ} formation of He-ion complexes in the trap \textit{via} three-body attachment processes. The resulting composition of ions after such a long initial He pulse (70 ms, \(n_{\text{He}} = 5 \times 10^{14} \text{ cm}^{-3}\)) in the trap can be seen in Fig. 2 (lower panel) for the case of protonated methanol, where around 1/3 of primary ions are converted to He-ion clusters, and, moreover, around 1/9 are converted to doubly He-tagged clusters. After the He atoms are pumped out of the trapping volume (which takes several tens of ms at 4 K), photon absorption and subsequent pre-dissociation are used to measure an IR action spectrum.

![Fig. 2](image)

**Fig. 2** Time sequence of a single measurement (upper panel). Upon injection aided by the high He number density inside the trap, ions are irradiated with subsequent laser shots (here at 10 Hz), prior to extraction. Lower panel: number of ions in the trap (values in parentheses) produced from protonated methanol and a strong initial He pulse at 4 K.
For the actual spectrum acquisition, the number of He-ion clusters is recorded as a function of infrared excitation frequency. When the laser is in resonance with a vibrational band of the He-ion complex, a decrease of the number of complexes is observed.

For all spectra shown in this work the intensity ($I$) is given in units of a relative cross section, i.e. we plot the logarithm of the ratio of the measured number of clusters ($S$) over the baseline counts ($B$), normalised to the total deposited power $E \cdot N$, with $E$ being the energy in a single pulse (in mJ) and $N$ being the number of IR laser pulses during the storage time,

$$I = -\frac{\ln(S/B)}{E \cdot N}.$$  

(1)

Using this definition, the intensity is always a positive quantity. The baseline signal $B$ is obtained from a spline interpolation of the recorded ion counts in regions where no absorption occurs. In this way, we correct for fluctuations in the ion counts over a spectral scan, e.g. due to variations in He number density or ion production drifts. With this procedure, spectra taken under varying experimental conditions (e.g. laser power, storage time, absolute number of clusters) can easily be averaged and compared to each other. A comparison to calculated infrared intensities should be taken with care as the photon absorption is only the initial step in a sequence of mechanisms leading to the measured IR-PD signal.

3.1.2 Infrared multiple-photon dissociation IR-MPD. With the advent of intense, widely tunable free electron lasers operating in the IR domain, the method of infrared multiple-photon dissociation (IR-MPD) spectroscopy has become one of the dominant tools for vibrational spectroscopy and structural characterization of gas-phase molecular ions. Applications include biomolecular structure determination, and spectroscopy of organometallic and proton-bound systems, and of astronomically relevant polycyclic aromatic hydrocarbon (PAH) ions. IR-MPD relies on the resonant non-coherent absorption of multiple photons to deliver enough energy to the molecule to dissociate a covalent bond. It generally works best for large molecules with high enough density of states for efficient intra-molecular vibrational redistribution (IVR).

In order to record IR-MPD spectra in the FELion instrument, the experimental conditions are slightly varied compared to those used for IR-PD. Mass-selected ions are again thermalized with a He pulse when entering the trap, but the He pulse’s density is reduced to avoid complex formation. It is apparent that high photon densities (pulsed operation, 10 Hz) and a tight focusing of the laser beam are required for IR-MPD to work. We used 1500 mm focusing mirrors in combination with FELIX (and a pulsed OPO), resulting in a laser focus better than $d = 1$ mm in the trap region translating to a photon flux of up to roughly $10^{19}$ s$^{-1}$ mm$^{-2}$ at 1000 cm$^{-1}$.

The IR-MPD data are processed in a similar way as the pre-dissociation signal, with the only exception that in addition to recording the depletion of the parent ion, we can alternatively also count the number of a specific fragment ion $S_{\text{frac}}$ as a function of wavelength. We generally present the fragmentation yield ($S_{\text{frac}}/P$, with $P$ being the number of parent ions) normalized to laser pulse energy and number of applied pulses, as signal intensity in the corresponding figures.
Since the IR-MPD technique is not limited to low ion temperatures as in the case of IR-PD, we could record spectra of the ethanol radical cation as a function of temperature from room temperature down to 4 K (see Section 5 and Fig. 12), by either using the built-in heater to keep a fixed temperature, or by switching off the cold-head at the desired trap temperature, which leads to a temperature change of typically less than 5 K over the time of spectra acquisition (~15 min).

3.2 Quantum chemical calculations

Several previous quantum-chemical studies of ionized and protonated methanol and ethanol can be found in the literature (CH$_3$OH$^+$/CH$_2$OH$^+$; 25,57–60 CH$_3$OH$_2^+$; 61–63 C$_2$H$_5$OH$^+$; 26,64,65 C$_2$H$_5$OH$_2^+$ (gauche/anti forms); 66–68). Complementary calculations (at common theoretical levels) to support analysis of the present study were performed using density functional theory (DFT) with the B3LYP functional and coupled-cluster theory in its variant CCSD(T). All calculations were performed using the Gaussian and CFOUR programs.

Structural parameters and harmonic vibrational frequencies of a total of seven bare ions as well as eight of their He-tagged variants (Fig. 3) were calculated using B3LYP (opt = tight, int = ultrafine) in combination with the aug-cc-pVTZ basis set. As dispersion interactions are not treated adequately in standard DFT, the B3LYP/aug-cc-pVTZ calculations were performed also using GD3BJ as implemented in Gaussian (Grimme D3 dispersion with Becke–Johnson damping). Only complexes with Helium attached to hydrogen atoms of hydroxyl-/oxonium groups were studied explicitly (Fig. 3) as those were shown earlier to be energetically favored for Ar-, Ne- and N$_2$-complexes. As can be seen from Fig. 3, all singly He tagged oxonium species are structurally equivalent except for the gauche form of C$_2$H$_5$OH$_2^+$ where the two binding sites to –OH$_2^+$ are different. Detailed results of the calculations (energies, structural parameters, vibrational frequencies also including anharmonic values calculated for a subset of the species considered here) are given as part of the ESI.*

At the CCSD(T) level, molecular structures of all bare ions as well as force fields of selected species were calculated using the ANO1 basis as this level of theory has been shown to provide accurate vibrational frequencies. For the radical cations (CH$_3$OH$^+$, CH$_2$OH, C$_2$H$_5$OH$^+$) unrestricted Hartree–Fock (UHF) reference wave functions were used. Owing to computational cost, CCSD(T)/ANO1 anharmonic force fields were calculated for two of the simpler species only, i.e., the methanol derivatives CH$_2$OH$_2^+$ and CH$_3$OH$_2^+$. Calculation of the CCSD(T) anharmonic force field of the CH$_3$OH$^+$ radical cation was impractical due the problems of second-order vibrational perturbation theory (VPT2) with large amplitude motions occurring in this ion. All relevant results obtained using CCSD(T) are given in the ESI.*

The interactions of He atoms and ions are rather weak. Without explicit consideration of dispersion interactions, B3LYP binding energies calculated here are on the order of 50 to 150 cm$^{-1}$ only, with dispersion increasing these values to 120 to 225 cm$^{-1}$. Consequently, He tagging does not change the fundamental vibrational frequencies of the bare ions by very much, typically on the order of a few cm$^{-1}$, except for the OH stretching bands and several other bands involving inversion modes (some 10–40 cm$^{-1}$, see Section 1 and 2.2 of the ESI* for details). Calculations of CH$_3$OH$_2^+$ and its He-cluster at the CCSD(T)/aug-cc-pVTZ level were
used to derive a coupled cluster-value for the He-binding energy. The value of 150 cm$^{-1}$ compares favorably with the corresponding B3LYP-GD3BJ value (175 cm$^{-1}$).

As is common practice, in the following, for discussion and assignment of vibrational frequencies, the B3LYP/aug-cc-pVTZ harmonic frequencies of He-tagged clusters (scaled by a common factor of 0.966) were used. As can be seen from a comparison for protonated methanol (Section 3 of the ESI†) differences between the various sets of calculated vibrational frequencies (untagged, He-tagged, scaled harmonic and anharmonic frequencies) are generally rather
small. Finally, it should be noted that the mechanisms underlying conventional absorption and action spectroscopies are different as pointed out in the discussion of eqn (1), thus making infrared band intensities not necessarily instrumental in the analysis of intensities in action spectra. As a consequence, the calculated infrared intensities in Tables 1 to 6 and in the ESI† are given for the sake of completeness but need to be viewed with caution in the evaluation of the experimental action spectra presented.

4 Measurements and results: spectroscopy of simple alcohol radical ions and protonated alcohols

In order to demonstrate the capabilities of the FELion instrument coupled to FELIX' FEL-2, we used the He IR-PD technique at 4 K in the frequency range 300–1800 cm\(^{-1}\) to record the spectra of four primary alcohol ions: methanol and ethanol, in their radical ion and protonated forms. Additional data were taken using the pulsed OPO system in the 2850–3600 cm\(^{-1}\) range. The experimental spectra are summarized in Fig. 4 and compared to results of quantum chemical calculations (cf. Section 3.2). Experimental and calculated vibrational band positions are summarized in Tables 1–6.

For the experiments, commercial methanol and ethanol samples (HPLC grade >99.9%, and technical grade 99%, resp.) were purified with several freeze–thaw cycles at −195 °C and leaked directly into the ion source as precursor gas for the respective ionic species (source pressure of the order 10\(^{-5}\) mbar). Radical methanol and ethanol ions were produced by electron impact ionization with electron energies in the range 20–40 eV. Both alcohols possess high proton affinities (754 and 776 kJ mol\(^{-1}\) for methanol and ethanol, resp.), effectively producing protonated forms through ion molecule reactions with water, or even more likely with another neutral molecule of the same alcohol in the storage ion source. For all ions multiple spectra over the frequency range were taken, and then normalized, averaged and concatenated to produce the final spectra displayed in Fig. 4.

4.1 Methanol cation vs. methylene-oxonium – \(m = 32\) u

The mass 32 u ion with the nominal formula \([\text{CH}_4\text{O}]^+\) produced from electron impact ionization of methanol (\(\text{CH}_3\text{OH}\)) has two stable isomers, with methylene-oxonium (\(\text{CH}_2\text{OH}_2^+\), structure 1b in Fig. 3) being the most stable structure, and the methanol cation (\(\text{CH}_3\text{OH}^+\)) lying 6.9 kcal mol\(^{-1}\) higher in energy (structure 1a in Fig. 3, see also Sections 1.1–1.2 and 2 in the ESI†). In a recent IR-PD spectroscopic study of the CH– and OH–stretching band region using Ar tagging, Mosley et al.\(^{25}\) predominantly observed features belonging to the methanol cation, which they explained with a high isomerization barrier (30.8 kcal mol\(^{-1}\)) between the lowest energy methylene-oxonium isomer and the methanol cation, with the latter being produced as the primary ionization product in their molecular beam discharge source.

Based on a comparison of the experimental \([\text{CH}_4\text{O}]^+\)–He spectrum and the predicted theoretical spectra of both isomers (Fig. 4, top panel) we can also clearly attribute the majority of strong bands to the less stable \(\text{CH}_3\text{OH}^+\). In Table 1 we list the theoretically predicted band positions from the highest to lowest frequency as
well as the experimental bands when they could be associated and assigned to the theoretical bands. The additional unassigned band progressions to the blue of the main features in the 900–1400 cm\(^{-1}\) region are likely due to combination bands with the He stretching and bending modes, which have predicted fundamental frequencies in the range 50–150 cm\(^{-1}\). This conclusion is supported by the spectra shown in Fig. 5, where H\(_2\) was used as a tagging agent instead of He, and the position of the main bands but also the structure of the progression bands significantly changes.

However, we also clearly see a feature at 1635 cm\(^{-1}\) at the predicted band position of the diagnostic OH\(_2\) scissor mode of CH\(_2\)OH\(_2^+\) (1a) where naturally no vibrational feature of CH\(_3\)OH\(^+\) (1a) is predicted. Additionally, we attribute the observed band at 3480 cm\(^{-1}\) to one of the two OH stretching bands of methyleneoxonium (the other one might overlap with the OH band of CH\(_2\)OH\(^+\) as indicated by the vertical lines of the theoretical predictions), whereas the assignment of the OH\(_2\) inversion bands around 630 cm\(^{-1}\) remains ambiguous (see Table 2). The fact that we can rather efficiently produce both isomers in our experiment can be attributed to isomer quenching in our storage ion source, where primary ions created via electron impact ionization undergo many collisions (and possibly reactions) within the storage time (of up to several seconds) and are thus pre-cooled to the temperature of the storage ion source (~400 K). This behaviour has been observed previously in the case of hydrocarbon ions.\(^{79}\)
4.1.1 Influence of tagging agent and comparison to earlier work. Additional He IR-PD spectra were recorded for the $m = 32$ u ions in this work in the 2300–2800 cm\(^{-1}\) region using the 3rd harmonic mode of FEL-2. These data (together with the OPO data already shown in Fig. 4) are presented in Fig. 6 and compared with the recent work of Mosley \textit{et al.}\(^{25}\) using Ar and Ne as tagging agents. As can be seen for the OH stretching band of the CH\(_3\)OH\(^{+}\) ion at \(\approx 3400\) cm\(^{-1}\), the use of Ne

![Image](image_url)

**Fig. 5** Comparison of infrared pre-dissociation spectra of the methanol ion ($m = 32$ u) using tagging with a single He atom at 4 K (upper panel) or H\(_2\) at 10 K (lower panel).
only induces a small redshift of 15 cm$^{-1}$ with respect to the He IR-PD spectrum, whereas the redshift of the Ar tagged species is substantial (232 cm$^{-1}$), demonstrating the relative “innocence” of the He tag, i.e. its small influence on the observed band positions (see also Table 3). Our calculations (Section 1.1 in the ESI†, anharmonic B3LYP/aug-cc-pVTZ) predict a redshift of only $\approx$10 cm$^{-1}$ for this band upon attachment of a He atom to the bare ion. However, the true shift due to the attached He and thus the quality of the calculated band positions can only be found by comparison to a spectrum of the bare ion.

Interestingly, Mosley et al.\textsuperscript{25} observed a pronounced substructure in the region from 2400–2900 cm$^{-1}$ adjacent to the totally symmetric and anti-symmetric CH

### Table 2 Vibrational wavenumbers of CH$_2$OH$_2^+$–He (1b) (in cm$^{-1}$)$^a$

<table>
<thead>
<tr>
<th>Mode</th>
<th>Meas. He IR-PD</th>
<th>Calc. B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pos.</td>
<td>Int.</td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>3478</td>
<td>1.44*</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>3478</td>
<td>1.44*</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>3037</td>
<td>0.34</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>1635</td>
<td>0.88</td>
</tr>
<tr>
<td>$\nu_5$</td>
<td>1363</td>
<td>0.68</td>
</tr>
<tr>
<td>$\nu_6$</td>
<td>1247</td>
<td>0.89*</td>
</tr>
<tr>
<td>$\nu_7$</td>
<td>905</td>
<td>1.48</td>
</tr>
<tr>
<td>$\nu_8$</td>
<td>900</td>
<td>7</td>
</tr>
<tr>
<td>$\nu_9$</td>
<td>639</td>
<td>85</td>
</tr>
<tr>
<td>$\nu_{10}$</td>
<td>599</td>
<td>0.84</td>
</tr>
<tr>
<td>$\nu_{11}$</td>
<td>167</td>
<td>13</td>
</tr>
<tr>
<td>$\nu_{12}$</td>
<td>102</td>
<td>2</td>
</tr>
</tbody>
</table>

*a* Scaling factor 0.966. Intensities in km mol$^{-1}$ (calc.) and mJ$^{-1}$ (meas.), see text. * denotes multiply assigned bands.

![Fig. 6 Observed IR-PD spectra of the methanol ion (m = 32 u) in the CH– and OH– stretching region, tagged with He (blue, this work) in the cold ion trap, as well as with Ne (magenta) and Ar (red) in a supersonic expansion and consequent mass selection (data digitized from Mosley et al.\textsuperscript{25}). The intensities are arbitrarily scaled for best comparability.](image-url)
stretching bands (see red trace in Fig. 6), which they attributed to combination bands of the CH stretching modes with the low-lying torsional bands and an overtone of the HOC bending mode. This substructure is not observed in our He IR-PD spectrum, however, we see a clear doublet structure with peaks at 2442 cm\(^{-1}\) and 2477 cm\(^{-1}\), which we assign to the totally symmetric and antisymmetric CH stretching bands. However, judged from the relative intensity of the two bands, and in light of the large anharmonicities and interactions with the torsion, the absolute assignment remains ambiguous.

4.2 Protonated methanol – \(m = 33\) u

Protonated methanol (CH\(_3\)OH\(_2^+\)) is the only stable isomer with the [CH\(_5\)O]\(^+\) composition (\(m = 33\) u).\(^{61}\) It was long discussed to be involved in the formation of the ubiquitous methanol molecule in the interstellar medium (via dissociative recombination with electrons), triggering several kinetic studies.\(^{81-83}\) In addition, collisions of the dominant molecular ion H\(_3^+\) with methanol will lead to the formation of CH\(_3\)OH\(_2^+\). However, no previous spectroscopic investigations of this fundamental ion have been reported to date. Here we present the first vibrational spectrum of protonated methanol, recorded via He IR-PD and displayed in Fig. 4 (second panel). The comparison with quantum-chemical calculations allows a clear assignment of all strong experimental features above 700 cm\(^{-1}\) to fundamental bands (see Table 4), with the dominant peaks belonging to the CO stretching band (800 cm\(^{-1}\), \(v_{13}\)), the three overlapping modes involving the CH\(_3\) group (1447 cm\(^{-1}\), \(v_{7-9}\)), the HOH scissor mode (1636 cm\(^{-1}\), \(v_6\)), and the symmetric and antisymmetric OH stretching bands (3504 and 3507 cm\(^{-1}\), \(v_1\) and \(v_2\)). The observed bandwidth (43 cm\(^{-1}\)) for the HOH scissor mode is considerably larger than those observed for the other bands, and larger than the intrinsic FEL bandwidth of around 0.5–1%, see Section 4 in the ESI† for a comparison of fitted bandwidths. This we attribute to a fast predissociation process of the order 0.1 ps upon excitation of this mode. This seems likely since the attached He is located at one of the equivalent hydrogens of the HOH group (see Fig. 3 and Section 1.3 in the ESI† and also the discussion in Section 4.2.1).

In the region below 700 cm\(^{-1}\) the assignment is not so clear. The scaled harmonic B3LYP band position of the strong OH\(_2\) inversion mode lies at 678 cm\(^{-1}\), well above the strong observed feature at \(~540\) cm\(^{-1}\). However, anharmonic corrections for this mode are significant, predicted from DFT and CCSD(T) calculations (see Section 1.3 in the ESI†), shifting the band to 580 cm\(^{-1}\) for the He-ion complex, as is shown in Section 3 of the ESI†. We, therefore, tentatively assign this strong band accordingly and attribute the observed

<table>
<thead>
<tr>
<th></th>
<th>He IR-PD, this work</th>
<th>Ar IR-PD</th>
<th>Ne IR-PD</th>
<th>VUV-IR</th>
<th>VUV-IR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol(^+)</td>
<td>2442</td>
<td>2473 (^{25})</td>
<td>3156 (^{25})</td>
<td>3373 (^{25})</td>
<td>2900 (^{80})</td>
</tr>
<tr>
<td></td>
<td>3387</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol(^+)</td>
<td>2947</td>
<td>3156 (^{25})</td>
<td></td>
<td>3373 (^{25})</td>
<td>2900 (^{80})</td>
</tr>
<tr>
<td></td>
<td>3479</td>
<td></td>
<td></td>
<td></td>
<td>3470 (^{80})</td>
</tr>
<tr>
<td>Protonated ethanol</td>
<td>3499</td>
<td>3377(25) (^{68})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3576</td>
<td>3547(22) (^{68})</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
progression of features to the blue as combination bands of the OH$_2$ inversion mode with the bending and stretching modes involving the attached He, whose scaled harmonic frequencies are at 49 cm$^{-1}$, 77 cm$^{-1}$ and 148 cm$^{-1}$, but likely affected by large anharmonicity effects.

In order to verify this reasoning, we also recorded spectra of the same spectral region with two He atoms attached to protonated methanol. A comparison of both spectra is shown in Fig. 7. Apart from a general shift of the bands, the observed substructure in the progression clearly starts to collapse. This might be expected upon the addition of a second He atom to the HOH moiety as vibrational modes of the two He atoms and the core ion will lead to even lower frequency vibrations.

Estimates from the CCSD(T)/ANO1 anharmonic force field predict the low-lying torsional mode and its first two overtones at 203, 367 and 490 cm$^{-1}$. If the observed feature near 540 cm$^{-1}$ corresponded to the second overtone we also should have clearly detected the first overtone, which lies well above the calculated dissociation energy of $D_0 = 106–177$ cm$^{-1}$ (depending on the level of theory, see Section 2 in the ESI†). Therefore, the interpretation of the bands being associated with modes involving the attached He seems more likely.

4.2.1 Pre-dissociation and the lifetime. The pre-dissociation lifetime of the He tag does not lead to a significant broadening of the observed bands, except for the significantly broadened HOH scissor mode discussed above. The experimental bandwidth on the order of cm$^{-1}$, determined using the LaserVision OPO and FELIX, corresponds to lifetimes on the order of ps. However, the effect of lifetime broadening can dominate the observed linewidth when using cw lasers of small intrinsic bandwidths.$^{55,56}$ In an additional study on the protonated methanol ion we

<table>
<thead>
<tr>
<th>Mode</th>
<th>Meas. He IR-PD</th>
<th>Calc. CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>3571</td>
<td>15.1</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>3504</td>
<td>12.3</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>3100</td>
<td>1.21*</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>3100</td>
<td>1.21*</td>
</tr>
<tr>
<td>$\nu_5$</td>
<td>3002</td>
<td>1.1</td>
</tr>
<tr>
<td>$\nu_6$</td>
<td>1636</td>
<td>13.2</td>
</tr>
<tr>
<td>$\nu_7$</td>
<td>1433</td>
<td>18</td>
</tr>
<tr>
<td>$\nu_8$</td>
<td>1447</td>
<td>15.6</td>
</tr>
<tr>
<td>$\nu_9$</td>
<td>1238</td>
<td>1</td>
</tr>
<tr>
<td>$\nu_{10}$</td>
<td>1165</td>
<td>1.5</td>
</tr>
<tr>
<td>$\nu_{11}$</td>
<td>922</td>
<td>3.1</td>
</tr>
<tr>
<td>$\nu_{12}$</td>
<td>802</td>
<td>21.2</td>
</tr>
<tr>
<td>$\nu_{13}$</td>
<td>678</td>
<td>281</td>
</tr>
<tr>
<td>$\nu_{14}$</td>
<td>148</td>
<td>10</td>
</tr>
<tr>
<td>$\nu_{15}$</td>
<td>49</td>
<td>3</td>
</tr>
</tbody>
</table>

* Scaling factor 0.966. Intensities in km mol$^{-1}$ (calc.) and mJ$^{-1}$ (meas.), see text. * denotes multiply assigned bands.
have used a continuous-wave (cw) OPO (Aculight Argos), with a line width of a couple of MHz, coupled to a similar ion trap instrument\textsuperscript{33,84} with the aim of recording high-resolution ro-vibrational spectra of the CH\textsubscript{3}OH\textsuperscript{2+}–He cluster.

In Fig. 8, the results using the high-resolution cw and pulsed OPOs are compared. In both cases the relative depletion yield, \textit{i.e.} the number of ions with radiation relative to the number of ions in the trap without the laser present, is plotted. The observed widths of the predissociation bands are nearly identical, a clear indication that the linewidth is dominated by the pre-dissociation lifetime (of the order of 2 ps). This prevents a ro-vibrational study of this He-ion complex with IR-PD. Furthermore, we were also unsuccessful in recording the infrared ro-vibrational spectrum of the bare ion using the techniques of Laser Induced Inhibition of Complex Growth (LIICG).\textsuperscript{27,33,55,85} Therefore, other techniques of action spectroscopy need to be explored to unravel the rotational spectrum of protonated methanol.

4.3 Ethanol cation – \textit{m} = 46 u

The third panel in Fig. 4 shows the experimental He IR-PD spectrum of the ethanol radical cation together with a theoretical prediction. As in earlier studies,\textsuperscript{26,86} our calculations predict the \textit{C\textsubscript{1}} structure of this ion to be more stable than the \textit{C\textsubscript{3}} form by 2.5 kcal mol\textsuperscript{-1} (see Section 2 in the ESI†), and the corresponding predicted vibrational bands of both isomeric structures tagged with He on the OH\textsuperscript{+} group (see Fig. 3, structures 3a and 3b, resp.) are displayed for comparison. As expected, we observe a good match of our experimental spectrum with the lower lying isomeric structure (3a). The two earlier reported vibrational spectroscopic studies of the ethanol cation were performed in the 2400–7100 cm\textsuperscript{-1} region covering the CH and OH fundamental and overtone stretching bands by VUV-IR double resonance schemes.\textsuperscript{26,80} Our observed CH and OH stretching band positions using He tagging

![Fig. 7 Pre-dissociation spectra of protonated methanol using He tagging at 4 K. Upper panel – singly tagged ion. Lower panel – doubly tagged ion.](image-url)
are slightly blueshifted compared to the VUV-IR measurements, see Table 3. This is surprising, since the attached He atom is expected to induce a red-shift of the vibrational band (of ~15 cm\(^{-1}\), see Section 1.4 in the ESI\(^\dagger\)). However, the VUV-IR double resonance method relies on either preparing the cation in a highly excited Rydberg state prior to IR excitation or in an IR multiple photon process to induce the observed dissociation of the ion.\(^{87}\) Both processes might lead to a red shift of the vibrational bands.

In the present study we record and assign all fundamental vibrational transitions down to 900 cm\(^{-1}\), see Table 5. The formation of only one, the most stable isomeric C\(_1\) structure, upon electron impact ionization of ethanol is corroborated not only by the close match of the observed and calculated spectra (and the absence of an additional OH stretching band belonging to the second isomer), but also by saturation depletion measurements as described in detail in Section 5.2. The two unassigned observed vibrational features at ~610 and ~680 cm\(^{-1}\) are likely combination bands involving the strong OH torsional motion (\(v_{19}\)) and lower lying bands involving the CH\(_3\) torsion (\(v_{20,21}\)).

### 4.4 Protonated ethanol – \(m = 47\) u

Protonated ethanol features two distinct rotamers with the gauche form being more stable than the anti form by about 0.3 kcal mol\(^{-1}\) (see also Sections 1.6 and 1.7 in the ESI\(^\dagger\)). The calculated vibrational band positions of both isomers complexed with He are shown as stick diagrams in Fig. 4 (bottom panel), together with our observed He IR-PD spectrum of protonated ethanol (\(m = 47\) u). Where in the anti rotamer the two preferred binding sites of the He ligand (on the OH groups) are equivalent (structure 4b in Fig. 3), they are different in the gauche rotamer (4a and 4a'), leading to slightly different induced band shifts (of the order of ~5 cm\(^{-1}\)). Based on the nearly identical predicted spectra, \(i.e.\) the absence of a diagnostic band only present in one of the isomeric forms, we cannot unambiguously assign the observed spectrum to either one or the other rotamer. In general, however, the predictions for both isomers (and both He binding sites) agree well with the observed spectrum, and an assignment of the vibrational

---

Fig. 8 Pre-dissociation spectrum of CH\(_3\)OH\(_2^+\)–He. The magenta line represents data recorded with a pulsed OPO (\(\sigma = 2\) cm\(^{-1}\)), while the yellow points represent data recorded using a narrow line width cw OPO (\(\sigma <\) MHz). The data is shown as the relative depletion of complexes.
bands is summarized in Table 3. One rather intense observed band at \( \nu \approx 520 \text{ cm}^{-1} \) cannot be accounted for by the calculated fundamental bands. At the moment we can only speculate that this is a combination band involving the CH\(_3\) torsional mode (\( \nu_{24} \)), predicted with high intensity. The band position of this mode is in fact strongly influenced by the attachment of the He atom (predicted blue-shift of \( \approx 40 \text{ cm}^{-1} \), see Section 1.6–1.7 in the ESI†). It would certainly be interesting to extend the measurements to lower wavenumber regions covering the fundamental CH\(_3\) torsional mode in future studies.

In an earlier study, Solcà and Dopfer\(^a\) reported vibrational spectra of protonated ethanol in the OH stretching region, using Ar and N\(_2\) IR-PD. As expected, the use of those more strongly bound ligands introduces a significant red-shift of the observed bands (see Table 3). Compared to our He-tagged spectra in this region, the shift is significantly more pronounced for the lower lying symmetric bands (122/341 cm\(^{-1}\) for Ar/N\(_2\), resp.) than for the antisymmetric (29/25 cm\(^{-1}\) for Ar/N\(_2\)) OH stretching band.

## 5 Discussion

### 5.1 Comparison of He IR-PD to IR-MPD

In addition to the He IR-PD measurements presented in Section 4, we also recorded IR-MPD spectra of the ethanol radical cation and protonated ethanol, in

<table>
<thead>
<tr>
<th>Mode</th>
<th>Meas. He IR-PD</th>
<th>Calc. B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_1 )</td>
<td>3476</td>
<td>3494</td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>3096</td>
<td>3112</td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td>3073</td>
<td>3084</td>
</tr>
<tr>
<td>( \nu_4 )</td>
<td>3011</td>
<td>3044</td>
</tr>
<tr>
<td>( \nu_5 )</td>
<td>2947</td>
<td>2956</td>
</tr>
<tr>
<td>( \nu_6 )</td>
<td>2947</td>
<td>2939</td>
</tr>
<tr>
<td>( \nu_7 )</td>
<td>1407</td>
<td>1397</td>
</tr>
<tr>
<td>( \nu_8 )</td>
<td>1375</td>
<td>1366</td>
</tr>
<tr>
<td>( \nu_9 )</td>
<td>1336</td>
<td>1319</td>
</tr>
<tr>
<td>( \nu_{10} )</td>
<td>1259</td>
<td>1258</td>
</tr>
<tr>
<td>( \nu_{11} )</td>
<td>1233</td>
<td>1219</td>
</tr>
<tr>
<td>( \nu_{12} )</td>
<td>1105</td>
<td>1091</td>
</tr>
<tr>
<td>( \nu_{13} )</td>
<td>1087</td>
<td>1066</td>
</tr>
<tr>
<td>( \nu_{14} )</td>
<td>920</td>
<td>908</td>
</tr>
</tbody>
</table>

\(^a\) Scaling factor 0.966. Intensities in km mol\(^{-1}\) (calc.) and mJ mol\(^{-1}\) (meas.), see text.
order to compare these two methods under otherwise identical conditions (e.g. ion production, laser power and linewidth, and ion kinetic and internal temperature, which was close to 4 K in both cases). In general, IR-MPD does not work for small molecules because the necessary IVR process for the absorption of more than one photon of the same energy is too slow. Therefore, IR-MPD is a standard method to characterize molecules more complex than ethanol and in fact attempts to record such spectra for the methanol species failed.

The IR-MPD process can lead to the production of several fragments, the dominant ones (showing higher S/N ratio) being the dehydrogenated form ($m = 45$ u) for the ethanol radical cation and $\text{H}_3\text{O}^+$ ($m = 19$ u) for protonated ethanol, and these were used to record the IR-MPD spectra shown in the lower panels of Fig. 9 and 10, respectively. The upper panel in each figure displays the corresponding He IR-PD spectrum.

As is directly evident from these figures, there are major differences in the observed spectra with respect to the number of bands, band intensities and line

<table>
<thead>
<tr>
<th>Mode</th>
<th>Meas. He IR-PD</th>
<th>Calc. B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>3576</td>
<td>1.8</td>
</tr>
<tr>
<td>$v_2$</td>
<td>3499</td>
<td>1.5</td>
</tr>
<tr>
<td>$v_3$</td>
<td>3069</td>
<td>0.1</td>
</tr>
<tr>
<td>$v_4$</td>
<td>3033</td>
<td>0.1</td>
</tr>
<tr>
<td>$v_5$</td>
<td>2977</td>
<td>0.2*</td>
</tr>
<tr>
<td>$v_6$</td>
<td>2977</td>
<td>0.2*</td>
</tr>
<tr>
<td>$v_7$</td>
<td>2949</td>
<td>0.1</td>
</tr>
<tr>
<td>$v_8$</td>
<td>1605</td>
<td>4.38</td>
</tr>
<tr>
<td>$v_9$</td>
<td>1465</td>
<td>1.2</td>
</tr>
<tr>
<td>$v_{10}$</td>
<td>1445</td>
<td>4</td>
</tr>
<tr>
<td>$v_{11}$</td>
<td>1441</td>
<td>1.7</td>
</tr>
<tr>
<td>$v_{12}$</td>
<td>1389</td>
<td>4.7</td>
</tr>
<tr>
<td>$v_{13}$</td>
<td>1353</td>
<td>12</td>
</tr>
<tr>
<td>$v_{14}$</td>
<td>1244</td>
<td>3</td>
</tr>
<tr>
<td>$v_{15}$</td>
<td>1157</td>
<td>1.8</td>
</tr>
<tr>
<td>$v_{16}$</td>
<td>1129</td>
<td>1.6</td>
</tr>
<tr>
<td>$v_{17}$</td>
<td>949</td>
<td>8.98</td>
</tr>
<tr>
<td>$v_{18}$</td>
<td>904</td>
<td>2.0</td>
</tr>
<tr>
<td>$v_{19}$</td>
<td>808</td>
<td>2.1</td>
</tr>
<tr>
<td>$v_{20}$</td>
<td>665</td>
<td>31.5</td>
</tr>
<tr>
<td>$v_{21}$</td>
<td>617</td>
<td>19.2</td>
</tr>
<tr>
<td>$v_{22}$</td>
<td>369</td>
<td>2.0</td>
</tr>
<tr>
<td>$v_{23}$</td>
<td>249</td>
<td>6</td>
</tr>
<tr>
<td>$v_{24}$</td>
<td>215</td>
<td>48</td>
</tr>
<tr>
<td>$v_{25}$</td>
<td>128</td>
<td>5</td>
</tr>
<tr>
<td>$v_{26}$</td>
<td>40</td>
<td>3</td>
</tr>
<tr>
<td>$v_{27}$</td>
<td>37</td>
<td>4</td>
</tr>
</tbody>
</table>

$^a$ Scaling factor 0.966. Intensities in km mol$^{-1}$ (calc.) and mJ$^{-1}$ (meas.), see text. * denotes multiply assigned bands.
widths. Most striking is the absence of clear bands in the low energy region of the spectrum; the bands below 1000 cm\(^{-1}\) are missing in the IR-MPD spectrum since even with the brilliant FEL radiation not enough photons can be absorbed during one laser pulse to cause dissociation. However, other vibrational bands are strongly enhanced in the IR-MPD spectrum, e.g., the observed band of protonated ethanol at around 3100 cm\(^{-1}\), which might correspond to the CH stretching fundamental bands, but is more likely the overtone of the HOH scissor mode, which is observed as a very broad and intense feature in the IR-MPD spectrum at 1650 cm\(^{-1}\).

In general, the width of the measured vibrational bands is significantly higher for IR-MPD than for He IR-PD, e.g., we observe a FWHM of 22 and 14 cm\(^{-1}\), respectively, for the 3480 cm\(^{-1}\) OH stretching band of protonated ethanol at the same ion temperature of 4 K, a behaviour that is inherent to the multiple photon process.\(^{12,88,89}\) The reduced band width and the very small shift associated with the attached He atom in the case of the IR-PD method turns this method into a nice tool for unraveling the structure of molecules with many more close lying bands. Also, the access to lower lying bands as illustrated in Fig. 9 and 10 gives IR-PD a higher diagnostic value than IR-MPD.

An even more detailed view of the differences between IR-PD and IR-MPD band structures and positions is given in Fig. 11, in the example of the cold (4 K) OH stretching band of the ethanol radical cation. The band recorded via IR-MPD in two different fragmentation channels shows a significantly larger bandwidth (intrinsic OPO FWHM \(\approx 3\) cm\(^{-1}\), calibration accuracy \(1–2\) cm\(^{-1}\) ) compared to that in the He IR-PD spectrum, whereas the He tag introduces a small red-shift in band position (by \(2–3\) cm\(^{-1}\) ). This is even smaller than predicted from our calculations (see Section 1.4 in the ESI\(^\dagger\)). However, the IR-MPD process is also known to introduce red-shifts due to anharmonicity,\(^{88}\) although the extent of this effect has been discussed in only a few studies.\(^ {5,90}\)

---

Fig. 9  Comparison between the observed IR-PD (He tagging, upper panel) and IR-MPD (lower panel, monitoring the hydrogen loss channel, \(m = 45\) u) spectra for the ethanol radical ion, performed at \(T = 4\) K.

Published on 07 May 2019. Downloaded by Radboud University Nijmegen on 10/28/2019 3:19:45 PM.
Since the IR-MPD technique is not limited to low ion temperatures as is the case of IR-PD, we recorded spectra of the ethanol radical cation as a function of temperature from close to room temperature (245 K) down to 4 K, revealing the efficient cooling of the rotational level population via an observed substantial narrowing of the band profile. In Fig. 12 we present the corresponding IR-MPD spectra in the CH₃ (upper panel, m = 31 u) and hydrogen (middle panel, m = 45 u) neutral loss channels. The first thing to notice is the change in absolute and more importantly relative band intensities for the two fragmentation channels with temperature. The rotational band contour visible in the spectra at the highest temperatures, revealing the characteristic P, Q and R-substructure, is seen to collapse in the spectra taken at the lowest temperatures, as is qualitatively expected. To address this quantitatively, the lower panel shows a simulation of the rotational band contour, based on rotational constants of the ethanol cation–He complex and transition moments calculated from anharmonic force fields. The calculated stick spectrum was convoluted with the OPO linewidth (FWHM ~3.5 cm⁻¹), which is clearly dominating the observed linewidth of the 4 K band. Fig. 12 thereby demonstrates the advantages of a low temperature ion trap for IR-MPD spectroscopy compared to room temperature experiments, in particular for small molecular ions, effectively reducing the band width by a large factor while increasing the intensity in the band center, provided the spectral brightness allows for the IR-MPD process. In this respect the decreasing intensity at the lowest trap temperatures in the case of the energetically less favoured CH₃ abstraction channel (18.6 vs. 10.7 kcal mol⁻¹ for CH₃ vs. hydrogen loss, resp.) might be an indicator that even with the brilliant FELIX light source the cold, “small” ethanol cation cannot be heated as efficiently as the warm one, which already stores many times k⋅T in all its vibrational modes.

![Fig. 10](image-url) Comparison between the observed IR-PD (He tagging, upper panel) and IR-MPD (lower panel, monitoring the H₂O⁺ loss channel, m = 19 u) spectra for protonated ethanol, performed at T = 4 K.
5.2 Saturation depletion measurements – distinguishing isomers

In the FELion instrument, the ions undergoing spectroscopic interrogation have a well defined mass to charge ratio (due to selection in a quadrupole mass filter). Furthermore, the charge of the ion can be assessed using He (or any other ligand) attachment. Attachment of He to the singly charged ion leads to the appearance of +4 u from the bare ion mass, whereas for doubly charged ions it leads to appearance of +2 u in the mass spectrum. This phenomena allows us to safely assume that only singly charged ions contribute to the vibrational spectra presented in this study.

Nevertheless, as shown for the spectra of the methanol cation and methylene oxonium (both $m = 32$ u) the question on the isomeric structure of the stored ion remains. In Fig. 13 we show an example of a so-called saturation depletion measurement recorded for the ethanol radical cation. In these experiments the relative peak depletion signal, $D = 1 - S/B$, is recorded as a function of deposited energy $E$ at a wavelength coincident with the band center of a specific vibrational band. Here $S$ denotes the ion counts at a resonant frequency and $B$ denotes the counts at an off-resonance frequency for the same storing time and laser power, to account for the effects of ion losses from the trap by non-radiative processes. The energy can be varied by changing the irradiation time (equivalent to the storage time in the trap, which can be extended to tens of seconds) and/or the light intensity. As can be seen, the depletion shows a saturation trend towards a maximum convergence value at high energies. This value, under certain conditions, may reveal the ratio of “active”, i.e. absorbing, ions at this wavelength, see also Jašik et al. for a description of a similar method.

If we assume the presence of two isomers, one of which is active (absorbing) at the specific wavelength and contributing an ion signal $S_a$, and another one which is not active with an ion signal $S_n = S - S_a$, then the observed depletion signal will
follow the function \( D(E \cdot N) = \frac{S_{a0}}{S_{a0} + S_{n0}} (1 - \exp(-kE \cdot N)) \). Here \( S_{a0} \) and \( S_{n0} \) indicate the initial ion–He complex number of active and non-active isomers, and \( k \) reflects the efficiency for the IR-MPD process of the specific band. From a fit of this function to the observed depletion signal, we directly obtain the fraction \( \frac{S_{a0}}{S_{a0} + S_{n0}} \) of the active isomer. This is demonstrated in the case of He IR-PD in the upper panel of Fig. 13 for the OH stretching band of the ethanol radical cation at 3476 cm\(^{-1}\). From the fitted fraction (0.96(6), i.e. full depletion) we can infer that only one isomer is present, i.e. in this case isomeric structure 3a (see Fig. 3), produced upon electron impact ionization of ethanol in our storage ion source. However, this method can obviously not be applied to systems where multiple isomers are all active at the chosen wavelength. In the case presented here, our calculations predict the corresponding band of the higher-lying \( C_5 \) isomer (structure 3b) to be red-shifted by more than 50 cm\(^{-1}\) relative to the assigned \( C_1 \) form, i.e. the two bands are clearly resolvable with the OPO laser linewidth used.

The observation of full depletion described above also verifies that we are able to address all ions stored in the ion trap. Even if the laser beam (diameter of ∼1
mm) is significantly smaller than the cross section of the ion cloud (diameter of up to 6 mm), the large field free area of the 22-pole ion trap allows the ions to freely move in and out of the laser beam on microsecond timescales, which is much smaller than the typical experimental timescale of several seconds.

In the case of IR-MPD, where several branching ratios into different dissociation product channels are possible, we focus on the sum of these branching channels, and the corresponding depletion signal monitoring the loss of the parent ion is shown in the lower panel of Fig. 13. Obviously, the IR-MPD method does not lead to full depletion of the ion signal as observed for He IR-PD. We can exclude varying source conditions leading to the formation of different isomeric ratios, and account for all fragmentation channels by monitoring the depletion of the parent ions. Therefore, if we indeed have only one isomer of the ethanol cation produced and stored in the trap, this discrepancy needs to be explained via intrinsic processes pertaining to the different methods applied. Due to the addition of considerable energy during the multiple photon process prior to dissociation, ions may undergo isomerisation, suddenly becoming not active at the set wavelength. In the present case of the ethanol cation, this might be the isomerisation from the energetically lower lying $C_t$ structure (3a in Fig. 3) to the $C_s$ form of the ion (structure 3b), lying 2.15–2.5 kcal mol$^{-1}$ higher in energy with an isomerization barrier of only 3 kcal mol$^{-1}$, i.e. less than the photon energy of a single IR photon at 3476 cm$^{-1}$. The energy needed to be stored in the ion prior to the observed dissociation is significantly larger than this (10.7 (18.6) kcal mol$^{-1}$ for hydrogen (CH$_3$) loss, resp.). The OH stretching band is shifted by >50 cm$^{-1}$ to the red in the $C_s$ isomer, well out of the exciting OPO linewidth.

In general, this observed effect may lead to situations where full depletion (recorded via the sum of all channels, or via depletion of the parent ion) is not achievable, even in cases where only one isomer is present. As a consequence, not achieving full depletion when using IR-MPD cannot be related to the presence of multiple isomers. However, this observation opens up the possibility of investigating the isomerization process itself via dedicated two-colour experiments.

---

**Fig. 13** Relative depletion $D$ of the ethanol cation irradiated at $\sim 3476$ cm$^{-1}$ (OH stretching band position) as a function of deposited energy $E\cdot N$ for He IR-PD (upper panel) and IR-MPD monitoring the loss of the parent ions (lower panel). Full line – exponential fit with saturation (dashed line, saturation value).
where one isomer is pumped via a specific vibrational excitation and another one is probed via IR-MPD on a corresponding vibrational transition. Further studies to investigate this effect are needed.

6 Conclusion

With the combination of the low temperature ion trap instrument FELion and the widely tunable FELIX free electron laser facility a very versatile tool for the determination of the structure and reactivity of molecular ions has been developed and is described in detail in this work. In particular, we demonstrate that cooling to temperatures of 4 K and below allows the tagging of molecular ions with one or more He atoms. These complexes can be easily destroyed by a single infrared photon thus leading to spectra mimicking the fundamental bands of the bare parent ion. In fact, these bands are perturbed only very little by the He attachment, i.e., only very small band shifts are observed and most importantly the bands are rather narrow due to the low temperatures and due to the single photon absorption event. Therefore, these spectra can be used to unravel the structures of molecular ions, which are hard to obtain otherwise.

In the present study, corresponding spectra have been obtained for the ionized and protonated variants of the astrophysically relevant molecules methanol and ethanol. In fact, this work presents the first vibrational spectra for protonated methanol. The measured spectra have been compared to results from high-level ab initio calculations and very good agreement is found over a wide range of infrared energies. Therefore, different isomeric forms can be safely distinguished and identified in the experiment. Moreover, the method of depletion saturation has been applied to determine the isomeric composition of the ion cloud in the trap. This can be turned into a tool to study the process of photon induced isomerisation via a two color scheme with a He attachment step in between. A candidate for such an isomeric change has been identified for the ethanol cation. Examples of isomeric switching with an associated change in reactivity can be of wider chemical relevance.

IR-PD in combination with the wide frequency range of FELIX revealed interesting vibrational features at low frequencies (<800 cm\(^{-1}\)), which are not always associated with fundamental band positions. This opens up the range of low energy internal motions associated with conformational degrees of freedom. These bands can act like a fingerprint for molecules with various isomeric and conformational forms and thus be used as a diagnostic tool. They might also shed more light on the interplay between structure and reactivity. In that respect the use of the FLARE laser at FELIX will address even lower frequency bands (6–100 cm\(^{-1}\)).

Another aspect of this work was a detailed comparison of IR-PD and the standard IR-MPD method. The benefit of low temperature trapping for IR-MPD was clearly demonstrated by showing how the rotational contours of vibrational bands led to rather narrow bands. This shall be exploited in further experiments on larger species with richer vibrational spectra as compared to the comparatively small molecules in this study.

One limitation of predissociation spectroscopy lies in lifetime broadening. For the analysis of the vibrational bands shown here this does not lead to significant restrictions since the resolution is limited by the pulsed nature of the free electron laser. However, for high-resolution studies where the rotational structure shown
for the ethanol radical cation or any other example should be fully resolved, lifetime broadening can be a severe limitation as shown for the case of protonated methanol. This hints at a limitation of IR-PD which has been observed before when only Ar, N₂, Ne or other more strongly bound tags could be used in photodissociation studies. However, broadened lines and thus very short lived states can also be helpful in identifying states close to the dissociation limit and thus experimentally determining the dissociation energy.

Overall it is important to realize that there is a whole suite of methods available for action spectroscopy, where IR-PD and IR-MPD are only two choices. In both cases a uni-molecular process is employed as a way to obtain a spectrum of a molecular ion. However, bimolecular or even higher order processes can also be used as tools. In fact, laser induced bimolecular reactions are a perfect tool to obtain spectra of unperturbed molecular ions, even without the shifts or broadening effects of an attached He. This has been demonstrated already 20 years ago for rotationally resolved N₂⁺ spectra and later on a large number of other ions. These methods have been extended by double-resonance techniques to obtain even ro-vibrational and rotational spectra of molecular ions and also by using the state-dependence of the three-body association process with He to record the pure rotational spectrum of C₃H⁺ and other molecules.

In summary, FELion, its sibling Coltrap and other cryogenic ion trap instruments are extremely flexible and versatile tools to unravel the structure of molecular ions, whether it be extremely rich spectra because of chemical complexity or due to large amplitude motions like those for He tagged species or whether it be simple molecules with simple spectra. The versatility is even increased by the use of different color schemes of excitation, addressing different degrees of freedom in UV-IR, IR-IR, FIR-NIR or FIR-IR double resonance setups, all demonstrated in recent years in different laboratories. In any case, the future of FELion is bright especially in combination with the highly intense light of FELIX.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support from the DFG Gerätezentrum “Cologne Center for Terahertz Spectroscopy” is acknowledged. S. B. and St. S. acknowledge support from DFG SPP 1573 grant BR 4287/1. O. A. is supported by grant DFG AS 319/2-2. P. J. acknowledges support from the Alexander von Humboldt-Stiftung. J. O. and A. S. acknowledge financial support through VICI grant #724.011.002 from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). We gratefully acknowledge the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) for the support of the FELIX Laboratory. The authors gratefully acknowledge the work of the electrical and mechanical workshops of the I. Physikalisches Institut, and the support from the FELIX staff. We thank Michael Harding for helpful discussions. The Regional Computing Center of the Universität zu Köln (RRZK) is acknowledged for providing computing time on the DFG-funded High Performance Computing (HPC) system CHEOPS.
References


