Leak-out Spectroscopy, a universal method of action spectroscopy in cold ion traps

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Abstract

A novel method of spectroscopy in ion traps termed leak-out spectroscopy (LOS) is presented. Here, mass selected, cold ions are excited by an infrared laser. In a subsequent collision with a neutral buffer gas particle their internal energy is then transferred to kinetic energy. As a result, these ions leak out from the ion trap and are detected. The LOS scheme is generally applicable, very sensitive and close to background free when operated at low temperature. The potential of this method is demonstrated and characterized here for the first time by recording the rotationally resolved spectrum of the C-H stretching vibration $\nu_1$ of linear C$_3$H$. Besides performing high-resolution spectroscopy, this method opens up the way for analyzing the composition of trap content, e.g., determining isomer ratios, by selectively expelling isomers or other isobaric ions from the trap. Likewise, LOS can be used to prepare clean samples of structural and nuclear spin isomers.

Graphical TOC Entry

Keywords

C$_3$H$, ro-vibrational spectroscopy, ion traps, action spectroscopy, V-T-transfer, isomer selection
Introduction

Over the last 35 years spectroscopy of molecular ions made tremendous progress on the basis of action spectroscopy, where the absorption of a photon is detected as a change of an ion signal. Following the pioneering work of Y.T. Lee and coworkers\textsuperscript{1,2} especially infrared multiple photon dissociation (IRMPD) of mass selected ions and the photo-dissociation of loosely-bound ion-complexes, in particular in the form of messenger spectroscopy, became popular and very productive methods of ion spectroscopy. They have been applied to ions in molecular beams, ion guides and ion traps and even in commercial mass spectrometers.\textsuperscript{3–6}

For cases where the accuracy and resolution of IRMPD and messenger spectroscopy is not sufficient, alternative methods of action spectroscopy, e.g., various forms of Laser Induced Reactions (LIR) have been developed\textsuperscript{7,8}. Here, the products of a bi-molecular reaction are employed to detect the photo-absorption of the parent ion. This method requires appropriate reactions which are promoted by the internal excitation of the ion. A more general method, first developed by J. Maier and coworkers\textsuperscript{9}, uses the inhibition of complex formation (LIICG\textsuperscript{1}) of the parent ion with a rare gas atom, in particular with He. For this purpose cryogenic temperatures are required such that ion-rare-gas clusters are formed and this signal is then altered by the internal excitation of the parent ion of interest.

All these methods are predominantly used in tandem mass spectrometers where the parent ions are mass selected by the first mass filter, then subjected to the exciting radiation in a cryogenic ion trap and the product ions are analyzed in the second mass filter before they are detected with near unit efficiency. With this repertoire of methods spectra of a large variety of molecular ions have been recorded. Even pure rotational spectra could be obtained by the use of double resonance schemes combining millimeter wave excitation of rotational states with infrared lasers to create an action spectroscopic signal which is altered by the rotational excitation.\textsuperscript{10} Despite the success story of action spectroscopy, many important ions could not be studied in high resolution so far, the reason being, e.g., a missing adequate

\textsuperscript{1}The method was termed Laser Induced Inhibition of Complex Growth, in short LIICG
reaction for LIR, or ineffective complex formation for LIICG.

![Figure 1: Thermal distribution of trapped ions. Ions which are accelerated by a vibration-to-translation energy transfer collision such that $E'_{\text{kin}} > 10 \, kT$ will leave the trap when the trap depth $E_A$ is of this order too.](image)

Here we report on a new, very universal approach of action spectroscopy, where the action relies on the inelastic energy transfer of an excited ion with a neutral collision partner. As a consequence, the ion gains kinetic energy and leaves the cold ion trap. The signal can then be detected as a loss of stored parent ions or as an arrival of escaping parent ions, even when the trap is nominally closed for cold ions. Based on the action at work we term this method *leak-out spectroscopy* (LOS). The idea of this method is depicted in Fig. 1 where a thermal Maxwell-Boltzmann distribution of the kinetic energy of trapped ions is displayed. The most probable kinetic energy is on the order of $E_{\text{kin}} = kT$ and only very few ions are found with $E_{\text{kin}} > 10 \, kT$ (see vertical line in Fig. 1). Based on this fact, the trap can be closed by applying an appropriate voltage to the exit electrode of the trap, resulting in a barrier ($E_A$) along the trap axis which exceeds this value, i.e., $E_A > 10 \, kT$. Thus the ions can be stored for very long times. If, however, an initially thermal ion is excited internally, e.g., to a vibrationally excited state, a subsequent collision with a neutral collision partner may transfer vibrational to translational energy (V-T-transfer). This results in a change of
kinetic energy $\Delta E_{\text{kin}}$, such that the kinetic energy after this collision can easily exceed the ion trap barrier height, $E_A$, as indicated by the horizontal arrow in Fig. 1. The accelerated ion can now escape the trap resulting in the desired action spectroscopy signal which only appears upon tuning the radiation source to resonant absorption.

**Experimental**

In order to prove this idea the cryogenic 22-pole ion trap LIRtrap was employed. It is the same instrument as already used for the first LIR experiments. Fig. 2 a) shows schematically the tandem mass spectrometer with the central cryogenic 22-pole ion trap.

Ions are created in the storage ion source (SIS) by electron bombardment. In the present case, $C_3H^+$ and other small hydrocarbon ions are created from allene precursor molecules ($C_3H_4$) which is admitted to the source at a pressure of about $10^{-6}$ mbar. At the beginning of a trapping cycle a train of ions is extracted from the source by pulsing the ion source exit electrodes as shown in the top blue trace of Fig. 2 b). These ions are mass selected in mass...
filter I for mass 37 u (C₃H⁺) which are then admitted to the trap for several ten milliseconds termed *accumulative trap filling*. During this time a pulse of He buffer gas (turquoise trace in Fig. 2b)) stops the ions in the potential of the 22-pole ion trap and ensures thermalisation of ions to the cryogenic temperatures. At the end of this initial trapping phase the voltages of the entrance (red trace) and exit electrodes (green trace) of the trap are adjusted to keep the stored ions but to allow fast ions to escape via the exit electrode as described in the introduction. During the following 200 ms the laser is admitted to the trap on the axis of the apparatus and the detector gate is opened to detect the fast ions leaving the trap (orange trace). For our first LOS experiments, the trap is constantly filled with N₂ gas at a density of about 10¹²/cm³ and thus a collision rate of approximately 10³/s.

In order to avoid freezing of this gas, the ion trap is held at about 40 K. Most collisions are elastic or change the rotational state of the molecules. But some collisions lead to the desired V-T-transfer described above and the ions leaving the trap upon an inelastic collision with the N₂ buffer gas are again mass analysed by *mass filter II* as shown in Fig. 2a). In contrast to other forms of action spectroscopy where the mass of the stored ion is changed, here the second mass filter is also transmitting mass 37 u detecting the C₃H⁺ ions leaving the trap. At the end of each trapping cycle any remaining ions are expelled from the trap to ensure that the next cycle starts with an empty trap. Before the next trapping cycle the laser frequency is stepped by about a tenth of the Doppler-width (0.0005 cm⁻¹) of an absorption line and the experiment is repeated again. Instead of detecting the ions expelled from the trap during the trapping period also the ions remaining in the trap can be detected in another series of experiments such that the kinetics of the ion loss can be followed as a function of time as will be described below.
Figure 3: Number of trapped $\text{l-C}_3\text{H}^+$ as a function of the trapping time. Less than 10% of the ions leave the trap without laser excitation. With the laser resonant to the R(5) transition the parent ions are lost with a 1/e time constant of approximately 1.5 s.

Results

As a first example for LOS, the C-H stretching vibration of the linear $\text{C}_3\text{H}^+$ ($\text{l-C}_3\text{H}^+$) molecular ion is excited by the intense light of a high-resolution infrared OPO system (Toptica Topo). As described above, the exit electrode of the trap is tuned in a way that the cold ions are barely held in the trap, i.e. some are constantly leaving the trap but with a very small rate only. When the exciting radiation is, however, in resonance with a ro-vibrational transition of $\text{l-C}_3\text{H}^+$, a vibrationally inelastic collision leads to a considerable redistribution of the internal excitation ($E_{\text{vib}} \sim 3170 \text{ cm}^{-1} \sim 0.393 \text{ eV}$) to the kinetic energy of both collision partners. In case of $\text{l-C}_3\text{H}^+$ ($m = 37 \text{ u}$) and $\text{N}_2$ ($m = 28 \text{ u}$) the kinetic energy release is well shared between the two partners in the laboratory frame, with $\text{C}_3\text{H}^+$ taking a maximum of $\Delta E_{\text{kin}} = 28/(28 + 37) \cdot 393 \text{ meV} = 169 \text{ meV}$. Now the fast $\text{C}_3\text{H}^+$ ions resulting from this V-T-transfer leave the trap across the $E_A$ barrier with a significantly enhanced rate.

Fig. 3 shows the result of such an experiment as a function of the trapping time. Without
laser excitation 90% of the about $10^4$ parent ions are kept in the trap for more than 4 seconds. When the laser excites the R(5) transition of the C-H stretch of l-C$_3$H$^+$, the ion number drops exponentially to only a few percent after 4 s. This large enhancement of the ion loss rate can now easily be used to record the ro-vibrational spectrum of l-C$_3$H$^+$. A spectrum recorded this way is given in Fig. 4, plotting the number of ions leaving the trap during the irradiation period as a function of the excitation wavenumber, measured by a wavemeter (Bristol Instruments, model 621 A IR, accuracy $\sim$0.001 cm$^{-1}$). Only several ten ions leave the trap with the OPO off-resonant and the signal rises to more than 2000 ions on some lines of the R-branch. Thus the recorded spectrum is almost background-free. The whole spectrum was measured in one scan which lasted only about 10 hours. The signal-to-noise ratio of this spectrum exceeds that of any action spectrum recorded in our laboratory by the aforementioned methods. It is in fact so high, that even a hot band of l-C$_3$H$^+$ is visible with an intensity of a few percent of the main band as will be discussed below.

Figure 4: Leak-out spectrum of the C-H stretching mode $\nu_1$ of l-C$_3$H$^+$, recorded by counting the number of escaping ions during the 200 ms lasting irradiation time. The $\nu_5 + \nu_1 \leftarrow \nu_5$ hot band is observed with an intensity of a few percent of the fundamental mode. The inset shows a zoom on the R(17) line fitted by a Gaussian profile corresponding to a kinetic temperature of $T_{\text{kin}} = 62(8)$ K.

The main spectrum shows a harmonic structure with a spacing of $2B \approx 0.75$ cm$^{-1}$=22.5 GHz. It belongs to the linear C$_3$H$^+$ molecule for which the rotational constant of the ground vibra-
tional state was determined with very high precision ($B = 11244.950(2)$ MHz) in an earlier experiment using the rotational-state-dependent attachment of He. Fig. 4 represents the first rotationally resolved vibrational spectrum of 1-C$_3$H$^+$, the $\nu_1$ C-H stretching band obtained in the present study. It exhibits a clear $P$- and $R$-branch with an intensity distribution which qualitatively follows that of an absorption spectrum of a linear species. For spectroscopic analysis the spectrum has been fitted to a standard linear molecule Hamiltonian. The molecular parameters derived from this analysis are given in Table 1. Also the spectroscopic parameters of a weak hot band, identified as $\nu_1+\nu_5 \leftrightarrow \nu_5$, and originating from the lowest energy C-C-C bending mode $\nu_5$, are given in this table. Detection of a $Q$-branch and $\ell$-type doubling in these weaker lines is a clear indication of the involvement of a degenerate bending vibration of the linear molecule. For comparison, Table 1 also reports results from previous experiment and high-level quantum-chemical calculations at the fc-CCSD(T)/ANO2 level of theory. The latter were performed using the CFOUR program$^{12}$ and complement other high level calculations reported in the literature earlier (e.g., Refs.$^{13–15}$ and references therein).

Overall good agreement between the experimental and calculated values is found. The new data may be reproduced to within experimental accuracy with just a few molecular parameters, i.e., the lower and upper state rotational constants $B_v$ (alternatively, one rotational and a rotation-vibration interaction constant $\alpha_i$), centrifugal distortion terms, an $\ell$-type doubling constant $q_i$ for the states involving the $\nu_5$ bending mode as well as the vibrational band centers $\tilde{\nu}_i$. The $\nu_1$ vibrational wavenumber of untagged C$_3$H$^+$ derived here is found blueshifted by some eight cm$^{-1}$ relative to C$_3$H$^+$–Ne studied earlier with infrared photodissociation.$^{14}$ This finding is in qualitative accord with that in other linear proton-bound weakly bound complexes (see, e.g., Ne–HCO$^+$, Ref.$^{10}$) and in good agreement with a harmonic estimate of 13 cm$^{-1}$ calculated at the CCSD(T)/aug-cc-pCVQZ level.$^{14}$ Further information and details on the spectroscopic analysis and calculations is given in the electronic supplementary material.

Besides the spectral parameters additional information has been derived from the recorded
Table 1: Molecular parameters of l-C$_3$H$^+$ in selected vibrational states. (in MHz unless noted otherwise).

| | $v=0$ | $v_1=1$ | $v_5=1$ | $v_5=v_1=1$ |
|---|---|---|---|---|
| $\tilde{\nu}_i / \text{cm}^{-1}$ | $3169.97769(16)^a$ | $3168.76964(12)^a$ | | |
| $\tilde{\nu}_i / \text{cm}^{-1}$ | $3162.2^b$ | | $3168.734^c$ | |
| $\chi_{ij}/ \text{cm}^{-1}$ | $\ldots$ | | $-1.244d/-1.20842(23)^a$ | |
| $B_v$ | $11244.9502(22)^e$ | $11209.120(19)^a$ | $11397.90(33)^a$ | $11362.97(33)^a$ |
| $\alpha_i$ | $\ldots$ | $-35.831(19)^a$ | $152.95(33)^a$ | $118.02(33)^a$ |
| $\alpha_i$ | $\ldots$ | $-32.673^d$ | $151.892^d$ | $119.219^d$ |
| $D_v \times 10^3$ | $7.710(75)^f$ | $8.49(83)^f$ | $\ldots$ | $\ldots$ |
| $H_v \times 10^6$ | $0.76(28)^f$ | $\ldots$ | $68.348(96)^f$ | $\ldots$ |
| $q_i$ | $\ldots$ | $\ldots$ | $65.468^d$ | $\ldots$ |

$a$ Experimental, this work.

$b$ From infrared photodissociation (IRPD) of the C$_3$H$^+$–Ne complex.$^{[3]}$

c From observed $\nu_1$ band center and calculated anharmonicity constant $\chi_{ij}$ (this work).

d Calculated at the fc-CCSD(T)/ANO2 level, this work.

e Combined fit of $\nu_1$ band (this work) and pure rotational data (Ref.$^{[11]}$).

$^f$ Common constant for both vibrational states, this work.

The kinetic temperature of the trapped ions is determined from the Doppler profile of the spectral signal as shown in the inset in Fig.4 for the R(17) line to be $T_{\text{kin}} = 62(8)$ K which is somewhat elevated w.r.t. the trap wall temperature. Still, we conclude that $10kT_{\text{kin}} = 54$ meV is much smaller than $\Delta E_{\text{kin}} = 169$ meV as considered for the LOS-principle. The rotational temperature has been determined from a Boltzmann-plot of the line intensities, $I_J$, of the spectrum shown in Fig.4 using the equation

$$ \ln \left( \frac{I_J}{S_J^{\text{PR}}} \right) \sim - \frac{E_J}{kT_{\text{rot}}} $$

where $S_J^{\text{PR}}$ is the Hönl-London factor for a linear molecule and $E_J$ is the rotational energy of the molecule in its vibrational ground state as determined from the spectroscopic parameters given in Table$^{[1]}$. The rotational temperature derived from this procedure is $T_{\text{rot}} = 50$ K. This temperature is determined by the collisions of the neutral gas at $T_{\text{neutral}} = 40$ K with the ions at $T_{\text{ion}} = 62$ K. The effective collision temperature is thus calculated to be
\[
T_{col} = \frac{(m_{\text{ion}}T_{\text{neutral}} + m_{\text{neutral}}T_{\text{ion}})}{(m_{\text{ion}} + m_{\text{neutral}})} = 49 \text{ K}
\]

in very good agreement with the measured rotational temperature.

**Discussion**

This work presents a first example of LOS for \( \text{C}_3\text{H}^+ \), a molecular of astrophysical importance. High-quality spectroscopic parameters have been derived from the high-resolution ro-vibrational spectrum of this linear molecule. On the basis of the findings in this work it is possible to discuss the principle of the LOS method, more specifically how the spectral contrast of LOS arises. In the LOS process the vibrational energy of about \( E_{\text{vib}}/hc = 3170 \text{ cm}^{-1} \) is eventually distributed between the various degrees of freedom of both collision partners. The V-T energy transfer is very inefficient due to the large energy mismatch between vibration and rotation. As a consequence only a small amount of energy is redistributed among the rotational states of the collision partners. The efficiency of a V-V energy transfer is also rather small by the same argument, i.e., there is a large mismatch between the various energetically allowed vibrational states of the two collision partners. Therefore, vibrational quenching is known to be a rather inefficient process altogether. For specific systems we and others found that only about one in 100 collisions lead to a V-T-transfer.\[17]\] Thus, quite a high number density of buffer gas is needed to promote this process as part of the LOS method. Although being unlikely, upon vibrational quenching a considerable fraction of the vibrational energy is thus transferred to translation. For molecules with many vibrational degrees of freedom quenching might leave the molecular ion in another vibrationally excited state which then yields less kinetic energy for the LOS process.

Preliminary studies on LOS of more complex ions such as protonated methanol or even protonated methane in our laboratory show that LOS also works perfectly for these molecules. For ions containing many more heavy elements it might be necessary to operate the trap at considerably lower temperatures to still observe a LOS signal. But at present we
don’t see a fundamental limit for the application of LOS for complex molecular ions.

Our considerations of the V-T-transfer process show that a considerable fraction of the vibrational energy $\Delta E_{vib}$ will be converted into translational energy, $\Delta E_{kin}$, with $\Delta E_{vib} \approx \Delta E_{kin}$ in the present case. For the success of LOS the molecular ion should take a considerable fraction of this energy. This can be achieved best for a heavy neutral collision partner, e.g., a heavy rare gas atom like Ar, Kr or Xe. In particular, for these partners energy dissipation in internal degrees of freedom is excluded. But also $N_2$ will only transfer a small fraction of the energy into molecular rotation as argued above. One more critical point for the method to work is that these neutral collision partners should not freeze to the walls of the trap. In that respect $N_2$ is a favorable choice for temperatures down to some 30-40 K. At lower temperatures condensable buffer gases will need to be supplied in a beam along the trap axis rather than as a background gas to avoid freezing. Another approach is to dilute these condensable gases in helium and admit them to the trap in a short pulse at the beginning of the trapping cycle. Using 3:1 mixtures of He:Ne or He:Ar, we already succeeded to record high-resolution spectra of a handful of cations at a trap temperature of 4 K. The corresponding publications are in preparation.

As a result of these considerations we find that the collisions with the buffer gas are essential for LOS to work. The efficiency of the V-T-transfer process is only small compared to that of the thermalizing collisions, i.e. rotationally inelastic or elastic collisions, which prevent the ions from leaving the trap. Therefore, one finds a competing situation, where the V-T-transfer process is desired but subsequent thermalizing collisions are not. Thus the temporal behavior of the LOS process needs to be considered to find optimal conditions for LOS.

The LOS sequence starts with the absorption of a photon, which we assume to be rather efficient, only limited by the spectral brightness of the available radiation source. Since the V-T-transfer should occur on time scales below a second, which is a typical trapping time, the number density $n$ of the buffer gas has to be on the order of $10^{12}$ cm$^{-3}$. With
this density about 1000 ion-neutral collision occur per second, and on average one to ten
V-T-transfer collisions. Under these conditions, the fast ion produced after the V-T-transfer
process collides about once per millisecond (\(\tau \sim 1\text{ms}\)) and will eventually be thermalized,
i.e., it can no longer leave the trap. Radiative decay also happens on a similar time scale,
i.e. \(\tau_{\text{rad}} \sim \text{ms}\). Therefore, the fast ion has to leave the trap on this natural time scale, \(\tau\),
for LOS to work.

The chance to escape from the trap during this time increases with the velocity of the fast
ion, \(v\), and decreases with the linear dimension of the trap, \(d\), which is of the order 0.1 \(m\). Thus, the escape rate scales as \(v/d\) and the escape probability as \(v/d \cdot \tau\) because after the
average collision time \(\tau\) the ion is slowed down and trapped again for long. To increase the
escape probability one would choose \(\tau \sim 1/n\) long and thus the neutral gas density, \(n\), low.
However, a high gas density is needed to promote the V-T-transfer on the scale of typical trapping time. Therefore, in the experiments we find an optimum number density for the
best LOS signal.

To evaluate the contrast of LOS the escape rate of the thermal ensemble of ions needs
to be considered. Here \(v\) is on the order of 100 \(m/s\). Ions from the hot tail of the Maxwell-
Boltzmann distribution may leave the trap when the escape barrier is chosen as \(E_A \approx 10 \text{kT}\)
as described above. This fraction of fast ions leaving the trap, \(P\), is given by integrating the
Maxwell-Boltzmann distribution from \(E_{\text{kin}}=E_A\) to \(\infty\). In summary, we estimate the loss rate
without laser excitation to be given by \(R = v/d \cdot P\) which is plotted in Fig. 5 as a function
of the barrier height \(E_A\) in units of the thermal energy \(kT\).

It can be seen from this graph that the escape rate drops to less than 1/s (horizontal
line in Fig. 5) for \(E_A\) larger than 10 kT, which means the ions are kept a fraction of a
second under these conditions. In fact, the off-resonance loss rate determined in Fig. 3 is
considerably smaller, namely \(2.3 \cdot 10^{-2}\text{ s}^{-1}\). On-resonance with the R(5) transition of l-C\(_3\)H\(^+\),
it increases by a factor of about 30 to \(6.6 \cdot 10^{-1}\text{ s}^{-1}\). Thus apparently we have chosen \(E_A\)
somewhat larger in the present experiments, but the process of LOS seems to be rather well
Figure 5: Escape rate of ions from a thermal ensemble in a trap with a potential barrier of height $E_A$ in units of thermal energy $kT$ for three different trap temperatures. Escape rates below $1/s$ (horizontal line) ensure a safe long time trapping.

described by the estimated escape rates on-resonance and off-resonance.

From Fig. 5 one reads that as long as $E_A$ is chosen in the right range, LOS should work also at room temperature (300 K). While this is true, the contrast between on- and off-resonance is given by the amount of energy transferred from vibrational to translational energy and how much this value lies above the thermal average $kT$. Therefore, LOS will work better under cryogenic conditions as demonstrated in this work.

In summary, we present a universal technique of action spectroscopy in cryogenic ion traps. The method relies on the inelastic collision with a buffer gas which should be chosen to promote the energy transfer. In the present case we used the vibrational excitation of the ion followed by the V-T-transfer. Our estimates show that the process of LOS is well described by deviations from a thermal ensemble in the trap. Other energetic processes like electronic excitations may be used as well to record a LOS signal. Also, the vibrational LOS introduced here can be combined with rotational spectroscopy. In this double resonance approach one would detect the change in the LOS signal when the rotational population of the ensemble of trapped ions is changed by a mm-wave radiation source as demonstrated
earlier for other action spectroscopy methods. Moreover, LOS reveals the spectrum of the bare ion, $\text{C}_3\text{H}^+$ in the present case, and does not suffer from spectral shifts due to a tag as the comparison with the spectra of the photodissociation (IRPD) of the $\text{C}_3\text{H}^+–\text{Ne}$ complex shows. Therefore, LOS opens a whole suite of possibilities to record spectra of mass selected ions with an unprecedented sensitivity.

Finally, similar to many methods of action spectroscopy in traps LOS also offers the chance to analyse the finite content of the trap. This is seen in Fig. 3 where on-resonance most of the ions leave the trap. This means that there is only one isomeric form of $\text{C}_3\text{H}^+$ in the trap, namely l-$\text{C}_3\text{H}^+$. In case a larger fraction of ions of a different species with the same nominal mass ($m = 37$ u) would be co-trapped, these ions would not be addressed by the radiation and stay in the trap. This would be observed as a remaining number of ions in the trap in Fig. 3. As such, LOS provides the possibility to determine the isomer composition of the initially trapped ensemble. Moreover, the escape of a specific isomer can be used to prepare a clean sample of selected isomers, conformers and nuclear spin isomers. In a preliminary experiment on an ensemble of $\text{H}_3^+$ we were able to isolate the para or ortho fraction by leaking out the respective other fraction through resonant ro-vibrational excitation of the $(J,K) = (1,0)$ ortho- or $(1,1)$ para-state, respectively. In this sense, LOS is the beginning of new kind of experiments where reactant isomers can be selected and product isomer ratios can be analysed. This we already showed for tagged ions in previous work but with LOS it works for bare ions.

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