

Electronic Spectroscopy of Toluene in Helium Nanodroplets: Evidence for a Long-Lived Excited State

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Manuscript submitted to *J. Phys. Chem. A*

Abstract

Optical excitation of toluene to the S_1 electronic state in helium nanodroplets is found to alter the rate of production of the fragment ions $C_7H_7^+$ and $C_5H_5^+$ when the droplets are subjected to subsequent electron ionization. The optical excitation process reduces the abundance of $C_7H_7^+$ ions delivered into the gas phase whereas $C_5H_5^+$ ions become more abundant beyond a minimum droplet size. This process contrasts with normal optical depletion spectroscopy, where the optical absorption of a molecular dopant in a helium nanodroplet shrinks the helium droplet, and thus the electron impact cross sections, because of dissipation of the absorbed energy by evaporative loss of helium atoms. The observations here are interpreted in terms of formation of an excited state in the neutral molecule which survives for several hundred μs . This long-lived excited state, which is assumed to be the lowest triplet electronic state, shows different cross sections for production of $C_7H_7^+$ and $C_5H_5^+$ relative to the S_0 state.

Keywords: laser, ion, dynamics, triplet

Introduction

Molecules trapped in superfluid helium nanodroplets can be probed spectroscopically using a *depletion* technique. Depletion spectroscopy works on the basis of heat dissipation after a molecule absorbs radiation, almost always from a laser source, which causes the helium droplet to shrink in size by evaporative loss of helium atoms. The absorption process is then registered by observing the reduction in the helium droplet size. Two practical means of achieving this have been employed: (1) through a reduction in electron ionization cross section as the droplet shrinks, which manifests itself as a reduced ion signal detected by a mass spectrometer;^{1,2} (2) the use of a bolometer, which detects the decrease in helium droplet size through the reduction in heat delivered when the droplet beam collides with the bolometric sensor.^{3,4}

In contrast to spectroscopic techniques such as laser-induced fluorescence (LIF) or resonance-enhanced multiphoton ionization (REMPI), which are unsuitable for many molecules due to competition from rapid excited state relaxation, depletion spectroscopy has much wider scope for detecting light absorption by atoms or molecules in helium droplets. Nevertheless, like LIF and REMPI, depletion provides an indirect means of detecting spectroscopic transitions, since it relies on relatively efficient transfer of energy from the excited dopant atom/molecule into the surrounding helium on the timescale of the experiment, which is typically on the order of a millisecond. Transfer of energy from a vibrationally excited molecule to the helium matrix is normally rapid, and thus depletion spectroscopy has been widely used to record vibrational spectra of molecules in helium nanodroplets (for a summary valid to 2004, see ref. 5). However, the depletion method tends to be less efficient for detecting electronic transitions because non-radiative relaxation is normally far slower than in the vibrational case. As a result, if molecules fluoresce from their excited electronic states then LIF is a better approach for recording their electronic spectra.⁶

An exception to the assumption of fast vibrational relaxation in a helium droplet has been identified for HF in its $\nu = 1$ vibrational state.⁷ Using a bolometer as the detector Nauta and Miller observed a positive-going signal when exciting the $\nu = 0 \rightarrow \nu = 1$ transition, which is consistent with excess energy being delivered to the detector as a result of laser excitation of the HF. The explanation was that the high vibrational frequency of HF dramatically slows the vibrational relaxation and therefore the $\nu = 1$ state is long-lived relative to the average transit time of helium nanodroplets from the point of laser excitation to the detector, which was estimated as 0.5 ms.

Here we present evidence for a long-lived excited state observed during an attempt to record the S_1 - S_0 electronic depletion spectrum of toluene. Toluene has been investigated only once before in helium nanodroplets, when Boatwright *et al.* studied a series of substituted benzene molecules to determine the effect of the substituent on the shift of the S_1 - S_0 origin transition relative to the corresponding gas phase value.⁸ Depletion spectroscopy was used by Boatwright *et al.*, with mass spectrometric detection registering the change in helium droplet size, but the depletion effect was found to be very weak. Using a similar experimental approach in the present study we have revisited the case of toluene and observed unusual behaviour. The most significant finding is that of signal *enhancement* in one particular fragment ion channel following resonant excitation of the neutral toluene. This suggests that the toluene enters a relatively long-lived excited state that goes on to affect subsequent electron ionization dynamics. The survival of a metastable excited state in helium nanodroplets for a molecule as large as toluene is surprising and we present the findings here.

Experimental

The overall helium droplet apparatus has been described in detail elsewhere.⁹ One important difference in the current experiments is the use of a continuously flowing helium droplet

beam instead of the pulsed source used in previous work. The continuous source consists of a 5 mm diameter disk (Pt/Ir (95/5) electron microscope aperture produced by Frey Precision), with a 5 μm circular aperture. This disk is compression sealed between a copper cylinder, with a 1 mm diameter straight channel cut through its centre, and a copper face plate with a 0.5 mm diameter aperture and conical angle of 90° extending outwards into the vacuum chamber. The complete assembly is mounted between copper brackets on the tip of a closed cycle cryostat, which in turn is mounted on an XY translation stage. The droplet beam is collimated by a skimmer with a 0.5 mm diameter aperture (Beam Dynamics) at a distance of 1.2 cm downstream from the nozzle.

To generate helium nanodroplets gaseous helium (99.9999% purity) with a stagnation pressure of 15-30 bar was cooled to temperatures in the range of 12-18 K and expanded into vacuum. The conditions employed in the current work generated droplets with a mean size ranging from 2500 to 19000 helium atoms, as deduced by comparison with the conditions reported by Lewerenz *et al.*¹⁰ At a distance of 20 cm from the nozzle the droplet beam entered a pickup region filled with toluene at pressure such that most droplets captured no more than one toluene molecule. Further downstream the droplet beam enters a quadrupole mass spectrometer (QMS; Extrel ELQ-400), where it is bombarded with 70 eV electrons. We also have the option of recording mass spectra with a time-of-flight mass spectrometer (a reflectron model built by Kore Technology), which improves the resolution but is not suitable for optical spectroscopy experiments because of the limited duty cycle and shot-to-shot signal fluctuations.

In order to record electronic transitions of toluene, ions in specific mass channels were monitored as a function of laser wavelength. The UV laser light (2 mJ per pulse) was generated by frequency doubling the output from a dye laser (Sirah Cobra Stretch) pumped by a Continuum Surelite II-10 Nd:YAG laser. The unfocused laser beam was directed in a

counter-propagating direction to the helium droplet beam to ensure maximum spatial overlap. To process the ion signal, an SR400 two-channel gated photon counter was employed. Two gates were defined, one to coincide with any change in the ion signal induced by laser excitation and the second to coincide with the background QMS signal level (*i.e.* at a period in time when the laser beam was not overlapping the helium droplet beam). An optical spectrum was then obtained by subtracting the laser enhanced/depleted ion signal from the background ion signal obtained when the laser beam was absent, and the residual was then normalized against the background ion signal at the same laser wavelength.

Results

Mass spectrometry

Figure 1 shows a mass spectrum obtained under the same conditions used to record optical spectra (see below). The main spectrum shows a scan over a relatively wide range of masses and includes the regions where both the toluene monomer and dimer cations would appear. For the monomer the two major ions produced by electron impact on toluene-doped helium nanodroplets are the parent ion, $C_7H_8^+$, and the dehydrogenated species, $C_7H_7^+$. These are also the most prominent ions in electron ionization and photoionization mass spectra of toluene in the gas phase.¹¹⁻¹³

Fragment ions other than $C_7H_7^+$ are relatively minor products in the mass spectrum of gaseous toluene.¹¹⁻¹³ Among these more scarce ions the most abundant is at $m/z = 65$, which corresponds to $C_5H_5^+$. This product is also readily seen in our mass spectra recorded for toluene in helium droplets, as illustrated in the expanded view in Figure 1. Other fragment ions from toluene, including $C_5H_3^+$ and $C_3H_3^+$, gave exceedingly low intensities in the mass spectra and so will not be considered any further. Again, these relative fragment ion abundances are consistent with previous gas phase studies using electron ionization and

photoionization, showing that the helium droplet does not have a large effect on the branching ratios for the ionization of toluene.

Laser spectroscopy

Attempts were made to record electronic spectra of toluene by monitoring various mass channels but we start by presenting the findings for the C_7H_7^+ and C_5H_5^+ ions. The upper panel in Figure 2 show the spectrum obtained by monitoring C_7H_7^+ for a mean helium droplet size of 15000 helium atoms. A series of resonances were observed which caused a decline in the C_7H_7^+ signal. This includes the $\text{S}_1\text{-S}_0$ 0_0^0 transition and transitions to several excited vibrational states in the S_1 manifold. The degree of signal depletion at the peak maximum for the $\text{S}_1\text{-S}_0$ 0_0^0 transition was roughly 15%. The acquisition times were relatively long so data have been recorded only over relatively narrow ranges near the expected peak positions. All of the peaks can be readily assigned to known transitions of toluene¹⁴ and these assignments are given in the figure. A uniform blue shift of the spectrum by *ca.* 50 cm^{-1} relative to the gas phase is observed, which agrees with a previous study of the $\text{S}_1\text{-S}_0$ 0_0^0 transition of toluene in helium droplets.⁸

When detecting C_5H_5^+ very different behaviour is seen. Instead of signal depletion the ion signal *increases* as the laser is tuned into resonance with specific vibronic features. Consequently, the spectrum observed (see the lower half of Figure 2) is essentially the mirror image of that seen in the C_7H_7^+ ion channel.

Attempts were also made to record depletion spectra in other mass channels, including the parent ion channel, C_7H_8^+ , and also for various He_n^+ cluster ions, including He_2^+ and He_3^+ . Although depletion features could be seen in these mass channels, the spectra obtained were

exceptionally weak when compared with those recorded in the $C_7H_7^+$ and $C_5H_5^+$ channels, an observation discussed later.

Droplet size dependence

To extract further information the spectroscopic signals in the $C_7H_7^+$ and $C_5H_5^+$ channels were recorded as a function of helium droplet size. These measurements focused on the S_1-S_0 0_0^0 transition only. The droplet size was found to have a modest effect in the case of $C_7H_7^+$, with the signal showing depletion at all droplet sizes but the magnitude of the laser-induced depletion showed a small decline with increasing droplet size. However, the signal in the $C_5H_5^+$ channel showed more unusual behaviour, with exceptionally weak depletion being observed at the small droplet end of the range and a switch to signal enhancement once the droplet contained more than 9000 helium atoms. The degree of signal enhancement progressively increased up to the maximum mean droplet size used in this work, *ca.* 19000 helium atoms.

Discussion

The observation of both ion depletion *and* enhancement effects in the optical spectrum following laser excitation of a molecule in helium droplets has, as far as we can tell, not been reported previously. A particularly interesting aspect is that the dominant effect is found when fragment ions are detected, namely $C_7H_7^+$ and $C_5H_5^+$, rather than for the parent ion, $C_7H_8^+$. Thus in the experiments reported here any signal depletion is primarily the result of a reduction in the probability of producing a specific ion, $C_7H_7^+$, and delivering these ions into the gas phase following resonant laser excitation, rather than resulting from a reduction in helium droplet size due to heat dissipation. Similarly, the enhancement signal suggests that formation of the fragment ion $C_5H_5^+$ increased in the presence of the laser at the appropriate

resonant frequency when compared to its absence. Consequently, the laser must deposit the toluene molecule into an excited state that affects the outcome of the subsequent ionization event.

Furthermore, we can obtain information on the lifetime of the excited state. Figure 3 shows an illustrative decay profile obtained by detecting C_5H_5^+ following laser excitation of the $\text{S}_1\text{-S}_0$ 0_0^0 transition. In conventional depletion spectroscopy the entire illuminated portion of the droplet beam shows a depletion effect, which in our instrument generates a depleted signal extending for more than 1 ms as the full extent of the illuminated beam travels through the mass spectrometer. On the other hand the enhancement effect in the current study is a shorter-lived phenomenon.

To try and explain the experimental observations we start by considering energy disposal following excitation to the zero point level of the S_1 state. Given that laser excitation affects the outcome of subsequent ionization events, the excess energy deposited by the photon must be retained by the neutral toluene molecule until the helium droplet undergoes electron impact. The S_1 state of toluene itself is not expected to survive this journey, since it will undergo rapid radiative and non-radiative decay if its behaviour is at least reasonably similar to that of toluene in the gas phase. The fluorescence lifetime for the zero point level of the S_1 state of toluene in the gas phase is 86 ns and internal conversion (IC) is known to be a minor decay channel.^{14,15} However, intersystem crossing (ISC) competes effectively with fluorescence and the respective quantum yields in the gas phase have been determined to be 0.64 and 0.3 for the zero point level of the S_1 state. Thus, if similar values apply for toluene in helium droplets, then ISC should be the major product channel following population of the S_1 state of the neutral molecule.¹⁵

In the isolated molecule the zero point level of the lowest triplet state (T_1) lies 8400 cm^{-1} below that of the S_1 state and so ISC will convert this excess energy into vibrational

energy in the toluene. The molecule will most likely relax fully to the zero point level of the T_1 state on a relatively short timescale and evaporation of a minimum of 1680 helium atoms is expected if each helium atom removes 5 cm^{-1} of energy.⁵ This could account for the conventional signal depletion seen in the parent ion and helium cluster ion mass channels. Once in the fully relaxed T_1 state the toluene molecule either travels inside the droplet to the point of ionization unchanged, or it could conceivably undergo a second intersystem crossing into the S_0 state. If the former were true then we would not expect to see an observable lifetime effect, since signal depletion in the $C_7H_7^+$ channel or signal enhancement in the $C_5H_5^+$ channel would continue over the timescale defined by the fully illuminated droplet beam, *i.e.* $\sim 1\text{ ms}$.

The experimental evidence therefore suggests that a second ISC takes place, giving the T_1 state a measurable lifetime as it transfers into the highly vibrationally excited S_0 state. Previous estimates suggest that this $T_1 \rightarrow S_0$ ISC occurs on a timescale of seconds when it takes place from the zero point level of the T_1 state, although it is much faster for excited vibrational levels.¹⁶ A lifetime of several seconds is clearly incompatible with the decay curve shown in Figure 3. A possible explanation is that this second ISC is accelerated by the surrounding helium, thus accounting for the observed $230\text{ }\mu\text{s}$ lifetime. Even if this were so, it introduces a second difficulty, namely production of very highly vibrationally excited toluene, with an initial vibrational energy near 29000 cm^{-1} . The dissipation of this energy into the helium matrix is expected to be rapid and would lead to a much stronger conventional depletion effect than for the initial ISC ($S_1 \rightarrow T_1$ ISC), since ~ 5800 helium atoms should be evaporated. However, this is contrary to the experimental observations. Two other ways of dissipating this excess energy can be ruled out. One option would see this excess energy funnelled into bond dissociation, but the lowest bond dissociation threshold of toluene, that for the benzylic hydrogen atom, is $\sim 30900\text{ cm}^{-1}$ and so is not accessible.¹⁷ Equally,

phosphorescence from the T_1 state into the S_0 state can also be ruled out since the known phosphorescence lifetime of toluene in solid matrices is several seconds.¹⁸

The only other way we can account for this apparent lack of vibrational energy dissipation into the helium matrix is that the vibrationally excited molecules in the S_0 state undergo rapid ejection from the helium droplets before complete vibrational relaxation can occur. There is precedent for such behaviour in the case of ions, where non-thermal ejection has been reported even for relatively low levels of vibrational excitation.¹⁹ Smolarek *et al.* have suggested that this non-thermal ejection of ions may be the result of localized heating of the helium in the immediate vicinity of the ion on account of the relatively strong interaction between the ion and the helium in the first few solvation shells. This leads to a bubble which migrates to the droplet surface and bursts before the heat can be dissipated throughout the droplet. Solute-solvent interactions will be weaker for neutral toluene but the vibrational energy content is exceptionally high when the S_0 state is reached from the T_1 state. If this is sufficient to overwhelm the thermal dissipation process then a temporary bubble could form to transport the toluene to the surface. We hasten to add that this is highly speculative and is not supported by any firm evidence at present. Further studies, which might include other substituted aromatic molecules, could help to resolve this matter.

Finally, we make some brief comments about the ionization process. The ionization energetics and dynamics of toluene molecules has been studied in considerable detail, particularly using photoionization.^{12,13} The production of $C_7H_7^+$ and $C_5H_5^+$ in such studies is well known and the evidence, as shown by a clear anti-correlation between the $C_7H_7^+$ and $C_5H_5^+$ signals near the threshold for forming the latter, suggests that $C_5H_5^+$ is a secondary product derived from formation of $C_7H_7^+$,¹¹ which itself is formed by H atom loss following photoionization of toluene. In our experiments the main source of ions is charge transfer from He^+ , which is formed by electron ionization of a helium droplet. Nevertheless, we might

expect the photoionization and charge transfer ionization mechanisms to be similar when the energy content is comparable. However, the C_5H_5^+ and C_7H_7^+ signals in the current study do not show any strong correlation or anti-correlation, *e.g.* with helium droplet size. A possible explanation for this is that the C_5H_5^+ is formed by a different mechanism, ejection of the vinyl radical, C_2H_3 , from the parent molecule. This change in mechanism when compared with previous photoionization studies might be the result of occupation of the T_1 state rather than the S_0 state, although there is currently no independent evidence on the ionization dynamics of the T_1 state of toluene to support or refute this suggestion.

Conclusions

An attempt to record depletion electronic spectra of neutral toluene in helium nanodroplets has led to the observation of a surprisingly long-lived excited state (*ca.* 230 μs) that leads to enhancement of the signal for the fragment ion C_5H_5^+ and depletion of the signal for C_7H_7^+ when the droplets are subject to electron impact. It is suggested that the excited state involved here is the first excited triplet state of toluene, which is occupied by laser excitation to the S_1 state followed by intersystem crossing.

In the form of depletion spectroscopy ordinarily used to observe spectra of molecules in helium droplets the best signal-to-noise ratio is obtained by working with relatively small helium droplets, with no more than a few thousand helium atoms. In this way the relative change in droplet size between on-resonance and off-resonance laser wavelengths is maximized. On the other hand, the enhancement signal reported in this paper improves up to a droplet size of at least 20000 helium atoms. Most likely this will continue up to the size limit imposed by the ability of molecular ions to form and escape from helium droplets after electron impact, which previous studies suggest is reached between 4×10^4 and 6×10^4 helium atoms.^{20,21} Thus signal enhancement of the type reported here could potentially be

used as a technique for recording optical spectra in helium droplets much larger than those typically used for conventional depletion spectroscopy experiments. However, a necessary pre-condition is that optical excitation must generate a long-lived excited state and must also deliver some measurable change in the ionization cross section when compared to the ground state molecule, otherwise no effect will be registered.

Acknowledgements

The authors wish to thank the UK Engineering and Physical Sciences Research Council and the Leverhulme Trust for grants in support of this work. Ben Shepperson and Andrew Shirley are grateful to the University of Leicester for providing research studentships.

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Figure captions

1. Mass spectra showing both the toluene monomer and dimer parent ion regions and, in the inset, an expanded view highlighting the C_5H_5^+ , C_7H_7^+ and C_7H_8^+ peaks. In addition to ions derived from toluene a clear series of peaks (not labeled) arising from He_n^+ ions can be seen. This mass spectrum is for toluene molecules inside helium nanodroplets was recorded using s TOF-MS (see text for further details), which provides a wider accessible mass range and a higher mass resolution than the QMS.
2. Spectra recorded in the $\text{S}_1\text{-S}_0$ region of toluene, acquired by monitoring the $m/z = 91$ (C_7H_7^+) channel (upper panels) and the $m/z = 65$ (C_5H_5^+) channel (lower panels). The assignments given were taken from ref. 10. 400 laser shots were used to acquire each point in the spectrum and the laser step size was 0.3 cm^{-1} .
3. Ion signal recorded for C_5H_5^+ showing a transient effect due to laser excitation (tuned to the $\text{S}_1\text{-S}_0\ 0_0^0$ transition). A clear signal enhancement is seen almost immediately following laser excitation and thereafter exponential decay occurs.

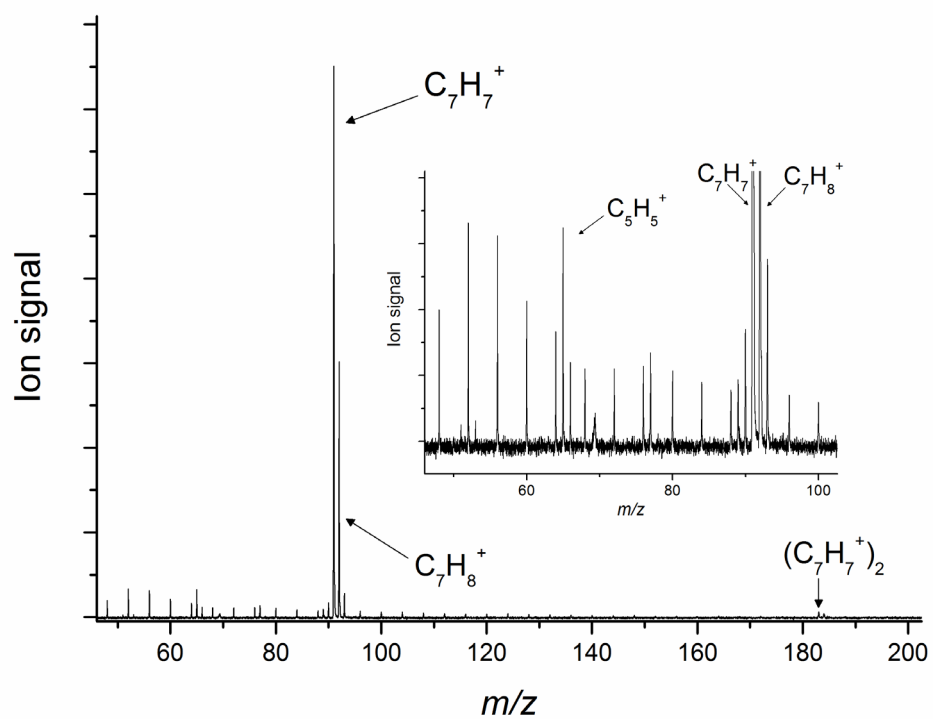


Figure 1

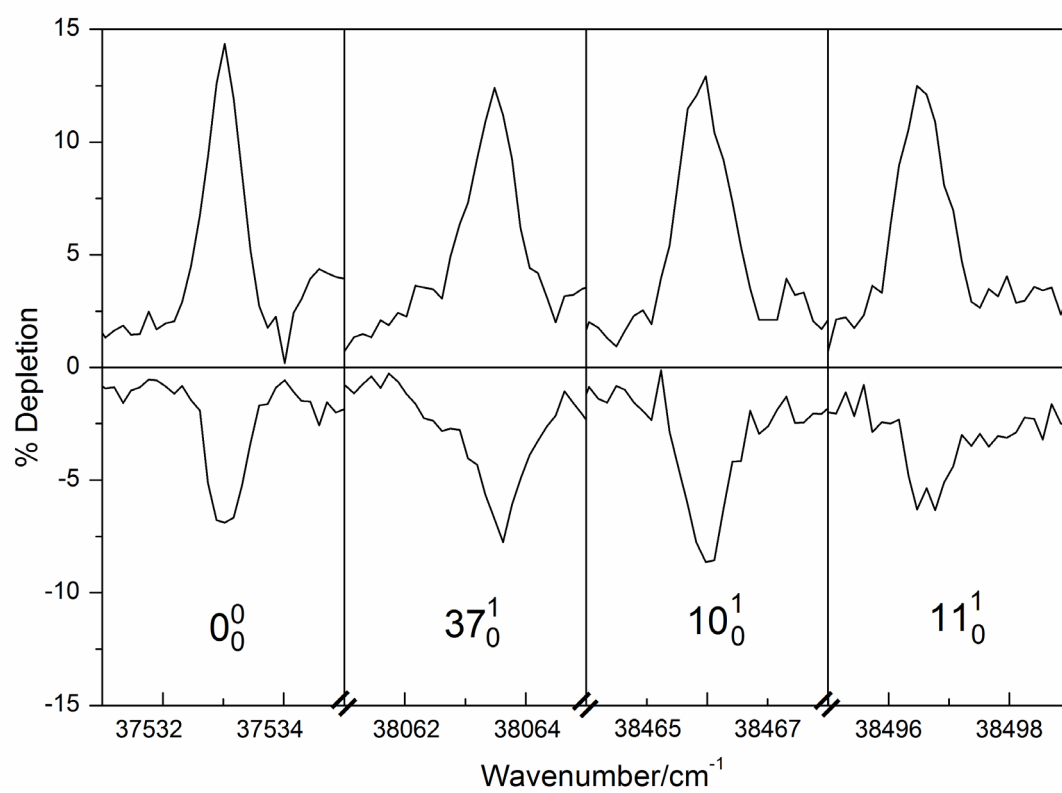


Figure 2

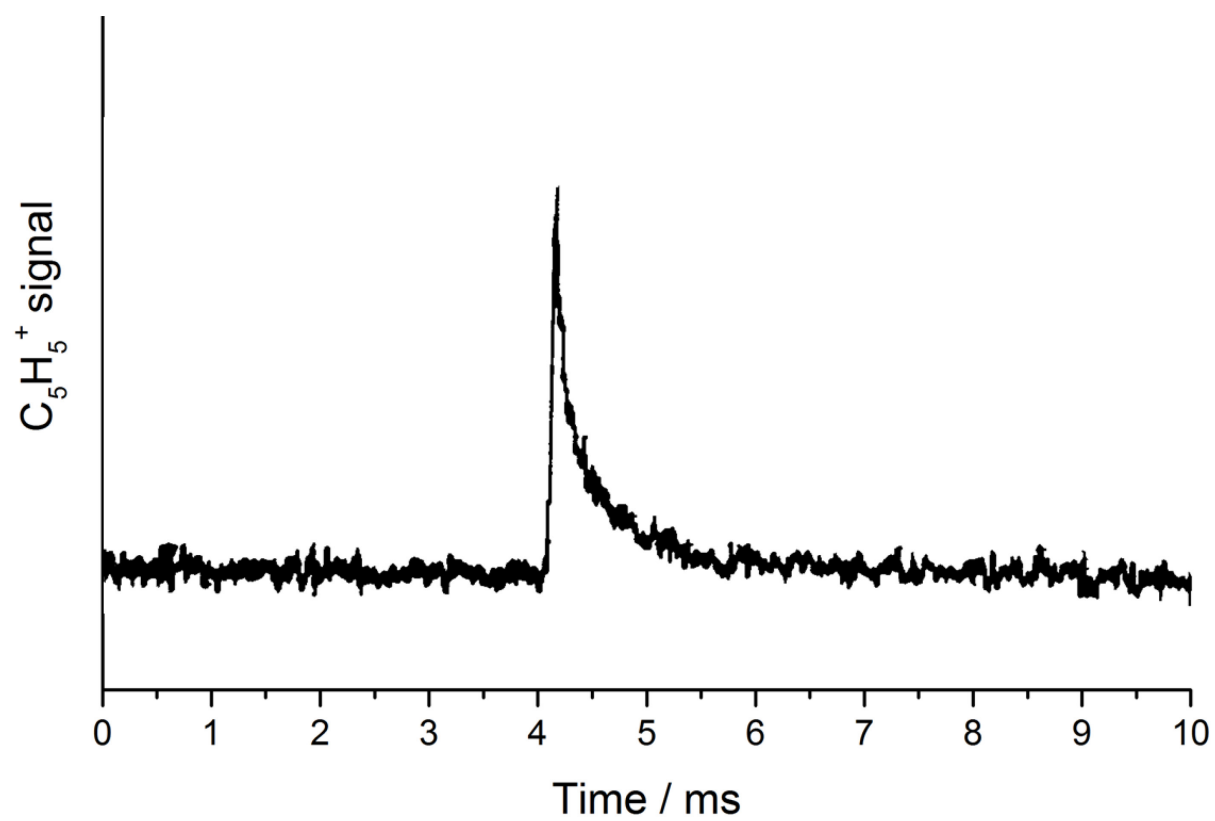


Figure 3

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