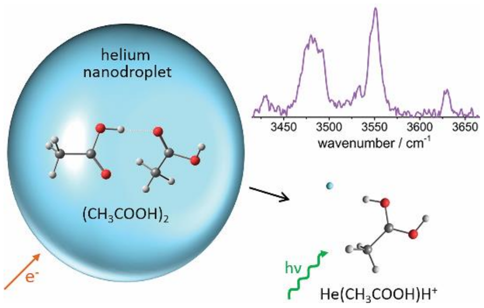
Accessing challenging molecular species by combining helium droplets with IR spectroscopy



Andrew M. Ellis

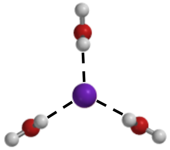
Department of Chemistry

University of Leicester, UK

QFC 2019, Bad Honnef

Research programme

Microsolvation complexes *motivation* – probing solute-solvent interactions

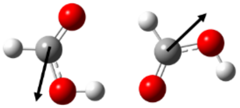


CsI-water

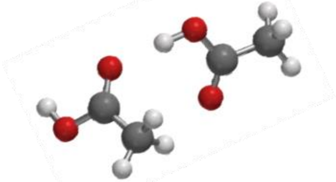
Acetic acid-water

Incipient aerosol nucleation *motivation* – understanding secondary aerosol formation mechanism

Metastable clusters *motivation* – link to extended structures



Formic acid dimer – the basic structural component of crystalline formic acid

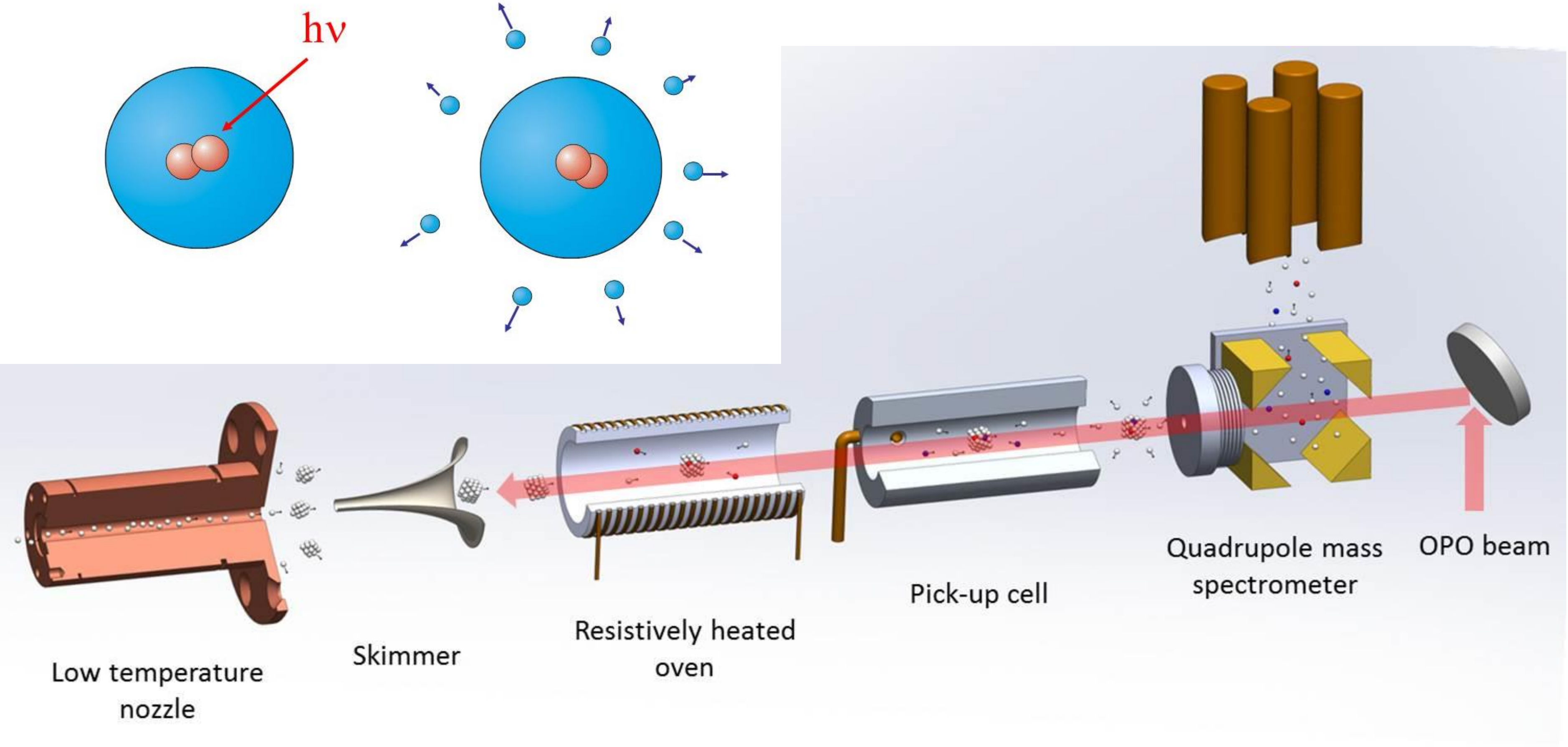


Acetic acid dimer

Helium-messenger spectroscopy of cations formed from doped helium droplets

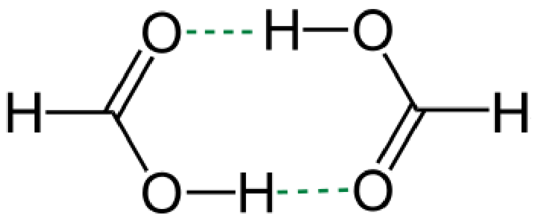
Infrared (IR) depletion spectroscopy

Infrared depletion spectra measured utilizing <u>mass-selective ion detection</u>

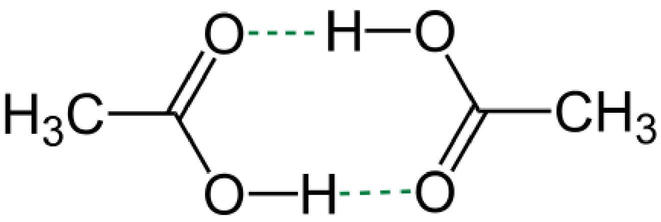


$e^- + M@He_N \rightarrow He^+[M@He_{N-1}] + 2e^- \rightarrow\rightarrow M^+$ in gas phase

Carboxylic acid clusters



Formic acid (FA) dimer



Acetic acid (AA) dimer

Global potential energy minimum of FA and AA dimers have two strong H-bonds

No electric dipole moment

Strongly red-shifted OH stretching bands

JOURNAL OF CHEMICAL PHYSICS VOLUME 120, NUMBER 22 8 JUNE 2004

Polar isomer of formic acid dimers formed in helium nanodroplets

Frank Madeja and Martina Havenith
*Department of Physical Chemistry II, Ruhr-Universität Bochum, Universitätsstraße 150,
D-44780 Bochum, Germany*

Klaas Nauta and Roger E. Miller
Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599

Jana Chocholoušová and Pavel Hobza
*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic and Center
for Complex Molecular Systems and Biomolecules, Dolejškova 3, 18223 Prague, Czech Republic*

(Received 3 November 2003; accepted 27 February 2004)

The infrared spectrum of formic acid dimers in helium nanodroplets has been observed corresponding to excitation of the "free" OH and CH stretches. The experimental results are consistent with a polar acyclic structure for the dimer. The formation of this structure in helium, as opposed to the much more stable cyclic isomer with two O–H···O hydrogen bonds, is attributed to the unique growth conditions that exist in helium droplets, at a temperature of 0.37 K. Theoretical calculations are also reported to aid in the interpretation of the experimental results. At long range the intermolecular interaction between the two monomers is dominated by the dipole–dipole interaction, which favors the formation of a polar dimer. By following the minimum-energy path, the calculations predict the formation of an acyclic dimer having one O–H···O and one C–H···O contact. This structure corresponds to a local minimum on the potential energy surface and differs significantly from the structure observed in the gas phase.
[DOI: 10.1063/1.1709942]

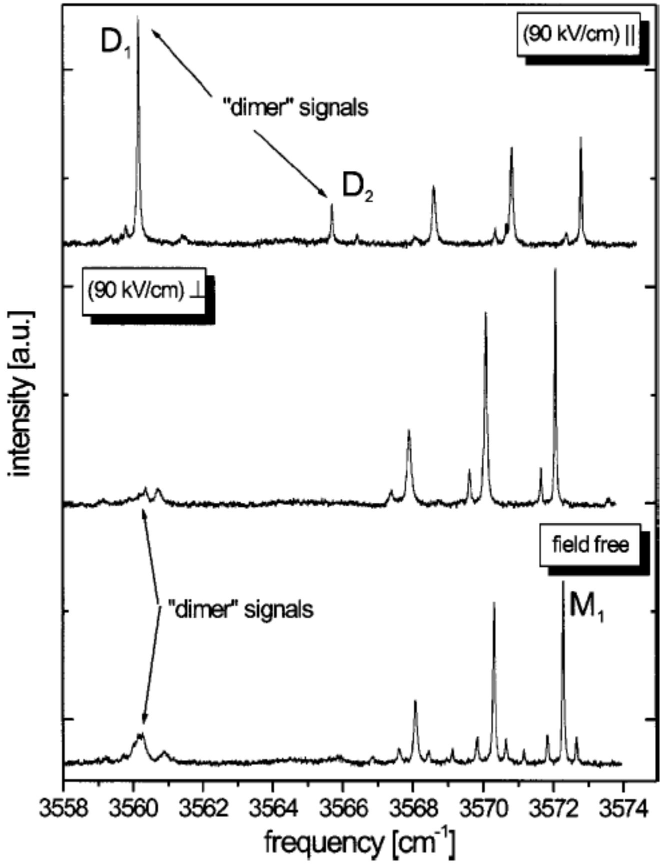


FIG. 2. "Field-free" and pendular spectra (taken with ⊥ and ∥ laser polarization) of h_2-formic acid inside liquid helium droplets at the OH stretching frequency. All dimer bands are marked with arrows. The three bands on the right side can be attributed to monomer bands.

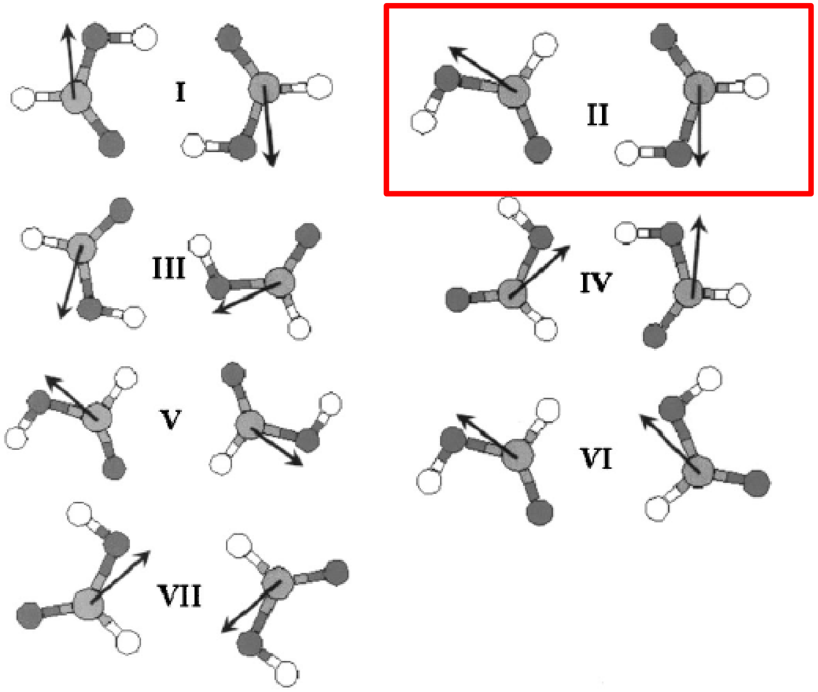


FIG. 1. Formic acid dimer isomers, predicted by MP2 calculations (Ref. 37), explained in Sec. V. Associated vibrational frequencies and binding energies can be found in Table I. The arrows indicate the orientation of subsystem dipole moments.

'Pendular' effect in free OH stretching region – shows the dimer has a substantial electric dipole moment

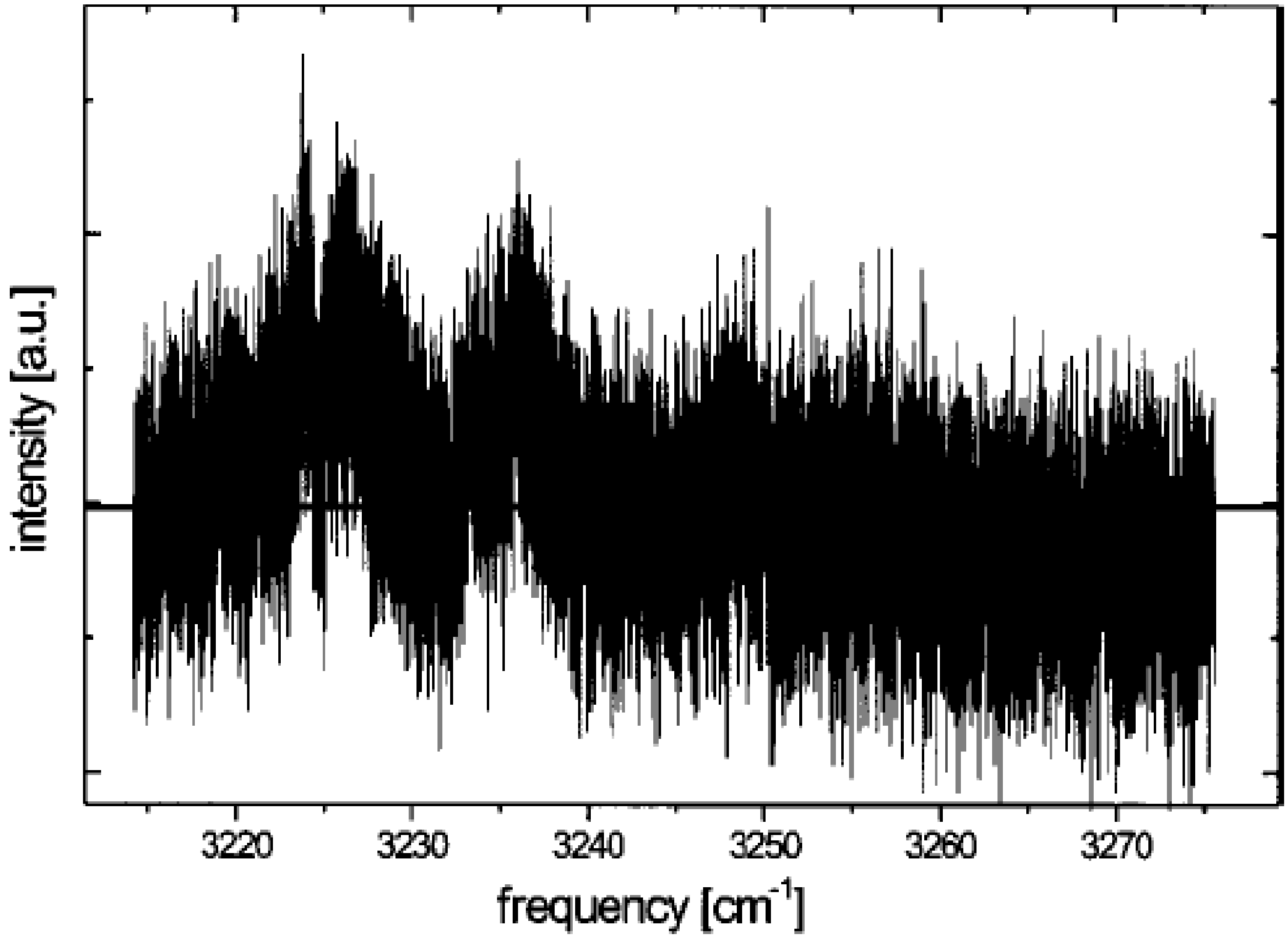
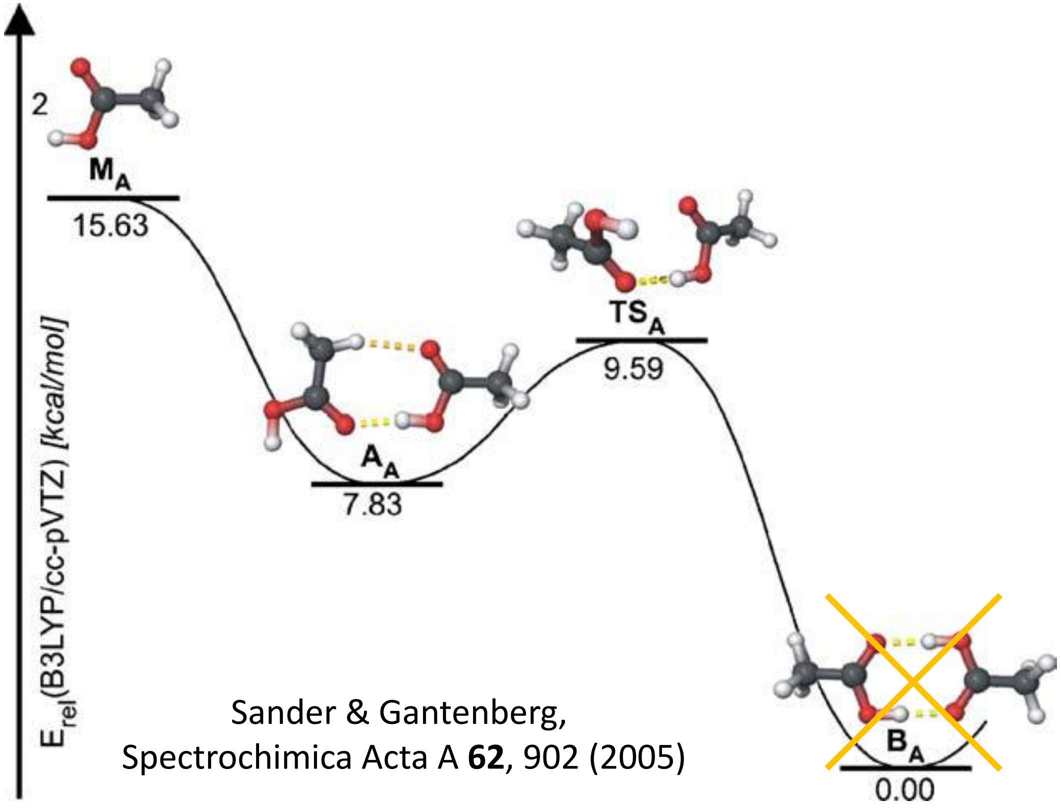


FIG. 6. Pendular-state spectrum of formic acid in the hydrogen-bonded OH stretch region at the maximum field strength of 90 kV/cm (|| polarization).

Trapping metastable clusters

For the dimer, rapid cooling traps it in a higher energy structure



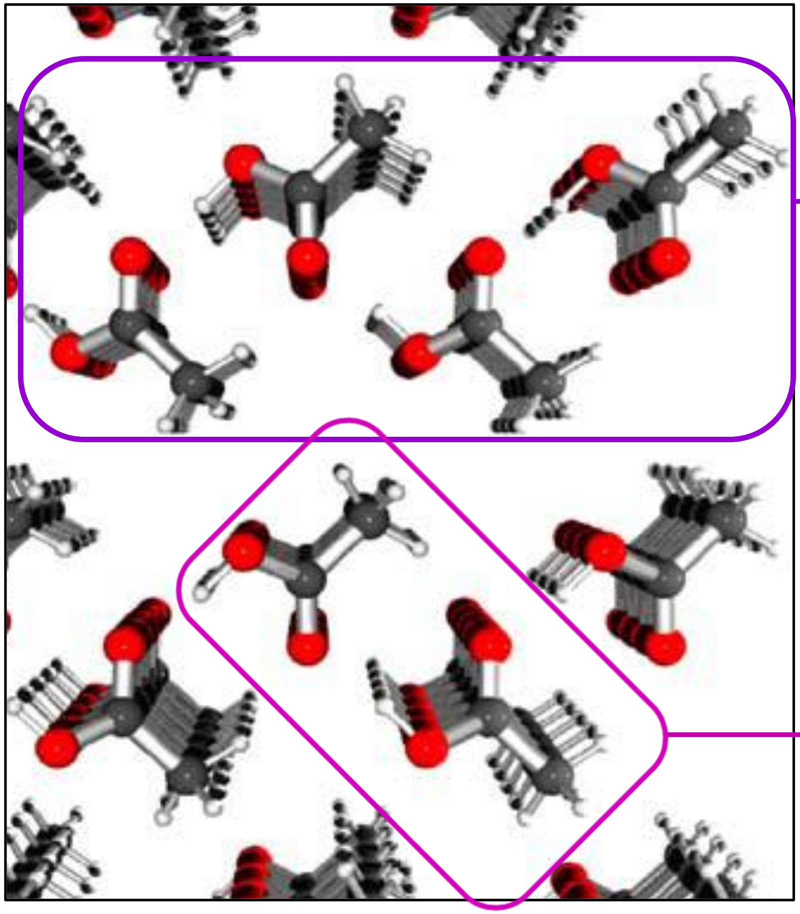
Sander & Gantenberg,
Spectrochimica Acta A **62**, 902 (2005)

Formation of clusters in HeDs is influenced by dipole-dipole interactions, which dominate at long range

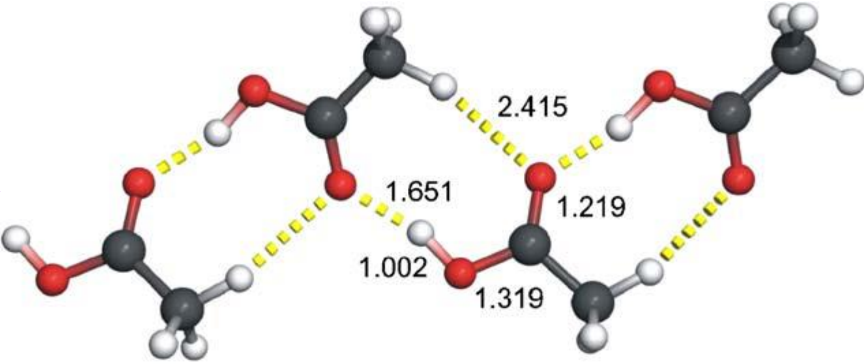
Crystalline acetic acid

Crystalline structure contains one strong C=O···H-O bond and a weak C=O···H-C bond between adjacent molecules

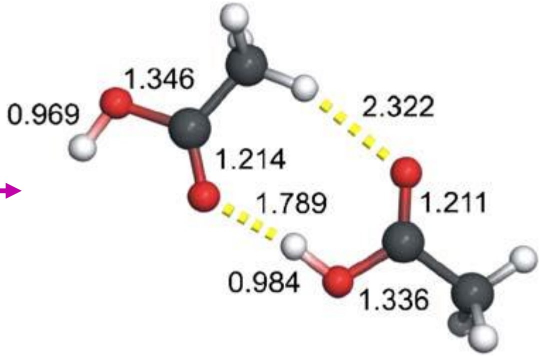
Crystalline structure



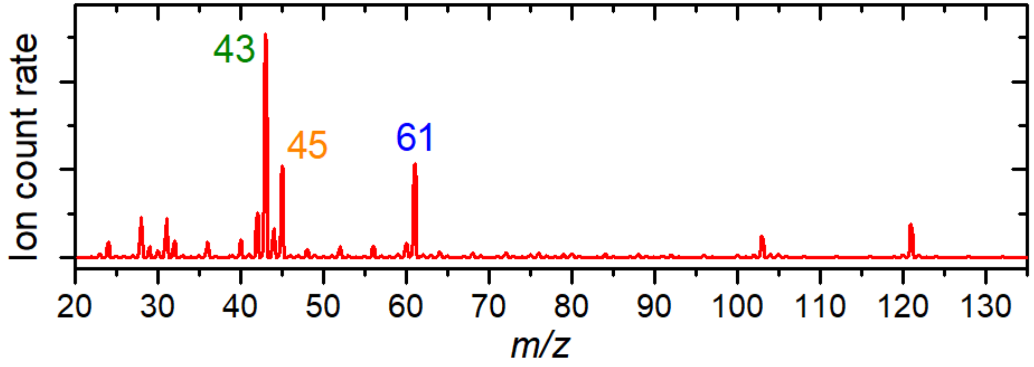
Section of an infinite chain



Dimer

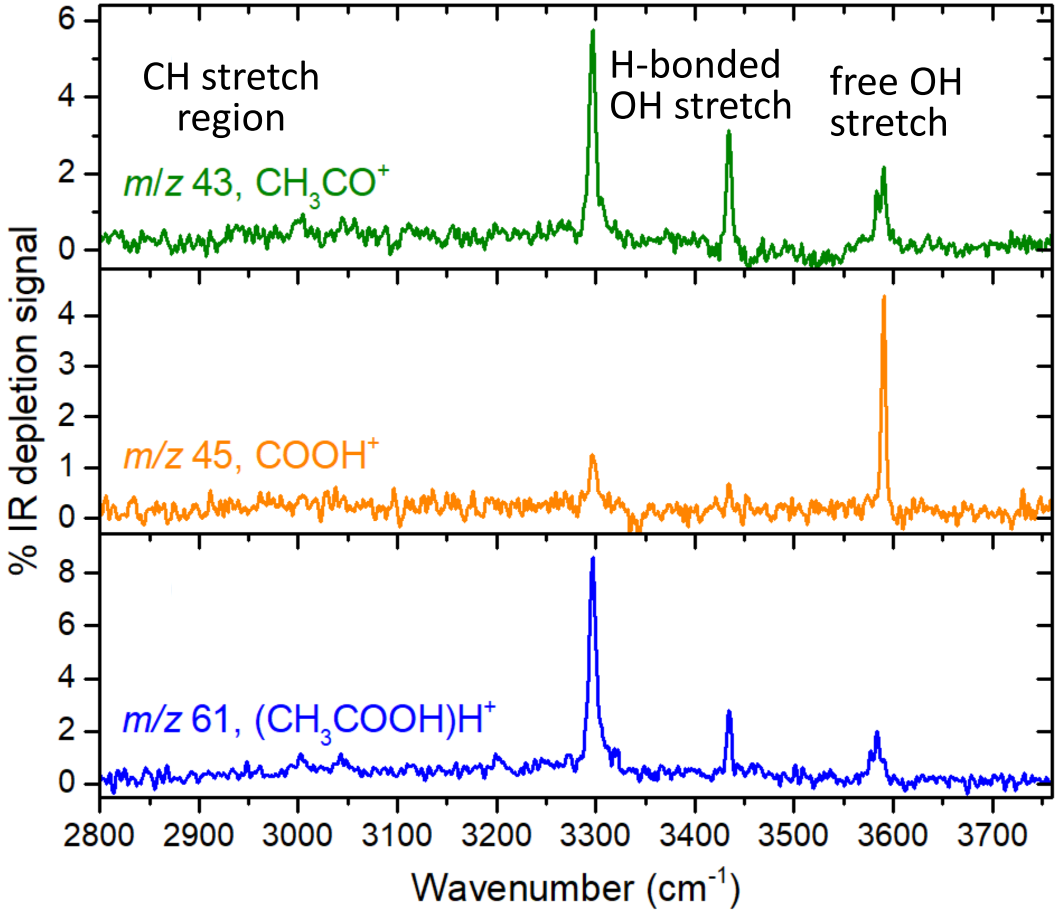


Results: Acetic acid clusters in HeDs



Mass spectrum at low pressure of AA

(N.B. molar mass of acetic acid = 60 g/mol)



$$(CH_3COOH) \xrightarrow{+\,He^+} CH_3CO^+\ (m/z\ 43) + OH$$

$$(CH_3COOH)_2 \xrightarrow{+\,He^+} CH_3CO^+\ (m/z\ 43) + CH_3COOH + OH$$

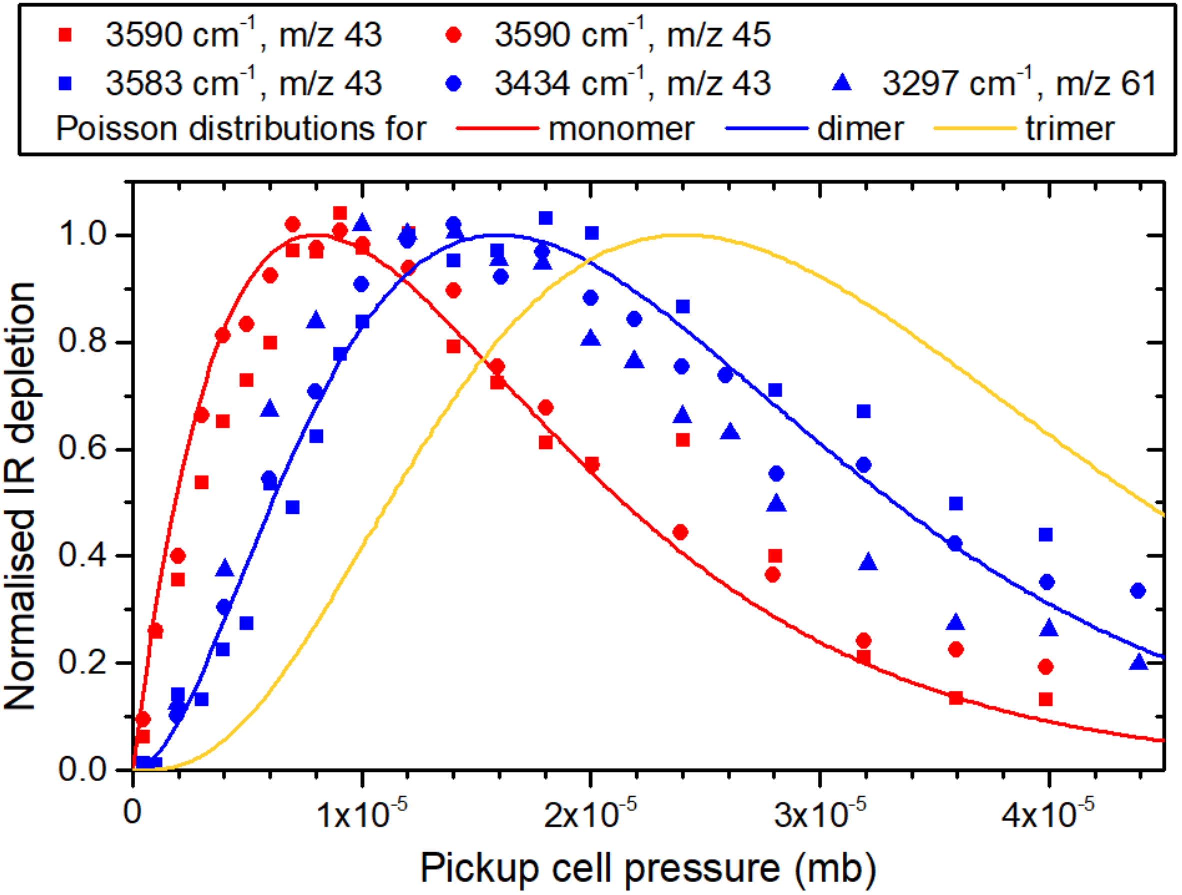
$$(CH_3COOH) \xrightarrow{+\,He^+} COOH^+\ (m/z\ 45) + CH_3$$

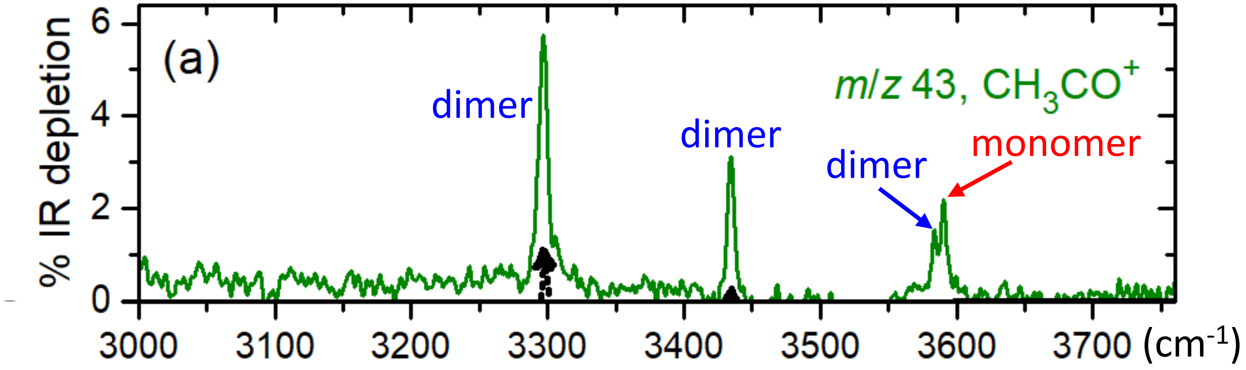
$$(CH_3COOH)_2 \xrightarrow{+\,He^+} COOH^+\ (m/z\ 45) + CH_3COOH + CH_3$$

$$(CH_3COOH)_2 \xrightarrow{+\,He^+} (CH_3COOH)H^+\ (m/z\ 61) + CH_3COO$$

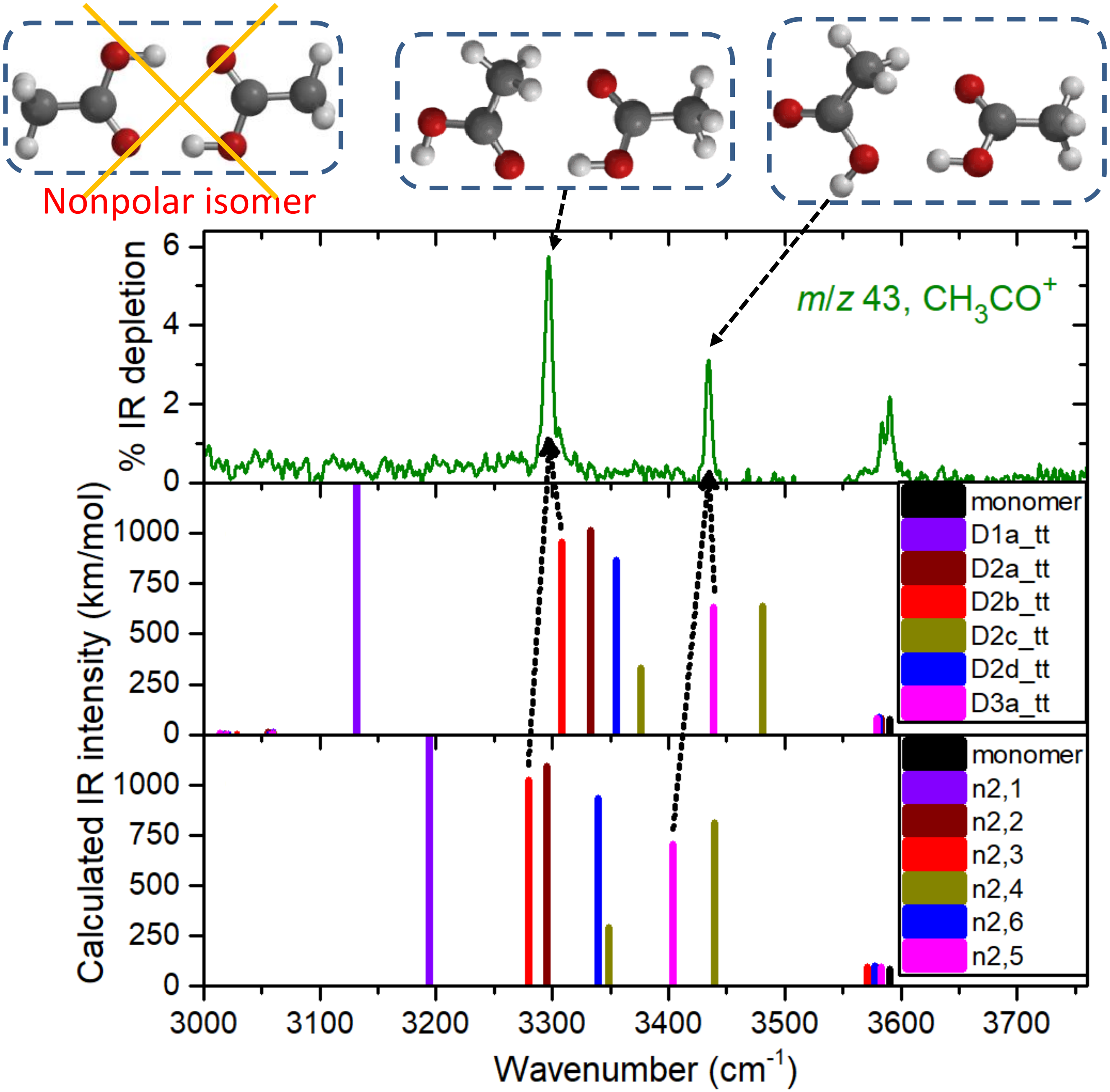
PCCP, 2019, DOI: 10.1039/c8cp05934a

Pressure dependence for IR peak intensities

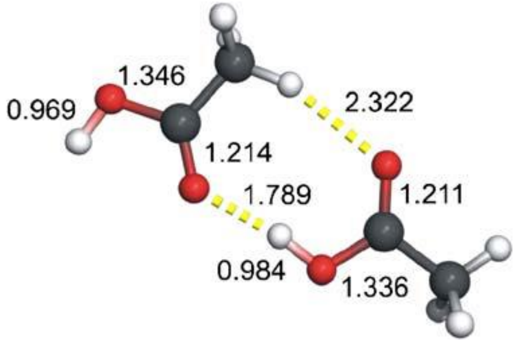




Assignment of dimer structures



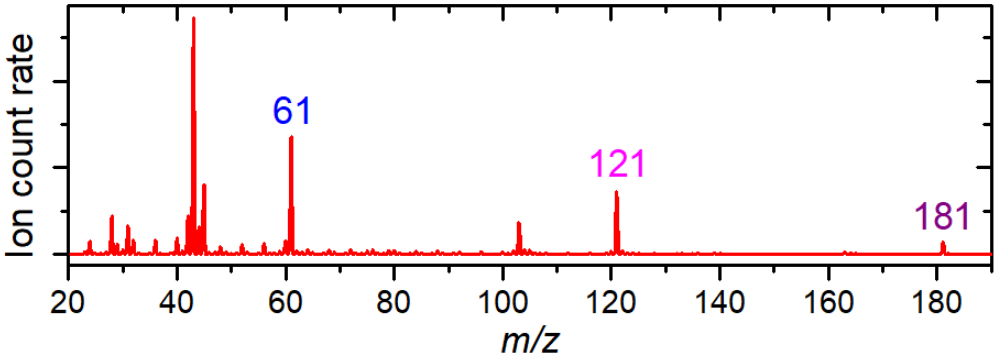
c.f. crystalline structure



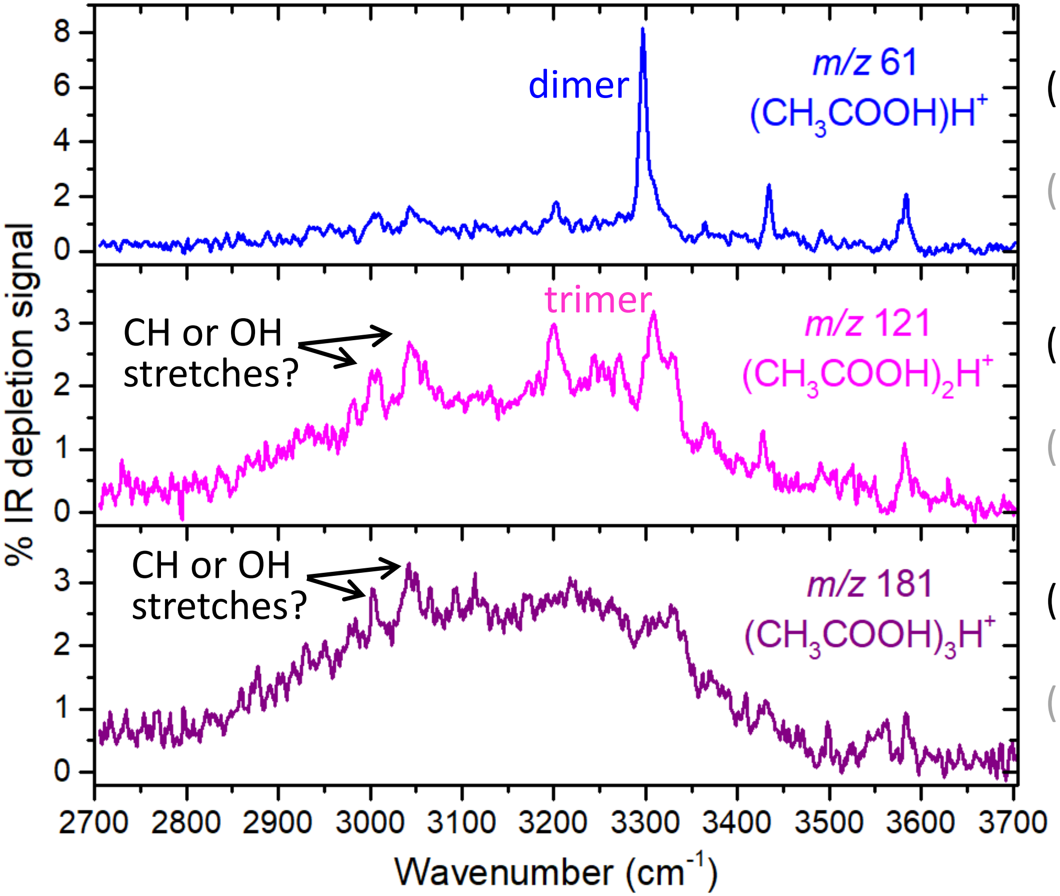
Ab initio calculations by Lopes *et al*, J Chem Phys 143, 104307 (2015) at the MP2/6-311++G(2d,2p) level of theory

DFT calculations by our collaborators at University of Nottingham at the M06/6-311++G(d,p) level of theory

Larger clusters



Mass spectrum at slightly higher pressure, <n> = 1.5



$(CH_3COOH)_2 \xrightarrow{+ He^+} (CH_3COOH)H^+$ (*m/z* 61)
$+ CH_3COO$

$(CH_3COOH)_3 \xrightarrow{+ He^+} (CH_3COOH)H^+$ (*m/z* 61)
$+ CH_3COO + CH_3COOH$

$(CH_3COOH)_3 \xrightarrow{+ He^+} (CH_3COOH)_2H^+$ (*m/z* 121)
$+ CH_3COO$

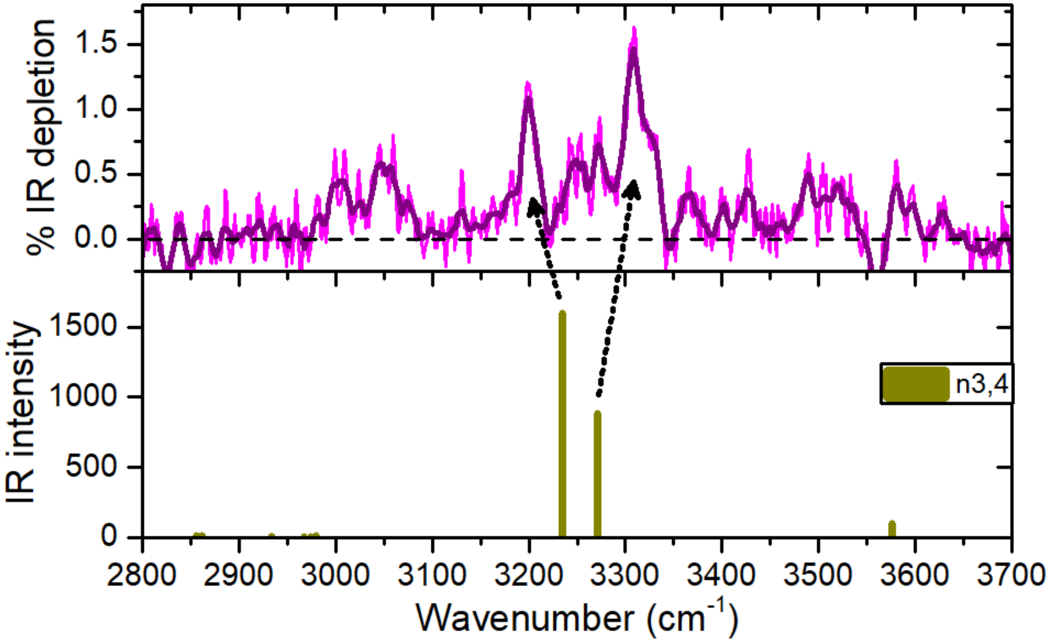
$(CH_3COOH)_4 \xrightarrow{+ He^+} (CH_3COOH)_2H^+$ (*m/z* 121)
$+ CH_3COO + CH_3COOH$

$(CH_3COOH)_4 \xrightarrow{+ He^+} (CH_3COOH)_3H^+$ (*m/z* 181)
$+ CH_3COO$

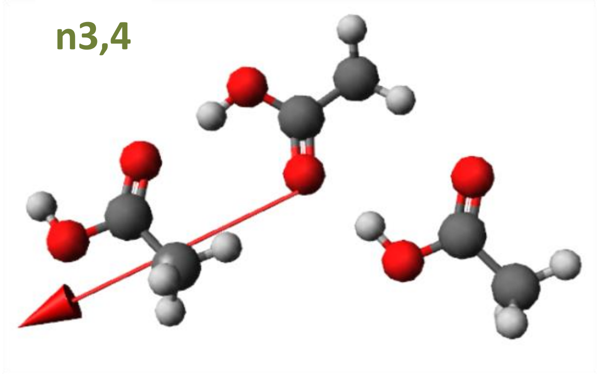
$(CH_3COOH)_5 \xrightarrow{+ He^+} (CH_3COOH)_3H^+$ (*m/z* 181)
$+ CH_3COO + CH_3COOH$

Acetic acid clusters in HeDs

Difference spectrum obtained by subtraction of *m/z* 181 spectrum from *m/z* 121

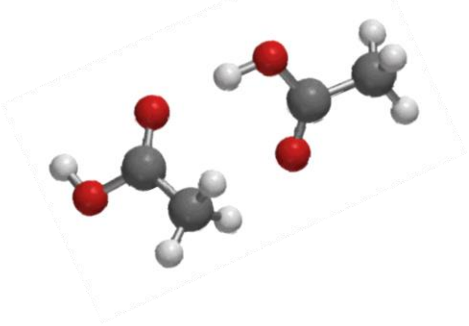


Polar isomer with large dipole moment

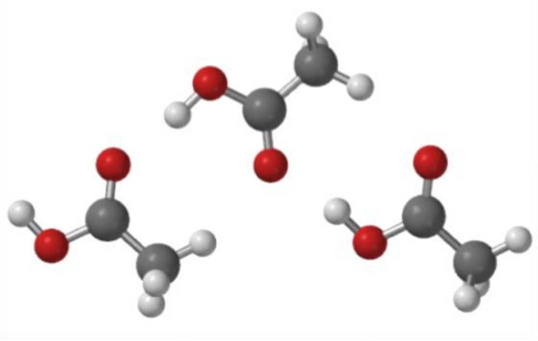


If this assignment is correct then this means (1) the 2 peaks at ~3000 cm^{-1} are most likely due to CH (and not OH) stretches and (2) one trimer structure dominates in HeDs

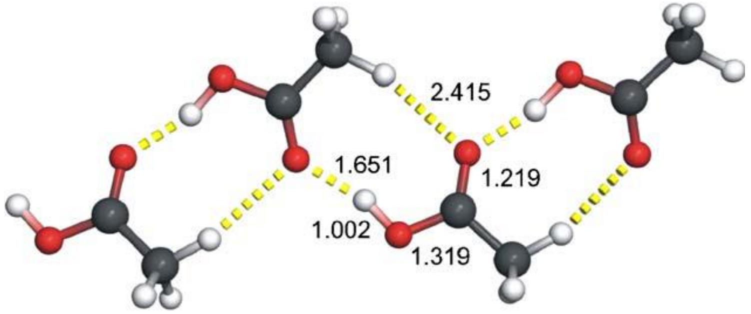
Assigned dimer



Trimer structure

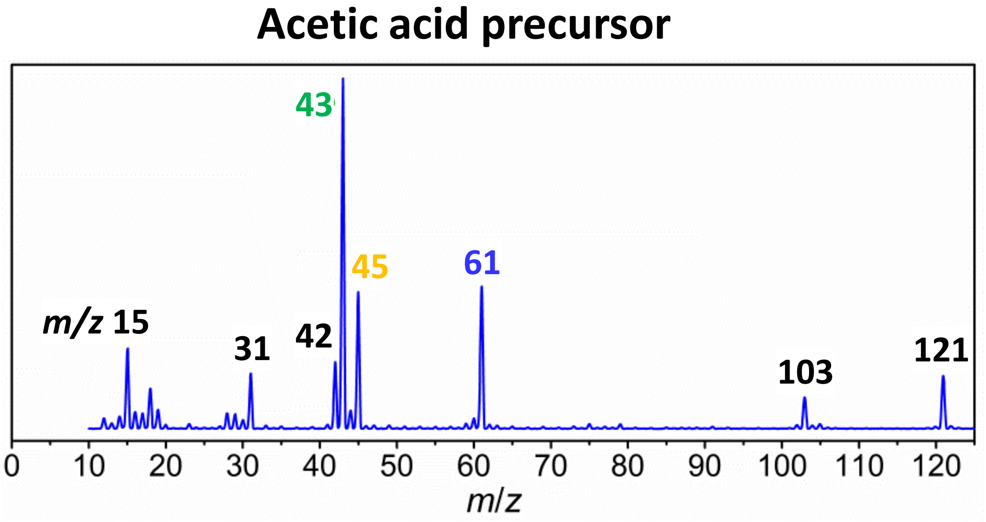


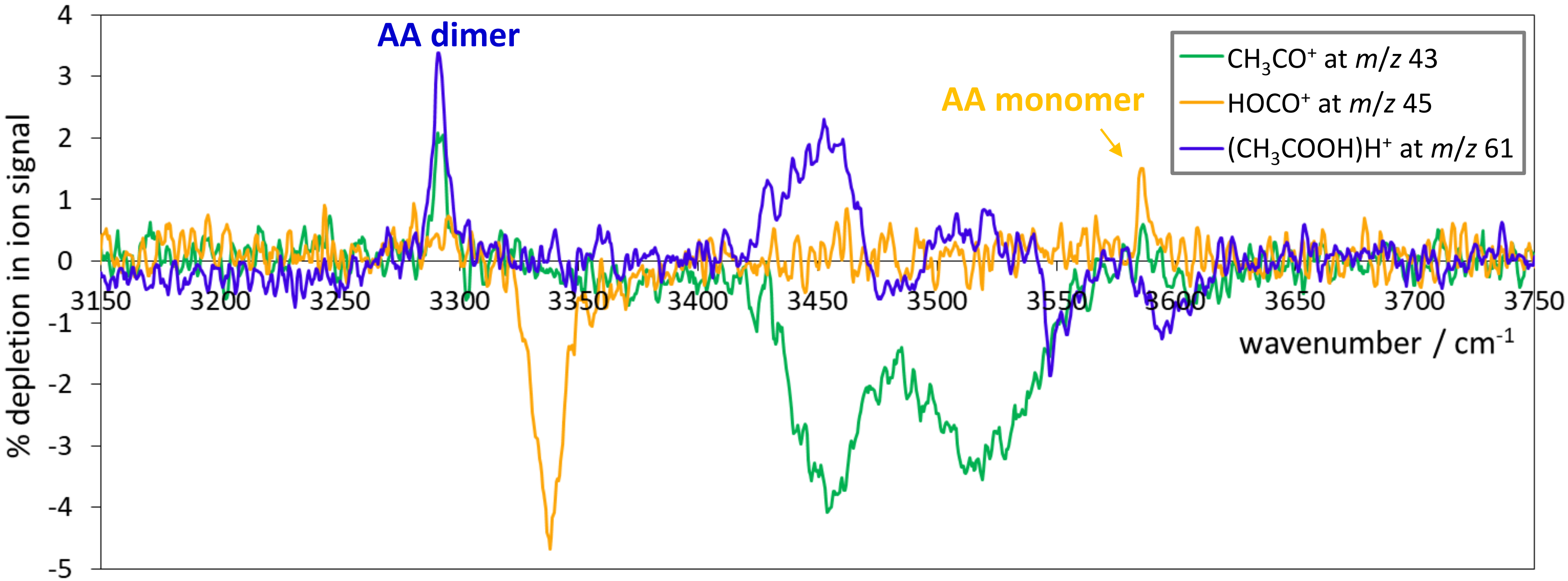
Crystalline structure (X-ray diffraction)



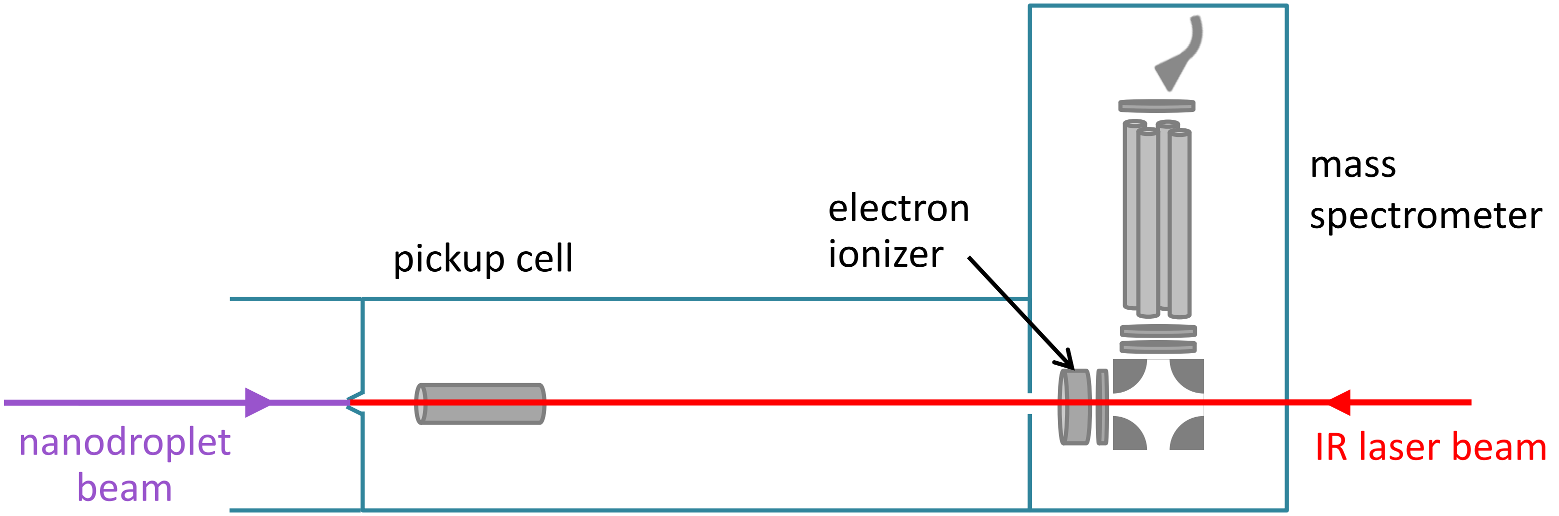
Complications

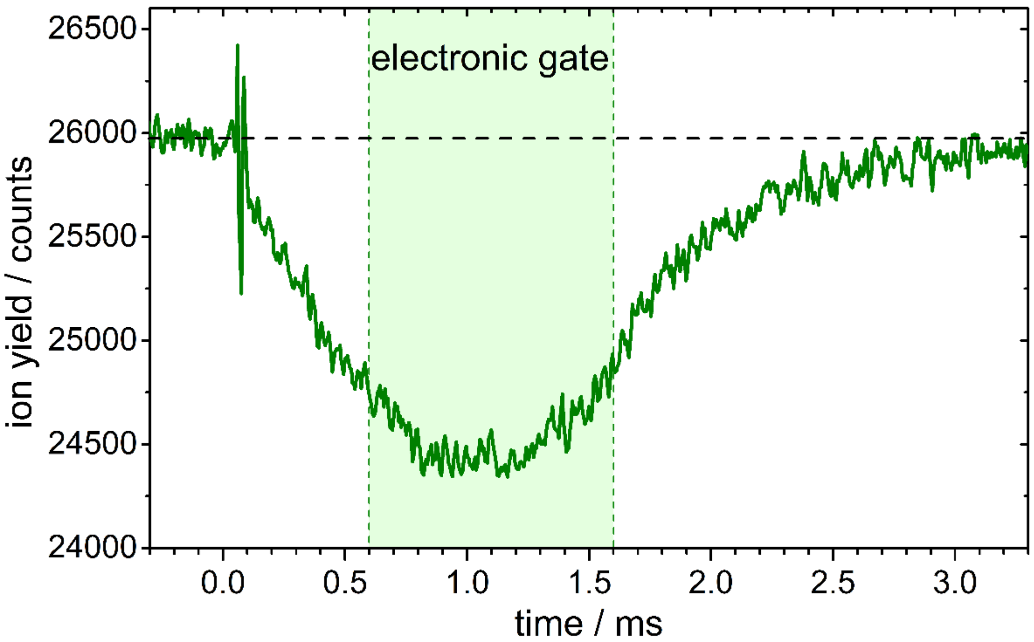
While tweaking the exptl conditions we came across wavelength-dependent ion signals that sometimes showed depletion and sometimes enhancement.





Depletion signal from neutral molecules

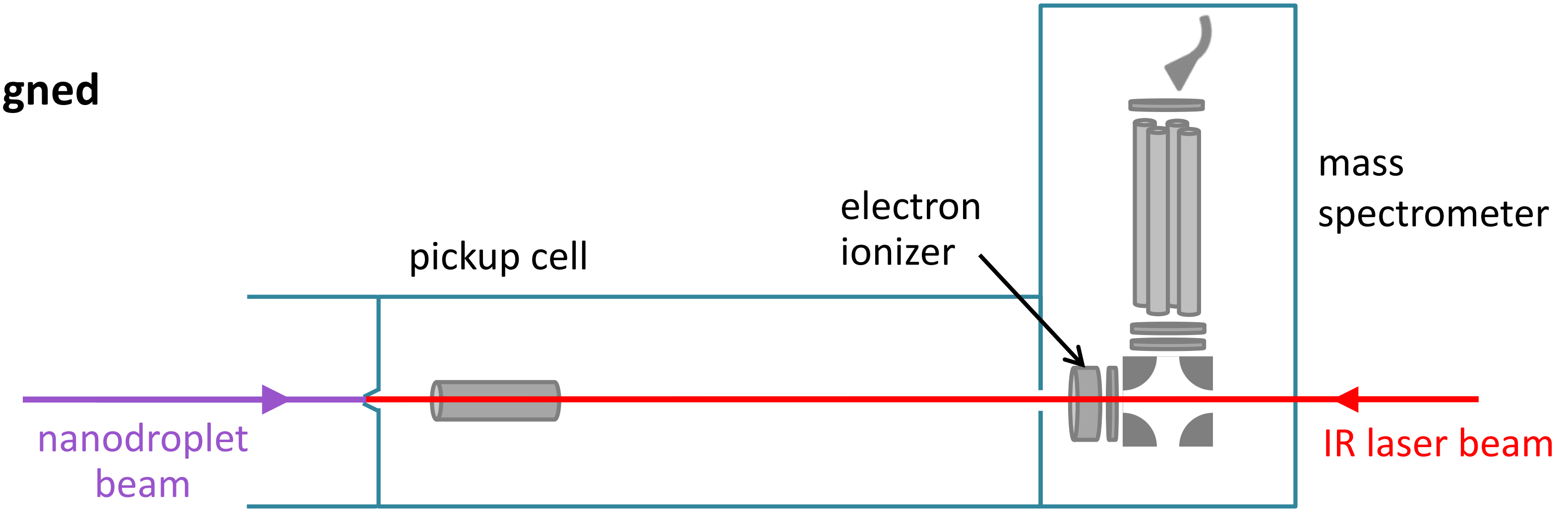




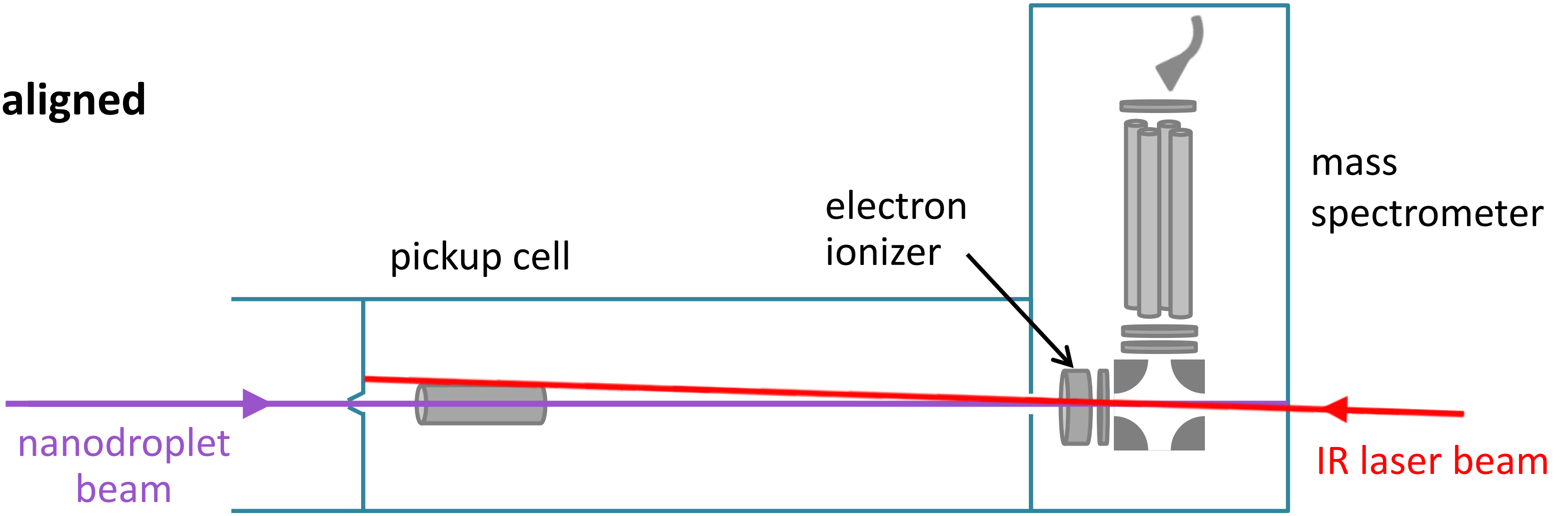
Wavelength @ resonance for a neutral molecule

Laser misalignment

Aligned

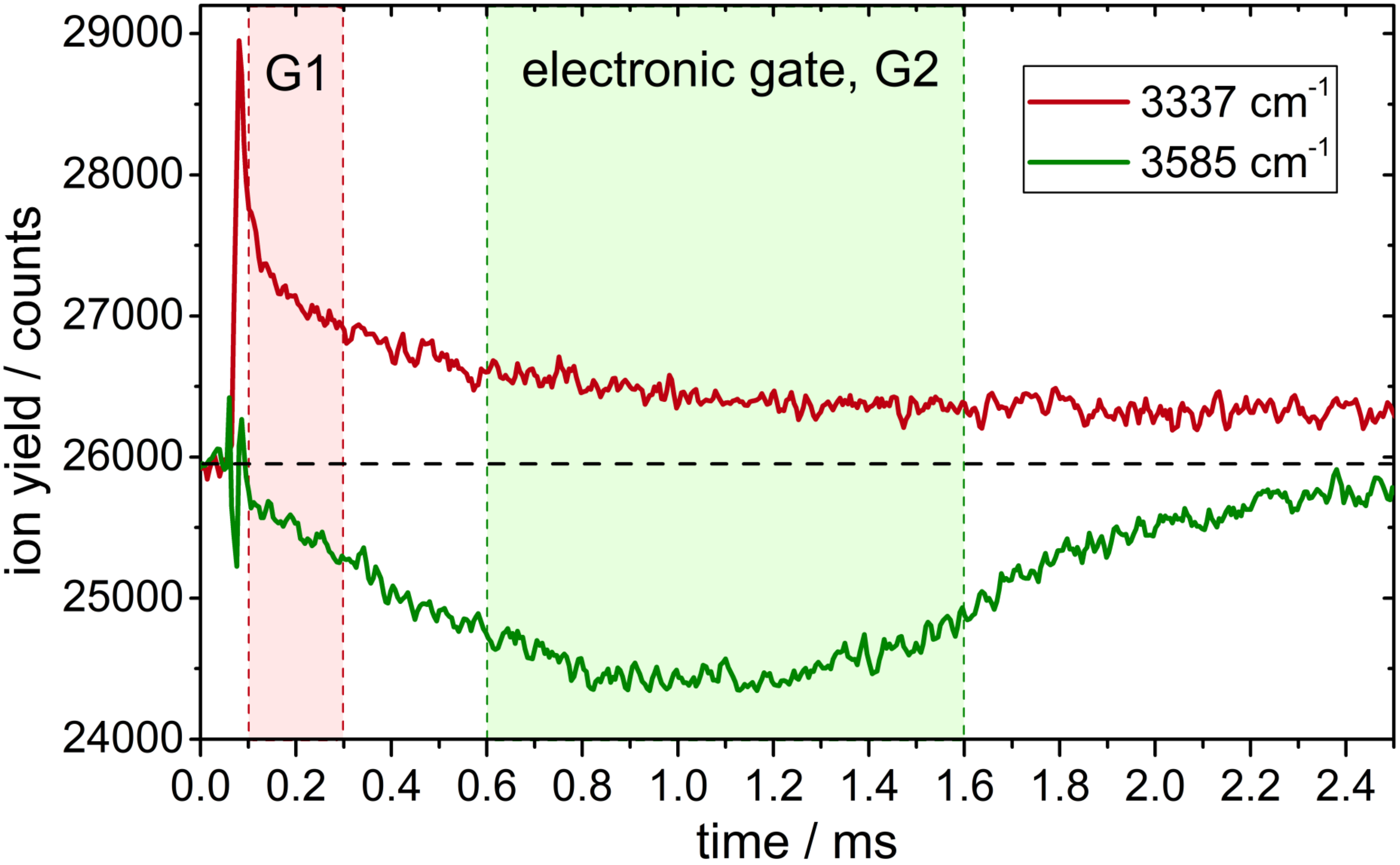


Misaligned

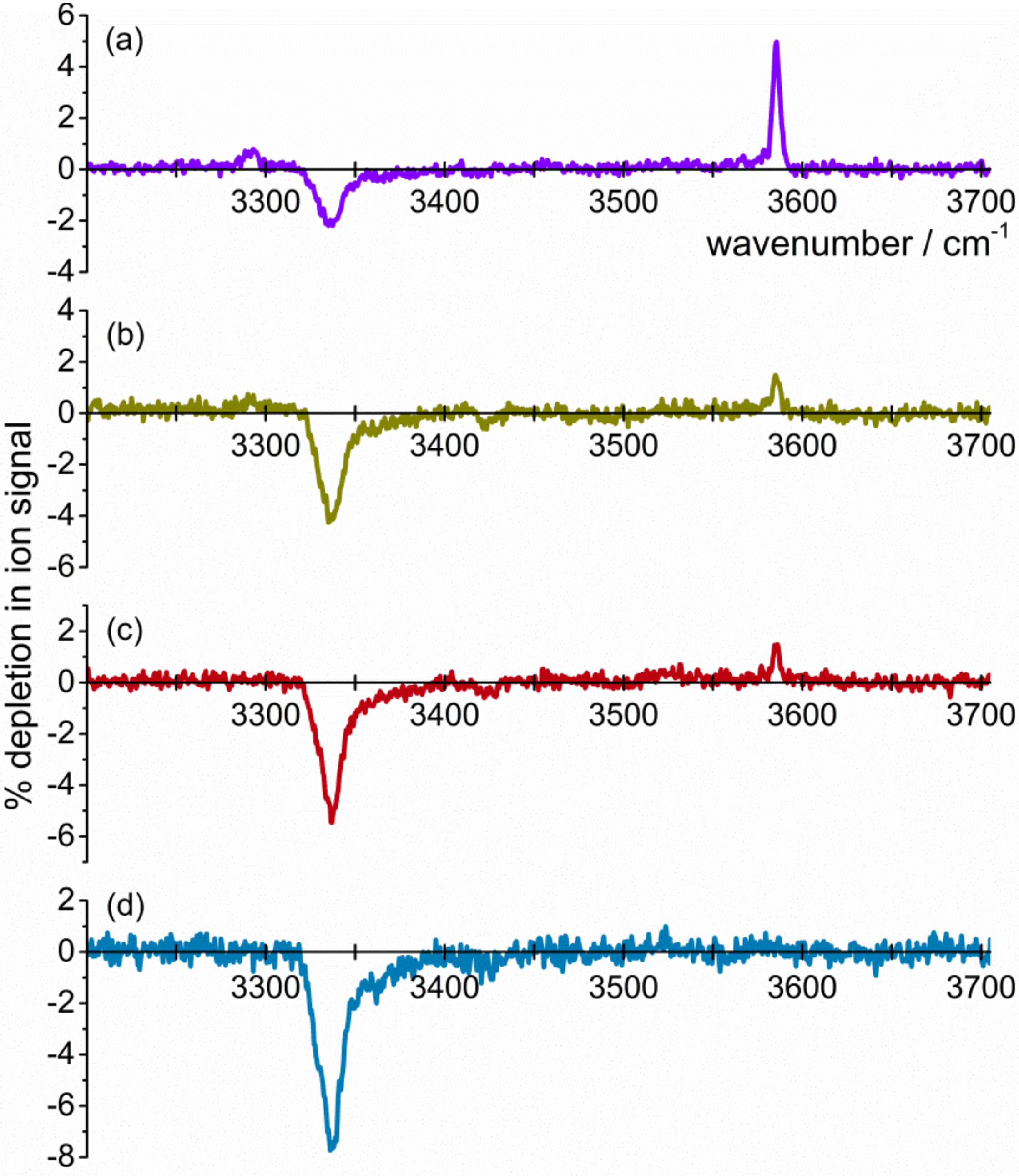


m/*z* 45 ($HOCO^+$)

Two different types of resonances



m/z 45 ($HOCO^+$)



T_0 = 16 K, wide gate (1 ms)

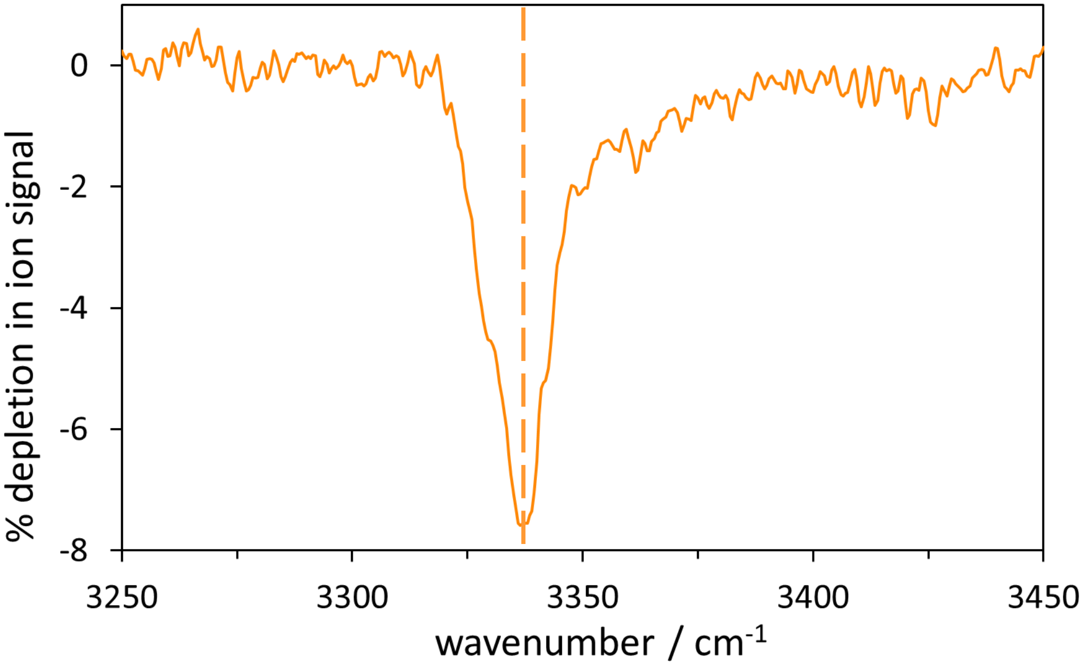
T_0 = 12 K, wide gate (1 ms)

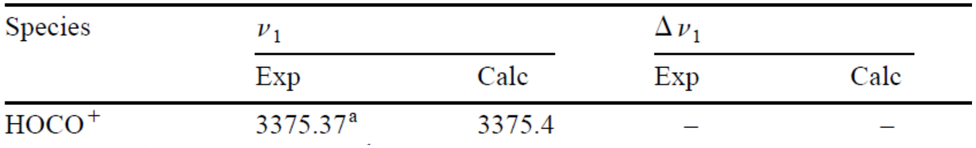
T_0 = 16 K, narrow gate (0.2 ms)

T_0 = 12 K, narrow gate (0.2 ms)

$HOCO^+$

Is this the IR spectrum of $HOCO^+$?



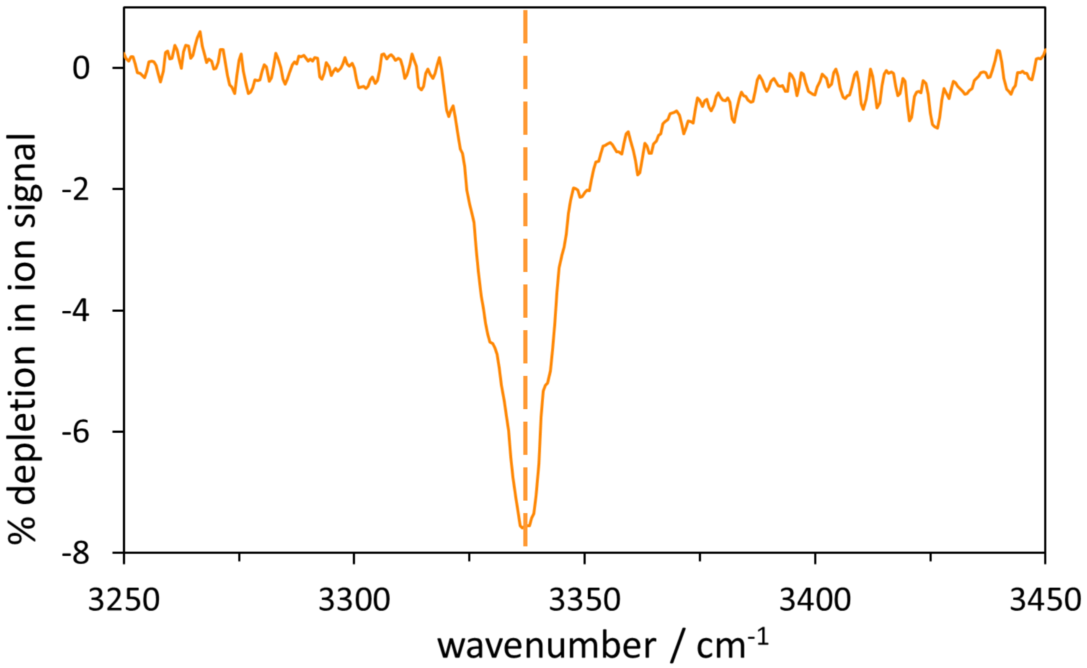


Species	ν_1		$\Delta\nu_1$	
	Exp	Calc	Exp	Calc
$HOCO^+$	3375.37[a]	3375.4	–	–

$HOCO^+$

Dopfer *et al.*, CPL 296, 585 (1998)

Is this the IR spectrum of $HOCO^+$?



Species	ν_1 Exp	ν_1 Calc	$\Delta\nu_1$ Exp	$\Delta\nu_1$ Calc
$HOCO^+$	3375.37[a]	3375.4	–	–
$He–HOCO^+$	3328.3(3)[b]	3317.8	47.1(5)	57.6
$Ne–HOCO^+$	3255.3(5)[c]	3248.9	120.1(5)	126.5
$Ar–HOCO^+$	2671(3)	2766.3	704(3)	609.1

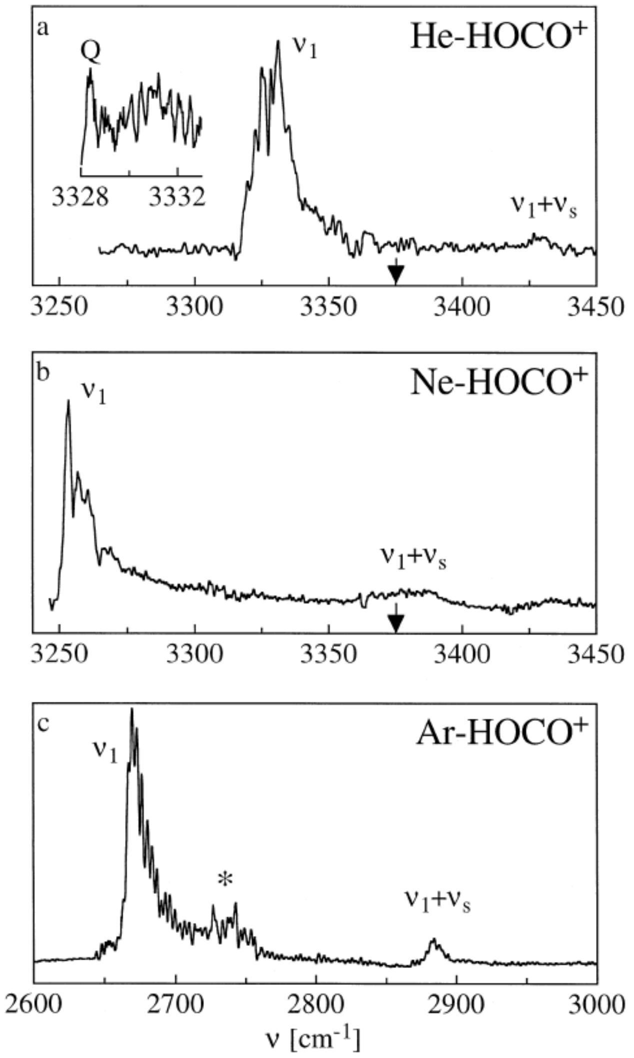


Fig. 2. Photodissociation spectra of $Rg–HOCO^+$ complexes (Rg = He/Ne/Ar) recorded in the $HOCO^+$ fragment channel. The arrows indicate the position of the ν_1 frequency of $HOCO^+$. The asterisk indicates sequence transitions.

Signal enhancement

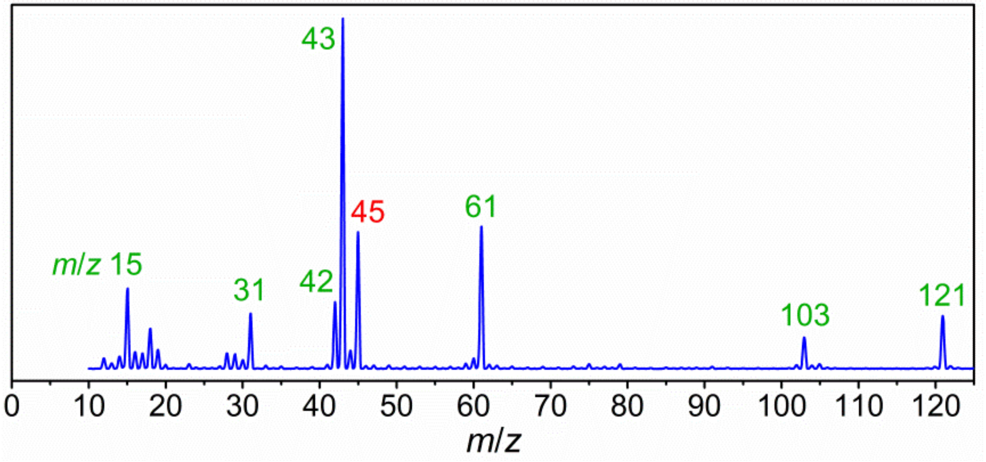
Previous spectrum detected in signal enhancement mode – why as ion signal gain?

$$e^- + CH_3COOH@He \rightarrow He_N\text{-}HOCO^+ + CH_3 + 2e^- + m\mathrm{He}$$

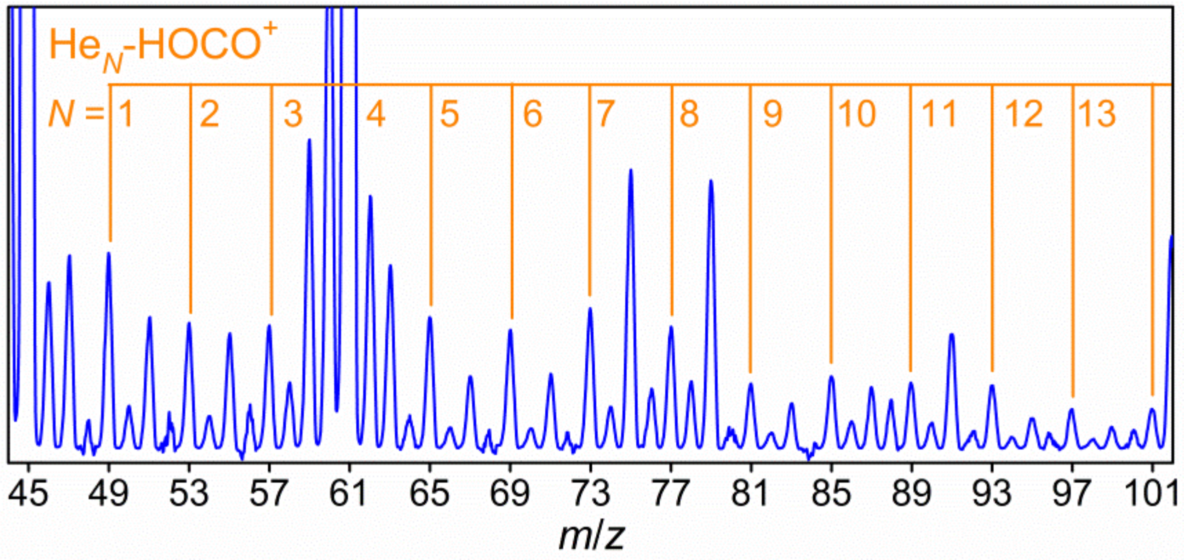
$$h\nu_{IR} + He_N\text{-}HOCO^+ \rightarrow He_N + HOCO^+$$

So IR absorption strips away the helium and thus increases the signal for bare $HOCO^+$ ions. The spectrum recorded is therefore an average of the spectra for different values of *N* weighted according to their abundance.

He_N-$HOCO^+$



Expand



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ARTICLES

Published on Web 09/20/2010

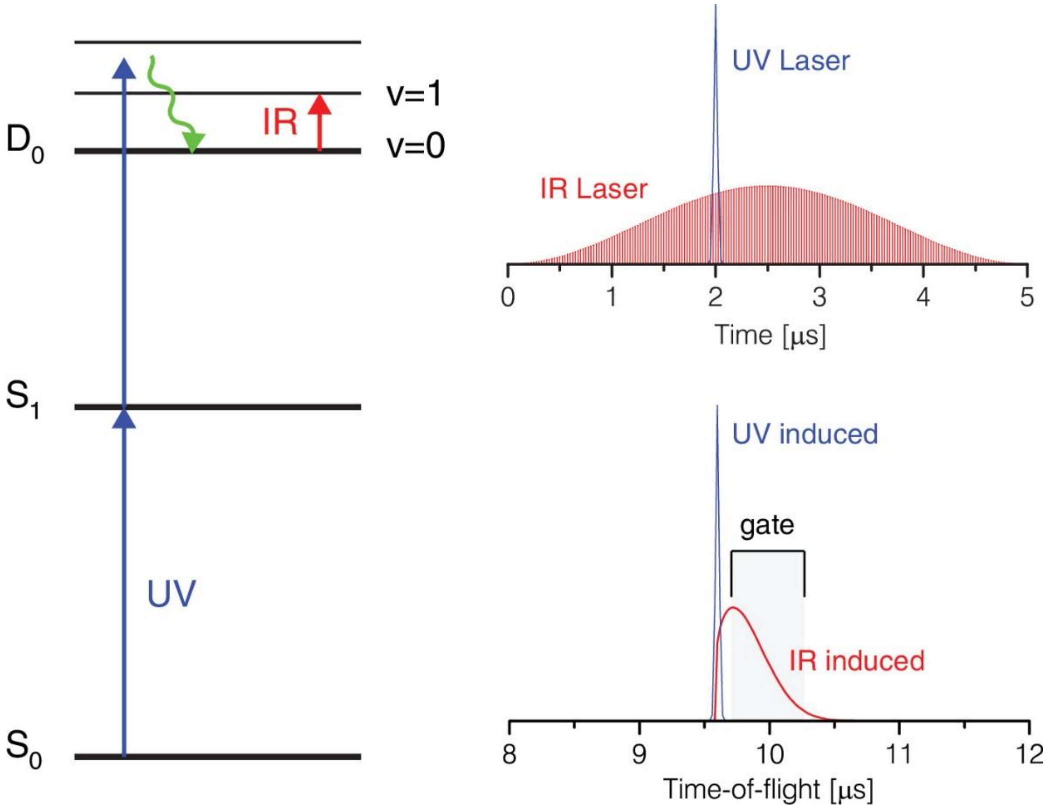
IR Spectroscopy of Molecular Ions by Nonthermal Ion Ejection from Helium Nanodroplets

Szymon Smolarek,[†] Nils B. Brauer,[‡] Wybren J. Buma,[†] and Marcel Drabbels*,[‡]

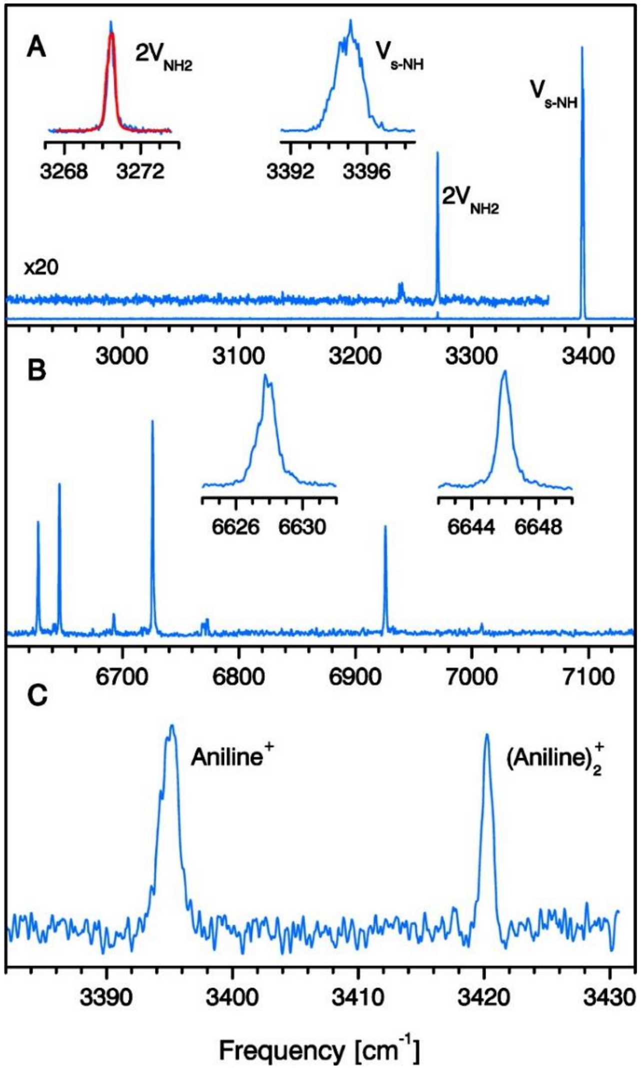
University of Amsterdam, P.O. Box 94157, 1090 GD Amsterdam, The Netherlands, and Laboratoire de Chimie Physique Moléculaire, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Received April 23, 2010; E-mail: marcel.drabbels@epfl.ch

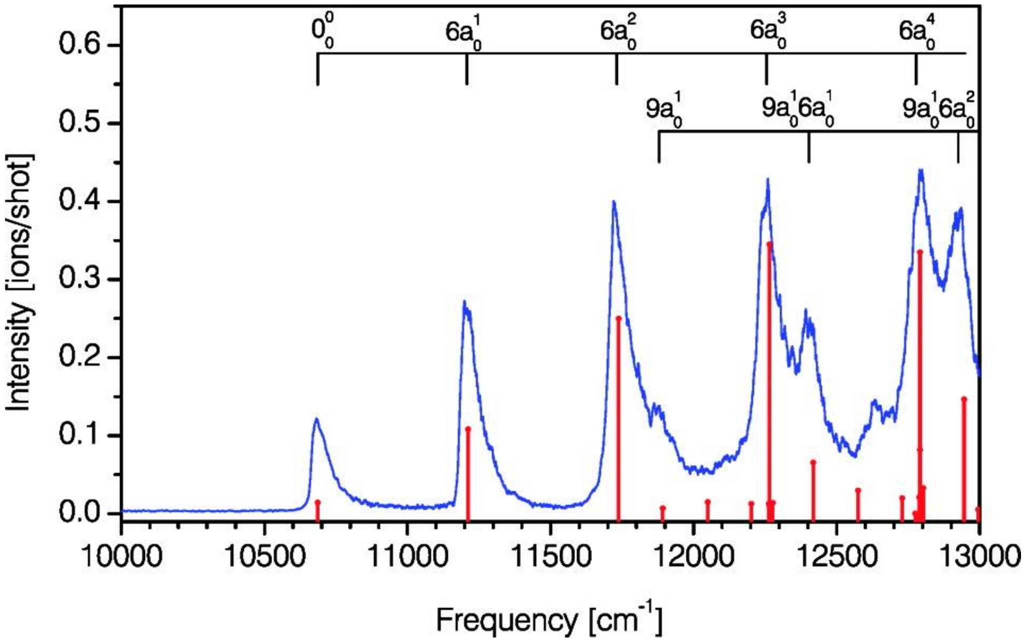
Abstract: Infrared spectroscopy provides a means to determine the intrinsic geometrical structures of molecules. Here we present a novel spectroscopic method that uses superfluid helium nanodroplets to record IR spectra of cold molecular ions, in this particular case aniline cations. The method is based on the detection of ions that are ejected from the helium droplets following vibrational excitation of these ions. We find that spectra can be recorded with a high sensitivity and that they exhibit only a small matrix shift. The widths of the individual transitions depend on the excited vibrational level and are thought to be related to the interaction of the ion with the surrounding helium solvent shells.



Energy level diagram indicating the resonant ionization scheme used to record IR spectra of ions (left). Timing diagram indicating temporal structure and timing of the ionization (UV) and excitation (IR) laser pulses (upper right). Schematic time-of-flight spectrum indicating the contributions of bare ions produced by the UV ionization of neutral molecules and those resulting from the IR excitation of ions in helium droplets.



Infrared spectra of aniline ions in helium droplets..



Excitation spectrum corresponding to the $\tilde{A}\ ^2A_2 \leftarrow \tilde{X}\ ^2B_1$ electronic transition of aniline cations in helium nanodroplets.

Brauer et al., *J. Phys. Chem. Lett*. **2**, 1563 (2011)

Complication: needs an accessible REMPI transition to generate the ions

nature COMMUNICATIONS

Corrected: Publisher correction

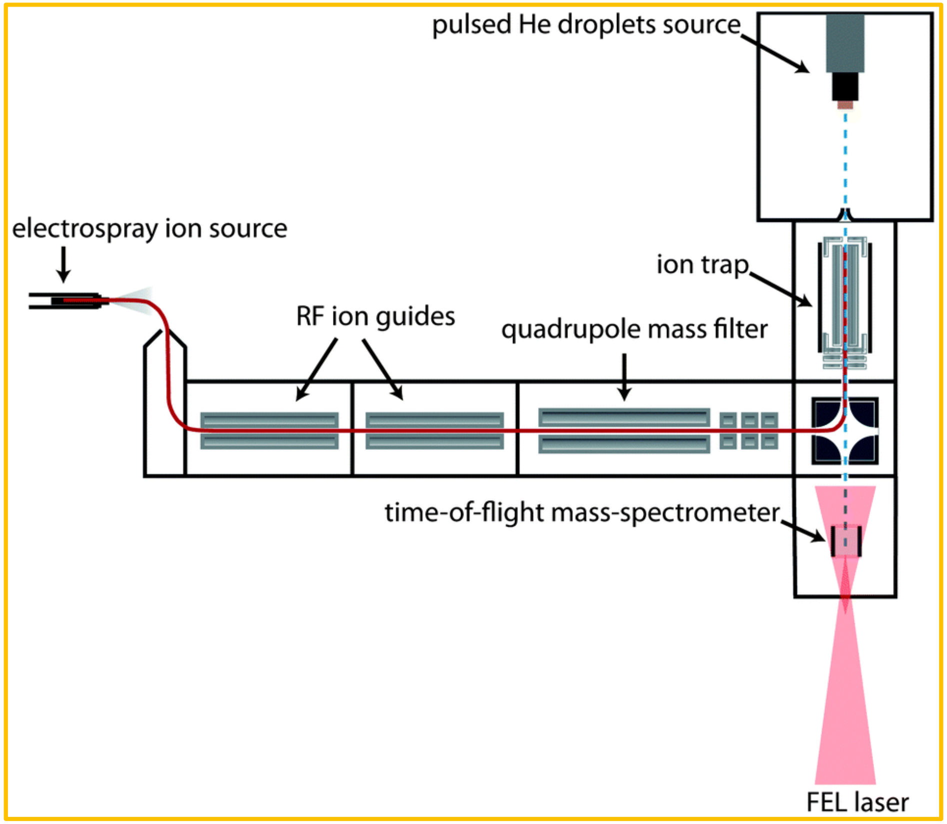
ARTICLE

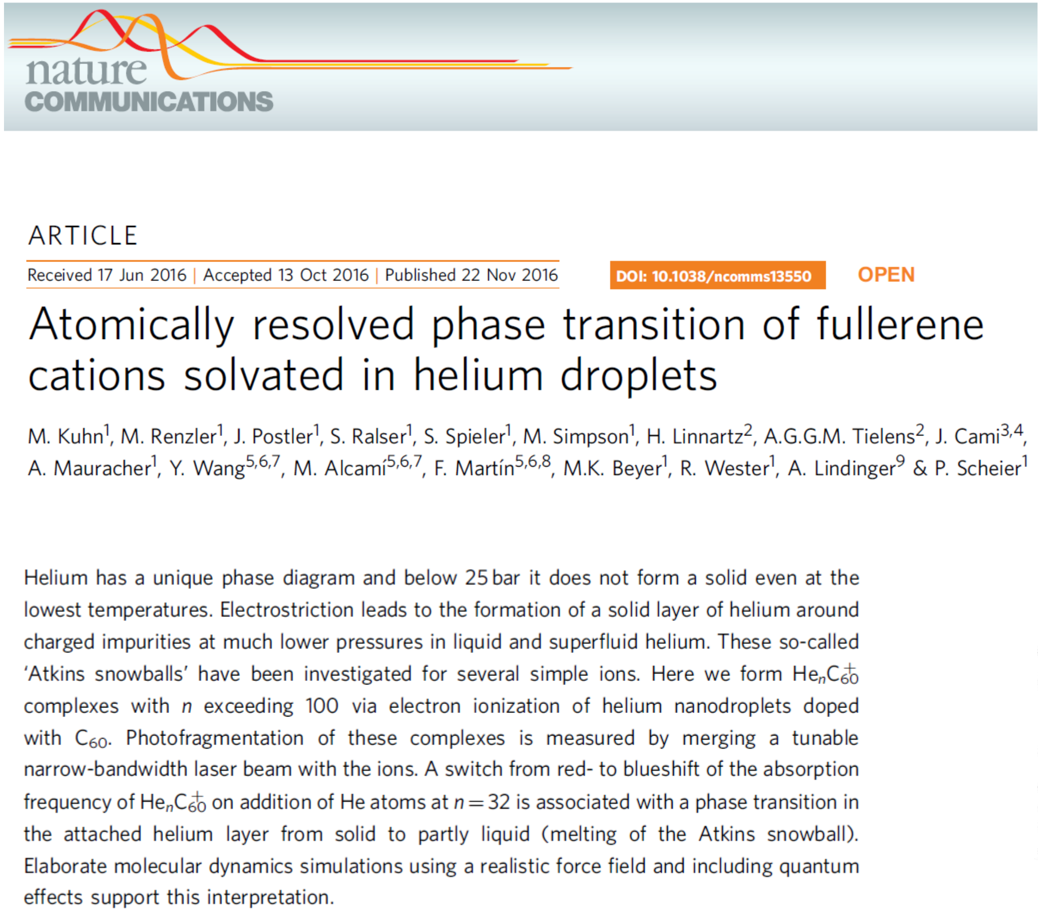
DOI: 10.1038/s41467-018-06764-3 OPEN

Unravelling the structure of glycosyl cations via cold-ion infrared spectroscopy

Eike Mucha[1,2], Mateusz Marianski[1,4], Fei-Fei Xu[3], Daniel A. Thomas[1], Gerard Meijer[1], Gert von Helden[1], Peter H. Seeberger[2,3] & Kevin Pagel[1,2]

Glycosyl cations are the key intermediates during the glycosylation reaction that covalently links building blocks during the synthetic assembly of carbohydrates. The exact structure of these ions remained elusive due to their transient and short-lived nature. Structural insights into the intermediate would improve our understanding of the reaction mechanism of glycosidic bond formation. Here, we report an in-depth structural analysis of glycosyl cations using a combination of cold-ion infrared spectroscopy and first-principles theory. Participating C2 protective groups form indeed a covalent bond with the anomeric carbon that leads to C1-bridged acetoxonium-type structures. The resulting bicyclic structure strongly distorts the ring, which leads to a unique conformation for each individual monosaccharide. This gain in mechanistic understanding fundamentally impacts glycosynthesis and will allow to tailor building blocks and reaction conditions in the future.





nature COMMUNICATIONS

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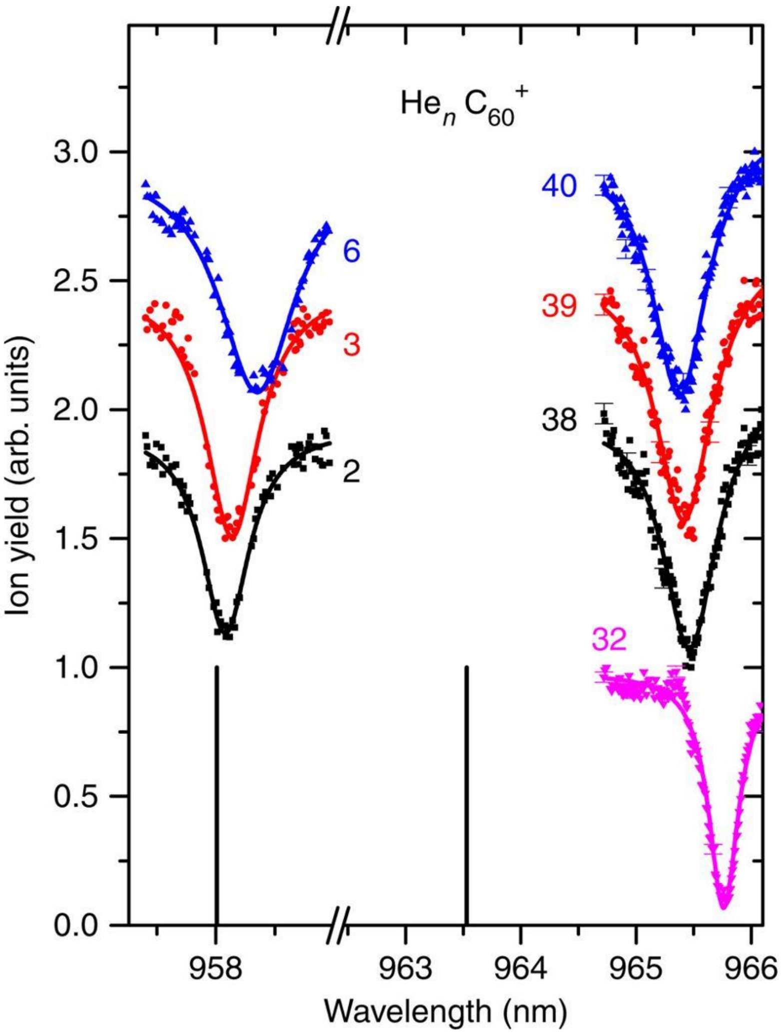
Received 17 Jun 2016 | Accepted 13 Oct 2016 | Published 22 Nov 2016 DOI: 10.1038/ncomms13550 OPEN

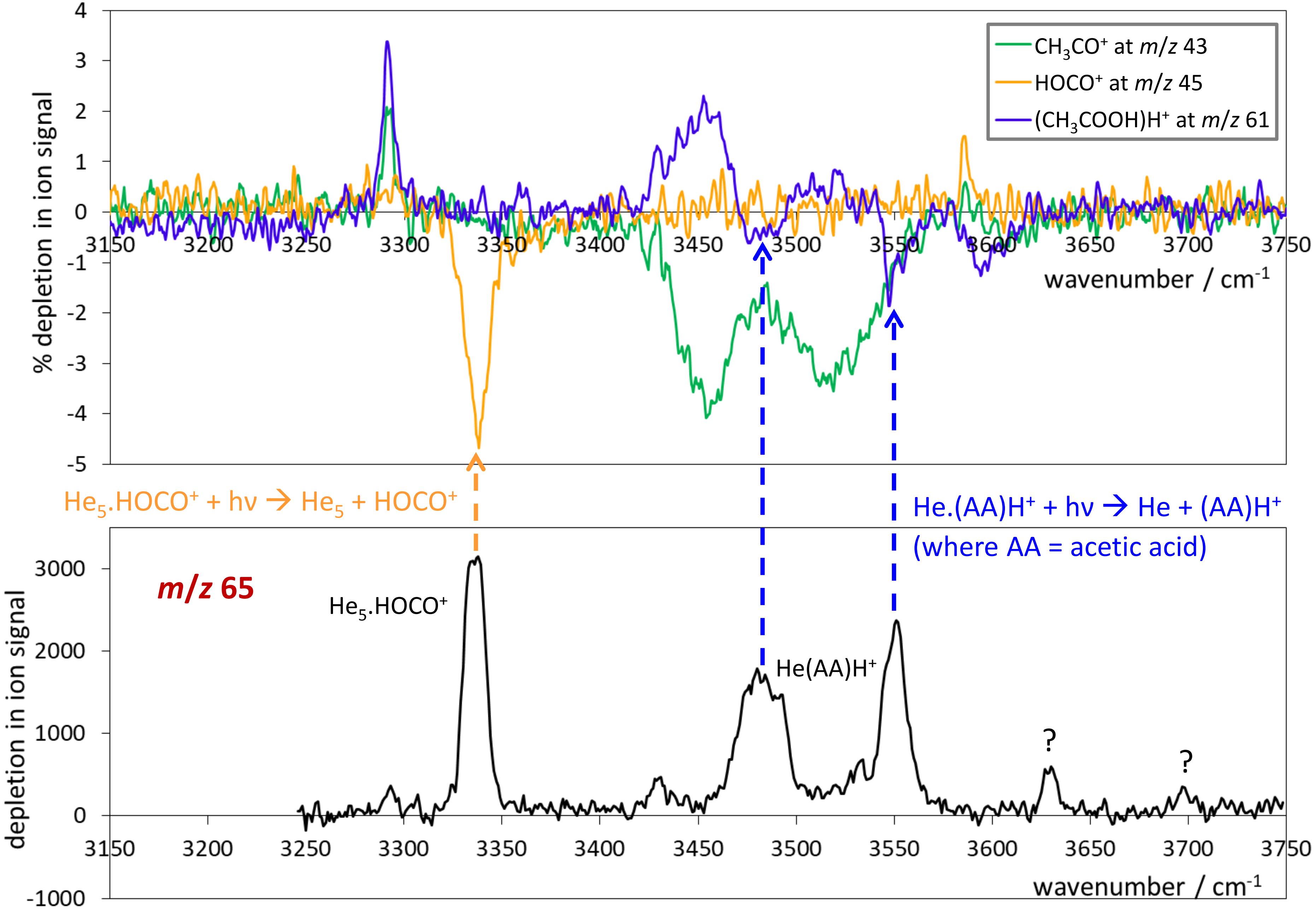
Atomically resolved phase transition of fullerene cations solvated in helium droplets

M. Kuhn[1], M. Renzler[1], J. Postler[1], S. Ralser[1], S. Spieler[1], M. Simpson[1], H. Linnartz[2], A.G.G.M. Tielens[2], J. Cami[3,4], A. Mauracher[1], Y. Wang[5,6,7], M. Alcamí[5,6,7], F. Martín[5,6,8], M.K. Beyer[1], R. Wester[1], A. Lindinger[9] & P. Scheier[1]

Helium has a unique phase diagram and below 25 bar it does not form a solid even at the lowest temperatures. Electrostriction leads to the formation of a solid layer of helium around charged impurities at much lower pressures in liquid and superfluid helium. These so-called 'Atkins snowballs' have been investigated for several simple ions. Here we form $He_nC_{60}^+$ complexes with n exceeding 100 via electron ionization of helium nanodroplets doped with C_{60}. Photofragmentation of these complexes is measured by merging a tunable narrow-bandwidth laser beam with the ions. A switch from red- to blueshift of the absorption frequency of $He_nC_{60}^+$ on addition of He atoms at $n = 32$ is associated with a phase transition in the attached helium layer from solid to partly liquid (melting of the Atkins snowball). Elaborate molecular dynamics simulations using a realistic force field and including quantum effects support this interpretation.



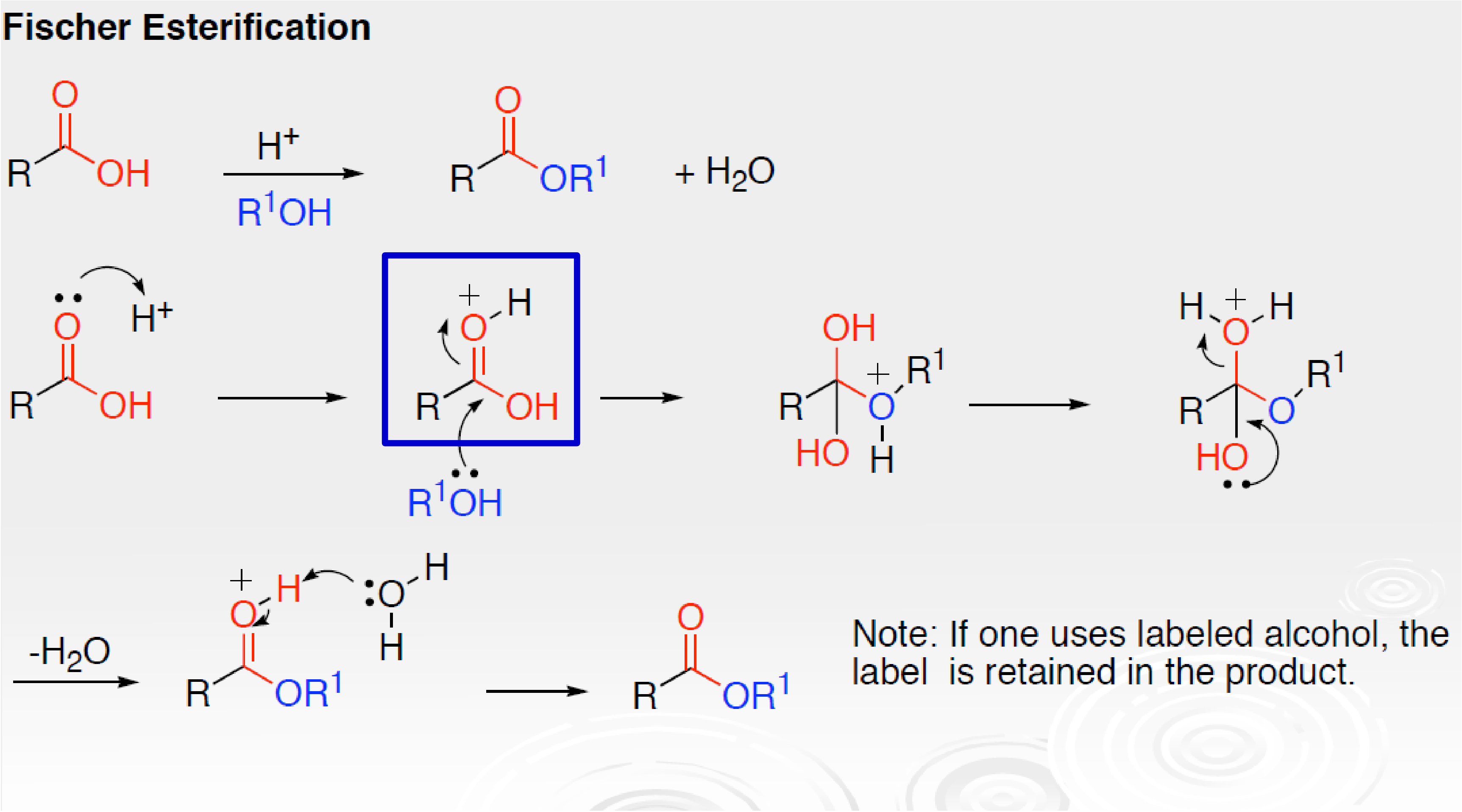
Protonated acetic acid



$He_5.HOCO^+ + h\nu \rightarrow He_5 + HOCO^+$

$He.(AA)H^+ + h\nu \rightarrow He + (AA)H^+$

(where AA = acetic acid)

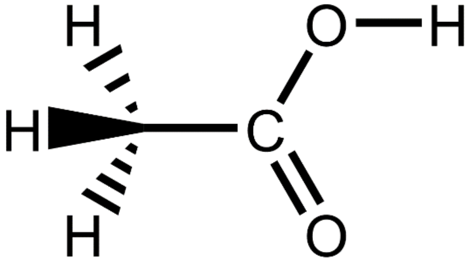


Fischer Esterification

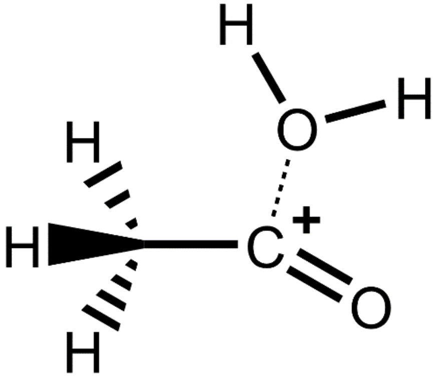
Note: If one uses labeled alcohol, the label is retained in the product.

Assumption that protonation always occurs at the carbonyl oxygen atom

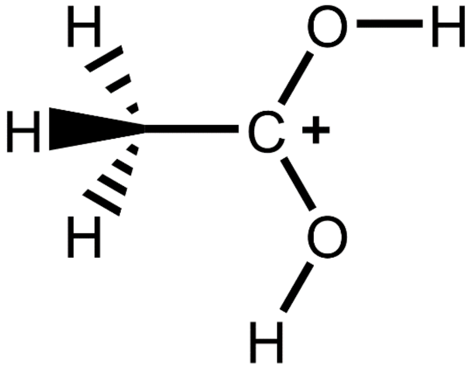
Protonated acetic acid – suggested structures



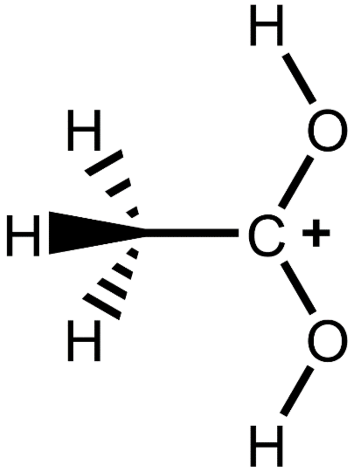
AA



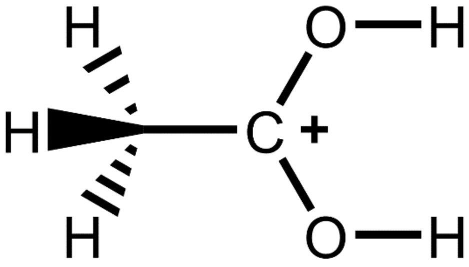
prot-OH



E,*Z*

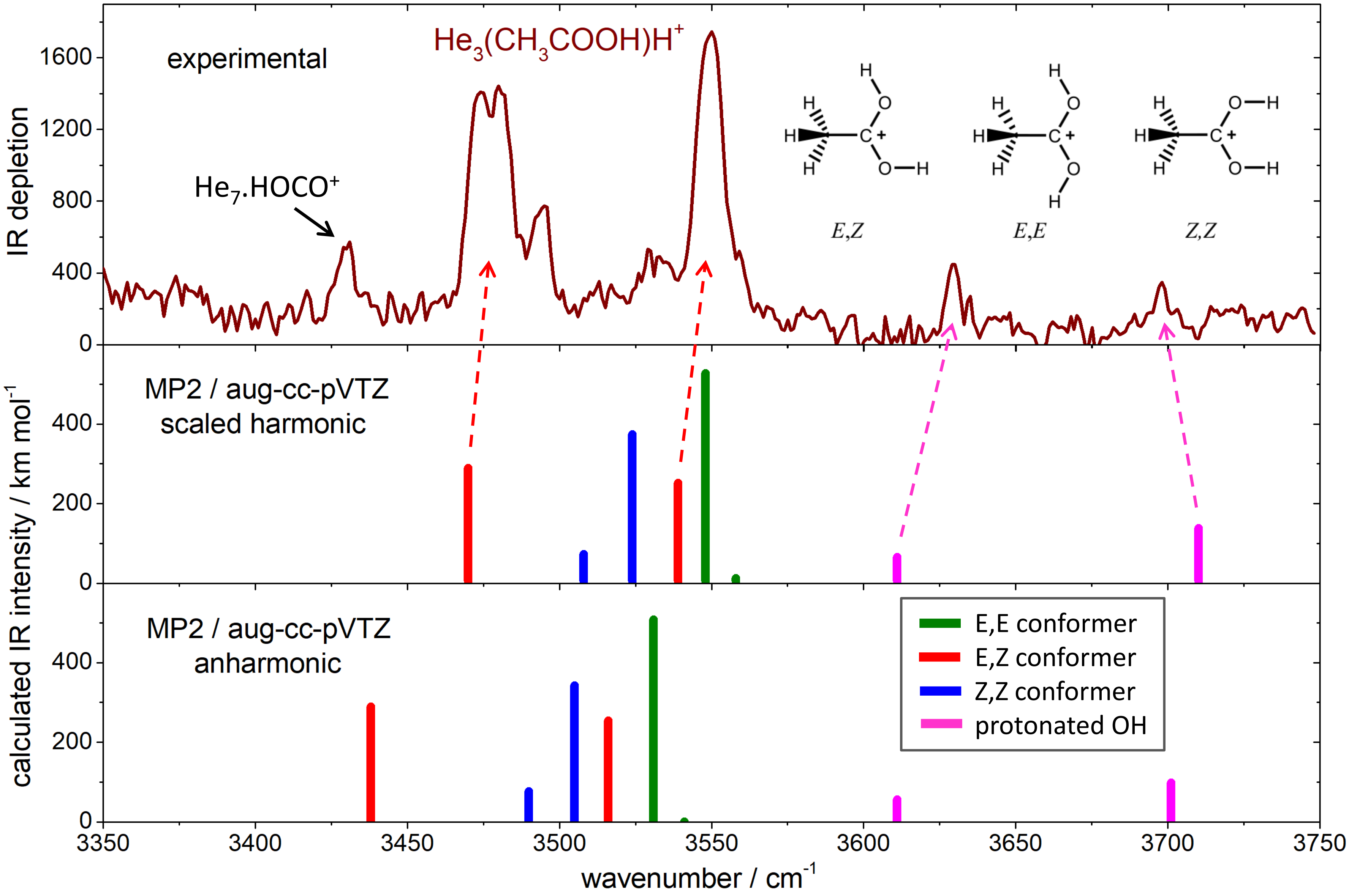


E,*E*



Z,*Z*

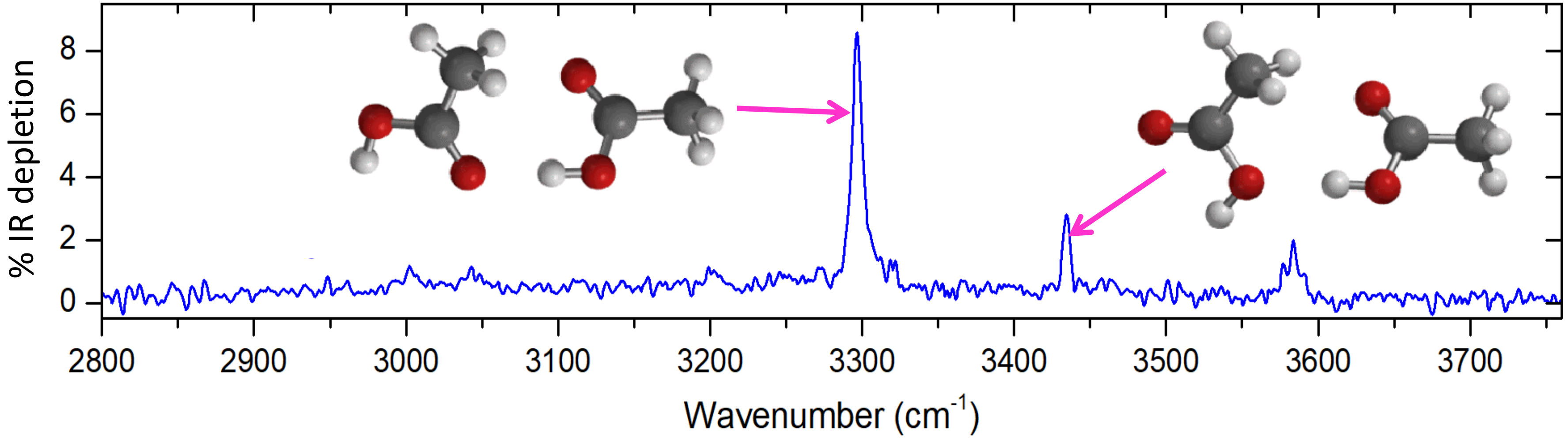
IR spectrum of protonated acetic acid



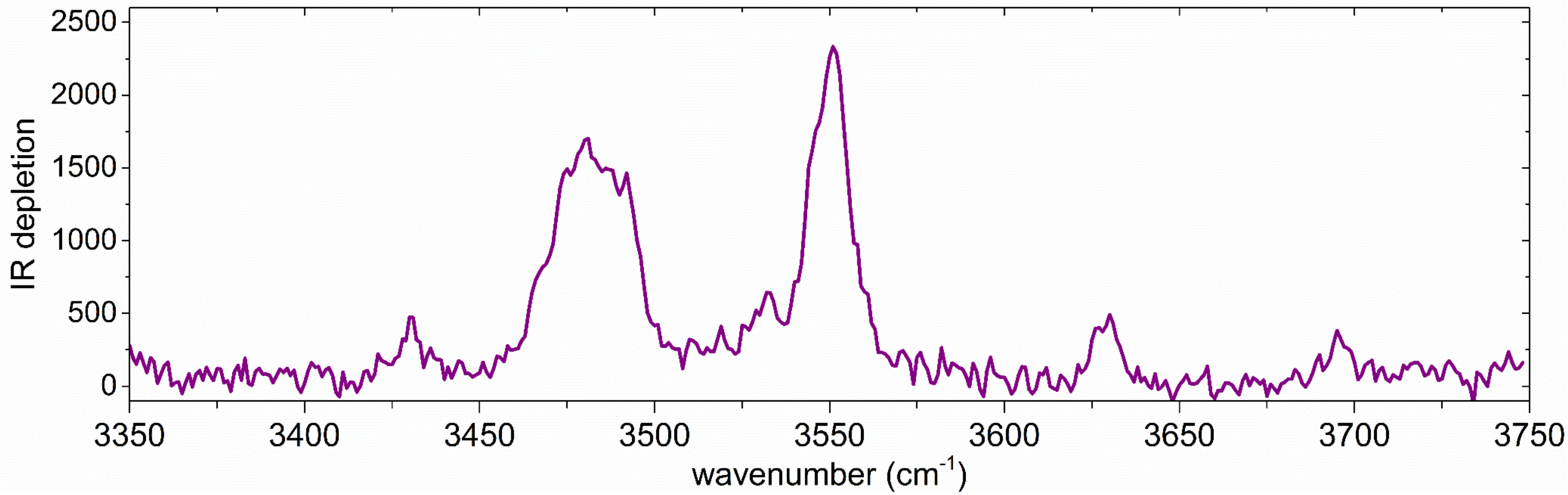
Davies et al. *J. Phys. Chem. Lett.* **10**, 2108-2112 (2019)

IR spectra for neutral precursors AND ion fragments

IR absorption by neutral dopant (acetic acid dimers)



IR absorption by ion fragment, He.(CH_3COOH)H^+



Spectra for neutral precursors AND ion fragments

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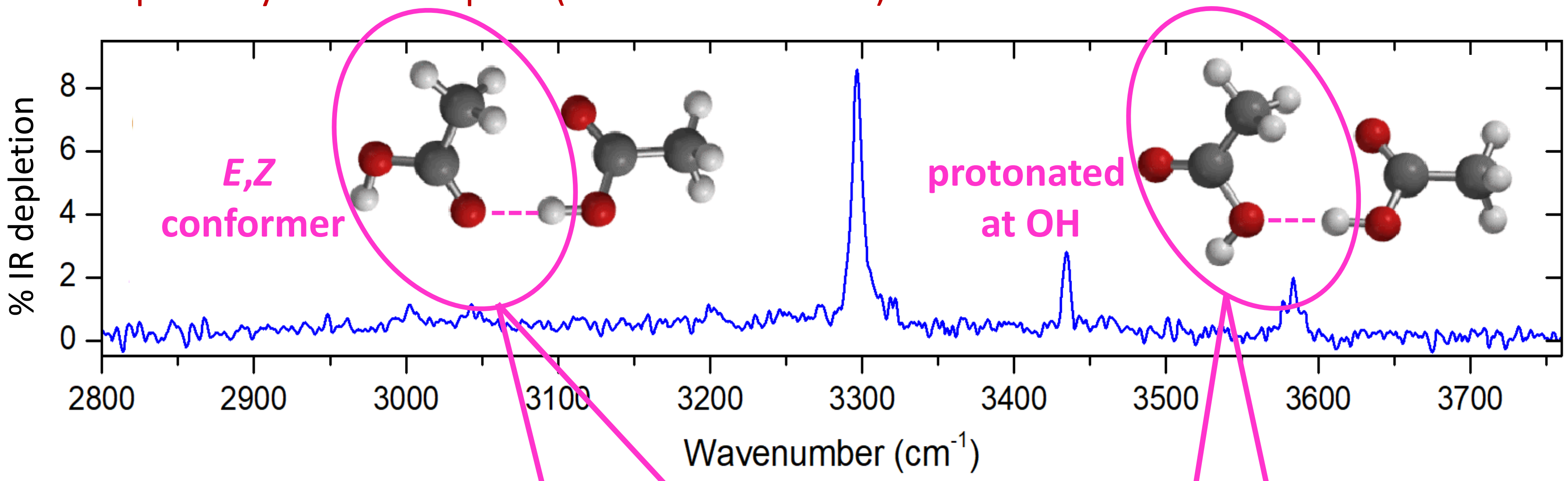

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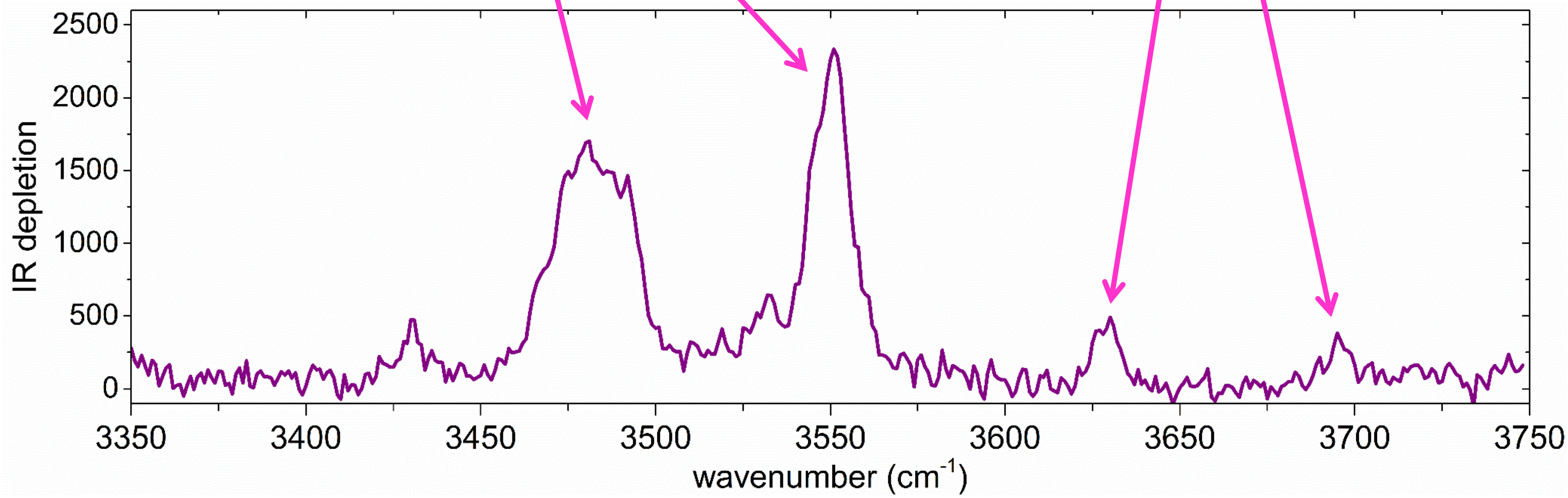


Quantum Solvation of Carbonyl Sulfide with Helium Atoms

Jian Tang,[1] Yunjie Xu,[2] A. R. W. McKellar,[1]* Wolfgang Jäger[2]*

High-resolution infrared and microwave spectra of He_N–carbonyl sulfide (He_N-OCS) clusters with N ranging from 2 to 8 have been detected and unambiguously assigned. The spectra show the formation of a solvation layer beginning with an equatorial "donut" of five helium atoms around the OCS molecule. The cluster moment of inertia increases as a function of N and overshoots the liquid droplet limit for $N > 5$, implying that even atoms in the first solvation shell are decoupled from the OCS rotation in helium nanodroplets. To the extent that this is due to superfluidity, the results directly explore the microscopic evolution of a phenomenon that is formally macroscopic in nature.

Table 1. Experimental vibrational frequencies and rotational parameters for ^4He_N-$^{16}O^{12}C^{32}S$ clusters. For $N = 1$ and 2, which are asymmetric rotors, B refers to $(B + C)/2$. The least significant digits given indicate the uncertainties of the parameters.

Species	Vibrational frequency (cm^{-1})	B (MHz)	D_J (MHz)
OCS (*20*)	2062.2008	6081.5	0.001
He-OCS (*12, 13*)	2062.3125	4582.8	0.94
He_2-OCS	2062.4263	3782.8	5
He_3-OCS	2062.5413	3104.6	5.11
He_4-OCS	2062.6539	2591.9	0.881
He_5-OCS	2062.7401	2225.2	0.234
He_6-OCS	2062.6753	1910.5	2.60
He_7-OCS	2062.6327	1683.0	1.29
He_8-OCS	2062.5676	1447.7	2.00
He nanodroplet-OCS (*4*)	2061.644	2194.5	11.4

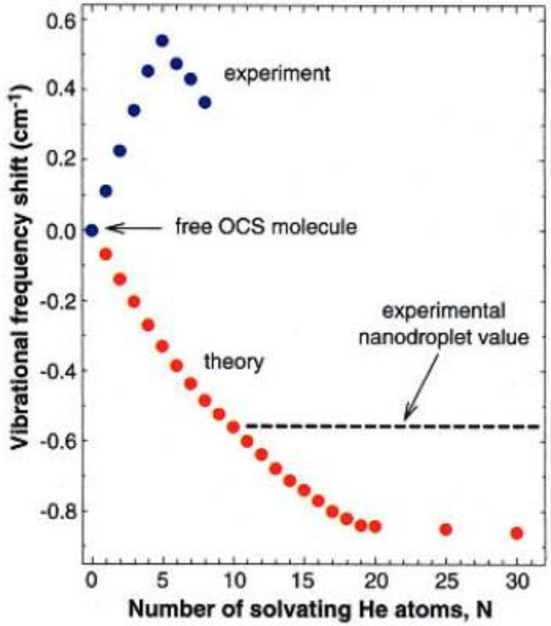


Fig. 2. Observed (blue circles, present work) and calculated [red circles (*9*)] vibrational frequency shifts for He_N-OCS clusters with N in the range from 0 to 30. The dashed horizontal line indicates the observed value for He nanodroplets where $N \approx 10^4$ (*4*).

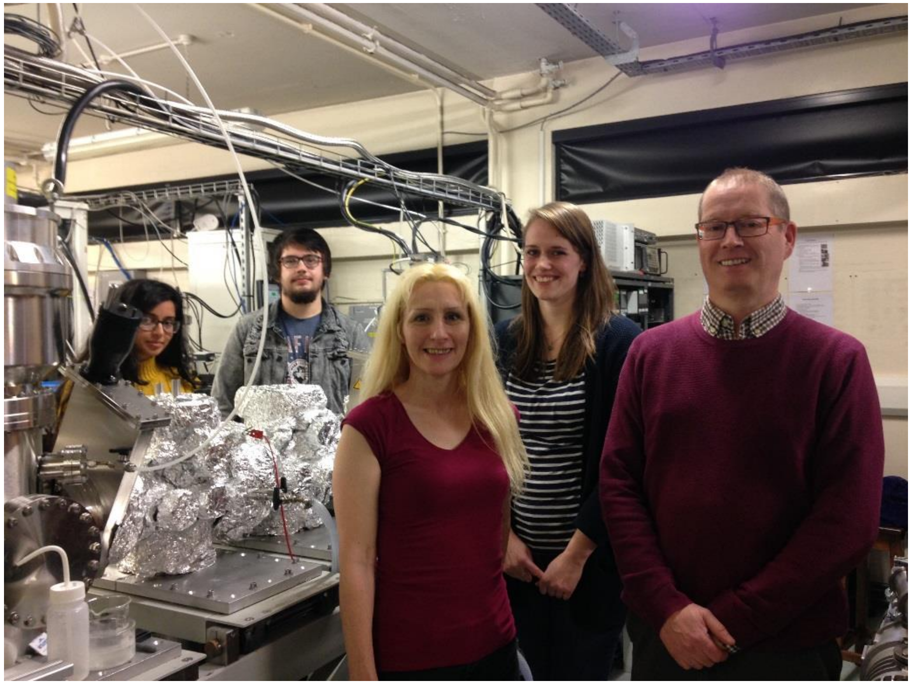
Take-home messages

❑ We can do ion spectroscopy using the same experimental configuration that we use for recording IR spectra of neutral species – does not require a more complex exptl setup

❑ We can use this approach to link the species we see as neutrals to those formed as ions, e.g. the structure of the neutral may dictate the structure of the ion

❑ We can use helium messenger spectroscopy to see how vibrational spectra are affected by the number of helium atoms attached to the ions

Acknowledgements



Martin Mugglestone, Julia Davies, Katharina Meyer

Shengfu Yang

The University of Nottingham

Nick Besley

Magnus Hanson-Heine

EPSRC

Engineering and Physical Sciences Research Council

The Leverhulme Trust