Ultrafast charge redistribution in small iodine containing molecules

M Hollstein, K Mertens, S Klumpp, N Gerken, S Palutke, I Baev, G Brenner, S Dziarzhytski, M Meyer, W Wurth, D Pfannkuche and M Martins

1 Department of Physics, University of Hamburg, Jungiusstraede 9, D-20355 Hamburg, Germany
2 Department of Physics, University of Hamburg, Luruper Chaussee 149, D-22761 Hamburg, Germany
3 DESY, Notkestrafte 85, D-22607 Hamburg, Germany
4 European XFEL GmbH, Holzkoppel 4, D-22669 Schenefeld, Germany
5 These authors contributed equally.
6 Author to whom any correspondence should be addressed.

E-mail: Maximilian.Hollstein@uni-hamburg.de and Karolin.Mertens@desy.de

Keywords: photoionization, free electron laser, xuv pump-xuv probe, charge rearrangement

Abstract
We present studies on intra-molecular charge redistribution in iodine containing molecules upon iodine-4d photoionization. For this, we employed an XUV-pump-XUV-probe scheme based on time-delayed femtosecond pulses delivered by the free-electron laser at DESY in Hamburg (FLASH). The experimental results show delay dependent and molecule-specific iodine charge state distributions that arise upon multiple iodine-4d photoionization. Using the example of CH3I and CH2I2, we compare the delay-dependent yields of I3- and I2- ions. We model the involved processes using advanced \textit{ab initio} electronic structure calculations which include electron correlations combined with a classical model of the nuclear motion. The qualitative agreement of our model with the experimental results allows us to relate the observed, strongly molecule-specific efficiencies of the intra-molecular charge rearrangement not only to molecule-specific fragmentation timescales but also to molecule-specific electronic structure and molecular environment.

1. Introduction

Charge rearrangement between atomic centers is vital for the formation and breaking of chemical bonds in molecules. It is often triggered by basic processes such as photoabsorption or electron impact. In general, the associated change in the electronic charge distribution triggers nuclear motion which can result in substantial structural changes. This has impact on applications such as imaging techniques [1], the processes involved are central to radiation damage in biological samples and they may trigger chemical reactions [2]. Due to its element-specificity, in particular core excitation is of special interest since it may give rise to site-specific fragmentation [3], which might be used, for instance, to selectively break molecular bonds [4].

The vacancies, that emerge during core excitation, inevitably decay radiatively or electronically [5]. They are thereby refilled by more weakly bound electrons. This refilling is accompanied by the emission of a photon or an Auger electron, which carries away the excess energy. In contrast to the initial core vacancies, which are usually strongly localized at the nuclei of a specific element, the emerging valence vacancies can be distributed among multiple atomic sites. With respect to the decay of core vacancies in isolated atoms, the decay in molecules can therefore be associated with a transfer of positive charge from photoionized atomic sites to their molecular environment. In experiments, this process has been observed to follow inner-shell photoionization of small molecules containing iodine or selenium [6, 6–10]. In the context of fragmenting molecules, the associated charge spreading is well estimated by the classical over-the-barrier model [11–14]. The occurrence of the process has been demonstrated for distances between molecular fragments up to 20 Å [14]. So far, charge rearrangement in fragmenting molecules has been modeled using the classical over-the-barrier model in the sequential single photon intensity regime. In the high intensity, multiphoton ionization regime the XMOLecule [15] approach is used which is based on a classical model of the fragmentation dynamics that is fed with atom and atomic ion
parameters obtained from the Hartree–Fock–Slater model of the individual atoms and atomic ions involved. In this work, we focus on the low-intensity regime and significantly extend the considerations based on the purely classical over-the-barrier model by treating the charge rearrangement within the molecule fully quantum mechanically using advanced electronic structure calculations that include electron correlations.

In this study, we report that the efficiency of charge rearrangement is not only determined by the fragmentation dynamics of the respective molecule but it is also strongly determined by the respective electronic structure.

For this purpose, we consider the iodine charge distributions that arise after XUV photoionization of CH$_3$I and CH$_2$I$_2$ molecules. These two methane derivatives serve as model systems to exemplify the effect. To stimulate intra-molecular charge rearrangement in these molecules, we used femtosecond pulses with a central photon energy in the vicinity of the iodine-4d giant resonance at 82.7 eV. At this photon energy, the iodine-4d photoionization cross section dominates the total cross section [16] and it exhibits a roughly constant value for the different initial charge states I$^{q+}$ ($q = 0$–2) [17]. This procedure allows us to selectively remove iodine-4d electrons from the molecules. After the decay of these photo-induced vacancies, which occur predominantly via Auger electron emission [18], the molecules are doubly charged and potentially unstable so that they can subsequently undergo fragmentation. In this situation, nuclear motion may cause the isolation of iodine fragments. Intra-molecular charge rearrangement is sensitive to this isolation. We can follow the separation of the iodine containing fragments by using the XUV-pump XUV-probe scheme. By controlling the delay time between the two XUV pulses we are able to put a timescale on the separation of the molecular fragments. The charge state distribution is changing over time, as charges can not be rearranged across isolated fragments. The final charge state distribution will be sensitive to the different triggered fragmentation pathways, so that the change in this distribution allows the reconstruction of fragmenting pathways.

To demonstrate the strong molecule specificity of these processes and the associated overall electron transfer, we used the following experimental scheme (see also figure 1): the first pulse is employed to photoionize one iodine atom in its respective molecular environment. This first interaction of the molecule with the XUV pulse and the subsequent ultra-fast electronic relaxation of the photo-induced iodine-4d vacancies occur in a situation where the nuclei are in the respective molecule’s ground state geometry. This pump pulse triggers nuclear motion, as it removes electrons from the system, and the molecule starts to dissociate because of Coulomb repulsion. The second and time-delayed pulse is then used to photoionize the iodine atom again. The larger the delay between the two pulses the more time elapses between the two photoionization events during which the fragmentation and isolation of iodine fragments takes place. To determine the charge state distributions that emerge from this fragmentation as a function of the time between the two XUV pulses we used ion-time-of-flight spectroscopy. This experimental scheme allows us to probe inter-atomic charge rearrangement at various stages of the fragmentation following the first interaction of the molecules with the XUV pulses—ranging from essentially intact molecules for vanishing pump-probe time delays ($\Delta t \to 0$) to fragmented ones for large time delays ($\Delta t \to \infty$).

2. Experimental details

The experiment was realized at the PG2 beamline [19–21] at the free-electron laser at DESY in Hamburg (FLASH) [22–24]. The time resolved XUV-pump XUV-probe studies have been performed at 82.7 eV photon energy using the split-and-delay unit (SDU) [25] of the PG2 beamline. It can split a XUV pulse into two and induces a jitter-free adjustable delay up to 5.1 ps between the splitted parts of the beam. The FEL pulse duration
was in the range of 40 fs full width half maximum (FWHM) for both molecules, which has been estimated by measuring the electron bunch length by the LOLA setup [26]. FLASH was operated in the multi-bunch mode generating 50 electron bunches with a bunch separation of 10 μs and a bunch train repetition rate of 10 Hz. This mode allows us to collect a sufficient number of single shot spectra at each pump-probe time delay within one beamtime campaign. The pulse energies, measured by the FLASH gas monitor detectors (GMD) [27], and the single shot ion spectra have been recorded on a shot-to-shot basis using a fast transient recorder (mTCA ADQ412-4G) and the FLASH fast data acquisition system. This guarantees a perfect synchronization of all measured properties and it allows a post-measurement sorting of the single-shot spectra. The created charged fragments of the gas phase molecules were detected by a Wiley–McLaren-type [28] ion time–of–flight spectrometer, which was mounted on a 90° angle to photon beam and gas needle, respectively. Further description of the setup can be found in [7]. A single count discrimination scheme was applied to the ion time–of-flight signal. Each single shot spectrum was sorted according to its GMD and SDU delay value into bins of finite size in terms of pulse energy and time delay. By summing over all single shot spectra of one bin, we obtained a mass–to–charge spectrum for each bin. The photon intensity is fluctuating due to the SASE (self–amplified spontaneous emission) process. By sorting the data by photon intensity and taking only data with low pulse intensity, we make sure to have single photon absorption within the pump and probe pulse, respectively. With a focused FEL beam of approximately 100 μm in diameter the intensity of a single pulse is approximately 10^{12} W cm^{-2}. By comparing this level of irradiance with the ionization scheme of xenon [29], we can relate that our spectra are in the regime of single photon absorption per molecule and pulse. No multiphoton ionization steps occur at these intensities and higher charge states can only be reached via sequential single-photon absorption.

3. Results and discussion

3.1. Ion time–of–flight spectra

Examples of ion time–of–flight spectra of CH3I and CH2I2 after photoionization at 82.7 eV photon energy are shown in figure 2. The most prominent peaks are labeled for both molecules. The presented spectra have been measured at the pump–probe delay of 400 fs and they show the ionized iodine fragments up to triply charged iodine and the carbon fragments. The CH2I2 peak of CH2I2 exhibits also features from atomic N+ of the residual gas, which has the same mass–over–charge ratio. The peak shapes of CH2I2 show a broadening for the charged iodine ions, as already shown in [7] for the multiphoton excitation for these two molecules. This broadening is due to the strong Coulomb repulsion between the two iodine ions and the resulting high kinetic energy release (KER) for the fragments. Correspondingly, for CH3I the broadening of the peaks is weaker because of the lower repulsion of the iodine atom.

The highest iodine charge state is I^{3+} and it is also the only peak showing a significant time–dependency. By integrating the area of the I^{3+} peak in the time–of–flight spectrum for each time delay bin, we can follow the increasing or decreasing of a signal over time. As I^{3+} charge state is the first charge state which can only be reached by two sequential photoionizations and their subsequent Auger decay, we will focus on this charge state distribution.

3.2. Time–dependency of the iodine 3+ charge state channel

For both molecules CH3I and CH2I2, the yield of the I^{3+} charge state shows a strong pump–probe time delay dependence between −400 and +400 fs as figure 3 shows.

Most notably, for both molecules the I^{3+} signals are strongly reduced for zero pump–probe delay with respect to large delay values. Since the I^{3+} charge state is the highest charge state observed in the experiment, the reduction of this charge state yield can be related to a shift of the charge state distribution towards lower iodine charge states. Although the lower charged fragments show an increasing charge state yield over time, their peaks are strongly dominated by direct photoionization and the subsequent decay processes which obscure the more delicate time dependent signal. However, the existence of the I^{3+} on the other hand indicates that two photons have been absorbed at the same atomic iodine site. The change in time of this signal shows that the two photons origin from pump and probe pulse which are delayed in time.

Our experimental findings can be concentrated on two main results:

1. The depletion of the normalized 1+ yield for zero pump–probe delay time is twice as strong for CH2I2 (-0.91 ± 0.1) as for CH3I (-0.47 ± 0.1). This indicates that even for perfectly overlapping pulses, less positive charge is transferred in CH3I than in CH2I2.

2. The characteristic timescales associated with the reduction of the I^{3+} yield (120(15) fs FWHM for CH3I and 292 (29) fs FWHM for CH2I2) are significantly different. This indicates that the isolation of iodine fragments associated with fragmentation occurs for CH3I more quickly than for CH2I2.
Lower iodine charge states indicate that positive charge is distributed more among the constituents of the molecule. Hence, the data indicate that for temporally well separated pulses, charge is not as efficiently redistributed as for simultaneously arriving ones. The key outcome of the experiment represents the fact that the quantitative manifestation of this behavior is strongly molecule specific.

Figure 4 shows a simple model for the time dependent production pathways of the $I^{3+}$ charge state for both molecules. For CH$_3$I$_2$, we can focus on the two main pathways: the pump pulse ionizes one iodine atom (step I) and the emission of the photoelectron and the subsequent Auger electron produces I$_2^{+}$ at one atomic iodine site of the molecule. Usually, charge transfer processes are happening faster than the dissociation process. Here, charges are rearranged between the two iodine atoms before the dissociation takes place (step II). For small or
zero delay between pump and probe, the probe pulse ionizes again one (after one charge transfer process now singly charged) iodine atom in the molecule. After the absorption of the second photon the emission of the photoelectron and the Auger electron produces now \( I_3^+ \). For the case of zero time delay the molecule will be still intact, again charges can be rearranged over the molecule. This leads to two doubly charged iodine atoms (step III) which then will undergo fragmentation, e.g. because of Coulomb repulsion. For increasing delay values between pump and probe pulse, the nuclei of the already ionized molecule (step II) will start to move away from each other. The probability increases with higher delay that the molecule is already fragmented and the probe pulse then ionizes isolated iodine atoms (step IV). For these isolated fragments no charges can be rearranged.

The model in figure 4(a) leads to a decrease in \( I_3^+ \) charge state yield within the time frame where charges can be rearranged over the molecule and to an increase in this charge state yield for longer delays.

The same two pathways can be observed for CH\(_3\)I. The range of a charge rearrangement process depends on the mass and charge and the distance of the involved atoms within the molecule and can be described by the classical over-the-barrier model \([11, 12]\). As in this case charges can only be rearranged between the iodine and the CH\(_3\) fragment, the nuclei are faster separated and the \( I_3^+ \) yield of CH\(_3\)I exhibits a shorter timescale on which charges are rearranged over the molecule.

To explain the differences in the depletion of the \( I_3^+ \) yield between the two molecules we need to take additional pathways into account which create more \( I_3^+ \) yield at zero delay values for CH\(_3\)I compared to CH\(_2\)I\(_2\). These additional pathways include only one single charge transfer either after the pump or the probe pulse. This adds step III\(_a\), where after the probe pulse no charges are rearranged and the molecule then fragments with a triply charged iodine atom. Another pathway would be that the first charge transfer does not take place (step V). The probe pulse ionizes \( I_2^+ \) and creates \( I_4^+ \). As long as the nuclei are not moving out of the range for the charge transfer, charges are rearranged leading again to a higher \( I_3^+ \) yield at zero delay values. As we do not see any \( I_4^+ \) in our spectra we can assume that either one of these charge transfers will happen and we therefore do not include that pathway in figure 4.

To explain the differences in the processes of both molecules we expand our considerations to theoretical calculations.

### 3.3. Theoretical calculations

In the following, we support this interpretation of the experimental data by theoretical considerations. Concretely, we demonstrate that the features observed in the experimental data (see figure 3) are reproduced by a simple model that is based on two mechanisms:

(A) The probability for the charge transfer associated with the molecular Auger decay is molecule-specific.

(B) The timescales on which the molecules fragment are strongly different.

We estimate the charge transfer probability (A) on the basis of \textit{ab initio} electronic structure calculations. The molecule specific fragmentation timescales (B) are estimated on the basis of classical models. On this basis, we estimate the delay dependent \( I_3^+ \) ion production whereby we are able to reproduce the trends observable in the experimental data.
To estimate the charge transfer probability \( A \), we use \textit{ab initio} electronic structure calculations. For this, we employ the following procedure: first, we determine the iodine partial charges after the decay of photo-induced iodine 4d vacancies in molecules in their ground state geometry. By comparison with the isolated iodine atoms, we deduce from these charges apparent charge transfer probabilities. Concretely, to determine the electronic states that are populated after Auger electron emission associated with the decay of iodine 4d vacancies, we employed the method of population analysis \cite{30}. The determined relative Auger intensities were applied to the dicationic states that we obtained from the configuration-interaction based approach described in \cite{31}. To determine the iodine partial charges \( Q_F \), we employed a Löwdin population analysis \cite{32, 33}:

\[
Q_F = Z - \sum_i \langle F | n_i | F \rangle.
\]

Here, \( \langle F | n_i | F \rangle \) denote the expectation values of number operators associated with Löwdin iodine spin orbitals. \( |F\rangle \) denotes an eigenstate of the dicationic Hamiltonian and \( Z \) is the iodine nuclear charge. Assuming that potential initial electronic coherences in the dication are rapidly suppressed on few-femtosecond timescales due to nuclear motion \cite{34, 35}, we quantify the average charge of the iodine atoms by incoherently averaging the partial charges associated with individual dicationic states weighted by their relative Auger intensity \( p_F \):

\[
Q = \sum_F p_F Q_F.
\]

Figure 5 shows the iodine partial charges for the electronic eigenstates of doubly and quadruply ionized CH\(_3\)I and CH\(_2\)I\(_2\) molecules. After the first photoionization and subsequent Auger decay, the molecule is doubly ionized. For CH\(_2\)I\(_2\), this procedure yields an iodine partial charge of \( Q_{\text{CH}_2\text{I}_2} \approx 1.0|e| \) (figure 5(c)) and for CH\(_3\)I \( Q_{\text{CH}_3\text{I}} \approx 1.4|e| \) (figure 5(d)). Noting that the iodine partial charges of isolated iodine atoms would be 2, these molecular iodine partial charges can be related to an apparent transfer probability of 1.0 for CH\(_2\)I\(_2\) (cp.)
figure 4(a) step II) and 0.6 for CH₃I (cp. figure 4(b) step I). For CH₃I we can motivate the splitting of step I of figure 4(b) into two pathways with different probabilities.

Applied to quadruply ionized molecules, after two photoionizations and their subsequent Auger decays the procedure described above yields for (CH₃I)⁴⁺ an iodine partial charge of 2.65 |e| whereas for (CH₂I₂)⁴⁺, an iodine partial charge of only 1.85 |e| is obtained. This can be related to an apparent transfer probability for two subsequent electron transfers to be 1 for CH₂I₂ (cp. figure 4(a) step III). For CH₃I, it indicates that also the second photoionization is followed by an electron transfer with a probability on the order of 0.6 (cp. figure 4(b) step IV). This again motivates the other pathway in figure 4(b): step IIIₚ with no charge transfer and step IIIₜ with a charge transfer after the second pulse.

We note that in both cases, most positive charge is distributed on the iodine atom (CH₃I) and on the two iodine atoms (CH₂I₂), respectively. Key result of these theoretical considerations represents the finding that the apparent probability for a charge rearrangement in the molecules in their ground state geometry is strongly molecule specific, i.e. the probability for charge rearrangement is significantly lower for CH₃I in comparison to CH₂I₂.

We now turn to aspect (B) concerning the fragmentation dynamics that follow the electronic charge rearrangement associated with the decay of photo-induced iodine 4d vacancies. The isolation of iodine fragments associated with the fragmentation can limit the charge rearrangement in situations in which multiple photons are sequentially absorbed. In the experiment, this concerns specifically the charge redistribution that follows the second photoionization event. To estimate the timescale on which isolation of iodine fragments can occur subsequent to an iodine 4d ionization and the ensuing Auger decay, we can employ classical models. Concretely, we estimate the distance from which on no charge transfer from the iodine fragments to other molecular fragments can occur on the basis of the over-the-barrier model [13, 14]. According to this model, charge can be transferred between two fragments as long as the energy of the most weakly bound valence electron is larger than the potential barrier formed by the core potentials of the two fragments involved. To estimate the timescale on which the critical distances between the iodine atoms and other fragments can be reached, we used a classical Coulomb explosion model consisting of two point charges located at the center of mass of a singly charged iodine ion and its singly charged molecular environment, respectively, interacting via their Coulomb repulsion. The ionization potentials of the iodine atom and its molecular environment, respectively, which are needed as input for the over-the-barrier model, were estimated on the basis of Koopmans’ theorem [36]. On this basis, we find that for CH₃I the iodine can separate from the methyl group already within 40 fs whereas isolation of the iodine atoms in CH₂I₂ can occur only after 180 fs.

When modeling the form of the time-dependent ionization rate in terms of a sum of two Gaussian functions:

\[
\Gamma(t) = \Gamma_{\text{max}} \exp \left( -\frac{(t - \tau)^2}{\tau^2} \right) + \Gamma_{\text{max}} \exp \left( -\frac{(t - \tau - \Delta t)^2}{\tau^2} \right),
\]

where \(\tau \sim 40\) fs is the pulse duration and \(\Delta t\) represents the pump-probe time delay, we can reproduce the key features present in the experimental data (see figure 3). The differences between the model and the experimental data are likely due to the potentially oversimplified fragmentation dynamic model considered. It suggests that more effort has to be made to develop a complete picture of the processes involved including a quantum chemical description of the dissociating molecules. Using the classical model the timescales on which the molecules stay intact are underestimated. The \(I^3\) charge state channel may be also produced by other fragmentation processes ending in this precise charge state channel but which are not connected to the calculated charge transfer processes. These additional channels may contribute to the overall difference between model and experimental data. Regardless, the model reproduces the key features in the experimental data and it visualizes the importance of the charge transfer efficiency in these fragmentation channels.

4. Summary

To conclude, we experimentally demonstrated molecule-specific iodine charge state distributions that arise upon multiple iodine-4d photoionization of CH₂I₂ and CH₃I molecules. We used 40 fs short XUV pulses of...
FLASH of different delay in a pump–probe scheme to create 4d holes with subsequent Auger decay at the iodine atoms. The delay dependent yield of I$^{3+}$ is strongly molecule dependent and allowed us to track down charge transfer mechanisms and fragmentation timescales in both molecules. As the molecules fragment on different timescales, the molecules exhibit different timescales for possible charge transfer. In CH$_3$I most charges are rearranged within a FWHM of 120(15) fs, in CH$_2$I$_2$ with a FWHM of 292(29) fs. These experimental results are in accordance with ab initio electronic structure calculations, which show that the differences in the I$^{3+}$ charge state yield result from molecule specific charge transfer probabilities. Charges are more efficiently distributed between the two iodine atoms in CH$_2$I$_2$ than between the iodine atom and the methyl group CH$_3$I in CH$_3$I. This leads to a higher I$^{3+}$ charge state yield in CH$_3$I for zero pump–probe delay which can be seen in the experimental data.

The experiments indicate that even the dissociation of simple molecules is non-trivial. We show, that charge transfer processes have to be considered specifically for every molecular environment. Using advanced electronic structure calculations including electron correlations, the charge rearrangement within the molecule can be treated fully quantum mechanically. The efficiency of charge rearrangement is not only determined by the fragmentation velocity of the respective molecule but it is also strongly determined by the respective electronic structure.

**Acknowledgments**

The work was funded by the DFG and performed within the framework of SFB925, projects A3, A5 and B2 and MA2561/4-1. SK acknowledges support from the European Cluster of Advanced Laser Light Sources (EUCALL) project, which has received funding from the European Union’s Horizon 2020 research and innovation programme under Grant Agreement No. 654220. The help of the DESY staff operating FLASH in an excellent way is gratefully acknowledged. MH and DP are grateful to Robin Santra for clarifying discussions.

**ORCID iDs**

K Mertens [https://orcid.org/0000-0002-0146-6318](https://orcid.org/0000-0002-0146-6318)

**References**

[1] Neutze R, Wouts R, van der Spoel D, Weckert E and Hайджу J 2000 Nature **406** 752–7
[2] Zewail A H 2000 J. Phys. Chem. A **104** 5660–94
[3] Eberhardt W, Sham T K, Carr R, Krummacher S, Strongin M, Weng S L and Wesner D 1983 Phys. Rev. Lett. **50** 1038–41
[4] Schmelz H C, Reynaud C, Simon M and Nenner I 1994 J. Chem. Phys. **101** 3742–9
[5] Krause M Ornd Oliver J H 1979 J. Phys. Chem. Ref. Data **8** 329–38
[6] Eberhardt W, Sham T K, Carr R, Krummacher S, Strongin M, Weng S L and Wesner D 1983 Phys. Rev. Lett. **50** 1038–41
[7] Nenner I 1986 J. Phys. B: At. Mol. Phys. **19** 2829–36
[8] Eberhardt W, Sham T K, Carr R, Krummacher S, Strongin M, Weng S L and Wesner D 1983 Phys. Rev. Lett. **50** 1038–41
[9] Neutze R, Wouts R, van der Spoel D, Weckert E and Hайджу J 2000 Nature **406** 752–7
[10] Takanashi T et al 2017 Phys. Chem. Chem. Phys. **19** 19707–21
[11] Ryufuku H, Sasaki K and Watanabe T 1980 Phys. Rev. A **21** 745–50
[12] Niehaus A 1986 J. Phys. B: At. Mol. Phys. **19** 2925
[13] Schneider K et al 2014 Phys. Rev. Lett. **113** 073001
[14] Zewail A H 2000 Nature **406** 752–7
[15] Hao Y, Inhester L, Hanasaki K, Son S K and Santra R 2015 J. Mod. Opt. **63** 383–93
[16] Hollstein M, Santra R and Pfannkuche D 2017 Phys. Rev. Lett. **118** 033017
[17] Ackermann W et al 2008 Rev. Sci. Instrum. **79** 073001
[18] Štrba J et al 2017 Opt. Lett. **42** 3583–86
[19] Riekel C, Hainzl M, Morgner U, Kisker C and Wabnitz H 2006 Struct. Dyn. **3** 386–91
[20] J. Phys. B: At. Mol. Opt. Phys. **39** 104301
[21] Zewail A H 2000 Nature **406** 752–7
[22] Ackermann W et al 2008 Rev. Sci. Instrum. **79** 073001
[33] Bruhn G, Davidson E R, Mayer I and Clark A E 2006 \textit{Int. J. Quantum Chem.} \textbf{106} 2065–72
[34] Vacher M, Bearpark M J, Robb M A and Malhado J P 2017 \textit{Phys. Rev. Lett.} \textbf{118} 083001
[35] Arnold C, Vendrell O and Santra R 2017 \textit{Phys. Rev. A} \textbf{95} 033425
[36] Koopmans T 1934 \textit{Physica} \textbf{1} 104–13