Closed-loop recycling of rare liquid samples for gas-phase experiments

View Online   Export Citation   CrossMark

K. Fehre,[1,a] M. Pitzer,[1] F. Trinter,[1,2] R. Berger,[3] A. Schießer,[4] H. Schmidt-Böcking,[1] R. Dörner,[1] and M. S. Schöffler[1,a]

AFFILIATIONS

[1] Institut für Kernphysik, Goethe-Universität Frankfurt, Max-von-Laue-Str. 1, 60438 Frankfurt, Germany
[2] Molecular Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany
[3] Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35039 Marburg, Germany
[4] Mass Spectrometry, Department of Chemistry, Technische Universität Darmstadt, Alarich-Weiss-Straße 4, 64287 Darmstadt, Germany

[a] Authors to whom correspondence should be addressed: fehre@atom.uni-frankfurt.de and schoeffler@atom.uni-frankfrut.de

ABSTRACT

Many samples of current interest in molecular physics and physical chemistry exist in the liquid phase and are vaporized for use in gas cells, diffuse gas targets, or molecular gas jets. For some of these techniques, the large sample consumption is a limiting factor. When rare, expensive molecules such as custom-made chiral molecules or species with isotopic labels are used, wasting them in the exhaust line of the pumps is quite an expensive and inefficient approach. Therefore, we developed a closed-loop recycling system for molecules with vapor pressures below atmospheric pressure. Once filled, only a few valves have to be adjusted, and a cold trap must be moved after each phase of recycling. The recycling efficiency per turn exceeds 95%.

Published under license by AIP Publishing. https://doi.org/10.1063/5.0037836

INTRODUCTION

Experiments on single molecules in the gas phase are particularly clean and powerful as the systems are isolated from any perturbing environment. Most of the simple molecular targets, such as H_2, N_2, O_2, or CO, which are naturally gaseous, have been extensively investigated in the past 20 years.[1–4] In the recent past, experimental techniques have improved dramatically,[5–8] and the research has shifted the focus on more complex targets. The drawback of "larger" molecules is that they are liquid at room temperature; many of them pose health risks or are problematic for vacuum pumps. Compounds from the large group of chiral molecules became of high interest in molecular physics.[9] In particular, enantiopure samples are usually quite expensive.[10] This is also the case for isotopically labeled species, which are often custom-made.[7,11]

Therefore, there is an effort to design the experimental setup in a way that reduces the sample consumption and minimizes contact with it. Experimental techniques that would benefit from such a reduction range from high order harmonics generation[8,12] over velocity map imaging,[13,14] hemispherical analyzers,[15] magnetic bottle spectrometers,[16,17] time-of-flight tubes,[18] and photon detection[19] to cold target recoil ion momentum spectroscopy (COLTRIMS)-type reaction microscopes.[20] While only a small fraction of the sample is really "used," the major part has to be pumped out of the apparatus in order to maintain the high or ultrahigh vacuum. Thus, the major part of the sample is lost when not recycled. Gas cells, effusive targets,[5,21,22] and supersonic gas jets are the most widely used target systems. We developed a closed-loop gas-recycling system to be used for these gas target systems. We have characterized it in connection with a free molecular gas jet, which is commonly used in COLTRIMS reaction microscopes.

We briefly discuss the key elements of a typical gas jet. The sample expands with its vapor pressure through a tiny nozzle (typically, 30 μm–200 μm), forming a supersonic gas jet when entering the vacuum chamber (referred to as expansion chamber). The expansion chamber is connected to a vacuum chamber in which the interaction takes place or to a series of differential pumping stages by a skimmer to keep the pressure in the interaction chamber as low

as possible. In the interaction chamber, only a minuscule portion of the sample is investigated in the interaction with single photons, strong laser fields, or charged particles, and the great majority of the molecules are guided out of the reaction chamber and are differently pumped. From the typical pressures and typical pumping speeds follows that >99.9% of the total gas load occurs in the first stage of the expansion chamber, where the gas nozzle is located. Capturing and recycling this majority of the unused sample will increase efficiency dramatically.

An easy approach to recycle the sample is a simple cold trap in the fore-vacuum line between the exhaust of a high-vacuum turbomolecular pump and a dry, oil-free fore pump, for instance, a roots-scroll pump combination. The "used" gas is deposited on the cold surface of the trap and transferred back into the initial reservoir for further use. This approach has some disadvantages: The gas line has to be physically opened and closed from time to time with the typical risks of leaks. The cold trap needs to defrost at a safe location (e.g., fume hood) where the sample can be transferred back into the initial reservoir or safely disposed. All these consume valuable time and even more importantly involve the danger of exposure to the sample and contamination. To avoid all these, we have developed a closed-loop recycling system, which is suited for samples that are liquid at room temperature; samples with vapor pressures between 10 mbar and 600 mbar have been used so far.

Figure 1 shows a sketch of the gas/vacuum lines, which are the main part of recycling. A photograph is shown in Fig. 3. The supply system (e.g., in 6 mm stainless steel tubing with standard tube fittings), sketched in red, connects the reservoir or one of the two cold traps with the nozzle. The fore-vacuum system (ISO-KF25 and ISO-KF40) is sketched in black and green from the outlet of the turbomolecular pump (in the expansion chamber) via the cold traps to the fore pump. Initially, the sample is taken from the original sample cylinder. Only valves R, 1, and 2 are opened [see Fig. 2(a)]. While the sample expands through the nozzle, >99.9% is pumped with a turbomolecular pump. In the fore-vacuum line, the gas passes through a cold trap made of glass. The trap is cooled in a liquid nitrogen filled Dewar flask. The sample undergoes deposition in the cold trap. This process is so efficient that when running the pure sample, the fore pump could be switched off. Obviously, when carrier gas is used (such as helium), the fore pump is needed.

When the original sample reservoir is empty, the first recycling phase is started. The sample is now located in the left of the two cold traps. This now will be used as the new reservoir from which the sample evaporates. The Dewar flask has to be removed and put underneath the other cold trap, in which for this cycle, the sample undergoes deposition. Valves 3 and 4 are opened, while valves 1 and 2 have to be closed. Additionally, valve A must be opened and valve R must be closed [see Fig. 2(b)], allowing the sample to reach the nozzle. The left glass cylinder acts now as the reservoir, and the right one acts as the cold trap. One can speed up the warming procedure by placing a container, filled with (warm) water underneath the left glass cylinder. The procedure is repeated for recycling, switching all valve positions (except for R) from one to the other for each turn. See Fig. 2(c) for the path in the second turn of recycling.

Care should be taken when opening the valves if, at room temperature, gaseous molecules (mostly N_2, O_2, and CO_2) from leaks
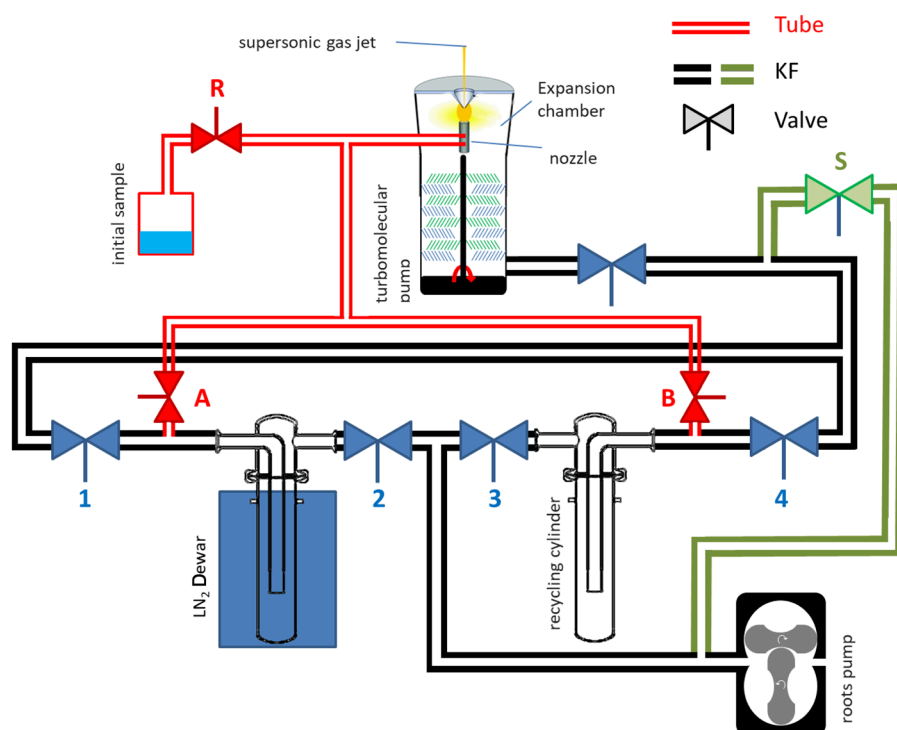

FIG. 1. Sketch of the closed-loop sample-recycling system. A photograph is shown in Fig. 3. The sample is fed to the nozzle in tube fittings (red) from the initial sample reservoir or recycling cylinder. In the stainless steel tube (red), the pressures typically range from 10 mbar to 500 mbar. The sample is returned from the exhaust of the turbomolecular pump to the recycling cylinder via KF pipes (black). In the KF fore-vacuum, the pressures range from 10^{-2} mbar to 10^{-4} mbar. A connection made of KF pipes makes it possible to bypass the gas recycling and connects the exhaust of the turbomolecular pump directly with the pre-vacuum pump (green).
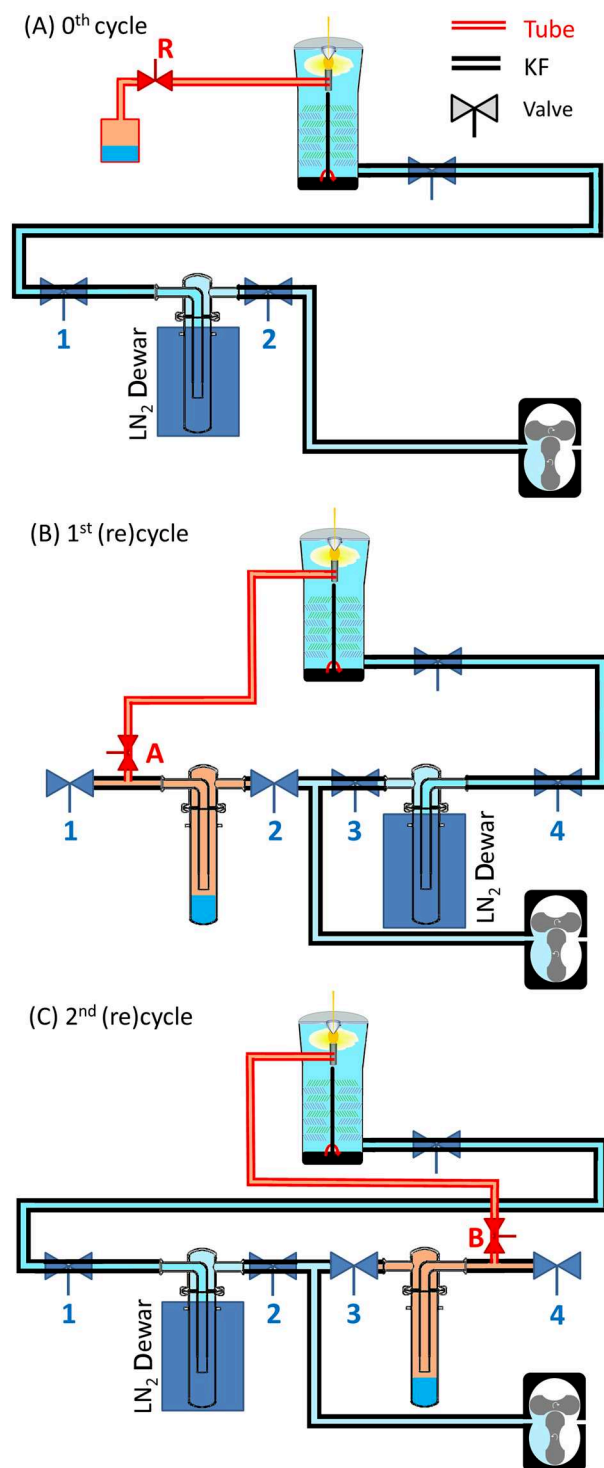
FIG. 2. Sketch of recycling with (a) the first filling and (b) the first and (c) the second turn on the recycling mode. The former cold trap on the left-hand side acts as the reservoir in the second turn, while the cylinder on the right-hand side captures the sample. Regions in the recycling system with pressures >1 (<1) mbar are highlighted in red (blue).

have condensed in the cold trap. When defrosting, there is a risk that they expand quickly and the glass cylinder will burst. This never happened, but as a precaution, we opened the valve to the backing pump slightly at the beginning during the thawing process. Another risk is posed by oxygen, which might leak into the recycling system and condensate there.[23]

Another possible solution to this potential problem is the installation of an overpressure release valve, which would open above atmospheric pressure directly to the (toxic gas) exhaust line.

In the first version, as depicted in the photograph (Fig. 3), the connectors at the glass recycling cylinders had a size of ISO-KF25 and the inner glass pipe had a diameter of 15 mm. When larger quantities of liquids (>20 ml) were used, the inner glass pipe was clogged by the frozen sample. This could be prevented by melting the clogged part or with a larger diameter of the inner tube of the cold trap. The latter approach was realized in a second version of this recycling system with 25 mm inner diameter of the glass pipe. As clogging still might occur, we installed a manual safety release valve to bypass recycling (the green line in Fig. 1). This can be opened in the case of a clogged inner tube and prevents excessive fore-vacuum pressure on the turbomolecular pump or even flooding of the expansion chamber. As protection against the potentially bursting glass of the cold traps, an acrylic transparent plate on both sides protects the equipment and the user. While a cold trap made of stainless steel does not carry this risk, the glass version has the important advantage that the sample level and any contamination can be checked visually. In addition, care should be taken that ISO-KF clamps and center rings are made of plastic to avoid damage to the glass.

If samples with rather low vapor pressures are used, the complete recycling system (the fore line, the cold trap, which acts as the reservoir, and the supply line) has to be carefully heated. Furthermore, minimizing the surface area is recommended, especially using ISO-KF pipes or tubes instead of flexible hoses, wherever possible. The flexible connectors that can be seen in Fig. 3 have been avoided in a second version for this reason.
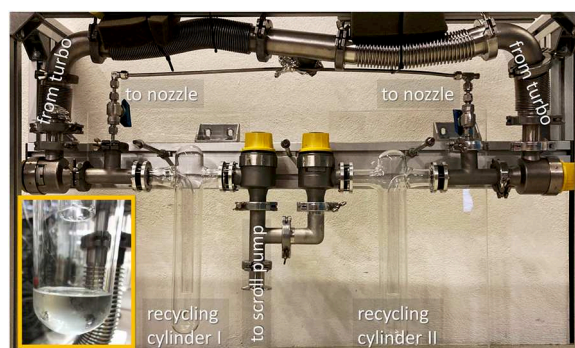

FIG. 3. Picture for the first version of closed-loop recycling. Cold traps (glass cylinders), ISO-KF, tubes and fittings, as well as valves and one Dewar flask sum to a total of about 2500 Euro. As can be seen in the inset, a cold trap made of glass allows the sample quantity and quality to be checked visually.

To examine the recycling efficiency, we recorded the pressure in the expansion chamber during an experiment with the closed-loop recycling system. The sample (here, ~10 ml liquid trifluoro-methyloxirane with a vapor pressure of ~600 mbar reduced with a needle valve to 100 mbar) expands through the nozzle into the expansion chamber and is pumped out with a 2300 l/s turbomolecular pump. The pressure in the expansion chamber is in very good approximation linked linearly to the sample flow through the nozzle. Consequently, the integral under the curves of the recycling steps in Fig. 4 gives a good estimate of how much sample was used in the respective recycling step. The properties of the supersonic jet (monitored via the event rate and the jet velocity) did not significantly change between $7.5 \cdot 10^{-5}$ mbar and $2.7 \cdot 10^{-4}$ mbar. The integrated area under the pressure–time curve is shown in Fig. 4(b). Assuming an exponential loss of the sample, more than 95% of the sample could be reused in each of the following recycling steps. This means instead of consuming 50 ml sample in 34 h, only 1.5 ml out of the initial 10 ml are lost.

After some recycling steps, we observed residue (probably oil from the turbomolecular pump) on the bottom of the glass cylinders. The amount of this residual contamination could be greatly reduced by thoroughly cleaning the (re-)supply and, especially, the fore-line vacuum tubes beforehand. The type of sample itself also influences the residual contamination in the glass cylinder: If solvents for oil (as ethanol or methanol) were used, more of the contamination was found on the bottom of the cold trap. Since only the distillate is returned to the experiment in each recycling step, the contamination did not affect our measurement. However, if the vapor pressure of the sample is very low, contaminations might interfere with the experiment. In addition, in the case of very reactive samples, it is conceivable that the sample interacts with the contamination in the glass cylinder. Additionally, the mass spectra of the first and last steps in the recycling were compared. This comparison did not show any noticeable change in the mass spectrum, which could be caused by any contamination of the sample by gas recycling.

CONCLUSION

In this article, we have presented the design and operation of a closed-loop recycling system for the safe handling of samples that are in the liquid phase at room temperature and standard pressure. With this setup, even small sample quantities can be examined in longer measurement series in the gas phase without much loss of time for the measurement or loss of sample due to difficult handling procedures. We achieved a recycling efficiency of >95% per cycle.

Experiments with this recycling scheme have successfully been performed using methyloxirane (C_3H_6O),[24] bromochlorofluoromethane,[11] halothane,[25] trifluoro-methyloxirane ($C_3H_3F_3O$), and deuterated formic acid (CHOOD),[26] with vapor pressures from 10 mbar to 600 mbar.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.
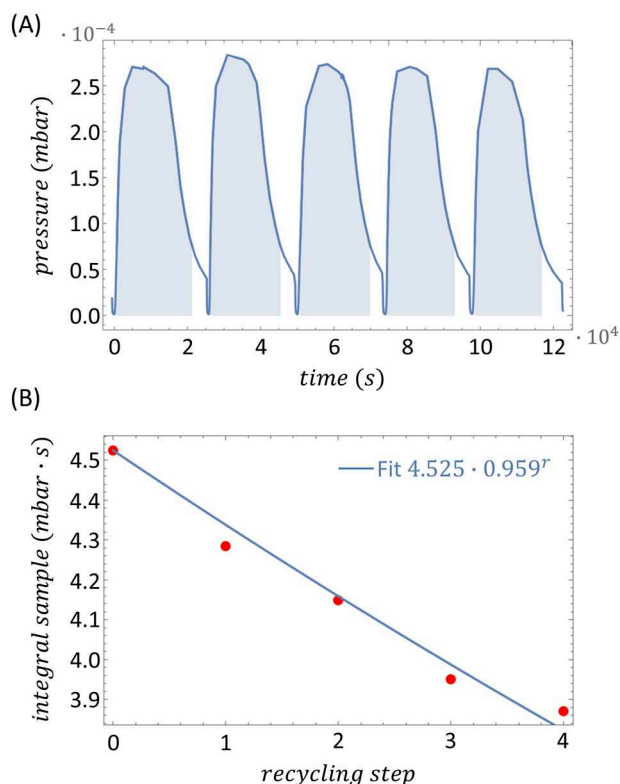

FIG. 4. Recycling efficiency of closed-loop recycling. (a) Pressure in the expansion chamber measured over several recycling steps. The blue areas under the curve fulfill the criterion *pressure* > $7.5 \cdot 10^{-5}$ mbar, separating the different recycling steps. (b) The integral of the blue areas indicates the amount of sample of every recycling step. Assuming an exponential loss of sample, more than 95% of the sample can be reused in every recycling step.

REFERENCES

[1] A. S. Sandhu *et al.*, "Observing the creation of electronic Feshbach resonances in soft x-ray-induced O_2 dissociation," Science **322**(5904), 1081–1085 (2008).

[2] D. Pavičić, K. F. Lee, D. M. Rayner, P. B. Corkum, and D. M. Villeneuve, "Direct measurement of the angular dependence of ionization for N_2, O_2, and CO_2 in intense laser fields," Phys. Rev. Lett. **98**(24), 243001 (2007).

[3] P. Salén *et al.*, "Experimental verification of the chemical sensitivity of two-site double core-hole states formed by an x-ray free-electron laser," Phys. Rev. Lett. **108**(15), 153003 (2012).

[4] M. S. Schöffler *et al.*, "Ultrafast probing of core hole localization in N_2," Science **320**(5878), 920–923 (2008).

[5] A. Comby *et al.*, "Real-time determination of enantiomeric and isomeric content using photoelectron elliptical dichroism," Nat. Commun. **9**(1), 5212 (2018).

[6] K. Fehre *et al.*, "Absolute ion detection efficiencies of microchannel plates and funnel microchannel plates for multi-coincidence detection," Rev. Sci. Instrum. **89**(4), 045112 (2018).

[7] P. Herwig *et al.*, "Imaging the absolute configuration of a chiral epoxide in the gas phase," Science **342**(6162), 1084–1086 (2013).

[8] R. Cireasa *et al.*, "Probing molecular chirality on a sub-femtosecond timescale," Nat. Phys. **11**(8), 654–658 (2015).

[9] A. Zehnacker, *Chiral Recognition in the Gas Phase* (CRC Press, Hoboken, NJ, 2010).

[10] M. Ilchen *et al.*, "Emitter-site-selective photoelectron circular dichroism of trifluoromethyloxirane," Phys. Rev. A **95**(5), 053423 (2017).

[11] M. Pitzer *et al.*, "Direct determination of absolute molecular stereochemistry in gas phase by Coulomb explosion imaging," Science **341**(6150), 1096–1100 (2013).

[12] F. McGrath *et al.*, "An apparatus for quantitative high-harmonic generation spectroscopy in molecular vapours," Rev. Sci. Instrum. **88**(10), 103108 (2017).

[13] A. T. J. B. Eppink and D. H. Parker, "Velocity map imaging of ions and electrons using electrostatic lenses: Application in photoelectron and photofragment ion imaging of molecular oxygen," Rev. Sci. Instrum. **68**(9), 3477–3484 (1997).

[14] G. A. Garcia, L. Nahon, and I. Powis, "Two-dimensional charged particle image inversion using a polar basis function expansion," Rev. Sci. Instrum. **75**(11), 4989–4996 (2004).

[15] H. Daimon and S. Ino, "Improvement of the spherical mirror analyzer," Rev. Sci. Instrum. **61**(1), 57–60 (1990).

[16] C. Strobel, G. Gantefoer, A. Bodi, and P. Hemberger, "A magnetic bottle time-of-flight electron spectrometer suitable for continuous ionization sources," Rev. Sci. Instrum. **90**(6), 063105 (2019).

[17] M. Mucke, M. Förstel, T. Lischke, T. Arion, A. M. Bradshaw, and U. Hergenhahn, "Performance of a short 'magnetic bottle' electron spectrometer," Rev. Sci. Instrum. **83**(6), 063106 (2012).

[18] R. S. Tranter, B. R. Giri, and J. H. Kiefer, "Shock tube/time-of-flight mass spectrometer for high temperature kinetic studies," Rev. Sci. Instrum. **78**(3), 034101 (2007).

[19] A. Hans *et al.*, "Setup for multicoincidence experiments of photons in the extreme ultraviolet to visible spectral range and charged particles—The solid angle maximization approach," Rev. Sci. Instrum. **90**(9), 093104 (2019).

[20] J. Ullrich, R. Moshammer, A. Dorn, R. Dörner, L. Ph. H. Schmidt, and H. Schmidt-Böcking, "Recoil-ion and electron momentum spectroscopy: Reaction-microscopes," Rep. Prog. Phys. **66**(9), 1463–1545 (2003).

[21] D. Trabert *et al.*, "Spin and angular momentum in strong-field ionization," Phys. Rev. Lett. **120**(4), 043202 (2018).

[22] C. Lux *et al.*, "Circular dichroism in the photoelectron angular distributions of camphor and fenchone from multiphoton ionization with femtosecond laser pulses," Angew. Chem., Int. Ed. **51**(20), 5001–5005 (2012).

[23] A. Beil, D. Luckhaus, and M. Quack, "Fermi resonance structure and femtosecond quantum dynamics of a chiral molecule from the analysis of vibrational overtone spectra of CHBrClF," Ber. Bunsen. Phys. Chem. **100**(11), 1853–1875 (1996).

[24] K. Fehre *et al.*, "Angular streaking in strong field ionization of chiral molecules," Phys. Rev. Res. **1**(3), 033045 (2019).

[25] M. Pitzer *et al.*, "Stereochemical configuration and selective excitation of the chiral molecule halothane," Rep. Prog. Phys. **49**(23), 234001 (2016).

[26] H. Kaur Gill, "Bestimmung der Konfiguration einfacher Moleküle mittels CEI," Master thesis, Goethe-University Frankfurt, 2015.