

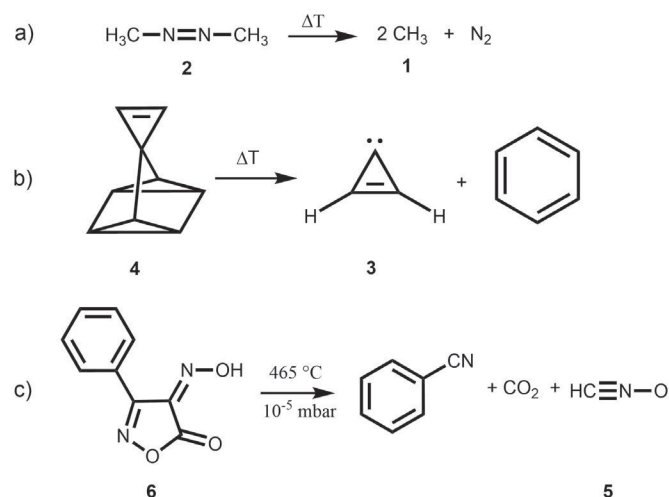
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# Photoionization and Photoelectron Spectroscopy of Reactive Species as Tools in Laboratory Astrochemistry

An inspection of online data bases like CDMS (Cologne Database of Molecular Spectroscopy) [1] reveals that more than 300 molecular species have now been identified in interstellar space, ranging in size from simple diatomics to C<sub>70</sub>. A large fraction of them are reactive molecules, like ions (cations as well as anions), radicals, biradicals or carbenes. Such species are unstable at room temperature and ambient pressure but survive under the cold and dilute conditions in space. Therefore, laboratory studies that help to identify reactive molecules in space and study their reactions are challenging. Experiments have to be carried out under isolated conditions, i.e., at high vacuum, to avoid reactive collisions. Typically, the species are diluted in a rare gas jet that expands adiabatically into the vacuum and potentially cools the species to some ten to hundred Kelvin. This molecular jet is then interrogated by a light source. In our group, we employ radiation from the Infrared to the soft X-ray to characterize the structure and reactivity of reactive species. Due to the high dilution, high photon flux light sources like lasers or accelerator-based sources (Synchrotron radiation, SR, or Free Electron Lasers, FEL) are often required.

In space, molecules are typically identified by radio- or Infrared astronomy [2]. While the former has successfully been employed for almost a century, the latter moved into the focus quite recently, partially due to the exciting data recorded by the James Webb space telescope (JWST). Thus, observational astronomy requires mostly laboratory data from rotational and vibrational spectroscopy. One might therefore ask, what laboratory studies using UV, VUV and soft X-ray radiation contribute to astrochemistry. However, many astrophysical regions are transparent to UV and VUV radiation [3]. In these so-called photon dominated regions (PDR), photoionization and photodissociation are important reaction pathways and have to be included in chemical reaction networks that model these regions in space [4]. Keeping this in mind, several relevant questions of astrochemistry are addressed in laboratory photoionization studies: (a) Vibrationally resolved photoelectron spectra help to identify molecular cations and complement the data from IR spectroscopy, (b) photoionization

in the PDR can form ions that are reactants in the formation of larger molecules. As ion-molecule reactions are among the most efficient processes in space [5], it is important to know the ratio of neutral and ionized molecules. Therefore, the rate of ionization has to be known [4], which requires the measurement of accurate energy-dependent ionization cross sections in the laboratory. (c) Radiation leads to the photodissociation or the dissociative photoionization of molecules and thus to new species. The energy-dependence of the processes and the product branching ratios are important input parameters for models of the reaction network [4]. The latter aspect is also important in the X-ray regime. Below, examples for the various aspects of photoionization and their relevance to astrochemistry will be presented.



**Fig. 1:** Preparation of selected reactive molecules discussed in the present work by thermal reactions (pyrolysis) of suitable precursors, from top to bottom a) formation of methyl radical **1** from commercially available azomethane **2**, b) formation of cyclopropenylidene **3** from quadricyclane **4** [6] and c) formation of fulminic acid **5** from 3-phenyl-4-oxoimino-isoxazolone **6** [7]. Note that the synthesis of **4** and **6** is quite elaborate.

## Generation of Reactive Molecules in the Laboratory

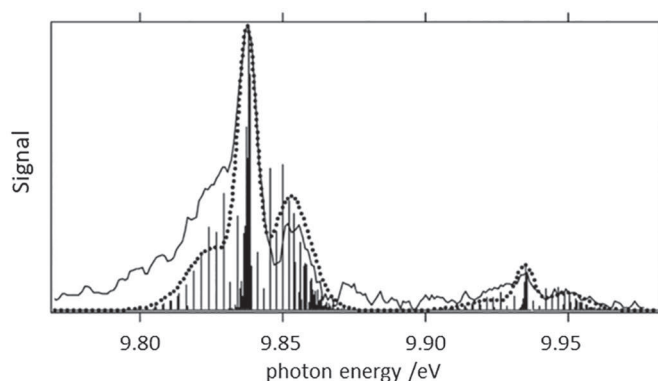
The high reactivity of radicals, biradicals, and carbenes requires in-situ synthesis from stable precursors, followed by experiments under collision-free conditions in the gas phase. Most work in our group is performed using pyrolysis, i.e., thermal reactions. Here, predetermined chemical bonds in a precursor are selectively broken in a SiC microreactor with <40 mm length and 1 mm inner diameter. A precursor is diluted in a rare gas,

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e.g. Ar, and the mixture is expanded through a small hole into the reactor. Here, the thermal reaction takes place, which forms the species of interest. At the microreactor exit, the molecule/argon mixture is adiabatically expanded into the vacuum and forms a molecular beam, which travels collision-free to the interaction region with light. Precursors with low bond energies are well suited and sometimes rather elaborate precursors, like **4** and **6** in Figure 1 are required to generate the desired species cleanly and in high number density. Some of the reactions in Figure 1 show that in pyrolysis, the challenge of producing a reactive species is turned into the chemical challenge to find and synthesize a suitable precursor.

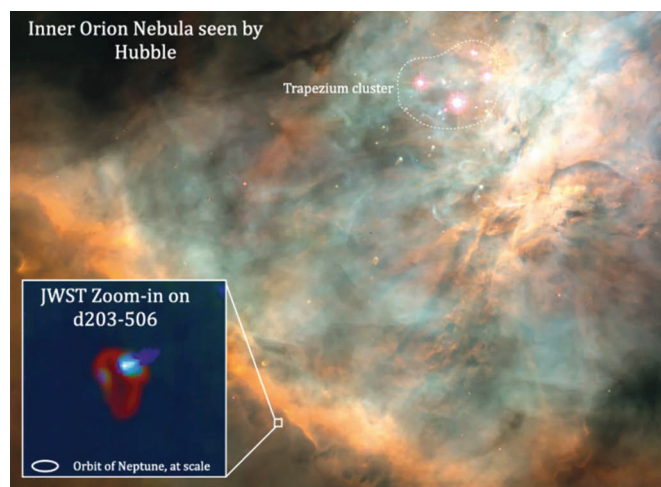
### Threshold Photoelectron Spectroscopy of CH<sub>3</sub>

Although radio astronomy and rotational spectroscopy are a good match, there is one requirement for observation that not all molecules fulfill: To record pure rotational spectra, a permanent dipole moment in the molecule is required. The methyl ion, CH<sub>3</sub><sup>+</sup>, is a planar molecule with D<sub>3h</sub> symmetry and thus an example for a molecule that cannot be detected based on its rotational spectrum. In such cases, high resolution photoelectron spectroscopy (PES) can yield vibrationally (and sometimes rotationally) resolved spectra of the ionic ground state that permit to extract spectroscopic constants, like the vibrational constants  $\omega_0$  and  $\omega_0x_0$ , as well as the rotational constant  $B_0$ . These constants can then aid in the identification of molecules in observations based on their infrared emission. The techniques applied to record mass-selected photoelectron spectra of reactive molecules have been described in two recent reviews [8, 9].



**Fig. 2:** Threshold photoelectron spectrum of the methyl radical together with a simulation of the origin band. At higher energies, a sequence band of the umbrella mode is visible. The solid line corresponds to the experimental spectrum, while the dotted line represents a simulation. Reproduced with permission from Ref. [10], American Chemical Society.

Figure 2 depicts part of the photoelectron spectrum of the methyl radical (i.e., a spectrum of the methyl cation **1**<sup>+</sup>) [10]. The spectrum is dominated by the origin band, i.e., the transition into the vibrational ground state of CH<sub>3</sub><sup>+</sup>. The wings on the main peak correspond to the unresolved rotational branches of the transition. In addition, a transition into the 2<sub>1</sub><sup>1</sup> sequence band of the umbrella mode (the symmetric C-H bending vibration) is observed. The umbrella mode appears quite prominently and is associated with large Franck Condon factors due to the geometry change from C<sub>3v</sub> to D<sub>3h</sub> upon ionization.

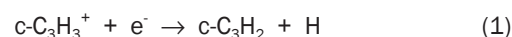


**Fig. 3:** CH<sub>3</sub><sup>+</sup> has been detected with the James Webb Space Telescope in the protoplanetary disc d203-506 located in the Orion Nebula. (Image credit: NASA/STScI/Rice Univ./C.O'Dell et al / O. Berné, I. Schrotter, PDRs4All)

In Figure 3, an image of a protoplanetary disk (a disk of gas and dust around a young star) in the Orion nebula is presented, recorded by the JWST. In this disk, a new species was detected, which has been assigned to the methyl cation **1**<sup>+</sup> by taking the spectroscopic constants from our work [10] as well as from recent IR spectra [12]. This is the first identification of **1**<sup>+</sup> in space, an ion that is assumed to be central for gas-phase organic chemistry in the interstellar medium. The work is also a perfect example for the potential of photoelectron spectroscopy in laboratory astrochemistry.

### Photoionization Cross Section of Cyclopropenylidene, c-C<sub>3</sub>H<sub>2</sub>

Despite its unusual structure, the singlet carbene cyclopropenylidene, **3** is one of the most abundant hydrocarbons in space. It was discovered in 1985 [13] and later found in a range of extraterrestrial environments [14]. Due to its high dipole moment, its rotational transitions can efficiently be detected and **3** is often employed as a probe for hydrocarbon chemistry in interstellar space. It is possibly formed by dissociative recombination, following (1):



In the photon-dominated regions, **3** can be ionized, which strongly influences the ratio between neutral and cation. To properly determine the ionization efficiency of a molecule  $M$ , its concentration  $[M]$ , the photon flux  $\Phi_{hv}$  and the ionization cross section  $\sigma_i$  are required. In laboratory experiments on stable molecules, the concentration can be adjusted, and the photon flux measured (which nevertheless can both be quite tedious), so determination of  $\sigma_i$  from (2) is straightforward.

$$[M^+] = [M] \cdot \sigma_i^M \cdot \Phi_{hv} \quad (2)$$

In contrast, this is not the case for reactive species, because the concentration is usually difficult to determine. One therefore often relies on the determination of **relative** cross sections, i.e., a reactive molecule is produced in a well-known

ratio relative to a stable molecule with a known cross section. We produced **3** by pyrolysis from the quadricyclane derivative **4** [15]. As visible from Figure 1b), benzene is generated as a second pyrolysis product. The latter's absolute photoionization cross section has been determined before [16] and its ionization energy (IE) of 9.244 eV is similar to the value of **3**. Mass spectra confirmed that both pyrolysis products are generated in a 1:1 ratio, so it is possible to determine the absolute photoionization cross section of cyclopropenylidene by comparing the photoionization efficiency (PIE) curves of  $c\text{-C}_3\text{H}_2$  and benzene. The determination is based on the relation (3):

$$\frac{S_{C_3H_2}}{S_{C_6H_6}} = \frac{[C_3H_2]}{[C_6H_6]} \cdot \frac{\sigma_i^{C_3H_2}}{\sigma_i^{C_6H_6}} \cdot \frac{A_{C_3H_2}}{A_{C_6H_6}} \quad (3)$$

$S$  stands for the detected ion signals of the respective species,  $[C_3H_2]$  and  $[C_6H_6]$  correspond to the concentrations of cyclopropenylidene and benzene,  $\sigma_i$  are the photoionization cross sections, and  $A$  represents an apparatus function. As the two pyrolysis products are generated in a 1:1 ratio, the fraction of the species concentrations equals 1. For the ratio of the apparatus functions, calibration studies yielded also a value close to 1. Thus, equation (3) reduces to:

$$\sigma_i^{C_3H_2} = \frac{S_{C_3H_2}}{S_{C_6H_6}} \cdot \sigma_i^{C_6H_6} \quad (4)$$

From (4), the absolute photoionization cross section of  $c\text{-C}_3\text{H}_2$  could then be determined from the ratio of the ion signals of **3** and benzene, as visible in Figure 4.

For application in any model, it is important to determine the error margin of the observed values. This includes inaccuracies in the determined apparatus function or deviations from the 1:1 concentration ratio in the pyrolysis. However, we found that the value of benzene's cross section itself accounts by far for the greatest source of error because its uncertainty is stated to be 20%. The overall error for the absolute photoionization cross section reported in this paper is therefore evaluated to be around  $\pm 30\%$  of  $\sigma_i$ , indicated in grey in Figure 6. The example demonstrates the need for determining accurate  $\sigma_i$  values in the laboratory even for stable molecules.

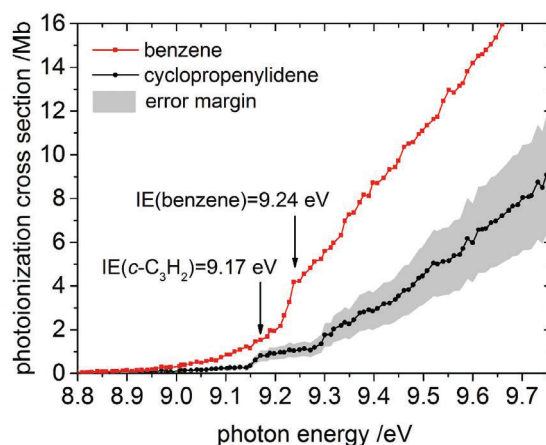


Fig. 4: Absolute photoionization cross section of **3** (black curve), generated in stoichiometric quantities from the precursor **4**. The second fragment is benzene (red curve), which acts as reference cross section. Reproduced with permission from Ref. [15], Royal Society of Chemistry.

### Fragmentation of HCNO upon X-Ray Excitation

In the late 1990's, two observatories were launched, XMM Newton and Chandra, which deliver observational data in the X-ray regime. This spectral region has for many years played only a minor role in astrochemistry. This is partly because X-ray spectra are very sensitive to atomic structure and thus very well suited to identify elements in various environments, but sensitivity to molecular structure is limited. In recent years, this view has slightly changed. First of all, X-rays can penetrate deeply into objects like dense clouds that are impermeable for UV photons and can initiate chemistry in the gas phase and on the surface of grains [17]. Second, it was found that young stellar objects, stars in an early stage of evolution, emit X-rays over a wide spectral range. Thus, X-ray induced photochemical processes will certainly modify molecular abundances and have to be included in the chemical networks. Unfortunately, laboratory data on the reactions of astrochemically relevant species in the X-ray regime are scarce. This is particularly true for reactive intermediates. To understand the challenges of the laboratory work, it is necessary to dwell briefly on the foundations of X-ray spectroscopy.

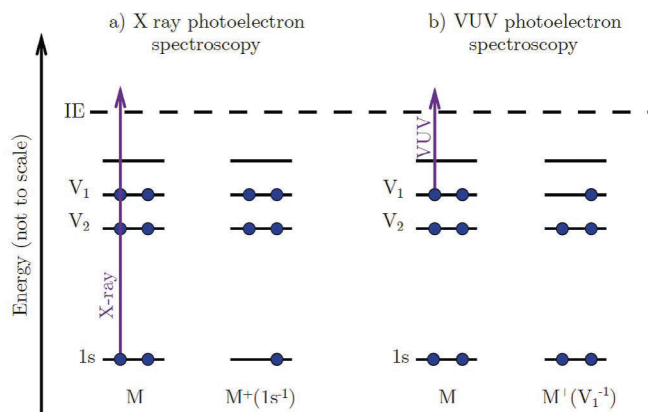


Fig. 5a: Photoionization with VUV radiation (right hand side) leads to the emission of valence electrons, while in X-ray ionization core electrons (mostly 1s) are emitted. Figure taken from [18].

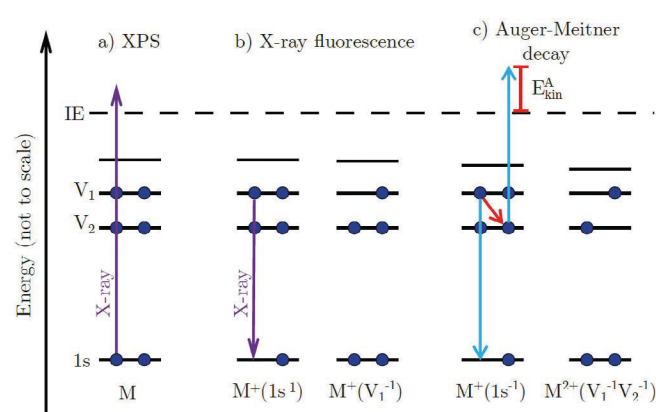


Fig. 5b: X-ray ionization a) forms a cation with a hole in a core orbital. When this vacancy is filled by a valence electron, the excess energy is either removed by emission of b) a photon, or c) a secondary electron. Figure taken from [18].



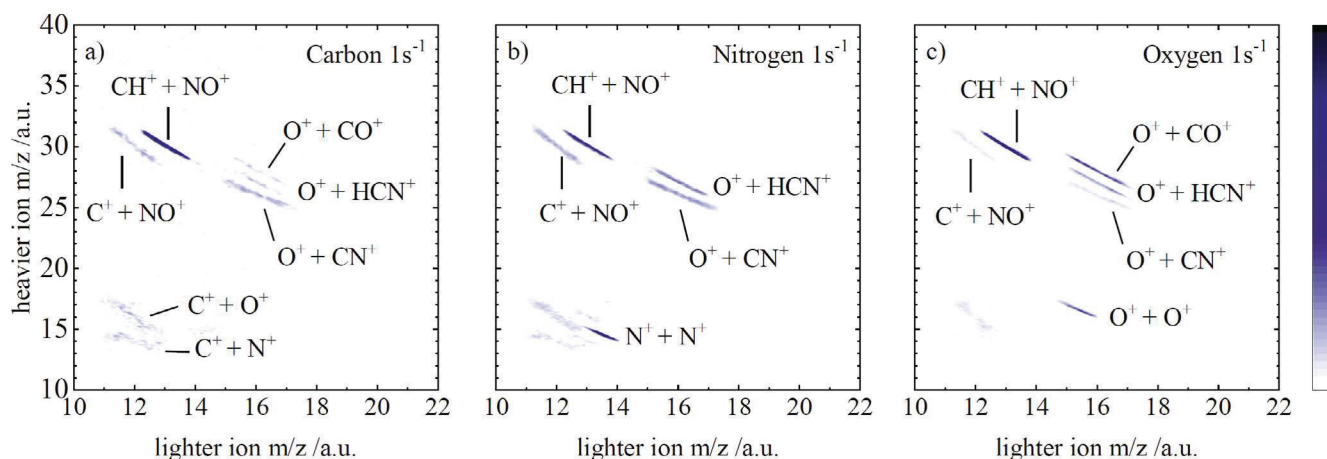
Figure 5 illustrates the differences between photoionization with VUV- and X-ray radiation. VUV light removes electrons from valence molecular orbitals, like  $V_1$  on the right-hand side of figure 5a. The valence orbitals are often involved in the chemical bonds, so analysis of the photoelectron spectra yields insight into the changes in chemical bonding upon photoionization (see section on  $\text{CH}_3$  above). In contrast, X-rays remove core electrons, for example from the  $1s$  orbital of first period elements. The  $1s$  electrons are close to the nucleus and not involved in the chemical bond, so the energy required for ionization is close to the value of the atoms. The  $1s$  ionization energy (IE) of carbon is around 290 eV, while the IE for a nitrogen  $1s$  is close to 410 eV and the one for O  $1s$  is around 540 eV. As these differences are huge, X-ray spectroscopy is an excellent tool to analyze **elemental** compositions. In contrast, details of the molecular structure have only a small influence on the  $1s$  IEs. Of course, a molecular ion with a hole in a  $1s$  orbital has a very high energy that it will try to reduce, see Figure 5b, e.g. a valence electron can fill the hole in the  $1s$  orbital and dispose the energy by X-ray emission. This process is efficient for heavy elements, so X-ray emission spectra are well-suited for elemental identification. In fact, X-ray observatories in space detected several atoms based on the emission signal. However, there is an alternative process, that is far more efficient for the lighter elements, Auger-Meitner decay [19], depicted on the right-hand side of Figure 5b. Here, also an electron returns to the  $1s$  orbital, but the excess energy is removed by emitting a **second** electron, the Auger electron. As a result, a dication is formed. The kinetic energy of this electron can be analyzed and gives important structural information. There are several possibilities both for the electrons that fill the  $1s$  hole and for the secondary electron. So even for small molecules many Auger-Meitner processes are possible and Auger spectra are difficult to disentangle. Most of the time, the dication formed in this process is not stable and will fragment. Thus, in space molecules exposed to X-rays will form various fragments and the branching ratios have to be included in the models that are supposed to describe regions with high X-ray flux in space. Here, laboratory studies on the fragmentation of interstellar molecules following X-ray excitation and ionization can contribute relevant information. Our group recently focussed on the

spectroscopy and dynamics of the isomers HNCO (isocyanic acid) [20] and HCNO (fulminic acid) [21]. Both are of interest, because they contain the basic atoms of organic chemistry and are considered to be potential precursors in the interstellar synthesis of prebiotic molecules.

Here, we will focus on one aspect, the fragmentation of the HCNO dications formed after emission of an Auger electron, investigated by photoion/photoion coincidence (PIPICO) spectroscopy [22]. In this method, two fragment ions that originate from the same event are detected, i.e., from dissociation of the same dication. This results in a PIPICO map like the one in Figure 6, which shows the ion pairs that originate from the same dissociation event. These maps consist of stripes, each corresponding to a specific product pair. The signal shape is due to the kinetic energy that is released in the fragmentation. Due to momentum conservation, the product ions are accelerated in opposite directions, the time of flight of one ion will decrease while the time of flight of the partner ion is increased by the same amount. As visible, at all three  $1s$  edges the  $\text{CH}^+ + \text{NO}^+$  pair is the dominant product but is twice as intense at the C and O  $1s$ -edge with 66% and 72% compared to only 37% at the N  $1s$ -edge. On the other hand, at the N  $1s$ -edge the  $\text{O}^+ + \text{HCN}^+$  and  $\text{O}^+ + \text{CN}^+$  are amplified and in general the branching ratios are more evenly distributed. Thus, the fragmentation pattern of HCNO varies strongly with the X-ray photon energy, which must be considered in models describing regions with high X-ray flux.

### Summary

In this article, we present three examples for the contribution of photoionization and photoelectron spectroscopy to laboratory astrochemistry. We focus on reactive molecules that are unstable under ambient conditions, but relevant in space. First, high resolution photoelectron spectra yield spectroscopic constants that help to identify molecular ions that cannot be observed by microwave spectroscopy. Second, ionization cross sections determined in the laboratory are required to model the amount of ions in interstellar space. Finally, investigations of photodissociation and dissociative photoionization of reactive species



**Fig. 6:** Photoion-photoion coincidence maps after a) carbon, b) nitrogen and c) oxygen  $1s$  ionization. While the  $\text{CH}^+ + \text{NO}^+$  channel dominates at the carbon and oxygen edge, the N  $1s$  map shows intensities for the various fragmentation channels that are more evenly distributed. The ion pairs  $\text{CO}^+ + \text{O}^+$ ,  $\text{N}^+ + \text{N}^+$  and  $\text{O}^+ + \text{O}^+$  are due to contaminations from carbon dioxide, nitrogen and oxygen. Reproduced with permission from Ref. [21], American Institute of Physics.

are necessary to unravel the chemistry in the so-called photon-dominated regions in space. These examples highlight the relevance of photoionization experiments for astrochemistry.

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Ingo Fischer studied chemistry at the University of Bonn from 1984 to 1989 and obtained his Dr. rer. nat. 1992 at the TU München with Vladimir E. Bondybey at the Institute of Physical Chemistry. From 1993 bis 1995 he worked as a research associate in the femtosecond science program of the Steacie Institute for Molecular Sciences in Ottawa with Albert Stolow. In 1995 he moved to the ETH Zürich and obtained his *Habilitation* 1999 with research on the photochemistry of hydrocarbon radicals. During this time, he was associated with the group of Peter Chen at the Laboratory of Organic Chemistry. Since April 2001 he is Professor of Physical Chemistry at the University of Würzburg. His group investigates the chemistry of reactive intermediates with a focus on the relevance for astrochemistry, atmospheric chemistry and combustion science.

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„Ich glaube, wir haben eine gute Chance, die Gesetze zu entdecken, die das ganze Universum regieren.“

**Stephen Hawking**

„Die Neugier ist die mächtigste Antriebskraft im Universum, weil sie die beiden größten Bremskräfte im Universum überwinden kann: die Vernunft und die Angst.“

**Douglas Adams**

„Zu fragen, was war vor dem Beginn des Universums, ist so sinnlos wie die Frage: Was ist nördlich vom Nordpol?“

**Stephen Hawking**

„Die Liebe ist der Endzweck der Weltgeschichte und das Amen des Universums.“

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