# Identification of isomeric hydrocarbons by Rydberg photoelectron spectroscopy

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## ARTICLE INFO

## ABSTRACT

Many saturated and unsaturated organic hydrocarbons can assume multiple isomeric forms. At high temperatures, the identification of such isomers is difficult with conventional spectroscopic techniques, posing a challenge to the exploration of important processes such as the combustion of hydrocarbons. A recently developed technology using resonance enhanced multi-photon ionization via Rydberg states shows promise as an analytical technique, because the resultant photoelectron spectra provide well-resolved peaks that are sensitive to the molecular structure even at high temperatures. We tested this new method on isomeric hydrocarbon systems with the chemical formulas $C_5H_8$, $C_6H_8$, $C_7H_8$, and $C_{11}H_{10}$. Three-photon ionization with femtosecond pulses near 400 nm shows that in all systems the observation of distinct Rydberg features can serve to identify the isomers. In the $C_5H_8$ system, the photoelectron spectra of the isomers show Rydberg peaks from different quantum states, making the spectral identification of those isomers especially facile. Thus it appears that photoionization from Rydberg states could be developed into an analytical tool that is capable of distinguishing isomeric hydrocarbons even under adverse conditions such as flames and other combustion phenomena.

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## 1. Introduction

The identification of isomeric molecular forms poses challenges in many areas of active research. Examples are the identification of tracer molecules of explosive materials, the determination of structural folding of biopolymers and the time-resolved exploration of chemical dynamics reaction sequences. In the context of the latter research, it has recently been shown that the binding energy of electrons in Rydberg states is a sensitive measure of the isomeric and conformeric structure of molecules [1–3]. In its simplest implementation, a molecule is elevated to a molecular Rydberg state in a single-photon or multi-photon excitation scheme. The binding energy of the electron in its Rydberg state $E_B$ is then determined by ejecting it with a third photon, and measuring its kinetic energy (see Fig. 1). Because the vibrational energy remains conserved during the ionization out of the Rydberg state ($\Delta v = 0$), the corresponding peaks in photoelectron spectra are distinctly sharper than those for ionization out of valence excited states, where no such selection rule applies. The photoelectron kinetic energy therefore reveals the vibrational energy content of the molecule in the Rydberg level and the ion level, as well as the purely electronic energy of the Rydberg state.

Rydberg states are highly excited electronic states that derive from those of the hydrogen atom. The sensitivity of the binding energy of an electron in a Rydberg state toward the molecular structure can be understood by considering the wave function of the electron (Fig. 1b). As the electron passes the positively charged ion core, it experiences a phase shift. After one round trip, the electron wave function must interfere constructively with itself, so that the phase shift must be reflected in the energy of the orbital. Analogous to an electron diffraction experiment, the phase shift depends on the charge distribution of the entire molecule, i.e. it depends on the structure of the molecule. Thus the molecular structure is encoded in the binding energy of the electron in the Rydberg state. Measurement of this binding energy can therefore provide a characteristic fingerprint of the molecular structure which is virtually independent of excitation energy. Since the ionization from the Rydberg orbit is independent of vibrational excitation, the resultant photoelectron spectra are independent of any thermal excitation in the molecule, minimizing the effect of high temperatures.

The concept of using Rydberg orbital binding energies to fingerprint molecular structures has been verified in many molecular systems. The idea has found interesting applications in the study of molecular ionization dynamics [4], and of molecular fragmentation processes [5–7]. Beyond isomeric structures, the sensitivity of the Rydberg spectra extends even to conformeric forms of molecules with many internal degrees of freedom with internal temperatures up to 1000 K [8], which made possible the study of conformational dynamics of hot, flexible hydrocarbons [9].
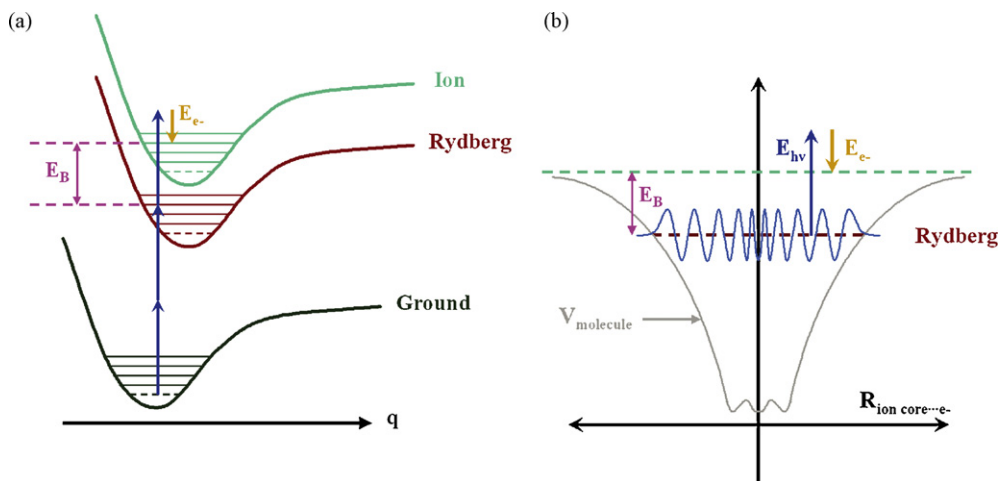
**Fig. 1.** The experimental scheme to measure the binding energy $E_B$ of an electron in a Rydberg state. Panel (a) shows the potential energy as a function of a molecular coordinate, while panel (b) plots it as a function of the distance of the electron from the ion core. A two-photon process prepares the molecule in a Rydberg state, and ionization in a one-photon step ejects the electron. The binding energy of the electron in the Rydberg state is obtained by subtracting the measured kinetic energy $E_{e^-}$ of the ejected electron from the photon energy.

Based on that knowledge, it appears that Rydberg photoelectron spectroscopy could be advantageously applied to achieve isomer-selective detection of many intermediates in combustion environments. As isomers can undergo quite different chemistries, isomer-specific information is critically important for the development of more efficient and cleaner combustion processes [10–12]. Not surprisingly, the experimental identification of isomeric species is a major task in current combustion chemistry research [13–16].

The objective of the present paper is therefore to explore if Rydberg spectroscopy is sufficiently sensitive toward molecular structure to distinguish the structurally very similar isomeric species that are found in flames of common fuels. We selected a group of chemically stable and commercially available molecules that form sets of isomeric pairs, consisting of closed-shell, linear and cyclic hydrocarbons. Specifically, we investigated the following sets of isomeric molecular pairs: the $C_5H_8$ systems cyclopentene and 1,3-pentadiene; the $C_6H_8$ systems 1,3-cyclohexadiene and 1,4-cyclohexadiene; the $C_7H_8$ systems toluene and 1,3,5-cycloheptatriene; and the $C_{11}H_{10}$ systems 1-methylnaphthalene and 2-methylnaphthalene.
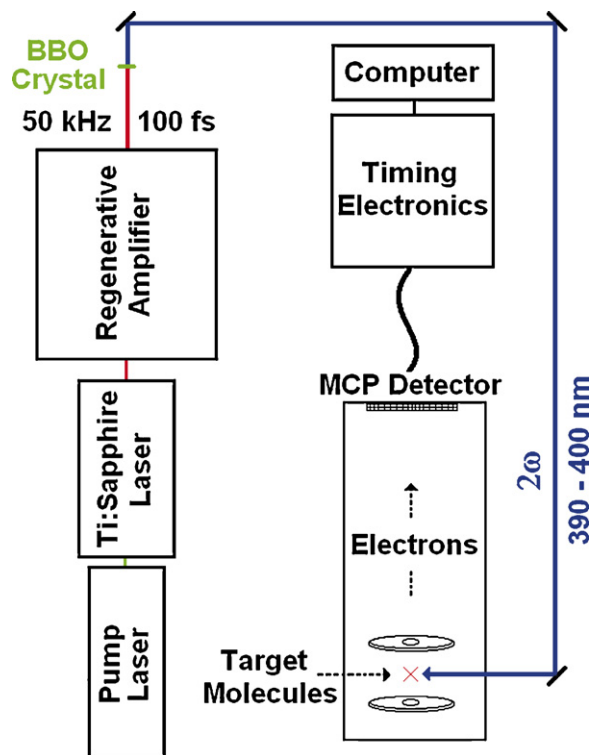
## 2. Experimental

The instrumental setup, including the photoelectron spectrometer and the laser system, has been described previously [17,18]. As illustrated in Fig. 2, a regenerative amplifier laser system generates pulses with a 50 kHz repetition rate and pulse duration of about 100 fs. The Ti:Sapphire gain medium affords a tuning range of 780–840 nm. For the current experiments, a single 0.3 mm BBO crystal is used for frequency doubling the fundamental beam to second harmonic ($2\omega$) wavelengths in the range of 390–400 nm. The resultant pulse energy is ~1.2 μJ.

The second harmonic laser beam is focused into an ultra high vacuum apparatus using a 200 mm UV-grade fused silica lens. The intensity at the focal spot is estimated to be $1.6 \times 10^{12}$ W/cm$^2$. A molecular beam is generated by expansion of sample vapors seeded in a Helium carrier gas (1 bar) through a 100 μm nozzle orifice and a 150 μm skimmer. Upon traversing the skimmer, the molecular beam crosses the laser beam at its focal spot. The kinetic energy of the ejected photoelectrons is measured with a time-of-flight analyzer using a 145 mm path length and time-resolved single par-

ticle counting electronics. In this scheme, photoelectron spectra are acquired at fixed ionization wavelengths, which are measured using a Spex 0.27 m Czerny-Turner grating monochromator.

1,3-Pentadiene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, 1,3,5-cycloheptatriene, and 1-methylnaphthalene were purchased from Sigma–Aldrich. Cyclopentene and 2-methylnaphthalene were purchased from Fluka, and toluene was purchased from Mallinckrodt Baker. All chemicals were used without further purification. While



**Fig. 2.** Diagram of the experimental setup: a laser system consisting of a diode pumped laser, a Ti:Sapphire oscillator laser, and a regenerative amplifier (itself pumped by another laser) generate a stream of 100 fs pulses with a repetition rate of 50 kHz. Upon second harmonic generation in a BBO crystal, the laser beam intersects a molecular beam. Photoelectrons are detected in a time-of-flight scheme by an MCP detector.