

## Correlated Rotational Alignment Spectroscopy of Isolated Molecules and Molecular Mixtures

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**Abstract.** We present a novel multi-pulse spectroscopic method for the correlated analysis of molecular mass, rotational structure and electronic structure. First experiments investigate carbon disulfide and butadiene.

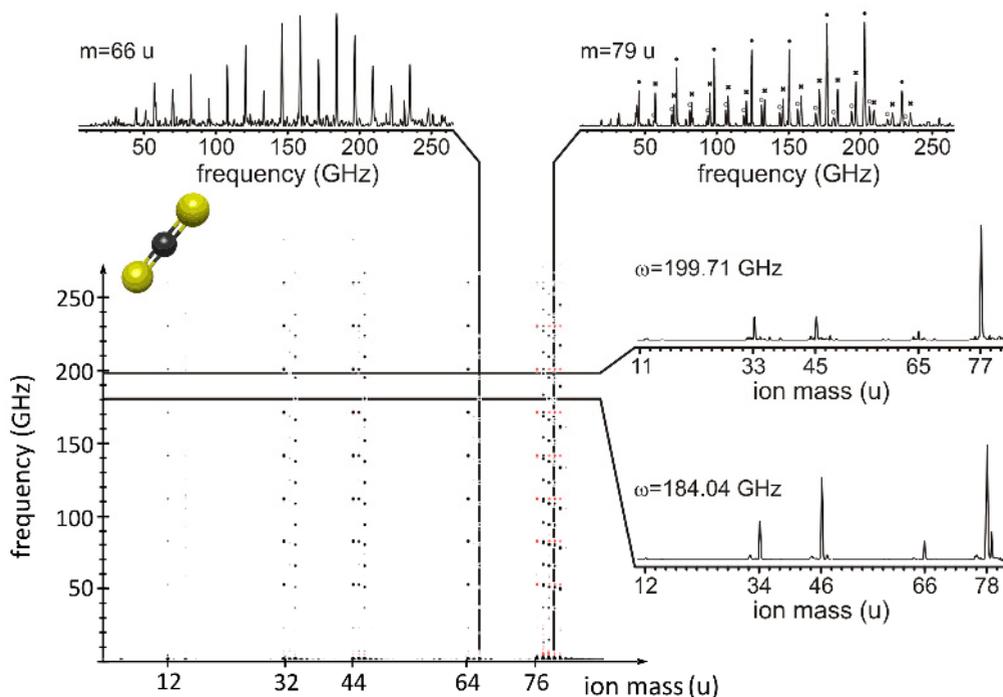
Electrons and ions formed in molecular ionization can be detected with quantum yields close to one, leading to an extraordinarily sensitive characterization of molecular mass and electronic structure. By using pump-probe ionization schemes, the characterization can be extended to photoexcited species to observe photochemical reactions in molecules and clusters [1-4]. The information content of such experiments, however, is insufficient for a spectroscopic assignment of molecular structure in all but the most trivial molecules. We recently presented the spectroscopic method of correlated rotational alignment spectroscopy (CRASY) to overcome this limitation [5]. CRASY allows the correlated (simultaneous) measurement of rotational structure, molecular mass, and electron binding energy for multiple molecules in a sample.

The presented method is based on the excitation of a rotational wave packet in the molecular electronic and vibrational ground state of molecules by means of non-adiabatic or (“impulsive”) alignment. The rotational motion influences the excitation probability in a subsequent photoexcitation event. By varying the delay between the wave packet creation and the photoexcitation steps, all spectroscopic observables tied to the photoexcitation event show a time-dependent modulation due to the evolution of the rotational wave packet.

Here a linearly polarized laser pulse (1 ps, 800 nm and 100  $\mu$ J) is used to create a rotational wave packet in the ground state of jet-cooled carbon disulfide and butadiene molecules. A delayed, parallel polarized UV laser pulse (60 fs, 200 nm and 2-3  $\mu$ J) ionizes the molecules via resonance enhanced multiphoton ionization (REMPI) and thereby probes the evolution of the rotational wave packet. Ions and electrons are detected in time-of-flight spectrometers to analyse molecular mass and electron binding energy. The observed time-dependent signals carry rotational structure information, which is encoded into signal modulations and can be extracted via Fourier transform. Resulting rotational Raman spectra are used to determine rotational transition frequencies and associated moments of inertia for all species in the jet. The technique allows the complete correlation between rotational structure, molecular mass (mass-CRASY) and electron binding energy (electron-CRASY).

Thus, CRASY has opened the door for the investigation of previously inaccessible spectroscopic properties, combining the high sensitivity and selectivity of mass spectrometry with high-resolution rotational structure. The direct observation of transient electronic structure is possible when REMPI is replaced by femtosecond pump-probe ionization.

Mass-CRASY data for  $\text{CS}_2$ , obtained in a single experiment, is shown in Figure 1. Mass signals in the range 76–82 u are due to the presence of  $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^{32}\text{S}$ ,  $^{33}\text{S}$ ,  $^{34}\text{S}$ , and  $^{36}\text{S}$  isotopes. In some cases, the isotopic composition is reflected in distinct masses (e.g.,  $^{32}\text{S}^{12}\text{C}^{32}\text{S}$  versus  $^{32}\text{S}^{13}\text{C}^{32}\text{S}$ ). In other cases, the composition leads to different moments of inertia and distinct rotational progressions (e.g.,  $^{32}\text{S}^{13}\text{C}^{32}\text{S}$  versus  $^{33}\text{S}^{12}\text{C}^{32}\text{S}$ ). REMPI also results in fragmentation into molecular and atomic fragments with masses 64–66 u ( $\text{S}_2$ ), 44–46 u (CS), 32–34 u (S) and 12 u (C).

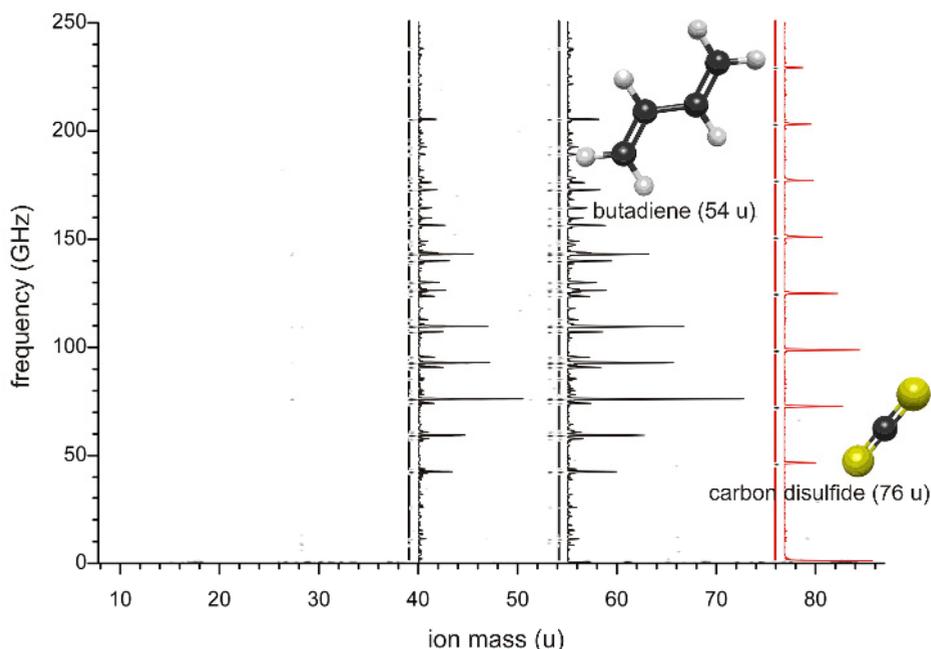


**Fig. 1.** Mass-CRASY data resolves multiple  $\text{CS}_2$  isotopologues and molecular ( $\text{S}_2$ , CS) and atomic (S,C) fragments. To show signal amplitudes spanning many orders of magnitude, signals are normalized to the noise amplitude in the rotational Raman spectrum. Vertical cuts through the data deliver rotational spectra for chosen masses. We show spectra for mass 79 u (top, right), containing a saturation signal from  $^{12}\text{C}^{32}\text{S}$  (dots) and progressions from two  $\text{CS}_2$  isotopologues  $^{33}\text{S}^{12}\text{C}^{34}\text{S}$  (circles) and  $^{32}\text{S}^{13}\text{C}^{34}\text{S}$  (crosses). The signal at mass 66 u (top, left) stems from  $^{32}\text{S}^{34}\text{S}$ , a fragmentation product of  $^{32}\text{S}^{13}\text{C}^{34}\text{S}$ . Vertical cuts yield mass spectra for a selected rotational transition frequency (right) and therefore show fragmentation products and parent for a single structure. Hence, observed fragment masses directly reflect the isotopic composition of the parent molecule.

A vertical cut through the data at a selected ion mass yields rotational Raman spectra of the neutral molecules before multiphoton ionization. Each spectrum contains information on the molecular moments of inertia and the relative angle of transition dipoles and thereby offers the required fingerprint for the assignment of molecular structure. The displayed dataset allowed the assignment of rotational constants for 10 of 20 naturally occurring  $\text{CS}_2$  isotopologues with abundances down to  $2 \times 10^{-6}$ . The ability to generate mass-selected rotational spectra with very high sensitivity will be useful for the structure determination of low-abundance compounds in impure samples.

A horizontal cut through the data at selected rotational frequencies delivers mass-spectra associated with well-defined rotational transition frequencies and distinct molecular ground state geometries. Fragments formed after the excitation process show the rotational spectrum of the parent molecule. Their masses appear in the same frequency-selected mass spectrum as shown in the right part of Figure 1. CRASY therefore allows the unambiguous assignment of fragmentation channels. If enough fragments are observed, even the atomic composition of a molecule can be directly assigned in complex samples.

CRASY experiments can be performed with heterogeneous samples. In Figure 2, we show the mass-CRASY dataset for a molecular mixture containing 1,3-butadiene and carbon disulfide. Corresponding parent ions and fragmentation products can be identified by their rotational Raman spectra. Structural data for butadiene is currently analysed.



**Fig. 2.** The figure shows mass-CRASY data for a heterogeneous sample of 1,3-butadiene and carbon disulfide. Vertical cuts at the masses of parent molecules and fragments reveal rotational Raman spectra which contain structural information about the parent molecules.

Similar experiments with electron detection were performed and give structure-selected electron spectra. This allows the indirect correlation of ion masses and electron binding energies via rotational transition frequencies.

CRASY offers new possibilities to determine rotational spectra, electronic structure, and photochemical dynamics and fragmentation channels for low-abundance compounds in impure samples or for inseparable molecular isomers. It should therefore become the method of choice to investigate structure and fragmentation pathways of complex (bio-) molecules and clusters. New data, measured with a rotational bandwidth of 62.5 MHz, offers sufficient resolution to assign molecular structure in fairly large and complex molecules. The technology for a simultaneous investigation of multiple molecular properties in heterogeneous samples is therefore established.

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