Isomer discrimination of polycyclic aromatic hydrocarbons in the Murchison meteorite by resonant ionization

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Abstract

We have used two-color resonant two-photon ionization (2C-R2PI) mass spectrometry to discriminate between isomers of polycyclic aromatic hydrocarbons in the Murchison meteorite. We measured the 2C-R2PI spectra of chrysene and triphenylene seeded in a supersonic jet by laser desorption. Since each isomer differs in its R2PI spectrum, we can distinguish between isomers using wavelength dependent ionization and mass spectrometry. We found both chrysene and triphenylene in sublimates from carbonaceous residue obtained by acid demineralization of the Murchison meteorite. Their R2PI mass spectra show only the molecular ion, even though these samples contain a complex inventory of organic molecules.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are among the most ubiquitous organic molecules in the universe [1, 2]. PAHs are very stable molecules and have been reported in interplanetary dust particles [3], meteorites [4-9], and comets [10]. They are also suspected to be in the interstellar medium [11]. On Earth, PAHs mainly originate from anthropogenic emissions such as combustion of fossil fuels.

Many structural isomers exist for PAHs and their differentiation by mass spectrometry is difficult. Electron ionization mass spectra of isomeric PAHs are virtually identical. Other mass spectrometric techniques have been applied with varying degrees of success. For example, Elson and Sim have demonstrated isomer discrimination of PAHs by chemical ionization mass spectrometry with carbon dioxide and analysis of characteristic fragment ions [12]. Ng et al. differentiated isomeric PAHs using ion intensity ratios from electrospray Ag(I) cat-ionization mass spectrometry [13]. Generally, additional techniques, e.g. gas chromatography, must be used to separate each isomer before mass spectral identification.

Laser desorption/laser multiphoton ionization mass spectrometry (L^2MS) has become a popular choice for analyzing PAHs in meteorites [3, 8, 9, 14-16]. The majority of these studies use 266 nm light for ionization since this wavelength is suitable for ionizing aromatic molecules by two photons via an electronic excited state. Isomer discrimination is not possible in a typical laser mass spectrometry setup and molecular assignment is

usually based on the isomer with the highest ionization efficiency at 266 nm. However, wavelength dependent resonant two-photon ionization (R2PI) spectra differ for specific isomers [17-22]. To capitalize on this property for isomer selectivity we couple laser mass spectrometry with supersonic jet expansion and resonant ionization. In a supersonic jet expansion, only a few rovibronic states of the entrained molecule are populated, leading to sharp R2PI spectra. We can thus achieve isomer selection by careful choice of wavelengths for excitation and ionization. In favorable cases, this approach also greatly simplifies the mass spectrum, since only the molecule of interest will be resonantly ionized and detected. Here we apply these concepts to measure the two-color R2PI spectra of chrysene and triphenylene and analyze for these molecules in a complex meteorite sample. These molecules are not resolved by gas chromatography-mass spectrometry, which makes their absolute identification in the Murchison meteorite difficult [23].

2. Experimental

Chrysene and triphenylene were purchased from Sigma-Aldrich Co. and used without further purification. Chrysene and triphenylene are PAH molecules that are isomers, with a monoisotopic mass of 228 (see figures 3 and 4 for structures).

The carbonaceous residue from an acid demineralization of Murchison meteorite was kindly provided by Dr. Luann Becker (Institute for Crustal Studies, University of California Santa Barbara). Powdered bulk meteorite was demineralized by HF-BF$_3$ to

isolate and concentrate organic matter [24]. We then extracted this carbonaceous residue by vacuum sublimation from a stainless steel micro-oven with a 1 mm orifice, depositing sublimates in a small spot of approximately 3 mm on a graphite substrate. We used sublimation temperatures of 200 °C and 600 °C with the collecting surface at room temperature while maintaining a vacuum pressure around 5×10^{-5} torr using a small diffusion pump. Attempts to vacuum sublime untreated, powdered samples of Murchison meteorite were unsuccessful. This was consistent with previous work where amino acids and nucleobases could be sublimed successfully but do not sublime from Murchison powder [25]. Possible explanations were that divalent cations or the kerogen-like components in the meteorite may inhibit sublimation.

The experimental setup has been described in detail elsewhere [26]. We laser desorb a thin layer of PAH from a graphite substrate in front of a pulsed nozzle. The desorption laser, a Nd:YAG operating at 1064 nm, is attenuated to 1 mJ cm^{-2} and focused to a spot approximately 0.5 mm diameter within 2 mm in front of the nozzle orifice. We translate the graphite substrate in order to expose fresh sample to successive laser shots. The nozzle consists of a pulsed valve with a nozzle diameter of 1 mm and a backing pressure of 6 bar of argon gas. The neutral molecules are skimmed and then ionized using a two-color two-photon process (2C-R2PI). The first photon from a tunable dye laser excites the molecule to an electronic excited state. Subsequently a second photon from another tunable dye laser ionizes the molecule of interest. For the second photon we used a fixed wavelength of 280 nm. A higher energy photon was needed since twice the one-color photon energy is less than the ionization potential for both triphenylene and chrysene. In

some cases, we also used 266 nm for both excitation and ionization for survey mass spectra. We detect ions in a reflectron time-of-flight mass spectrometer. Typical mass resolution ($m/\Delta m$) is 700 or higher.

We obtain resonant two-photon ionization (R2PI) spectra by monitoring mass selected peaks while tuning the excitation (i.e. first color) wavelength. When the spectroscopy of a compound is known, we can tune the wavelength to a given resonance in order to selectively ionize it and obtain an isomer specific mass spectrum. We observed that the graphite substrate alone does not contribute any significant signal in the mass spectrum.

3. Results and discussion

For an initial survey analysis of PAHs in the meteorite sample, we analyzed sublimates at a non-resonant wavelength of 266 nm. It is well documented that compound distribution and concentration in meteorites can be extremely heterogeneous and can be further altered by the type of extraction procedure used [27]. Figure 1 shows the mass spectrum of sublimate from the Murchison acid residue sublimed at 200 °C. Major peaks can be assigned to polycyclic aromatic hydrocarbons, including some fragmentation products. These peaks are very similar to those we observed previously and ascribed to PAHs [4]. In that earlier work we used isotope measurements to confirm the extraterrestrial nature of the extracted material. The mass spectrum is also similar to those of samples of ALH84001 analyzed by TOF-SIMS [28, 29]. Only the abundances are different; however, this is to be expected since fragmentation occurs during the SIMS process. In our mass

spectrum, the most intense mass peaks are at m/z 202, 226, and 228 corresponding to pyrene, benzo[ghi]fluoranthene, and triphenylene. Since many different structural isomers exist at each mass peak, the tentative assignments represent only examples of families of isomers; however we will investigate the isomers at m/z 228 in further detail below.

Figure 2 shows the mass spectrum of sublimate from the Murchison acid residue sublimed at 600 °C. Compared to the 200 °C sublimate, the mass spectrum is much more complex and contains higher molecular weight PAHs. At higher sublimation temperature, the less volatile, higher molecular weight compounds can be effectively extracted. PAHs with up to 8 rings are readily identified. We also detect the same lower masses in both the low and high temperature sublimates.

Figure 3 shows the two-color R2PI spectra of chrysene and triphenylene from 320 to 340 nm. In both cases, the second photon is 280 nm. The second color is necessary for efficient ionization out of the excited state since the energy of two photons in the one-color range does not suffice for ionization. The 2C-R2PI spectrum for triphenylene matches very well with the recently published laser induced fluorescence spectrum [30]. To our knowledge, the R2PI spectrum of chrysene probes a new wavelength region and only a laser induced fluorescence spectrum of the $S_1 \leftarrow S_0$ transition has previously been published [31]. Both 2C-R2PI spectra are sharp and well resolved and provide many distinct wavelengths to use for follow-up analysis.

Aside from the analytical application, gas phase spectra of large, neutral PAHs provide important data for comparison to the unidentified carriers of the diffuse interstellar bands [32]. The cold nature of the supersonic jet expansion mimics the conditions of the interstellar environment (e.g. low temperature and low density). Another potential application is differentiating PAH sources (e.g. extraterrestrial versus terrestrial) by ratio of isomer pairs, which could circumvent the immediate need for isotopic measurements. This type of analysis has been previously demonstrated to distinguish PAHs derived from automobile emissions, biomass, coal, and petroleum combustion [33, 34].

Figure 4 shows the mass spectra of sublimate from the Murchison acid residue at 200 °C measured at various one-color wavelengths while the second color is again fixed at 280 nm. The top trace was measured at 329.35 nm, a resonant wavelength of triphenylene. The middle trace was measured at 328.88 nm, a resonant wavelength of chrysene. The bottom trace was measured at an excitation wavelength of 329.30 nm, which is non-resonant for either species. In this analysis mode we observe only one peak in the mass spectrum, corresponding to the specific isomeric compound selected by the resonant wavelength. In contrast, a clean baseline is observed at the non-resonant wavelength. The R2PI technique *selectively* ionizes the specific PAH providing discrimination against a background of other compounds present in the low temperature sublimate. Since we obtain a signal at the resonant wavelength of each isomer, this result establishes that both chrysene and triphenylene are present in the Murchison acid residue.

Even without the unique selectivity of resonant ionization of a single compound, we can use wavelengths to optimize sensitivity for selected classes of compounds. For example, we can enhance the relative two-photon ionization efficiency of alkylated compounds by choosing a wavelength somewhat further to the blue. A higher density of vibronic states should exist because of the many possible low-frequency alkyl modes. Figure 5 shows the mass spectrum from the 600 °C sublimate at the non-resonant excitation wavelength of 322 nm with 280 nm ionization. In this mode of ionization we can identify three series of peaks with 14 Da increments, correlating with a possible alkylation series of the PAHs at base masses of 216, 228, and 240 Da. The unsubstituted base peaks are absent indicating the excitation wavelength is not resonant for the unsubstituted compounds. Elsila et al. have shown that higher abundances of alkylated PAHs correlate with a higher degree of aqueous activity in the meteorite [14]. In our mass spectrum, alkylation is clearly discernable and the complexity is reduced as a result of switching the wavelength (from 266 nm). Alkyl derivatives of PAHs have slightly shifted resonant absorptions, so in principle it is possible to further identify specific alkyl isomers by optimizing their resonant spectra. Future studies can thus take advantage of wavelength tunability to investigate important phenomena such as alkylation pathways to help elucidate the chemical history of meteoritic material.

4. Conclusion

Two-color resonant two-photon ionization mass spectrometry is a useful tool for isomer discrimination since it identifies molecules by both their mass and their vibronic

spectroscopy. This specificity is unique compared to other mass spectrometric techniques. We have used this approach to resonantly detect and differentiate triphenylene and chrysene in sublimates from the carbonaceous residue of the Murchison meteorite. The R2PI technique selectively ionizes the PAH, providing positive identification of specific isomers and discrimination against a background of other compounds. By tuning the excitation wavelength, we can also observe aromatic compounds with high degrees of alkylation.

Acknowledgements

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FIGURE CAPTIONS

Figure 1: Survey mass spectrum of 200 °C sublimate from Murchison acid residue. The photoionization wavelength is 266 nm. Since several structural isomers exist for all mass peaks, only examples are given for the labeled peak.

Figure 2: Survey mass spectrum of 600 °C sublimate from Murchison acid residue. The photoionization wavelength is 266 nm. Higher molecular weight peaks are labeled above. Refer to figure 1 for lower molecular weight peak assignments.

Figure 3: Two-color R2PI spectra of triphenylene (bottom) and chrysene (top). The first photon wavelength is scanned while the second photon wavelength is fixed at 280 nm for ionization.

Figure 4: Mass spectra of 200 °C sublimate from Murchison acid residue. Top trace is recorded at a resonant wavelength of triphenylene (329.35 nm), middle trace is recorded at a resonant wavelength of chrysene (328.88 nm), and bottom trace is recorded at a non-resonant wavelength (329.30 nm) for either species. The 2nd photon wavelength is 280 nm in all cases.

Figure 5: Mass spectrum of sublimate from Murchison acid residue at 600 °C. Excitation wavelength is 322 nm and ionization wavelength 280 nm. Circles indicate one series of alkylated compounds starting at 230 Da, triangles indicate a second of alkylated compounds starting at 242 Da, and squares indicate a third series of alkylated compounds starting at 254 Da.
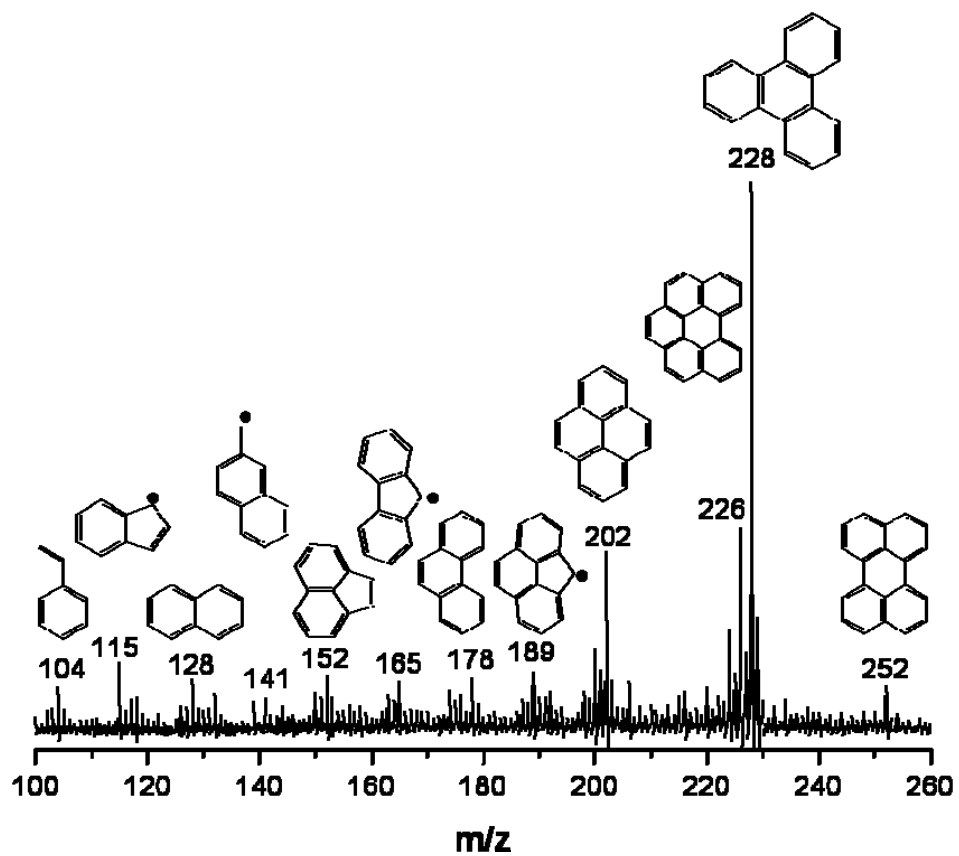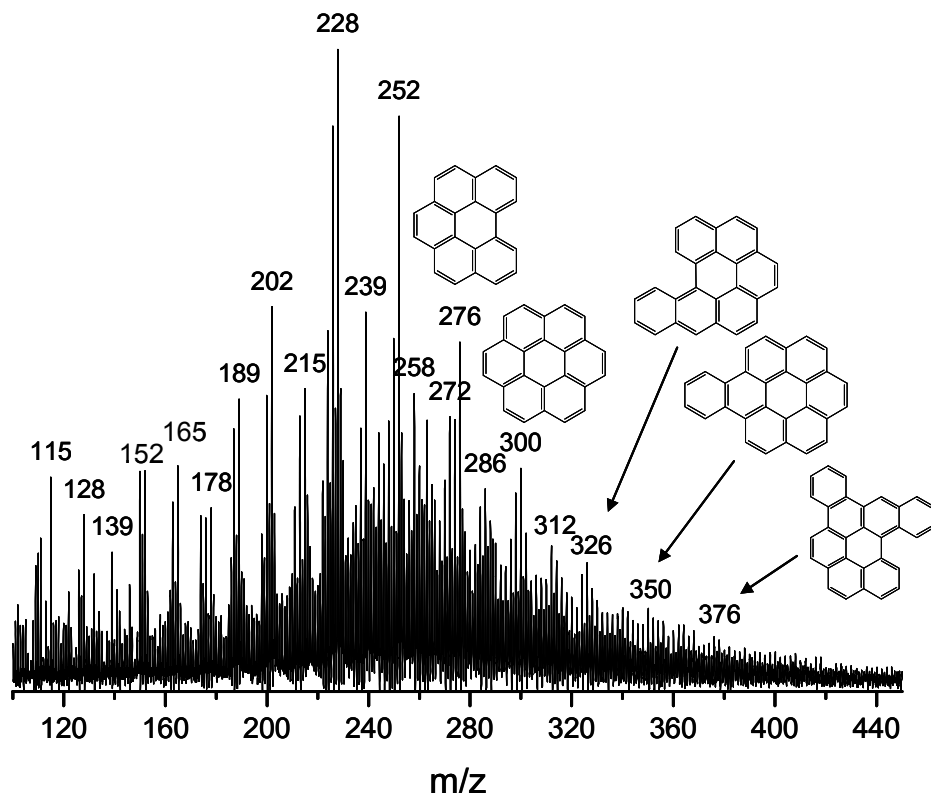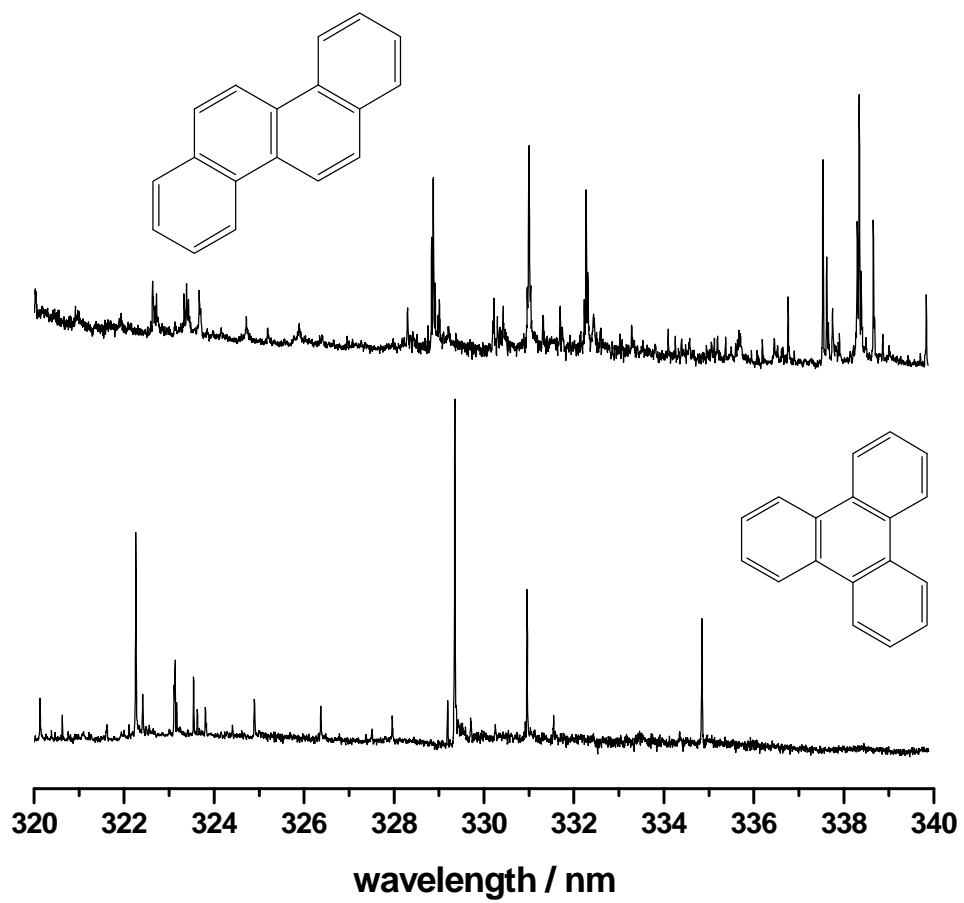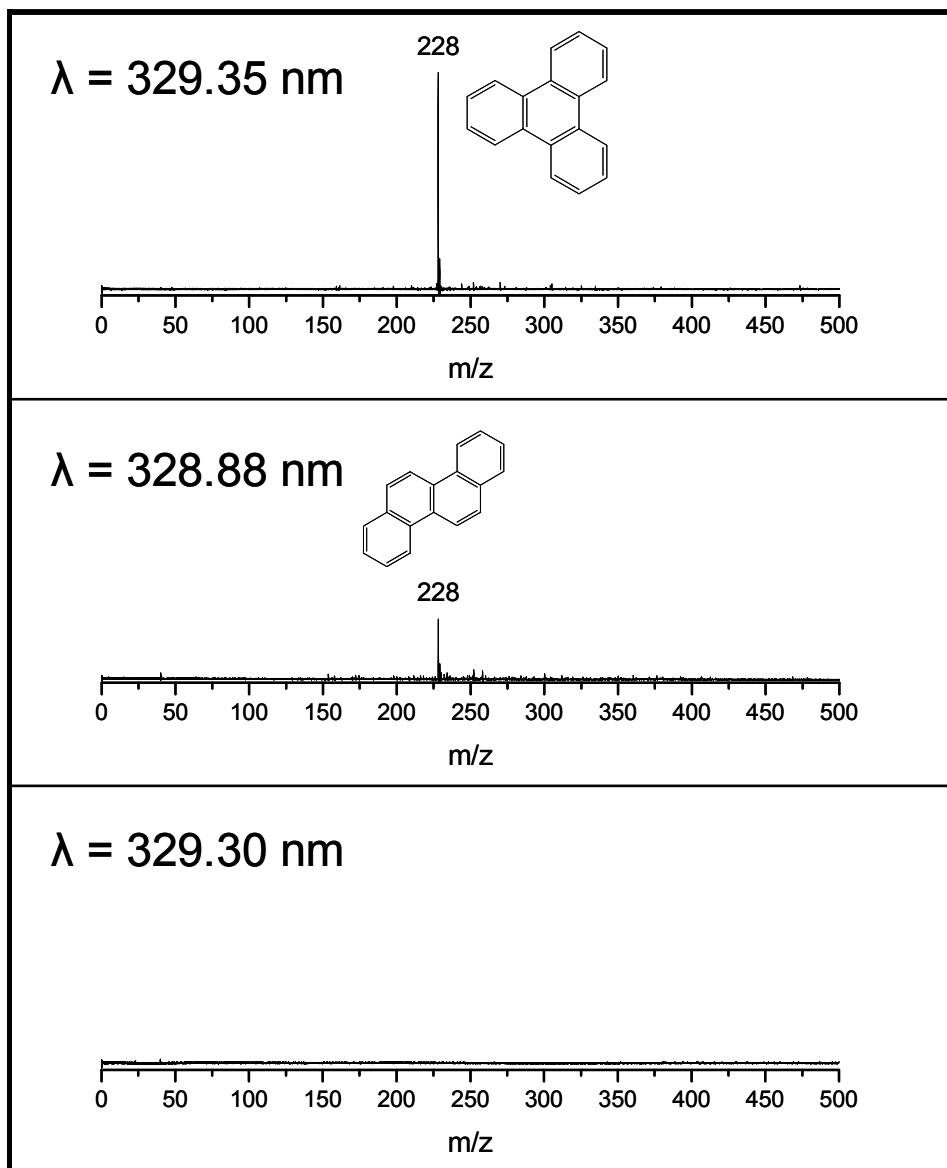
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