

QnAs with Daniel Neumark

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Polycyclic aromatic hydrocarbons (PAHs) are organic molecules composed of two or more rings of carbon and hydrogen atoms. Their role in combustion, soot formation, and possibly interstellar chemistry, as well as their adverse health impacts, raise the importance of understanding the structure and dynamics of PAH molecules. Daniel Neumark, a physical chemist at the University of California, Berkeley, and a recently elected member of the National Academy of Sciences, investigates the structures of chemical compounds using slow photoelectron velocity-map imaging (SEVI). The method spectroscopically represents the structure and vibrational frequencies of cryogenically cooled anions with high resolution. Neumark and colleagues sought to apply SEVI to study radical anions of anthracene, a three-ring PAH. He recently spoke to PNAS about his findings.

PNAS: How did you become interested in PAHs?

Neumark: Partly because they are important species, both in atmospheric and combustion chemistry, but also because we were interested in testing out the [SEVI] technique. One of the challenges of this method has been to see how large and complex a system we can apply it to. Hence, PAHs seemed like a very good model system because they're important in their own right, and from a spectroscopic view are technologically challenging, particularly the radicals, which are the species that we characterized in our experiments.

PNAS: PAHs have a wide range of compositions and chemistries. What are the fundamental characteristics of a polycyclic aromatic hydrocarbon?

Neumark: Well, you need at least two benzene rings fused together. Naphthalene, which would be two benzene rings, would be the smallest polycyclic aromatic hydrocarbon. And then they can grow to be very large. Ovalene, for example, comprises 10 fused rings.

PNAS: How can PAHs impact environmental or personal health?

Neumark: They play a key role in combustion chemistry. And they are generally thought to be soot precursors. So, understanding how flames produce soot often involves coming up with models for how when you burn small molecules, small hydrocarbons, like you do in your car or in a power plant, how those eventually get converted into PAHs or fragments of

PAHs, which then form macroscopic soot particles. So they're thought to be intermediates in soot formation. In that sense, they have significant environmental impact. They're also most likely carcinogenic, and they have adverse health effects.

PNAS: Some researchers are searching for signatures of PAHs in interstellar space. Why would we expect to find them there?

Neumark: The so-called diffuse interstellar bands are absorption bands, like you see in the visible and the infrared, and thus far they're unassigned, but many people believe that some form of PAHs are responsible. That's the main reason.

There's also an issue of how these species are formed in the first place. They are fairly complex molecules; they have to be thermodynamically stable and reasonably photoresistant to degradation in the interstellar medium. So, both from a kinetics point of view and the spectroscopic point of view, they're interesting from the perspective of the interstellar medium.

PNAS: How does your Inaugural Article (1) add to our understanding of PAH chemistry?

Neumark: We have characterized the deprotonated form of anthracene, which is a very common PAH, and we've done spectroscopy on the radical. There's basically three ways to pull a hydrogen off of anthracene and we, working with some synthetic organic chemists, came up with a scheme by which we could add a leaving group to the anthracene skeleton and then make three types of negative ions, depending on where you put the leaving group. That gave us access to the three isomers of the radical, and we were able to spectroscopically and energetically characterize the three isomers. And that's of interest because, just from the point of view of fundamental



Daniel M. Neumark. Image courtesy of Daniel M. Neumark (University of California, Berkeley, CA).

This is a QnAs of a recently elected member of the National Academy of Sciences to accompany the member's Inaugural Article on page 1698.

chemistry, the three isomers are different, and they have different electron binding energies. The degree of distortion that happens when you remove an electron differs, the vibrational frequencies differ, the excited-state energies differ. So, the article is an interesting demonstration of how fairly subtle structural effects can be characterized spectroscopically.

PNAS: This study was an effort to determine the capabilities of SEVI. What other research areas can the method be applied to?

Neumark: Well, this work is part of a larger effort to expand the boundaries of the cryo-SEVI technique. We've applied it to, for example, transition metal oxide clusters, which are very important model systems for catalysis. They've been largely intractable, spectroscopically. We're certainly interested in moving

through larger PAH systems, [i.e.] how many carbon rings we can actually add to these anions and radicals and still observe a highly structured spectrum that we can assign. We've also used SEVI to characterize the transition state of chemical reactions. We start with a stable negative ion, which is designed so that when we pull off the electron, we access the transition state of the neutral reaction and observe vibrational structure associated with the transition state. And we've been able to observe sharp structure in those spectra that are connected with a phenomenon called reactive resonances. This just appeared in a *Science* paper (2). So it's a very powerful technique in principle and we're trying to demonstrate the extent of its applicability.

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- 1 Weichman ML, DeVine JA, Levine DS, Kim JB, Neumark DM (2016) Isomer-specific vibronic structure of the 9-, 1-, and 2-anthracenyl radicals via slow photoelectron velocity-map imaging. *Proc Natl Acad Sci USA* 113:1698–1705.
 - 2 Kim JB, et al. (2015) REACTION DYNAMICS. Spectroscopic observation of resonances in the $F + H_2$ reaction. *Science* 349(6247): 510–513.