

Candian and her coauthors that the AIBs arise from individual, free-floating polycyclic aromatic hydrocarbon (PAH) molecules is widely accepted but has not been proven. (For a detailed critique of the PAH hypothesis, see reference 1.)

Candian and her coauthors state that no specific PAH has been definitively identified with any of the AIBs, which are sometimes referred to in the literature as the unidentified IR emission features. Also, the AIBs are conjectured to arise from the absorption of UV radiation by PAH molecules that then undergo IR fluorescence. Although evidence of PAH absorption in the UV is expected, none has been found so far.<sup>2</sup> It is difficult to understand how only a specific set of PAHs can arise from a wide range of astrophysical conditions.

The broad, smoothly varying shapes and widths of the AIBs are characteristic of solid-state emission bands. "Plateau" emission features underlying the main AIB peaks also suggest a solid-state or small-grains origin.<sup>3</sup>

Continuum emission in reflection nebulae and in the interstellar medium is consistent with nonequilibrium thermal emission from very small grains (nanoparticles) with tens to hundreds of carbon atoms.<sup>4</sup> PAHs do not explain the continuum emission because molecules have no absorption between absorption bands, nor to our knowledge do any laboratory or theoretical spectra convincingly replicate the continuum emission under the AIBs. A small-grain component may produce the continuum emission, which is consistent with the production of the plateau emission.

Amorphous carbonaceous nanoparticles might account for both the continuum emission and the AIBs. Many laboratory and amorphous carbonaceous materials—including hydrogenated amorphous carbon, soot, quenched carbonaceous composite, kerogen- and coal-like substances, and mixed aromatic and aliphatic organic nanoparticles—have been proposed as candidates for the AIB carriers.<sup>5</sup> In the interstellar medium, one would expect abundant elements such as nitrogen, oxygen, and sulfur rather than just the carbon and hydrogen of PAHs, since the dust grains are formed in many complex interstellar and circumstellar environments.<sup>1</sup>

All the above proposed AIB sources

would contain aromatic PAHs and aliphatic hydrocarbons in varying amounts. Such materials typically can explain some but not all of the emission bands, and the laboratory materials often show spectral bands that are not observed in the AIBs. Unfortunately, it is not yet possible to theoretically derive emission spectra of amorphous carbonaceous particles nor to closely simulate conditions in the interstellar medium in laboratory studies.

Efforts to pin down the carrier of the AIBs continue in astronomical and laboratory studies. The wonder is how nature can produce such a relatively simple spectrum from intrinsically complex organic material that has defied definite identification for nearly four decades.

## References

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**Alan T. Tokunaga**

([tokunaga001@gmail.com](mailto:tokunaga001@gmail.com))

University of Hawaii at Manoa  
Honolulu

**Roger F. Knacke**

([rknacke@gmail.com](mailto:rknacke@gmail.com))

Pennsylvania State University Behrend  
Erie

## ► Candian, Zhen, and Tielens reply:

Klavs Hansen and Piero Ferrari insightfully point out the importance of electronic fluorescence from thermally populated electronic states. Direct electronic fluorescence is a well-known process that occurs when excitation is temporarily trapped in, for example, the  $S_1$  state during the internal conversion cascade whenever relaxation to the ground state is hampered by a large energy gap. Because internal conversion is a reversible process, an excited electronic state can be revisited and electronic fluorescence can also compete with vibrational fluorescence later on during the relaxation process. Delayed electronic fluorescence emission was measured in the 1960s for small polycyclic aromatic hydrocarbons (PAHs), including coronene<sup>1</sup> ( $C_{24}H_{12}$ ). As Hansen and Ferrari point out, it was

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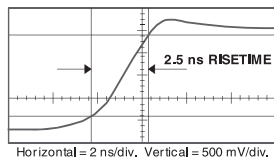
FET can be cooled

Noise: <100 e<sup>-</sup> RMS (Room Temp.)  
<20 e<sup>-</sup> RMS (Cooled FET)

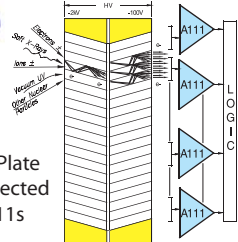
Gain-Bandwidth  $f_T$  > 1.5 GHz

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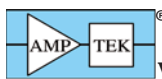


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also measured more recently in elegant thermo-ionic studies on small carbon-chain and fullerene anions.

Delayed fluorescence is controlled by the energy gap, which sets the fractional population of electronic states, and by competition between radiative and non-radiative processes, which depopulates electronic states. Despite the potential importance of delayed fluorescence, systematic studies of it are lacking, and it has received scant attention in astronomy. As Hansen and Ferrari emphasize, molecular stability in the interstellar medium may be closely tied to delayed fluorescence. Electronic fluorescence may also provide a means to characterize and identify specific molecules present in space. The narrow bands in the visible spectrum of the stellar outflow, the Red Rectangle, are generally ascribed to electronic fluorescence of large molecules, illustrating that further study of the processes involved might be beneficial.

Alan Tokunaga and Roger Knacke return to arguments first raised against the interstellar PAH hypothesis in the late 1980s. Studies driven by those arguments greatly elucidated the characteristics of the aromatic infrared band (AIB) carriers and helped to solidify the presence and importance of PAHs in space.<sup>2</sup> The AIBs are carried by 50 carbon-atom PAH species. Some very weak AIBs may be due to functional groups—for example, methyl or quinone groups—attached to an aromatic skeleton, but their fractional coverage is small compared with aromatic H. Although some of the debate may seem semantic, we emphasize that 50 C-atom species behave, emit, and evolve like molecules. A treatment based on solid-state physics is sometimes convenient but obfuscates the underlying molecular physics. Three issues raised by Tokunaga and Knacke—the AIB profile, the underlying continuum, and the dearth of electronic absorption features—are a result of thinking about the PAHs through a solid-state physics lens rather than from a molecular perspective.

Anharmonic behavior is a key aspect of vibrational spectroscopy. Recently, anharmonic density functional theory calculations of moderately sized PAHs have come within reach, and resulting spectra agree well with laboratory experiments.<sup>3,4</sup> Calculations following the energy cas-

cade of highly excited PAHs are in good agreement with AIB positions and provide a natural explanation for the observed, red-shaded AIB profiles.<sup>5</sup> Anharmonic interactions may also lead to a vibrational quasi continuum.<sup>6</sup> Alternatively, the delayed electronic fluorescence process pointed out by Hansen and Ferrari may result in a near-IR continuum.

Finally, the rapid (10–100 fs) nonradiative decay channels provided by conical intersections of highly excited electronic states<sup>7</sup> broaden UV absorption bands, and astronomical instruments are not well suited to detect resulting weak and broad features. The nano-grain approach misses those molecular-physics aspects and cannot explain the observations.

After the discovery of the first diatomic molecules some 100 years ago, astrophysicist Arthur Eddington lamented that “atoms are physics, but molecules are chemistry.” Ever since, astrophysicists have regretted that sometimes simple physical formulas have to give way to complex chemical solutions in a molecular universe. To us, though, interstellar molecules provide a tool to probe macroscopic aspects of the universe, whereas the harsh environment of space offers unique insight in microscopic processes controlling excitation and relaxation of isolated molecules.

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**Alessandra Candian**  
**Xander Tielens**

([tielens@strw.leidenuniv.nl](mailto:tielens@strw.leidenuniv.nl))

Leiden Observatory

Leiden University, Netherlands

**Junfeng Zhen**

University of Science and

Technology of China

Hefei