

Mass Spectrometers for Residual Gas Analysis

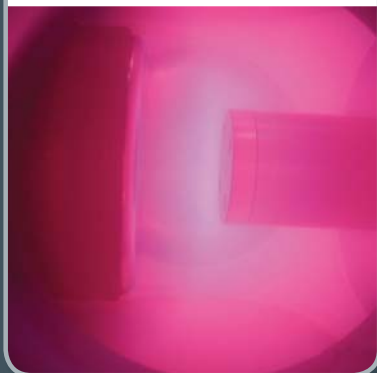
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The above-mentioned cases represent the tip of the iceberg. Anyone who has dual citizenship or is a doctoral student residing or studying in another country is taking serious chances when returning to Iran for a professional or family visit. Although the US sanctions contribute to the hardships experienced by our Iranian colleagues, the actions of the Islamic Revolutionary Guard Corps are largely responsible for making the lives of the Iranian scientists miserable.

References

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More whiffs of the aromatic universe

Authors Alessandra Candian, Junfeng Zhen, and Xander Tielens ("The aromatic universe," *PHYSICS TODAY*, November 2018, page 38) give us a glimpse of the remarkable progress made by astrophysicists and astronomers in identifying carbon-based molecules found in the interstellar medium. That progress includes the identification of a subset of the diffuse interstellar band, one of the most enduring astrophysical riddles.

In addition to the emission of IR vibrational radiation and absorption across the visible spectrum into the UV, polycyclic aromatic hydrocarbon (PAH) molecules can also emit radiation from thermally populated excited electronic states. That radiation can have an important stabilizing effect on the molecules. The effect, predicted by Abraham Nitzan and

Joshua Jortner in 1979, has been observed in several molecules, including fullerenes in which the radiation was seen to be enhanced two orders of magnitude or more relative to purely vibrational cooling.¹

Also, the hydrogen-containing PAH molecule anthracene was identified as a radiator,² and thermally emitted photons have been measured³ from pure carbon clusters as small as C_4^- and C_6^- . The large disparity in cooling rates for C_4^- and C_6H^- also illustrates the extreme variation caused by seemingly very small differences in molecular composition.⁴ At excitation energies in which radiation competes with electron emission from those species, the photon-emission rate constants are $8 \times 10^4 \text{ s}^{-1}$ for C_4^- , for example,⁵ and the energies removed (1.34 eV and 2.71 eV for the two allowed transitions) are an order of magnitude higher than vibrational quanta. Such extreme molecule-specific radiative cooling translates into strongly varying molecular survival probabilities after photoexcitation and may have significant implications for the populations of fullerenes, PAH molecules, and other molecules in interstellar space.

References

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The aromatic infrared bands (AIBs) discussed by Alessandra Candian, Junfeng Zhen, and Xander Tielens were discovered in interstellar and circumstellar environments in the 1970s. Since then, their origin has been a topic of interest. The hypothesis advanced by

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.² 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.³

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.⁴ 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.⁵ 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.¹

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.

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► 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 coronene¹ ($C_{24}H_{12}$). As Hansen and Ferrari point out, it was

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