oligomers can still be increased by a structural control of molecular organization, as shown in recent work (8). The solubility of these oligomers in chlorinated solvents, such as dichloromethane or 1.1.2.2 tetrachloroethane, is high enough to produce thin films by spin-coating or casting techniques (9), which widens the technological access to such all-polymer devices. Any kind of substrate can be considered in step 2, depending on the mechanical properties desired for the device. Concerning the gate, source, and drain electrodes, a silver paste-based polymer ink (Acheson) has also been successfully used in this work. However, other organicbased materials could be used, such as conducting polyaniline polypyrrole or polythiophenes (10-12), with achievable resolution as the goal. Although the present device is largely oversized, conventional printing techniques would allow us to reach some 50 µm for channel length, which means that channel widths of 0.5 to 1 mm would be required to effect significant amplification. These dimensions may appear large, but recent reports have pointed out that an interesting potential exists for macrosized chips in the display area (13). It must also be stressed that patterning techniques applied to organic conducting polymers have been shown to allow the realization of micrometer-sized electrode arrays, which should extend the possibilities of such all-polymer devices to a readily usuable device (10). This work has shown that devices fully based on polymer materials can be fabricated by only the use of printing techniques, and the interesting results appear promising for the development of large-area, low-cost plastic electronics.

REFERENCES AND NOTES

- 1. G. Horowitz, D. Fichou, X. Z. Peng, Z. G. Xu, F. Garnier, *Solid State Commun.* **72**, 381 (1989).
- 2. J. H. Burroughes et al., Nature 347, 539 (1990).
- F. Garnier, X. Z. Peng, G. Horowitz, D. Fichou, Adv. Mater. 2, 592 (1990).
- 4. G. Gustafsson et al., Nature **357**, 477 (1992).
- S. M. Sze, Semiconductor Devices, Physics and Technology (Wiley, New York, 1985), pp. 341–362.
 F. Garnier et al., J. Am. Chem. Soc. 115, 8716
- (1993).7. G. W. Neudeck and A. K. Malhotra, Solid State Elec-
- tron. 19, 721 (1976).
- 8. B. Servet *et al.*, *Chem. Mater.*, in press.
- B. Gorot et al., Orient Mater., in press.
 S. Hotta and K. Waragai, Adv. Mater. 5, 896 (1993).
 M. Angelopoulos et al., Polym. Eng. Sci. 32, 1535
- (1992).
- 11. O. Inganäs, G. Gustafsson, C. Svensson, *Synth. Met.* **41**–**43**, 1095 (1991).
- H. Naarmann, in Science and Applications of Conducting Polymers, W. R. Salaneck, D. T. Clark, E. J. Samuelsen, Eds. (Hilger, New York, 1990), p. 81.
 R. A. Street, Mater. Res. Soc. Bull. 17, 70 (1992).
- Yu Yu Cu Cec, *Iviater, ness. SUC. Bull.* 17, 70 (1992).
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The Unidentified Interstellar Infrared Bands: PAHs as Carriers?

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Infrared emission spectra of gas-phase naphthalene and pyrene have been measured in the range of 3 to 7.5 micrometers with ultraviolet laser desorption-excitation and a spectroscopic technique featuring single-photon counting in the infrared. The spectra were compared with the unidentified infrared emission bands that are observed in many astronomical objects. Marked discrepancies between those observations and the laboratory emission spectra in the wavelengths and relative intensities of principal spectral features led to the conclusion that small neutral unsubstituted polycyclic aromatic hydrocarbons cannot be the carriers of the unidentified infrared emission bands.

One of the most intriguing current problems in astrophysics is to identify the carriers of the visible diffuse interstellar absorption bands (DIBs) (1) and the unidentified infrared emission bands (UIRs) (2). These emission bands are observed from a variety of astronomical objects, including planetary nebulae (3), reflection nebulae (4, 5), HII regions (6), and galactic nuclei (7), all of which exhibit the same principal spectral features, which seem to correlate with the abundance of carbon (5). The identification of the carriers is important because they could account for a significant fraction of carbon in the interstellar medium. The hypothesis that the carriers of the UIRs are polycyclic aromatic hydrocarbon (PAH) molecules (8) has received much attention, supported by the identification of these species in interplanetary dust particles (9). According to the PAH hypothesis (2), individual PAHs absorb ultraviolet (UV) radiation emitted from nearby hot stars, undergo internal conversion or intersystem crossing followed by internal vibrational redistribution on a time scale shorter than UV fluorescence, and finally, emit infrared (IR) radiation characteristic of the aromatic C-H stretch [3.3 µm, (3040 cm⁻¹)], C-C stretch [6.2 µm (1615 cm⁻¹) and 7.7 µm (1310 cm⁻¹)], C–H in-plane bend [8.6 μ m (1160 cm⁻¹)], and C–H out-of-plane bend [11.3 μ m (885 cm⁻¹) and 12.7 μ m (785 cm^{-1})]. These six features correspond to the major UIRs.

The similarity of the observed UIRs to the absorption spectra of several PAH molecules has been described (2). However, emission and absorption spectra can differ markedly, especially if the vibrational energy content of the molecule is high and many overtones and combination bands are excited. Therefore, only laboratory emission experiments can test the PAH hypoth-

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esis in a rigorous way. Previous emission measurements were confined to the 3- to $4\text{-}\mu\text{m}$ wavelength range, characteristic of aromatic and aliphatic C–H stretch vibrations (10-14). The 3.3-µm features observed in previous experiments were found to coincide with essentially all astronomical UIR observations. Moreover, the emission spectra observed for different PAHs excited by different UV wavelengths are strikingly similar. Thus, the general notion that PAHs are responsible for the interstellar IR emission features seems supported by the available evidence. However, the 3.3-µm C–H stretch is ubiquitous to a wide variety of hydrocarbons; an identification of the UIR carriers from observation of the 3.3µm emission alone is impossible.

In this report we describe the measurement of IR emission spectra for two representative small neutral PAHs—naphthalene and pyrene—in the extended range of 3 to 7.5 μ m with the use of an infrared photon counting technique that we have developed. In these experiments we simultaneously monitor several of the principal UIR features, which allows us to assess the identification of their carriers in a more definitive manner than has been possible before.

Previous laboratory emission experiments addressing the PAH hypothesis have involved a direct simulation of the proposed mechanism with UV excitation of small PAH molecules under collision-free conditions (10, 11, 13). PAHs larger than benzene or naphthalene have vapor pressures suitable for spectroscopy only at high temperatures. Thermal sources of gaseous PAHs therefore emit intense blackbody radiation, which limits the sensitivity of conventional IR emission experiments and renders measurements beyond 4 μ m extremely difficult.

Our experimental approach is to use UV–laser-induced desorption (UV-LID) to vaporize PAH molecules adsorbed on a 77-K sample plate. The 248-nm excimer laser light also provides the requisite elec-

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tronic excitation. IR fluorescence of the desorbed molecules is then collected with the IR single-photon counting fluorescence spectrometer (IRSPCFS) we developed, which will be described elsewhere (15). In this experiment, an IR photon counting detector (16) is used in conjunction with a liquid helium–cooled Czerny-Turner mono-chromator. The detector is exposed only to the emission from the excited PAHs and the 77-K blackbody background radiation emitted by the cold sample Dewar, thus facilitating IR emission measurements at longer wavelengths.

With this technique, several important questions must be addressed before a meaningful comparison of laboratory emission spectra with the UIRs can be made. First, we carefully demonstrated that the emission actually originates from gas-phase molecules rather than from molecules adsorbed on the sample plate. Another possible concern is that the PAHs may photodissociate upon UV photolysis. Using a quadrupole mass spectrometer, we measured the photodesorption yield on the parent mass and on the masses of the most likely photofragments. At the laser fluences used in this experiment, the intensity ratios of all fragment masses observed with laser desorption to the parent mass correspond to the same ratios observed for a quiescent background of gaseous naphthalene and pyrene. We cannot rule out the production of ions in the UV-LID method. However, a comparison of the intensity ratios for several different emission features with ab initio predictions shows that they do not account for a significant fraction of the emission. Therefore, the emitters in these experiments are predominantly neutral parent molecules.

Finally, it must be shown that UV-LID approximates the proposed UV excitation of the PAH molecules in the interstellar medium. According to Leger and d'Hendecourt (17), internal conversion followed by internal vibrational redistribution is the dominant process in the photophysics of the PAHs in the interstellar medium. Therefore, one may think of the carriers of the UIRs as hot groundstate molecules. In our LID experiments, a 10- to 15-ns laser pulse at 248 nm (typically 1 MW cm⁻² to 10 MW cm⁻²) is absorbed by a thin, solid film of the sample molecules. This absorbed energy is dissipated by reflection, fluorescence of the excited monomer and dimer (excimer), heat conduction into the solid, and vaporization of the sample.

We have clearly shown that the emission observed upon UV-LID originates from the vaporized parent molecules, which we take to be hot ground-state species. There is no absolute proof that this mechanism is comparable to the proposed interstellar UV

excitation mechanism. However, we can compare the 3.3-µm feature obtained by UV-LID with similar results obtained in a collisionless free jet. Two IR spectra of naphthalene in the range of 3 to 4 μ m are shown in Fig. 1A (left). One spectrum (dotdash line) was taken in a free jet experiment involving the direct simulation of the PAH hypothesis, as described elsewhere (13), the other was taken with UV-LID (solid line). Both spectra exhibit the 3.3- μm feature; the linewidths and the shapes of the lines are essentially the same. The principal difference in the two spectra is a blueshift of the LID spectrum ($\Delta \lambda = 0.030$ μ m). Coupling between the various modes of these highly excited molecules leads to anharmonicity; emission from cooler molecules is therefore blueshifted relative to more energetic molecules. Brenner and Barker (10) observed such a blueshift due to gas kinetic collisions. In the case of benzene, they observed this blueshift to be a roughly linear function of internal energy.

In earlier UV-LID work it was reported that the vaporizing molecules undergo energy-exchanging collisions and actually form slightly supersonic molecular beams (18). In the free jet experiments, the entire energy of the absorbed UV photon is converted into vibrational excitation. For 248nm (40,000 cm^{-1}) excitation, we observed a 0.020- to 0.030-µm blueshift of the naphthalene 3.3-µm feature with respect to 193nm $(51,800 \text{ cm}^{-1})$ excitation, due to the lower degree of vibrational excitation. Assuming the peak position is linear with internal energy, we estimate that in the UV-LID experiment, the average vibrational energy per naphthalene molecule is around $30,000 \text{ cm}^{-1}$. Therefore, the IR emission in the UV-LID experiments originates from molecules that are colder than those in the collisionless, free jet experiment. We interpret the similarity of the types of spectra as evidence that both UV excitation mechanisms nevertheless leave the molecules very hot (vibrationally) in the S_0 ground state.

An IRSPCFS spectrum of pyrene in the 3- to 4- μ m region is shown in Fig. 1B (left). The 3.3- μ m emission feature is very similar to that of naphthalene. This similarity clearly shows that a carrier identification from the C–H stretch region alone is impossible. Moreover, all PAH spectra mea-



Fig. 1. Mid-IR emission spectra of **(A)** naphthalene and **(B)** pyrene obtained with the Berkeley IR single-photon counting fluorescence spectrometer (IRSPCFS). The corresponding stick diagrams indicate band positions and intensities of absorption spectra of the measured species in cryogenic matrices (20). IR fluorescence from UV laser–desorbed PAHs is imaged into the 0.5-m, liquid helium–cooled, f/7 monochromator. The wavelength-dispersed and time-resolved signal is collected with a solid-state blocked impurity band detector. For the spectra shown here the signal is integrated for 10 to 100 s after the UV laser pulse. The resolution is about 20 nm throughout the entire spectral range. The spectra are not corrected for the instrument response function, which is estimated to vary by a factor of 1.3 throughout the 5- to 7- μ m region. In (A) (left), IR fluorescence from UV laser–excited naphthalene in a free jet (dot-dash line) is compared with the corresponding emission from the UV-LID source (solid line). The similarity of the 3.3- μ m features from different methods indicates that UV-LID, as used in the remaining three panels, is a reasonable simulation to test the proposed PAH hypothesis. The appearance of emission in the 5- to 6- μ m regime is in agreement with the positions from matrix work but disagrees with the UIR observations. Relative intensities of the 3.3- μ m feature and the emission in the range of 6 to 8 μ m are further evidence that small neutral PAHs cannot be the carriers of the UIR emission.

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sured in this range, with both the free jet and UV-LID approaches, exhibit the same asymmetric line shape as do the naphthalene measurements of Brenner and Barker (10), Williams and Leone (14), and the unsubstituted PAH measurements of Shan, Suto, and Lee (12). In earlier benzene experiments, Brenner and Barker attributed shoulders to the red of the main feature to a progression of anharmonically shifted $\Delta \nu =$ -1 transitions in the C–H stretch modes (such as $\Delta \nu_{C-H} = 3 \rightarrow 2, 2 \rightarrow 1$) (10). The positions of these less intense transitions coincide with several minor UIR features. However, computer modeling (19) indicates that this effect should diminish for larger PAHs because the excitation energy is partitioned into more vibrations, thus leaving less energy for the requisite multiquantum excitation. Because both naphthalene and pyrene exhibit a similar asymmetry to the red of the 3.3-µm feature, and no distinct peaks are observed, we attribute this asymmetry to the presence of a multitude of sequence bands ($\Delta \nu = 1 \rightarrow 0$, with other modes simultaneously excited); this conclusion was independently reached by Williams and Leone (14). Alternatively, the minor UIR bands have been attributed to substituted PAHs with aliphatic side groups (methyl, ethyl, and others) (2). This notion is supported by the experiments of Shan and co-workers in which distinct bands to the red of the 3.3-µm feature are observed from methyl-substituted PAHs (12).

The IR spectra of naphthalene and pyrene at wavelengths longer than 4 μ m are shown in Fig. 1 (right panels). These are the first such emission spectra of these molecules measured under conditions that approximate the astrophysical environment. Whereas naphthalene shows strong emission throughout the 5- to 7.5-µm region, pyrene emits principally near 5.2 to 5.7 µm. All emission features in these spectra are attributed to C-C stretch vibrations, the C-H in-plane bending vibrations, overtones, and combination bands of these vibrations with C-H outof-plane bending motions as well as with cyclic C-C ring vibrational motions. The stick diagrams in each figure indicate the spectral assignment and band intensity found in recent IR absorption work carried out in 12-K argon matrices (20). For naphthalene, the present emission features largely coincide with the matrix absorption spectra; however, most emission bands are broader and extend to the red of the band positions found in (20), indicating that the emission originates from hot gaseous parent molecules. Accordingly, the intensities of the overtones and combination bands found in the present work are greatly enhanced with respect to the fundamental frequencies, as compared with the ratios found in the cold matrix work. For pyrene, this same trend is even more apparent.

The emission spectra measured in the present work were taken under conditions which approximate the astrophysical environment; therefore, a meaningful comparison of these spectra with the UIR bands is possible. All UIR spectra exhibit the same principal features at 3.3, 6.2, 7.7, 8.7, and 11.3 μ m; although the bands appear slightly shifted in different sources, all six bands appear very consistently as a group. Leger and d'Hendecourt pointed out that all PAH molecules show absorptions between 5 and 6 μ m (17); observations of some UIR sources reveal a distinct, albeit weak, band at 5.25 μ m (2, 21). The dominance of the 5- to $6-\mu m$ bands over the 6- to 7.5-µm bands in our laboratory emission spectra is in stark contrast to the UIRs in which features between 5 and 6 μ m are sometimes barely discernable and are considerably weaker than the consistently intense 6.2-µm UIR band, which did not appear in our experiments at all. Therefore, we interpret this as a strong indication that small PAH molecules are not the carriers of the UIRs.

A second critical test of the PAH hypothesis is the comparison of the emission strength of the C–C and C–H stretch bands. We found the 3.3- μ m feature comparable in strength to the 5- to 6- μ m features, and we did not measure strong emission at either 6.2 or 7.7 μ m. To obtain the C–C to C–H stretch intensity ratio, we therefore took our strongest bands in the 5-

Table 1. Comparison of the strength of the C–C stretch to C–H stretch emission. The UIR value is corrected for the fact that astronomical observations measure power densities rather than count photons. The values listed under "current work" include the instrument response function, and upper limits due to uncertainties in calibration are given in parentheses. The theoretical predictions of oscillator strengths for neutral and ionic naphthalene are given in (23). In the model for chrysene (2), an IR emission spectrum is calculated by weighing oscillator strengths with a 30,000-cm⁻¹ vibrational population distribution. Given the assumptions in this model, the values for chrysene and pyrene are expected to be similar.

Source	Intensity ratio / _{6.2 + 7.7} // _{3.3}
UIRs	4 to 25
Current work	
Pyrene	0.15 (0.6)
Naphthalene	0.19 (0.75)
Ab initio predictions	
Neutral naphthalene	0.22
Ionic naphthalene	20
Model	
Chrysene	0.19

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to 8- μ m range and compared those with the strength of the 3.3- μ m feature. In Table 1, we compare our findings with the range of values from seven other observations of UIR sources (6, 7, 22), with ab initio predictions of the ratios of integrated band intensities for neutral and ionized naphthalene (23), and with modeling results that include effects of vibrational excitation (2). Our present values for pyrene and naphthalene agree reasonably well with theoretical predictions for neutral naphthalene, but not at all for ionized naphthalene (23).

Therefore, we conclude that our emission originates from neutral species. More importantly, our results for naphthalene differ from the UIR results by one order of magnitude or more. This is further evidence that small neutral PAHs are not the carriers of the UIR emission.

The C–C to C–H stretch intensity ratio should rise strongly as the hydrogen/carbon ratio drops for larger PAHs, such as coronene ($C_{24}H_{12}$), as compared with naphthalene ($C_{10}H_8$), assuming that both the C–C modes and the C–H modes appear in a very narrow frequency range. Therefore, larger PAHs could certainly exhibit the observed UIR ratio and thus cannot be ruled out as possible carriers. However, even for coronene, one expects strong emission in the range of 5 to 6 μ m (17), which is inconsistent with the UIR observations.

Differences have also been found in the relative band intensities of the C-C stretch region (6.2 and 7.7 µm) and the 11.3-µm feature, which is attributed to the C-H out-of-plane bending mode (6). These discrepancies also favor a decreased hydrogen/ carbon ratio in the PAHs present in astronomical sources. Therefore, it was suggested that PAHs in the interstellar medium might be severely dehydrogenated (2). However, as one model (19) demonstrates, a population of sufficiently large PAHs can also explain this intensity ratio. Furthermore, calculations regarding radiative recombination (24) indicate dehydrogenated PAHs may readily accrete hydrogen without the aid of a third body. These considerations make the dehydrogenation hypothesis seem less palatable. IR emission measurements of PAH C-H out-of-plane bending modes (11 to 15 μ m) would be of considerable importance in addressing this question.

The PAH hypothesis has also been extended to molecular ions of PAHs (2). This extension seems reasonable, comparing the predicted C–C/C–H ratios with those found in the UIRs (see Table 1). Several groups have investigated the IR absorption spectra of molecular ions in cold matrices (20, 25). The absolute oscillator strengths of these ions are much larger (one order of magnitude or more) than for the corresponding neutrals (25). Moreover, these experiments show a favorable intensity ratio of the corresponding features. However, the band positions of the ionized species are shifted only slightly [80 cm⁻¹ or less (20)] with respect to the neutrals. It still remains to be shown that ionized gaseous PAHs do not carry the strong 5- to 6-µm emission.

Fulara et al. (26) have measured the near-IR, visible, and UV spectra emission from a different class of molecules, highly unsaturated hydrocarbons $[C_nH_m, n = 2 -$ 12 (even), m < 3]. They showed that the near-IR and visible features correspond to 15 DIBs. However, the absorption lines in the UV are inconsistent with astronomical observations. Nevertheless, this class of molecules also should be considered as possible carriers of the UIRs. IR emission spectra of these species as well as emission spectra from large neutral PAHs (for example, coronene or larger) and ionized PAHs must be measured to further explore the possible connections of these molecules with the UIRs and DIBs.

REFERENCES AND NOTES

- C. Joblin, J. P. Maillard, L. d'Hendecourt, A. Leger, *Nature* 346, 729 (1990).
- L. J. Allamandola, A. G. G. M. Tielens, J. R. Barker, Astrophys. J. Suppl. 71, 733 (1989).
- T. R. Geballe, in Proceedings of the Workshop on Laboratory and Observational Infrared Spectra of Interstellar Dust, Hilo, HI, USA, 18 to 20 July 1983, R. D. Wolstencroft and J. M. Greenberg, Eds., *R. Obs.* Occas. Rep. **12**, 93 (1984), R. W. Russel, B. T. Soifer, S. P. Willner, Astrophys. J. **217**, L149 (1977).
- T. R. Geballe, J. H. Lacy, S. E. Persson, P. J. McGregor, B. T. Soifer, *Astrophys. J.* 292, 500 (1985).
- 5. M. Cohen et al., ibid. 302, 737 (1986).
- J. D. Bregman, L. J. Allamandola, A. G. G. M. Tielens, T. R. Geballe, F. C. Witteborn, *ibid.* 344, 791 (1989).
- S. P. Willner, B. T. Soifer, R. W. Russel, R. R. Joyce, F. C. Gillet, *ibid.* **217**, L121 (1977); F. C. Gillet, D. E. Kleinmann, E. L. Wright, R. W. Capps, *ibid.* **198**, L65 (1975).
- A. Leger and J. L. Puget, Astron. Astrophys. **137**, L5 (1984); L. J. Allamandola, A. G. G. M. Tielens, J. R. Barker, Astrophys. J. **290**, L25 (1985).
- S. J. Clemett, C. R. Maechling, R. N. Zare, P. D. Swan, R. M. Walker, *Science* **262**, 721 (1993); L. J. Allamandola, S. A. Sandford, B. Wopenka, *ibid.* **237**, 56 (1987).
- J. D. Brenner and J. R. Barker, Astrophys. J. 388, L39 (1992).
- 11. I. Cherchneff and J. R. Barker, *ibid.* **341**, L21 (1989).
- J. Shan, A. Suto, L. C. Lee, *ibid*. **383**, 459 (1991); J. Shan, M. Suto, L. C. Lee, *J. Photochem. Photobiol.* A: Chem. **63**, 139 (1992).
- 13. S. Schlemmer et al., in preparation.
- 14. R. M. Williams and S. R. Leone, Astrophys. J., in preparation.
- 15. J. Harrison et al., in preparation.
- M. D. Petroff, M. G. Stapelbroek, W. A. Kleinhans, *Appl. Phys. Lett.* **51**, 406 (1985).
- 17. A. Leger and H. d'Hendecourt, Ann. Phys. Fr. 14, 181 (1989).
- 18. M. Buck and P. Hess, *Appl. Surf. Sci.* **43**, 358 (1989). 19. W. A. Schutte, A. G. G. M. Tielens, L. J. Allamandola,
- Astrophys. J. **415**, 397 (1993). 20. J. Szczepanski and M. Vala, *Nature* **363**, 699 (1993);
- Astrophys. J. **413**, 646 (1993). 21. L. J. Allamandola *et al.*, Astrophys. J. **345**, L59
- (1989).
- D. C. B. Whittet, A. D. McFadzean, T. R. Geballe, *R. Astron. Soc. Mon. Not.* **211**, 29 (1984); D. C. B. Whittet

et al., *ibid.* **233**, 321 (1988); D. K. Aitken and P. F. Roche, *ibid.* **196**, 39 (1981); T. R. Geballe, K. S. Noll, D. C. B. Whittet, L. B. F. M. Waters, *Astrophys. J.* **340**, L29 (1989); R. W. Russel, B. T. Soifer, S. P. Willner, *ibid.* **220**, 568 (1978); W. A. Schutte, A. G. G. M. Tielens, L. J. Allamandola, M. Cohen, D. H. Wooden, *ibid.* **360**, 577 (1990), and references therein.

- F. Pauzat, D. Talbi, M. D. Miller, D. J. DeFrees, Y. Ellinger, *J. Phys. Chem.* **96**, 7882 (1992).
 J. B. Barker, *ibid.*, p. 7361.
- 24, J. R. Barker, *İbid.*, p. 7361. 25. D. M. Hudgins, S. A. Sandford, L. J. Allamandola,

- *ibid.* 98, 4243 (1994).
 26. J. Fulara, D. Lessen, P. Freivogel, J. P. Maier, *Nature* 366, 439 (1993).
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X-ray Variability in the Hot Supergiant ζ Orionis

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Hot massive stars represent only a small fraction of the stellar population of the galaxy, but their enormous luminosities make them visible over large distances. Therefore, they are ideal standard candles, used to determine distances of near galaxies. Their mass loss due to supersonic winds driven by radiation pressure contributes significantly to the interstellar medium and thus to the chemical evolution of galaxies. All hot stars are soft x-ray sources; in contrast to the sun with its highly variable x-ray flux, long time scale x-ray variability is not common among hot stars. An analysis is presented here of an unusual increase in x-ray flux observed with the roentgen observatory satellite during a period of 2 days for the hot supergiant ζ Orionis, the only episode of x-ray variability that has been found in a hot star. These observations provide the most direct evidence so far for the scenario of shock-heated gas in the winds of hot stars.

X-ray observations carried out with the Einstein Observatory (1) and the roentgen observatory satellite (ROSAT) (2) have shown that all hot stars are soft x-ray sources with $\approx 10^{-7}$ (the typical range for the solar value is 10^{-7} to 10^{-6}) of their total luminosity emitted as soft x-rays (1-3). Early attempts to explain the observed x-ray emission in hot stars by a thin, hot corona at the base of the wind (4), similar to the solar x-ray corona, have become untenable. First, the absorption of the x-ray emission by the overlying wind requires an enormous emission measure of x-ray-emitting material (5). However, the search for the green corona emission line (Fe XIV, 530.3 nm), which is a direct indicator of gas at coronal temperatures, in the optical spectra of hot stars has been unsuccessful (6) and could not provide any observational evidence for the existence of hot gas in massive stars. Second, x-ray spectra of hot stars show no evidence for absorption at the 0.6-keV K shell ionization edge of oxygen (7) predicted in coronal models. Third, in contrast to cool stars like our sun, with its highly variable coronal activity, our long-term x-ray variability studies provide no evidence for x-ray time variability for hot stars over time scales of up to several years (2, 8).

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The theory of stellar winds driven by line radiation (9, 10), developed to explain the mass loss from hot stars, provides a different mechanism for the generation of x-rays in hot stars: The winds of hot stars are driven by the absorption of stellar radiation in a multitude of ultraviolet spectral lines, and stability analyses show that such line-driven winds are extremely unstable (11). In a more phenomenological way, Lucy and White (12) postulated (as a consequence of these instabilities) the presence of hot gas (and hence the x-ray emission) generated by shocks in the hot star winds. Detailed time-dependent calculations (13) show that the growth of instabilities naturally leads to the production of strong shocks that arise from the deceleration of high-speed wind material that impacts on slower material (thus driving a reverse shock). The combination of this effect with the results of our long-term x-ray variability studies of hot stars (2, 8), which indicate that the x-ray emission of hot stars remains very constant over long time scales, makes it seem likely that the observed x-ray emission is the average output from a larger number of shocks distributed in the wind of these stars.

A recently obtained ROSAT position sensitive proportional counter (PSPC) spectrum of the hot prototype star ζ Puppis (14) clearly shows the "self-absorption" of

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