

Topics in Current Chemistry

153

Editorial Board: M. J. S. Dewar J. D. Dunitz
K. Hafner E. Heilbronner S. Ito J.-M. Lehn
K. Niedenzu K. N. Raymond C. W. Rees
F. Vögtle

L. J. Allamandola: Benzenoid Hydrocarbons in Space

P. C. Hiberty: Distortive Tendencies of Delocalized π Electronic Systems

D. L. Cooper, J. Gerratt, M. Raimondi: Spin-Coupled Valence Bond Description

D. J. Klein: Semiempirical Valence Bond Views

J. Cioslowski: Scaling Properties of Topological Invariants

M. Zander: Molecular Topology and Chemical Reactivity

J. R. Dias: A Periodic Table for Benzenoid Hydrocarbons

P. John, H. Sachs: Calculating the Numbers of Perfect Matchings

F. J. Zhang, X. F. Guo, R. S. Chen: Existence of Kekulé Structures

W. C. He, W. J. He: Peak-Valley Path Method

R. Q. Sheng: Recognize Kekuléan Benzenoid Systems

R. S. Chen, B. N. Cyvin, S. J. Cyvin, J. Brunvoll, D. J. Klein: Enumerating Kekulé Structures

H. Hosoya: Clar's Aromatic Sextet

S. El-Basil: Caterpillar (Gutman) Trees

Advances in the Theory of Benzenoid Hydrocarbons



Springer-Verlag

Advances in the Theory of Benzenoid Hydrocarbons

Editors: I. Gutman, S. J. Cyvin

With contributions by

L. J. Allamandola, J. Brunvoll, R. S. Chen,
J. Cioslowski, D. L. Cooper, B. N. Cyvin,
S. J. Cyvin, J. R. Dias, S. El-Basil, J. Gerratt,
X. F. Guo, W. C. He, W. J. He, P. C. Hiberty,
H. Hosoya, P. John, D. J. Klein, M. Raimondi,
H. Sachs, R. Q. Sheng, M. Zander, F. J. Zhang

With 127 Figures and 3 Tables



Springer-Verlag Berlin Heidelberg New York
London Paris Tokyo Hong Kong

This series presents critical reviews of the present position and future trends in modern chemical research. It is addressed to all research and industrial chemists who wish to keep abreast of advances in their subject.

As a rule, contributions are specially commissioned. The editors and publishers will, however, always be pleased to receive suggestions and supplementary information. Papers are accepted for "Topics in Current Chemistry" in English.

ISBN 3-540-51505-4 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-51505-4 Springer-Verlag New York Berlin Heidelberg

Library of Congress Cataloging-in-Publication Data

Advances in the theory of benzenoid hydrocarbons/with contributions by L. J. Allamandola...[et al.]. (Topics in current chemistry; 153)

ISBN 0-387-51505-4 (U.S.)

1. Polycyclic aromatic hydrocarbons. I. Allamandola, L. J. (Louis J.), 1946-. II. Series. QD1.F58 vol. 153 [QD341.H9] 540 s--dc20 [547'.611] 89-21694 CIP

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, re-use of illustrations, recitation, broadcasting, reproduction on microfilms or in other ways, and storage in data banks. Duplication of this publication or parts thereof is only permitted under the provisions of the German Copyright Law of September 9, 1965, in its version of June 24, 1985, and a copyright fee must always be paid. Violations fall under the prosecution act of the German Copyright Law.

© Springer-Verlag Berlin Heidelberg 1990

Printed in GDR

The use of registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Bookbinding: Lüderitz & Bauer, Berlin

2151/3020-543210 — Printed on acid-free paper

Guest Editors

Professor Dr. *Ivan Gutman*

University of Kragujevac, Faculty of Science, P.O. Box 60,
YU-34000 Kragujevac, Yugoslavia

Professor Dr. *Sven J. Cyvin*

The University of Trondheim, The Norwegian Institute
of Technology, Division of Physical Chemistry,
N-7034 Trondheim NTH, Norway

Editorial Board

- | | |
|--------------------------------------|--|
| Prof. Dr. <i>Michael J. S. Dewar</i> | Department of Chemistry, The University of Texas
Austin, TX 78712, USA |
| Prof. Dr. <i>Jack D. Dunitz</i> | Laboratorium für Organische Chemie der
Eidgenössischen Hochschule
Universitätsstraße 6/8, CH-8006 Zürich |
| Prof. Dr. <i>Klaus Hafner</i> | Institut für Organische Chemie der TH
Petersenstraße 15. D-6100 Darmstadt |
| Prof. Dr. <i>Edgar Heilbronner</i> | Physikalisch-Chemisches Institut der Universität
Klingelbergstraße 80, CH-4000 Basel |
| Prof. Dr. <i>Shô Itô</i> | Department of Chemistry, Tohoku University,
Sendai, Japan 980 |
| Prof. Dr. <i>Jean-Marie Lehn</i> | Institut de Chimie, Université de Strasbourg, 1, rue
Blaise Pascal, B. P. Z 296/R8, F-67008 Strasbourg-Cedex |
| Prof. Dr. <i>Kurt Niedenzu</i> | University of Kentucky, College of Arts and Sciences
Department of Chemistry, Lexington, KY 40506, USA |
| Prof. Dr. <i>Kenneth N. Raymond</i> | Department of Chemistry, University of California,
Berkeley, California 94720, USA |
| Prof. Dr. <i>Charles W. Ress</i> | Hofmann Professor of Organic Chemistry, Department
of Chemistry, Imperial College of Science and Technology,
South Kensington, London SW7 2AY, England |
| Prof. Dr. <i>Fritz Vögtle</i> | Institut für Organische Chemie und Biochemie
der Universität, Gerhard-Domagk-Str. 1,
D-5300 Bonn 1 |

Preface

The editors of this volume of Topics in Current Chemistry have recently completed a book devoted to the theory of benzenoid molecules (Gutman I, Cyvin SJ (1989) Introduction to the theory of benzenoid hydrocarbons, Springer, Berlin Heidelberg New York). Due to its introductory nature the book could not embrace a number of relevant topics in which vigorous research activity is nowadays taking place. The aim of the present issue is to fill this gap. Outstanding and currently active researchers were invited to report on their contributions to the theoretical chemistry of benzenoid compounds.

Theoretical investigations of benzenoid molecules have a long history and are usually considered as a traditional, but somewhat obsolete, area of theoretical organic chemistry. This volume of Topics in Current Chemistry should document that in this field there still exists a variety of unsolved and partially solved problems, that there is still room for new ideas and that research activity shows no signs of slowing down.

Nashville and Trondheim, Spring 1989

Ivan Gutman
Sven J. Cyvin

Table of Contents

Benzenoid Hydrocarbons in Space: The Evidence and Implications	
L. J. Allamandola	1
The Distortive Tendencies of Delocalized π Electronic Systems. Benzene, Cyclobutadiene and Related Heteroannulenes	
P. C. Hiberty	27
The Spin-Coupled Valence Bond Description of Benzenoid Aromatic Molecules	
D. L. Cooper, J. Gerratt, M. Raimondi	41
Semiempirical Valence Bond Views for Benzenoid Hydrocarbons	
D. J. Klein	57
Scaling Properties of Topological Invariants	
J. Cioslowski	85
Molecular Topology and Chemical Reactivity of Polynuclear Benzenoid Hydrocarbons	
M. Zander	101
A Periodic Table for Benzenoid Hydrocarbons	
J. R. Dias	123
Calculating the Numbers of Perfect Matchings and of Spanning Trees, Pauling's Orders, the Characteristic Polynomial, and the Eigenvectors of a Benzenoid System	
P. John, H. Sachs	145
The Existence of Kekulé Structures in a Benzenoid System	
F. J. Zhang, X. F. Guo, R. S. Chen	181
Peak-Valley Path Method on Benzenoid and Coronoid Systems	
W. C. He, W. J. He	195

Rapid Ways to Recognize Kekuléan Benzenoid Systems	
R. Q. Sheng	211
Methods of Enumerating Kekulé Structures, Exemplified by Applications to Rectangle-Shaped Benzenoids	
R. S. Chen, S. J. Cyvin, B. N. Cyvin, J. Brunvoll, D. J. Klein	227
Clar's Aromatic Sextet and Sextet Polynomial	
H. Hosoya	255
Caterpillar (Gutman) Trees in Chemical Graph Theory	
S. El-Basil	273
Author Index Volumes 151 – 153	291

Benzenoid Hydrocarbons in Space: The Evidence and Implications

Louis J. Allamandola

NASA Ames Research Center 245-6, Moffett Field, California 94035, USA

Table of Contents

1 Introduction	3
2 The Interstellar Emission Spectrum	5
2.1 The 3200–2700 cm^{-1} Region	7
2.1.1 The 3050 cm^{-1} Major Band	7
2.1.2 The Minor Bands in the 3200–2700 cm^{-1} Region	10
2.1.3 The Broad Component in the 3200–2700 cm^{-1} Region	13
2.2 The 2000–1000 cm^{-1} Region	13
2.2.1 The 1610, 1350 and 1150 cm^{-1} Major Bands	13
2.2.2 The Minor Bands in the 2000–1000 cm^{-1} Region	16
2.2.3 The Broad Component in the 2000–1000 cm^{-1} Region	17
2.3 The 1000–500 cm^{-1} Region	20
2.3.1 The 890 cm^{-1} Major Band	20
2.3.2 The Minor Bands in the 1000–500 cm^{-1} Region	20
2.3.3 The Broad Component in the 1000–500 cm^{-1} Region	22
2.4 The Far Infrared	22
3 Conclusions	23
4 Acknowledgement	24
5 References	24

Many different celestial objects emit an infrared spectrum which has been attributed to infrared fluorescence from a family of highly vibrationally excited benzenoid hydrocarbons referred to as polycyclic aromatic hydrocarbons (PAHs). The most intense emitters contain between 20 to 50 carbon atoms, although larger species also contribute to the emission. This assignment is based on a rough resemblance of the interstellar emission spectra to the vibrational spectra of PAHs and related materials such as chars and soots which contain PAH mixtures. The spectroscopic assignments of the features between 3200 and 700 cm^{-1} are discussed in detail.

Much laboratory work on PAHs which are larger than those previously studied, isolated, ionized and dehydrogenated is called for to fully exploit this model. As PAHs are thought to be ubiquitous throughout the interstellar medium and more abundant than all other known polyatomic, interstellar molecules, they possess great potential as important probes of conditions in many different kinds of astronomical objects. Conversely, astronomical observations are extending our knowledge of these exotic materials by probing regions in which some conditions may be impossible to duplicate in the laboratory.

1 Introduction

An intriguing and exciting chapter of modern astrophysics was opened by Gillett, Forrest and Merrill in 1973 [1] with their discovery that some astronomical objects emitted a broad band which peaks near 3050 cm^{-1} . In the ensuing years, astronomers around the world found that this was part of a family of infrared emission features which were emitted by a large number of very different types of astronomical objects. Reviews of the ground breaking observations are in Ref [2] and [3]. The other prominent, well-known bands, or features as they are often called, peak near 1610, “1310”, 1160 and 890 cm^{-1} . They are broad, with a FWHH on the order of 30 to 50 cm^{-1} or more. The peak frequencies do not seem to vary by more than a few wavenumbers from object to object except for the case of the “1310” cm^{-1} feature in which it can differ by as much as 50 cm^{-1} .

As the list of astronomical objects which emit these features grew, it became clear that the emission came from regions where ultraviolet radiation was impinging on vast areas of space in which dust was known to be present. Surprisingly, the age and history of the dust seemed to be unimportant. Illumination from hot, UV-rich stars which had formed in – and emerged from – dense, dark dust clouds (age $\sim 10^6$ – 10^7 years) could excite the emission from the surface of the cloud. Examples of this type of object include H–II regions and some reflection nebulae. Similar spectra are emitted from some much younger, isolated objects known as planetary nebulae. These are stars near the end of their normal life which have produced copious amounts of dust during the past 10^4 – 10^5 years. This dust has a very different history and is much younger than the dust in dense clouds. During the late 1970s and early 1980s, the known extent of the phenomenon was extended to other galaxies as well. The intensities of the bands detected however, were far greater than those which would be expected from the individual objects which comprised the galaxies such as planetary nebulae, reflection nebulae, H–II regions and so on. The implication was that a substantial fraction of this extragalactic emission came from regions which were not associated with individual stars, but from the dark matter in the interstellar medium in these galaxies [4]. Subsequent observations of our galaxy, the Milky Way, by the Infrared Astronomical Satellite (IRAS) have shown that there are strips of interstellar IR emitting clouds, known as the IR Cirrus, that lie slightly above and below the galactic plane which seem to emit these bands as well [5]. Obviously, understanding the source of this completely unexpected, yet widespread, phenomenon became an important problem in astrophysics.

As the number and variety of objects found to emit the features increased, identifying the carrier and determining the emission mechanism became the key challenges. During the fifteen years since their discovery, a number of models had been proposed to account for both aspects of the problem. Many of the models proposed up to 1984 are reviewed in Ref [6]. The comparable intensity of the 3050 cm^{-1} feature to those at lower frequencies, and the close association with ultraviolet radiation led us to propose that the emission was due to the infrared fluorescence from molecule sized emitters excited by the absorption of ultraviolet and visible photons [7, 8]. Although the carrier we initially proposed (molecules, frozen on 10K dust grains) was incorrect, this excitation-emission mechanism is now generally accepted because of the important and analysis observations of reflection nebulae made by Sellgren which showed that

the ultraviolet and visible photon fluxes present were unable to sufficiently excite larger species to emit in the 3000 cm^{-1} region [9]. The idea, now gaining wide acceptance, that aromatic material may be the carrier of the features began with the suggestion made by Duley and Williams in 1981 that they arise from vibrations of chemical groups attached to the aromatic moieties which make up small (< 0.01 micron radius) amorphous carbon particles [10]. Subsequently, Léger and Puget [11] and Allamandola, Tielens, and Barker [12] proposed that individual polycyclic aromatic hydrocarbon molecules, referred to as PAHs in the astrophysical literature, were the band carriers.

The principal reason for this assignment was the suggestive, but not perfect, resemblance of the interstellar emission spectra with the infrared absorption spectra of benzenoid hydrocarbons in KBr pellets. This assignment was supported by the better match of the interstellar features with the vibrational spectra of chars and soots which are comprised of mixtures of polycyclic aromatic hydrocarbons [13]. The need to invoke emission from free molecules rather than from the aromatic building blocks of amorphous carbon particles was driven by the fluorescent nature of the emission. Energy deposited in a particular molecular structural unit of a larger particle or cluster is thought to become thermalized on timescales on the order of 10^{-11} to 10^{-13} seconds, many orders of magnitude shorter than the 10^{-3} to 10^{-2} second timescale appropriate for the emission of IR photons. Emission from molecular units in a particle implies extremely weak intermolecular coupling [14] and has yet to be demonstrated. This question is presently the matter of some debate.

The imperfect match between the IR spectra of benzenoid hydrocarbons with the interstellar emission bands has been taken to indicate that rather than pure benzenoid compounds being responsible, benzenoid-like (or PAH-like) species are present in the interstellar medium. In many regions of the interstellar medium PAHs are expected to be ionized [12] and those containing less than about 20 carbon atoms are expected to be dehydrogenated [10, 11, 12].

In addition to the spectroscopic evidence, related observations support an aromatic hydrocarbon carrier as well. In planetary nebula, the fraction of the IR emitted in the " 1310 " cm^{-1} feature, which is by far the most intense of the bands, is strongly correlated with the amount of carbon available [15]. As the carriers must be produced under harsh conditions in planetary nebulae, they must be carbon-rich compounds which are extremely stable. Finally, although there is some variation among the relative band intensities, the bands are correlated, implying that a single class of chemical species is responsible [15].

Apart from the "curiosity" value, why is the discovery of a previously unrecognized and surprisingly ubiquitous component of the interstellar medium important astrophysically? There are several reasons. Current estimates are that between 1 and 10% of all of the carbon in the galaxy is in PAHs comprised of roughly 15 to, say, 500 carbon atoms [16]. The PAHs responsible for the IR features are thought to be more abundant than all of the other known interstellar, gaseous, polyatomic molecules combined [11, 12]. Their proposed ubiquity and high abundance has serious ramifications for other spectral regions. They may well contribute to the strong ultraviolet interstellar extinction, measured between 100 to 200 nm, the weak, diffuse, visible absorption bands [17, 18, 19], and the far-IR Cirrus [12, 20]. Similarly their influence on many physical processes may be profound [21]. They may comprise much of the carbon in meteorites [22] and be responsible for maintaining interstellar

cloud temperature [23], moderating interstellar cloud chemistry [24], and contributing to the deuterium enrichment found in interplanetary dust particles and meteorites [25]. Comprehensive treatments of various aspects of the polycyclic aromatic hydrocarbon model can be found in Ref [26] and [27].

In view of the previous paragraph, it is important to realize that precious little information is available on important properties of individual PAHs. For example, little is known about the spectroscopic properties of PAH ions and radicals from the UV through the IR. Other important, but poorly understood properties include photo-ionization cross sections, electron capture cross sections, cluster geometry, *n*-mer binding energies and so on. Recently, important information of fragmentation patterns of doubly ionized PAHs has become available [28, 29]. The carbon chemistry in the stellar atmospheres in which they are produced is just beginning to be modelled and poses significant chemical kinetic challenges [30, 31]. There is much to be done both experimentally and theoretically before the PAH model can be reliably extended from a means to account for certain observations to the point where it can be exploited as a probe of interstellar and circumstellar processes and conditions.

It is becoming increasingly apparent that the interstellar emission includes contributions from both free PAHs and carbonaceous particles as well [13, 32]. As amorphous carbon is primarily made up of randomly oriented clusters of PAHs, cross-linked and interconnected by saturated and unsaturated hydrocarbon chains, the infrared spectra of amorphous carbons and hydrogenated amorphous carbons should resemble spectra of PAH mixtures with some of the individual bands blurred out due to solid-state intermolecular interactions. If the H content is high, in addition to the aromatic features, aliphatic CH bands between 3000 to 2900 cm^{-1} and 1500 to 1400 cm^{-1} should become evident in the spectra of carbonaceous materials. The aromatic signature of small amorphous carbon particles and PAH clusters will be largely determined by the properties of the PAHs of which they are made. Individual bands overlap as the particles get larger and broad features are produced which may retain some substructure indicative of the individual PAHs. For still larger particles, bulk properties dominate and broad components appear as substructure on a strong continuum. As with PAH molecules, the spectroscopic and physical properties of amorphous carbon must be studied in detail.

In this article the infrared spectroscopic evidence for interstellar PAHs will be reviewed. The spectroscopic properties of PAHs studied in salt pellets rather than amorphous carbons will be primarily used since a wealth of very detailed information is available (thanks to the sustained, dedicated effort of Cyvin and his colleagues over many years) and molecule-sized emitters can account for many details of the interstellar spectra. Infrared spectra of amorphous carbon particles and carbonaceous films, synthesized to study the connections with interstellar carbonaceous material, are just now becoming available. The work of Bussoletti and coworkers ([33] and references therein) and Sakata and colleagues ([34] and references therein) is particularly noteworthy in this regard.

2 The Interstellar Emission Spectrum

Infrared spectra of celestial objects are usually measured in narrow frequency ranges because the Earth's atmosphere is opaque in certain infrared regions and the most

sensitive instrumentation is region specific. Consequently, although nearly complete mid-IR spectra have been published for only a few objects, detailed spectroscopic information is available in certain frequency ranges for many objects. Spectra have been measured in regions which are obscured by telluric H₂O using NASA's Kuiper Airborne Observatory which can operate a telescope at 12 to 14 km altitude. Observations in the 2000 to 1000 cm⁻¹ region made in this aircraft have played a very important role in unraveling the mystery of the interstellar infrared emission bands. Reliable observations in the 2500 to 2100 cm⁻¹ and 700 cm⁻¹ to lower frequency regions must await spaceborne instrumentation. The former region is blocked by atmospheric CO₂ and the latter by a combination of CO₂ and the very rich H₂O rotation spectrum. Fortunately, the Infrared Space Observatory (ISO), an infrared satellite under construction by the European Space Agency (ESA), is planned to be launched in the early 1990s, and the Space Infrared Telescope Facility (SIRTF), a complementary infrared satellite at an earlier stage of development by the National Aeronautics and Space Administration (NASA) in the United States, is planned to be launched in the latter part of the 1990s.

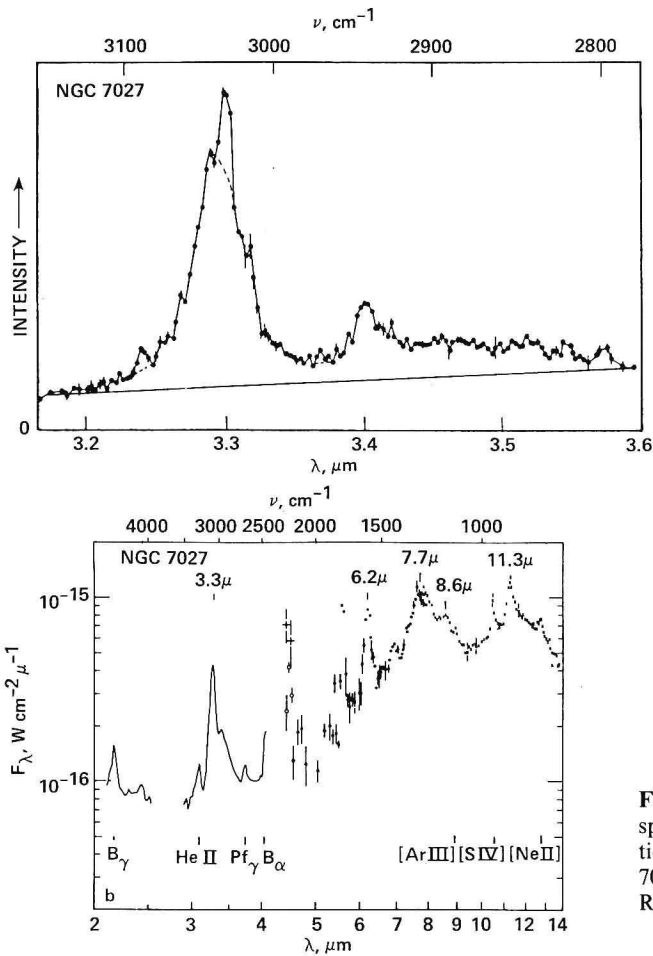


Fig. 1. The infrared emission spectrum from the high excitation planetary nebula NGC 7027 (a from Ref. [61], b from Ref. [60].)

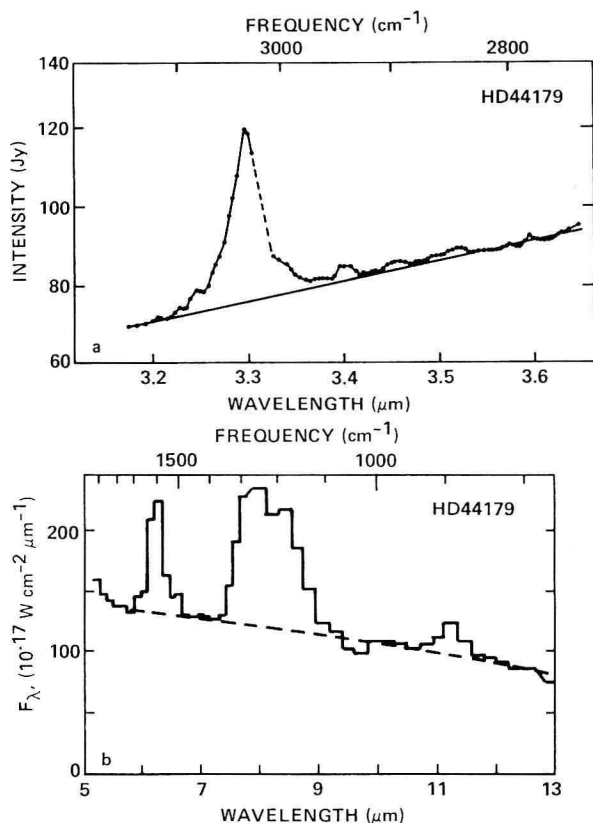


Fig. 2. The infrared emission spectrum from the reflection nebula HD 44179, the Red Rectangle (**a** from Ref. [44], **b** from Ref. [15].)

Good examples of nearly complete mid-IR spectra are shown in Figs. 1, 2 and 3 a, b. In addition to the family of bands at 3050, 1610, “1310”, 1160 and 890 cm^{-1} (3.3, 6.2, “7.7”, 8.6 and 11.3 μm), these figures show that there are striking variations in the underlying continuum and small changes in the “1310” band. Perusal of these figures also shows that there are 3 types of spectral components: major bands, minor (weak) bands and broad features. The broad features span roughly the 3100 to 2750 cm^{-1} , 2000 to 1100 cm^{-1} and 900 to 700 cm^{-1} regions. The band positions, widths and assignments are summarized in Table 1. In each of the following subsections these will all be discussed in this order: the major bands first, the minor bands next and the broad components last.

2.1 The 3200–2700 cm^{-1} Region

2.1.1 The 3050 cm^{-1} Major Band

Figures 1, 2, 3 a and 4 show that this region is dominated by the 3050 cm^{-1} emission band. This frequency is well known among IR spectroscopists as characteristic of

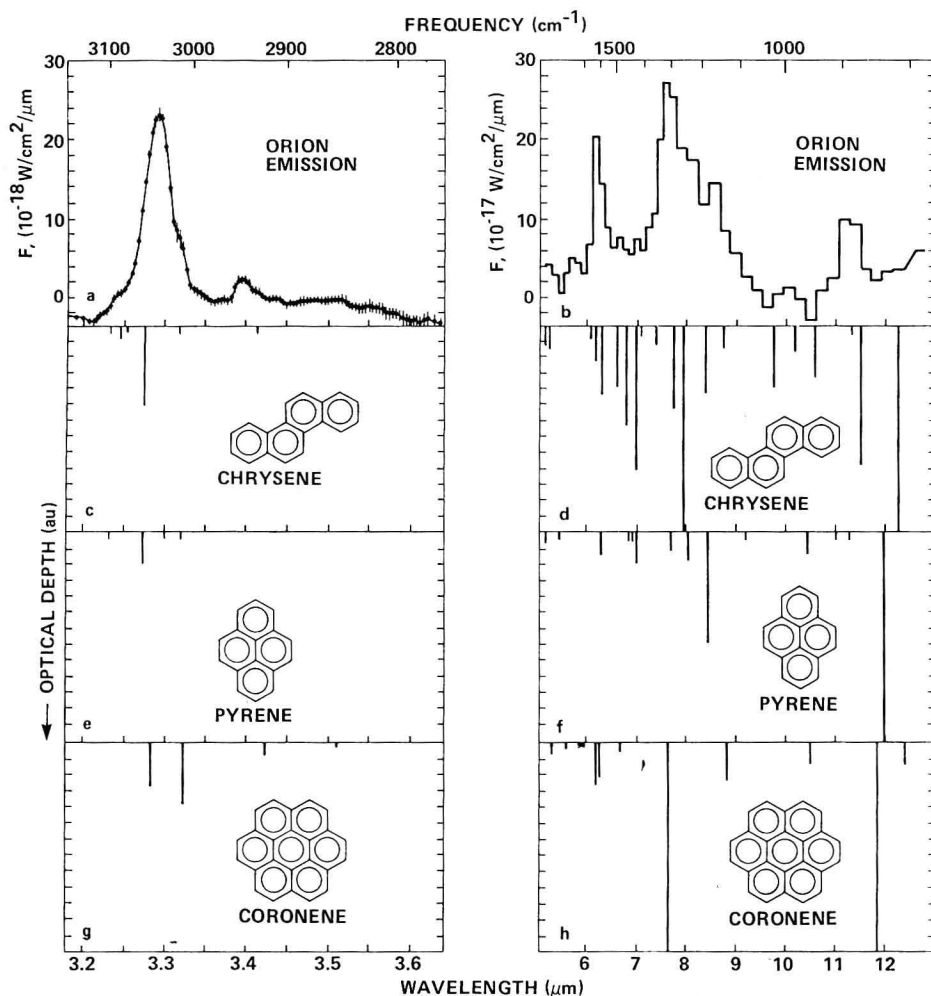


Fig. 3. The 3 to 13 micron emission spectrum from the Orion Bar compared with the absorption spectra of the PAHs chrysene, pyrene and coronene suspended in KBr pellets. (Orion, Ref. [47]; Chrysene, Ref. [38]; Pyrene, Ref. [37]; Coronene, Ref. [39].) A schematic representation for the absorption spectrum is used because the KBr pellet technique alters the spectrum compared to that of a free species

the aromatic CH stretch [35, 36, 37, 38, 39]. This frequency played a strong role in Duley and Williams first suggestion of an aromatic carrier of the interstellar spectra in 1981 [10]. The 30 cm^{-1} FWHH is probably due more to non-radiative vibrational energy redistribution times within an individual molecule rather than due to the overlapping of bands from different PAHs along the line of sight [12, 40]. A homogeneous linewidth of 30 cm^{-1} implies a redistribution time of about 0.2 picoseconds, a value consistent with the vibrational energy distribution time in other large molecules [41, 42]. It has recently been found that the band is narrower than shown in Fig. 2 by nearly a factor of two in the high flux vicinity of the star HD 44179 [43].

Table 1. Emission components: Properties and assignments¹

ν (cm^{-1})	λ (Microns)	FWHH (cm^{-1})	Assignment ²
The major bands			
3040	3.29	30	Aromatic C–H stretch ($\nu = 1 \rightarrow \nu = 0$)
1615	6.2	30	Aromatic C–C stretch
1315 1250	7.6–8.0	70–200	Blending of several strong aromatic C–C stretching bands
1150	8.7	–	Aromatic C–H in-plane bend
885	11.3	30	Aromatic C–H out-of-plane bend for non-adjacent, peripheral H atoms
The minor features			
3085	3.24	–	Overtone and/or combination involving fundamentals in the 1810–1050 cm^{-1} (5.52–9.52 μm) range
2995	3.34	–	Overtone and/or combination involving fundamentals in the 1810–1050 cm^{-1} (5.52–9.52 μm) range
2940	3.4	“20”	Aromatic C–H stretch ($\nu = 2 \rightarrow \nu = 1$)
2890	3.46	–	Overtone/combination band involving fundamentals in the 1810–1050 cm^{-1} (5.52–9.52 μm) range, aromatic CH stretch (high ν), aliphatic CH stretch,?
2850	3.51	–	Aromatic CH stretch ($\nu = 3 \rightarrow \nu = 2$), aliphatic CH stretch, overtone/combination band involving fundamentals in the 1810–1050 cm^{-1} (5.52–9.52 μm) range
2810	3.56	–	Aromatic CH stretch (high ν), aldehydic CH stretch, overtone/combination band involving fundamentals in the 1810–1050 cm^{-1} (5.52–9.52 μm) range
1960 1890	5.1–5.3	30	Combination of CH out-of-plane and in-plane bend,?
1785–1755	5.6–5.7	40	Aromatic C–C stretch; overtone of 885 cm^{-1} (11.3 μm) band; carbonyl C = O stretch,?
1470 1450	6.8–6.9	30	Aromatic C–C stretch, aliphatic CH deformation
840	11.9	–	C–H out-of-plane bend for doubly adjacent H atoms
790	12.7	–	C–H out-of-plane bend for triply adjacent H atoms
The broad components			
2940	3.5		Overlap of C–H stretching modes, shifted by anharmonic effects,
3115 2740 [†]	3.21–3.65 [†]	“300”	with overtones and combinations of C–C stretch fundamentals in the 1670–1250 cm^{-1} (6–8 μm) region, aliphatic CH stretch?, ?
~ 1200	~ 8.5	“400”	Blending of many weak aromatic C–C stretching bands
1810 1050 [†]	5.52–9.52 [†]		
880	12	“160”	Overlap of many aromatic C–H out-of-plane bending modes for non-adjacent as well as doubly and triply adjacent peripheral H-atoms
950–740 [†]	10.5–13.5 [†]		Electronic transitions between low-lying levels in ionized and complexed PAHs and amorphous carbon particles
Red-Near IR Continuum			
Mid-IR Continuum			Quasi-continuum formed by overlapping overtone and combination bands

“ ” Value estimated from several published spectra. † Rough limits of the feature.

1: When the assignment is not clear, several possible explanations are listed. The first seems most likely.

2: This table is extensively discussed in [16]