

Infrared Spectroscopy of Matrix Isolated Polycyclic Aromatic Hydrocarbons. 3. Fluoranthene and the Benzofluoranthenes

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Matrix isolation techniques have been used to measure the 4000–500 cm^{-1} infrared spectra of the polycyclic aromatic hydrocarbons (PAHs) fluoranthene, benzo[*a*]fluoranthene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, and benzo[*ghi*]fluoranthene. For the PAHs where previous matrix isolation and gas-phase laboratory studies are available, agreements between the data sets are generally very good. While the fluoranthenes as a class produce infrared spectra that share many of the same characteristics of the spectra of PAHs containing only benzenoid moieties, for comparably sized molecules, the fluoranthenes tend to produce more absorption bands overall and considerably more and stronger bands in the 1550–1350 cm^{-1} range. These differences are largely due to the presence of the five-membered cyclopentadienyl ring characteristic of the family.

I. Introduction

As discussed in part 1 of this series,¹ polycyclic aromatic hydrocarbons (PAHs) are prevalent in the terrestrial environment² and have been proposed as common components of many interstellar environments.^{3,4,5} To expand the available database on the fundamental spectroscopic properties of this ubiquitous family of compounds, we have undertaken a systematic survey of the mid-infrared (4000–500 cm^{-1}) spectra of neutral PAHs isolated in rare gas matrixes. This work is reported in parts 1, 2, and 3 in this journal issue.^{1,6} For an in-depth description of the experiment and applications, see part 1. This paper reports the results of studies involving six PAHs which incorporate a five-membered, cyclopentadienyl ring in their structures: fluoranthene, benzo[*a*]fluoranthene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, and benzo[*ghi*]fluoranthene. Related theoretical and experimental studies of the spectral properties of ionized and isotopically substituted neutral PAHs are reported elsewhere.^{7–10}

This paper is organized as follows. Relevant experimental details are summarized in section II. In section III.A, the conventions used in the presentation of the data are outlined. The spectra of the neutral PAHs and listings of band positions and strengths are presented in section III.B and, where available, compared to previous laboratory results. Finally, the unique astrophysical implications of the data are briefly discussed in section III.C, followed by a summary of the results in section IV.

II. Experimental Section

The matrix isolation and spectroscopy apparatus and methodology used in this study have been described in part 1 and elsewhere.^{1,7–9}

The PAHs used in this investigation, together with their deposition temperatures (T_{dep}), were: fluoranthene, Aldrich, 98%

purity, $T_{\text{dep}} = 45$ °C; benzo[*a*]fluoranthene, Bureau of Community Reference, Brussels, Belgium, 99+% purity, $T_{\text{dep}} = 95$ °C; benzo[*b*]fluoranthene (benz[*e*]acephenathrylene), Aldrich, 99% purity, $T_{\text{dep}} = 95$ °C; benzo[*j*]fluoranthene, Bureau of Community Reference, Brussels, Belgium, 99+% purity, $T_{\text{dep}} = 95$ °C; benzo[*k*]fluoranthene, Janssen Chimica, 99+% purity, $T_{\text{dep}} = 110$ °C; and benzo[*ghi*]fluoranthene, Bureau of Community Reference, Brussels, Belgium, 99+% purity, $T_{\text{dep}} = 65$ °C. All samples were used without further purification. Matheson prepurified argon (99.998% min) was used as the matrix material.

The Ar/PAH ratios in the samples were estimated using known argon flow rates and the integrated area of the strongest CH out-of-plane bending feature between 1000 and 500 cm^{-1} . Assuming an absolute absorption intensity of 110 km/mole, a value typical of these bands in other neutral PAHs,¹⁰ the argon/PAH ratios in all samples were found to exceed 1000/1.

III. Results and Discussion

A. Conventions Used in the Figures and Tables. In the following sections spectra and tabular summaries of the band positions and relative strengths as well as comparisons with other laboratory data (where available) are presented. The conventions adopted for the presentation of the data are identical with those discussed in detail in part 1. Only the salient features are summarized here. (i) The spectra reflect a small but significant level of H₂O contamination as evidenced by absorption bands in the 1625–1590 cm^{-1} range. Bands clearly due to H₂O are marked with a solid dot (•) in the spectra. (ii) In the tabulations, multiple bands are noted in one of two ways. If one band clearly dominates in strength, only its position is listed with a footnote indicating that it is the strongest member of a band “complex”. In those cases where there is no obvious dominant feature, or where there is reason to believe the bands may be associated with different vibrational modes, the position of each feature is specified. (iii) Due to complex overlapping of fundamental modes and confusion with overtones and combination bands, only the measured *positions* of the individual

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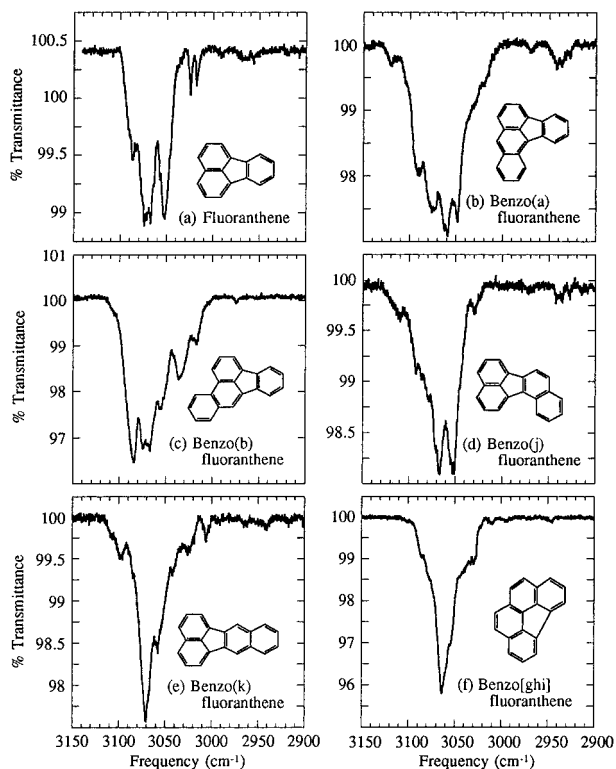


Figure 1. Spectra in the 3150–2900 cm^{-1} CH stretching region of the matrix isolated PAHs (a) fluoranthene ($\text{C}_{16}\text{H}_{10}$), (b) benzo[*a*]fluoranthene ($\text{C}_{20}\text{H}_{12}$), (c) benzo[*b*]fluoranthene ($\text{C}_{20}\text{H}_{12}$), (d) benzo[*j*]fluoranthene ($\text{C}_{20}\text{H}_{12}$), (e) benzo[*k*]fluoranthene ($\text{C}_{20}\text{H}_{12}$), and (f) benzo[*ghi*]fluoranthene ($\text{C}_{18}\text{H}_{10}$). All spectra were taken at a matrix temperature of 10 K. The argon to PAH ratio was in excess of 1000/1 in all cases.

features in the aromatic CH stretching region are tabulated together with the *total* integrated absorption over the *entire* region.

B. The Infrared Spectra of Neutral Matrix Isolated PAHs.

The 3150–2900 cm^{-1} spectra of the six PAHs fluoranthene ($\text{C}_{16}\text{H}_{10}$), benzo[*a*]fluoranthene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene (all $\text{C}_{20}\text{H}_{12}$), and benzo[*ghi*]fluoranthene ($\text{C}_{18}\text{H}_{10}$) are presented in Figures 1a–f, respectively. The 2000–500 cm^{-1} spectra of these PAHs are presented in the same order in Figures 2–7, and the positions and relative strengths of the absorption bands of these PAHs are listed in Tables 1–6.

The relative band strengths listed in Tables 1–6 have all been normalized to the strongest feature in the aromatic CH out-of-plane bending region between 1000 and 500 cm^{-1} . The bands used for normalization were fluoranthene, the 775.0/776.7 cm^{-1} band complex; benzo[*a*]fluoranthene, the 739.0/740.8 cm^{-1} band complex; benzo[*b*]fluoranthene, the 744.1 cm^{-1} band; benzo[*j*]fluoranthene, the 815.5 cm^{-1} band; benzo[*k*]fluoranthene, the 743.6/745.9 cm^{-1} band complex; and benzo[*ghi*]fluoranthene, the 828.1 cm^{-1} band. All bands having a relative strength greater than 1% are tabulated.

1. *General Properties of the Spectra.* In the absence of theoretical calculations it is difficult to assign individual bands to specific vibrational modes of the molecules. In general, the various fundamental vibrations (i.e., CH and CC stretching, CH in-plane and out-of-plane bending) are expected to fall in those regions characteristic of PAHs in general. Nevertheless, as a class, the spectra of fluoranthenes also show a few distinctive differences from PAHs containing only benzenoid rings. First, molecules that incorporate a cyclopentadienyl ring typically

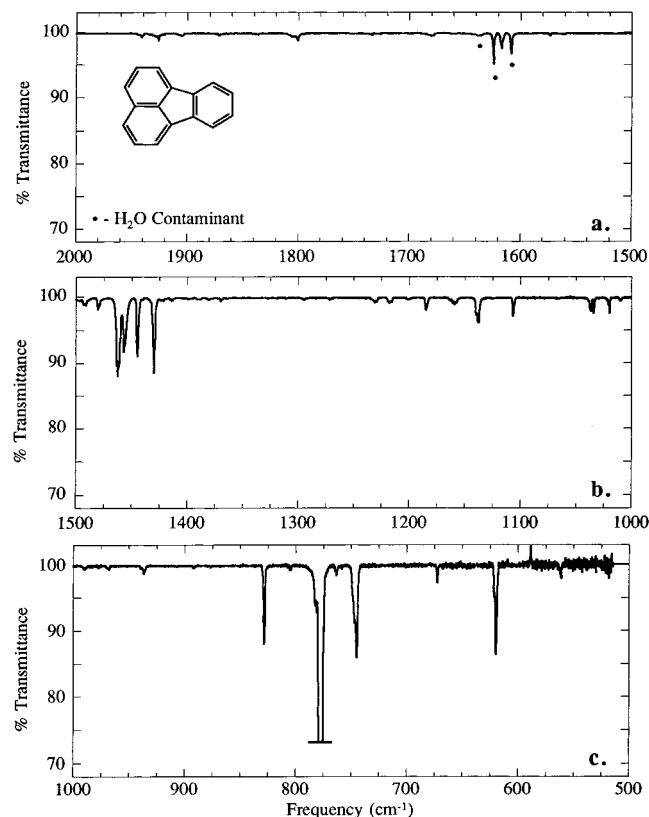


Figure 2. The spectra of matrix isolated fluoranthene ($\text{C}_{16}\text{H}_{10}$) through the aromatic CC stretching and CH bending regions: (a) 2000–1500 cm^{-1} , (b) 1500–1000 cm^{-1} , and (c) 1000–500 cm^{-1} . The spectrum was taken at a matrix temperature of 10 K and the argon-to-fluoranthene ratio was estimated to be in excess of 1000/1.

produce a somewhat larger number of absorption bands than do comparably sized, pure benzenoid PAHs of the same symmetry. This is particularly noticeable in the 1550–1350 cm^{-1} range, where the fluoranthenes typically exhibit $\geq 50\%$ more bands. The bands in this region are also considerably stronger in the fluoranthenes relative to other absorptions. Normalized to their strongest out-of-plane bending mode bands, the fluoranthenes typically produce between 2.5 and 5 times as much absorption in this region than do their benzenoid counterparts (approximately 3 times as much for PAHs in the comparable size range). This is undoubtedly linked to the distinctive geometry of the five-membered ring and, in the case of benzo[*ghi*]fluoranthene, the warping of the planar structure. Since this difference is associated with the carbon skeleton of the molecules, it is not surprising that the most dramatic changes are observed between 1550 and 1350 cm^{-1} and below 700 cm^{-1} where the aromatic CC stretching and the skeletal deformation modes, respectively, predominate.

In the following sections the spectra of each individual PAH is discussed and compared to previously published experimental work, when available.

2. *Fluoranthene, $\text{C}_{16}\text{H}_{10}$.* The spectrum of fluoranthene (Figures 1a and 2, Table 1) is fairly typical of all the PAHs in this series. Its spectrum is dominated by strong out-of-plane bending modes in the 800–700 cm^{-1} region, but it also produces a substantial number of moderately strong bands in the 1500–1400 cm^{-1} range. A significant fraction of the bands showed complex profiles presumably arising from matrix effects.

This spectrum can be compared to earlier matrix and gas-phase studies of fluoranthene. Mamantov et al.¹¹ used a nitrogen matrix and reported positions in the 1500–600 cm^{-1} range, but

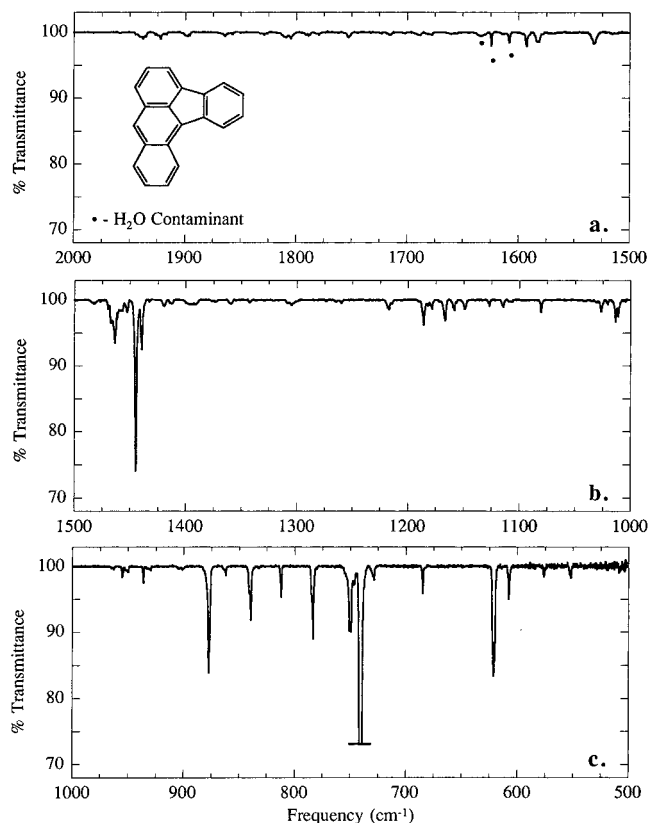


Figure 3. The spectra of matrix isolated benzo[*a*]fluoranthene ($C_{20}H_{12}$) through the aromatic CC stretching and CH bending regions: (a) 2000–1500 cm^{-1} , (b) 1500–1000 cm^{-1} , and (c) 1000–500 cm^{-1} . The spectrum was taken at a matrix temperature of 10 K and the argon to benzo[*a*]fluoranthene ratio was in excess of 1000/1.

did not list band strengths, so only a qualitative comparison can be made. Nonetheless, all of the reported frequencies agree to within 5 cm^{-1} or less of the moderate-to-strong bands (relative strength > 0.07) reported here. The earlier studies do not, however, report a band in the vicinity of the relatively strong 1429.2 cm^{-1} feature. Semmler et al.¹² measured the spectrum of fluoranthene in the gas-phase and provide both band positions and relative strengths (to the nearest 10%). Again, the agreement is generally quite good. Most reported positions fall within 5 cm^{-1} or less of the positions of the strongest argon-matrix-isolated bands and measured band strengths agree to within the stated precision of the data. The gas-phase studies do report a band near 1426 cm^{-1} that is similar in strength to the 1429.2 cm^{-1} band reported here. The biggest difference between the two data sets is that gas-phase studies do not report a feature which corresponds to the 1444.2 cm^{-1} feature reported here. A band is, however, reported at 1454 cm^{-1} with an intensity that is substantially stronger than that of the 1456.5 cm^{-1} argon matrix band alone, but which agrees well with the *sum* of the intensities of the 1444.2 and 1456.5 cm^{-1} matrix bands. Examination of the gas-phase spectrum shows that the 1454 cm^{-1} feature indeed exhibits a low-frequency shoulder. Together, this suggests that the 1444.2 and 1456.5 cm^{-1} features are blended in the gas-phase spectrum.

3. Benzo[*a*]fluoranthene, $C_{20}H_{12}$. The spectrum of benzo[*a*]fluoranthene (Figures 1b and 3 and Table 2) is qualitatively similar to that of fluoranthene in that it is dominated by strong out-of-plane bending modes in the 900–600 cm^{-1} region and contains substantial absorption in the 1500–1400 cm^{-1} range. The spectrum of benzo[*a*]fluoranthene contains a significantly larger number of absorption bands, in accordance with its lower

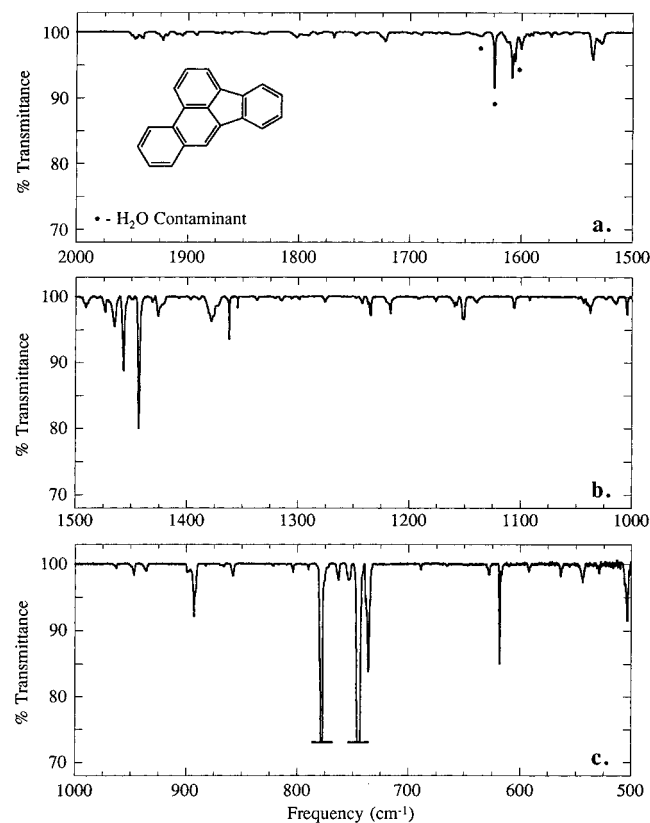


Figure 4. The spectra of matrix isolated benzo[*b*]fluoranthene ($C_{20}H_{12}$) through the aromatic CC stretching and CH bending regions: (a) 2000–1500 cm^{-1} , (b) 1500–1000 cm^{-1} , and (c) 1000–500 cm^{-1} . The spectrum was taken at a matrix temperature of 10 K and the argon to benzo[*b*]fluoranthene ratio was in excess of 1000/1.

symmetry (C_5). This is especially notable in the 900–500 cm^{-1} region. Again, a number of the bands show relatively complex profiles, presumably due to matrix effects. Neither theoretical nor experimental studies of the infrared spectroscopic properties of this molecule have been reported previously.

4. Benzo[*b*]fluoranthene, $C_{20}H_{12}$. Benzo[*b*]fluoranthene (benzo[*e*]acephenanthrylene) produces a spectrum (Figures 1c and 4, Table 3) with characteristic, strong out-of-plane bending mode bands in the 800–700 cm^{-1} region and substantial absorption in the 1500–1400 cm^{-1} range. Its spectrum contains a comparable number of absorption bands to that of benzo[*a*]fluoranthene; however, in this case the band profiles tend to be much simpler.

This molecule has not been studied previously by matrix isolation, but its gas-phase spectrum has also been reported by Semmler et al.¹² While comparison of the two data sets is somewhat complicated by the lower resolution (8 cm^{-1}) of the gas-phase data, for those bands with relative intensities greater than 15%, the matrix positions fall within 5 cm^{-1} of those reported in the gas-phase. There are, however, bands in the matrix spectrum with relative strengths that exceed 10% but which were not reported in the gas-phase studies, namely, the bands at 735.7, 1456.3, and 1464.6 cm^{-1} (two additional such bands at 503.3 and 617.9 cm^{-1} simply fall below the low-frequency limit of the gas-phase data). Presumably, at 8 cm^{-1} resolution, these bands are convolved with nearby bands. For example, the band observed at 735.7 cm^{-1} in an argon matrix likely blends with the 741 cm^{-1} band in the gas-phase spectrum. Assuming this is the case, the relative intensities reported in the two experiments can be compared by normalizing the

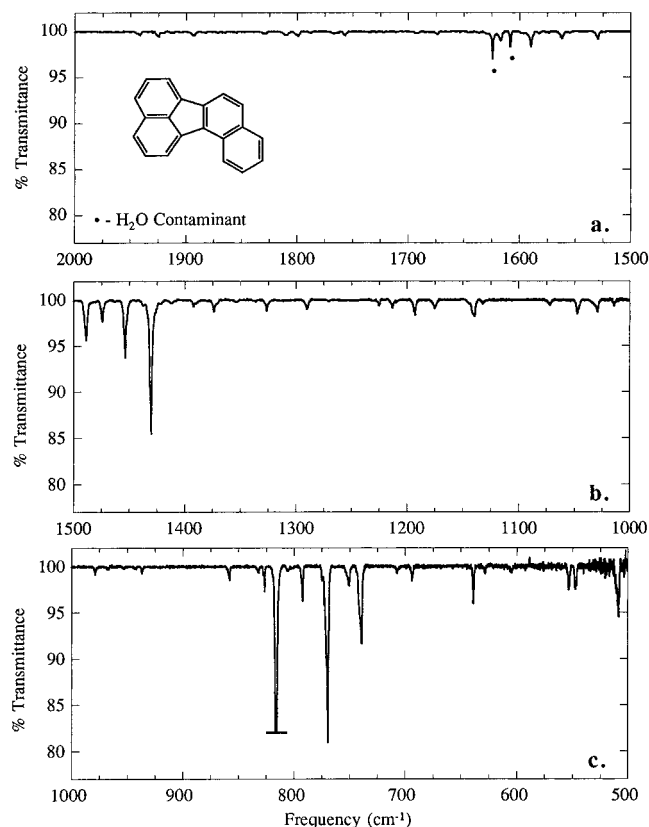


Figure 5. The spectra of matrix isolated benzo[*j*]fluoranthene ($C_{20}H_{12}$) through the aromatic CC stretching and CH bending regions: (a) 2000–1500 cm^{-1} , (b) 1500–1000 cm^{-1} , and (c) 1000–500 cm^{-1} . The spectrum was taken at a matrix temperature of 10 K and the argon to benzo[*j*]fluoranthene ratio was in excess of 1000/1.

intensity of the nominal 741 cm^{-1} gas-phase band to the *sum* of the 735.7 and 744.1 cm^{-1} matrix bands. Doing so shows that the relative band strengths of the two data sets generally agree to within 25–30% with only a few noteworthy discrepancies. For instance, the gas-phase data show a relatively strong band near 1599 cm^{-1} (0.20) where the matrix spectrum has only a weak band (1599.6 cm^{-1} , 0.04). This position, however, falls quite close to some strong matrix isolated H_2O lines, so contamination may be the source of this discrepancy. Also, three discrete matrix bands at 1442.6, 1456.3, and 1464.6 cm^{-1} are observed where only a single gas-phase band is reported (1442 cm^{-1}). If these bands are blended in the lower resolution, gas-phase data (the gas-phase band does appear to be somewhat broader than the other bands in the spectrum), then the total measured absorption in the matrix appears to be nearly twice as great as that reported in the gas phase. However, a qualitative comparison of the intensities of the 1442 and 887 cm^{-1} bands in the gas-phase spectrum reveals that, while these bands are tabulated as equal, the 1442 cm^{-1} band appears to be considerably larger. Thus, the reported relative strength of the 1442 cm^{-1} band may be underestimated and, in fact, more consistent with the measured matrix value. Thus, the overall agreement between the gas-phase and matrix isolation spectra of benzo[*b*]fluoranthene is excellent.

5. Benzo[*j*]fluoranthene, $C_{20}H_{12}$. The spectrum of benzo[*j*]fluoranthene (Figures 1d and 5 and Table 4) is dominated by strong out-of-plane bending modes in the 900–700 cm^{-1} region and contains substantial absorption in the 1500–1400 cm^{-1} range. Benzo[*j*]fluoranthene exhibits a rich spectrum that is qualitatively similar to that of benzo[*b*]fluoranthene. A substantial fraction of the bands have relatively broad profiles,

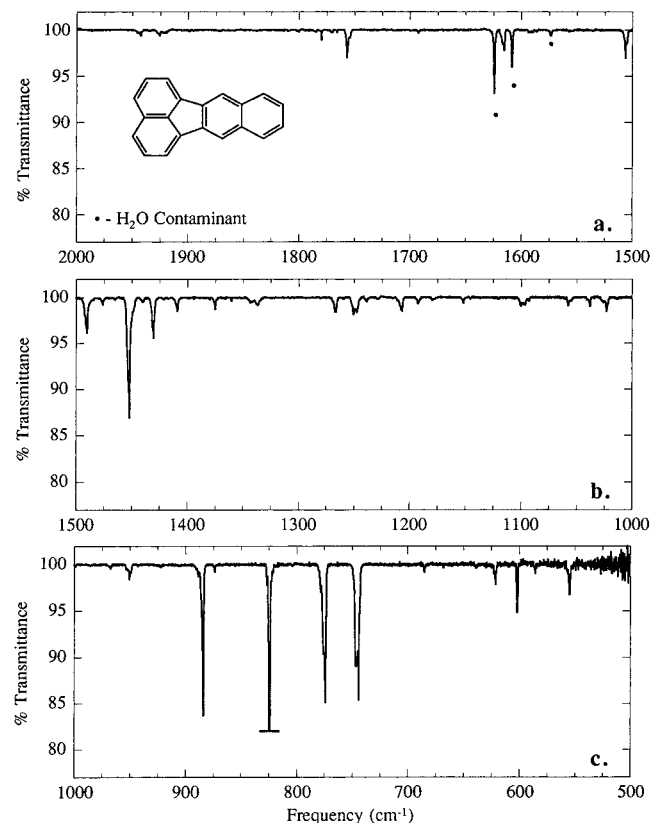


Figure 6. The spectra of matrix isolated benzo[*k*]fluoranthene ($C_{20}H_{12}$) through the aromatic CC stretching and CH bending regions: (a) 2000–1500 cm^{-1} , (b) 1500–1000 cm^{-1} , and (c) 1000–500 cm^{-1} . The spectrum was taken at a matrix temperature of 10 K and the argon to benzo[*k*]fluoranthene ratio was in excess of 1000/1.

although they do not show the same degree of complexity common in the band profiles of fluoranthene and benzo[*a*]fluoranthene. Again, the larger width is probably due to matrix effects. Neither theoretical nor experimental studies of the infrared spectroscopic properties of this molecule have been reported previously.

6. Benzo[*k*]fluoranthene, $C_{20}H_{12}$. Benzo[*k*]fluoranthene produces a spectrum (Figures 1e and 6 and Table 5) with the characteristic strong out-of-plane bending modes in the 900–700 cm^{-1} region and substantial absorption in the 1500–1400 cm^{-1} range. Its spectrum contains a comparable number of absorption bands to the spectra of the previous benzofluoranthenes and the bands tend to have simple profiles similar to those in the spectra of benzo[*b*]fluoranthene.

While this molecule has not been studied previously in a matrix, as was the case for fluoranthene and benzo[*b*]fluoranthene, it too has been studied in the gas phase by Semmler et al.¹² Despite the lower resolution (8 cm^{-1}) of this gas-phase data, where comparisons are possible, all of the reported gas-phase band positions fall within 5 cm^{-1} of the positions observed in the matrix. Furthermore, with the exception of the aromatic CH stretching region, the relative strengths of all bands agree to better than 30%. In the case of the CH stretching feature centered at 3069.3 cm^{-1} , the matrix band strength is about 75% higher than the previously reported gas-phase value. In addition, the matrix spectrum contains a number of bands with relative strengths greater than 10% that were not reported in the gas phase. Qualitative inspection of the gas-phase data does reveal the presence of unreported weak bands near 1760, 1500, 1340, and 1100 cm^{-1} which correspond to some of the matrix features. The remaining bands seen in the matrix experiments but not in

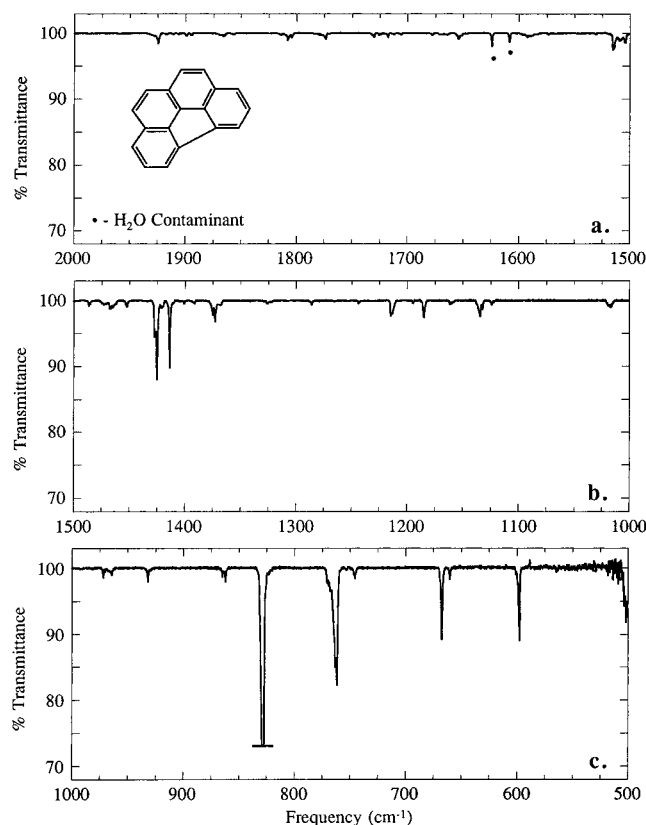


Figure 7. The spectra of matrix isolated benzo[ghi]fluoranthene ($C_{18}H_{10}$) through the aromatic CC stretching and CH bending regions: (a) 2000–1500 cm^{-1} , (b) 1500–1000 cm^{-1} , and (c) 1000–500 cm^{-1} . The spectrum was taken at a matrix temperature of 10 K and the argon to benzo[ghi]fluoranthene ratio was in excess of 1000/1.

the gas-phase are probably blended with other nearby bands at the lower resolution of that data. For example, the gas-phase band at 1265 cm^{-1} may represent a blending of the 1247.1/1250.1 and 1265.5/1266.7 cm^{-1} matrix isolation features. Thus, the overall agreement between the gas-phase and matrix isolation spectra of benzo[k]fluoranthene is quite good.

7. Benzo[ghi]fluoranthene, $C_{18}H_{10}$. While the spectrum of benzo[ghi]fluoranthene (Figures 1f and 7 and Table 6) is qualitatively similar to those of the previous fluoranthenes, it has some unique characteristics. The spectrum is remarkably simple given the large size and relatively low symmetry of the molecule (C_5). Like benzo[b]fluoranthene and benzo[k]fluoranthene, the band profiles in the spectrum are typically quite simple. Aromatic CH out-of-plane bending modes dominate the spectrum but, compared to the other fluoranthenes, it produces less than 50% as much absorption in the 1500–1400 cm^{-1} region. Together, these characteristics make the spectrum of benzo[ghi]fluoranthene qualitatively more similar to that of a pure benzenoid PAH. Note that the central cyclopentadienyl ring in benzo[ghi]fluoranthene warps the molecule into a shallow bowl or saucer shape, destroying the planarity characteristic of most of the PAHs studied to date. This warping presumably enhances the out-of-plane skeletal deformation modes leading to the moderate low-frequency absorptions (667.1 cm^{-1} , 0.13; 597.3 cm^{-1} , 0.12; and 501.1 cm^{-1} , 0.09). Neither theoretical nor experimental studies of the infrared spectroscopic properties of this molecule have been reported previously.

C. Implications for Astrophysics. A detailed consideration of the relevance of the infrared spectral properties of neutral PAHs to the family of discrete interstellar infrared emission features observed near 3050, 1920, 1725, 1610, 1310–1280,

TABLE 1: Infrared Frequencies (cm^{-1}) and Intensities for Neutral Fluoranthene

frequency in Ar	relative intensity ^a
561.1	0.02
619.3	0.13
672.0	0.01
744.5	0.25
762.9	0.01
775.0, 776.7	1.00
827.9	0.10
936.3	0.02
1019.5	0.02
1033.7	0.01
1036.7	0.02
1106.3	0.02
1137.3, 1139.4	0.07
1159 ^b	0.02
1184.4	0.03
1217.0	0.02
1230.6	0.02
1429.2	0.16
1444.2	0.13
1456.5	0.21
1461.8	0.32
1479.8	0.02
1490.6, 1492.7	0.02
1616.5	0.04
1678.9	0.02
1799.8 ^b	0.04
1904.8	0.02
1925.3	0.04
1940.4	0.02
3016.7	
3023.3	
3051.9 ^c	
3066.2 ^c	
3073.1 ^c	
3085.9	
Σ3100–3010	0.81

^a Intensities relative to that of the combined 775.0 and 776.7 cm^{-1} bands. ^b Position of strongest band in a “complex” of features. ^c Major features in the CH stretching region.

1160, 885, 840, and 790 cm^{-1} has been presented in part 1. Nevertheless, the distinctive spectral characteristics of the fluoranthenes presented here warrants some further comment.

As a class, the PAHs containing a cyclopentadienyl ring tend to produce considerably more and/or stronger bands in the 1500–1250 cm^{-1} range relative to those in the 900–600 cm^{-1} range. This tendency moves the ratio of total intensity in CC stretching and CH in-plane bending modes to that in CH stretching and CH out-of-plane bending modes into better agreement with the ratio observed in the interstellar spectrum where features in the 1600–1100 cm^{-1} region dominate. Nevertheless, PAHs containing five-sided rings still do not provide a particularly good match to the interstellar spectrum. While better than PAHs with only hexagonal rings, the fluoranthenes still produce out-of-plane bending mode bands that are much too strong relative to the CC and CH modes in the 1600–1000 cm^{-1} range. In addition, the strongest CC modes in the fluoranthenes tend to fall between 1500 and 1400 cm^{-1} , a position that lies between the strongest interstellar features near 1610 and between 1310 and 1280 cm^{-1} .

A more complete discussion of the astrophysical relevance of neutral PAHs can be found in part 1.¹

IV. Conclusions

The 4000–500 cm^{-1} infrared absorption spectra of six different argon matrix isolated PAHs that incorporate a cyclo-

TABLE 2: Infrared Frequencies (cm⁻¹) and Intensities for Neutral Benzo[*a*]fluoranthene

frequency in Ar	relative intensity ^a
481.5 ^b	0.10 ^b
551.7	0.02
575.7	0.02
607.2	0.05
619.8, 620.9	0.35
684.3	0.04
728.1	0.04
739.0, 740.8	1.00
748.7, 750.2	0.28
783.0	0.16
811.7	0.05
839.0 ^c	0.14
861.7	0.02
876.7	0.31
900.9, 904.2	0.02
929.3, 932.9	0.01
935.8	0.02
949.4 ^c	0.02
954.7	0.01
1010.5, 1013.1	0.08
1026.2	0.03
1080.0	0.02
1113.7	0.02
1126.2	0.01
1148.2	0.03
1157.8	0.03
1165.9	0.06
1177.8, 1185.3 ^c	0.12
1216.4	0.05
1304.1, 1307.9	0.03
1359.0	0.02
1394 ^d	0.05
1412.5	0.02
1418.9	0.02
1438.8	0.10
1444.1 ^e	0.43
1452.0	0.03
1463.2 ^c	0.27
1482.0	0.02
1531.5	0.08
1582.0	0.06
1592.2	0.04
1632 ^f	0.03
1677.1	0.02
1688.7	0.02
1714.9	0.01
1752.0	0.02
1779.0	0.01
1788.4	0.02
1804.1, 1808.9	0.05
1828.3	0.02
1857.2, 1863.7	0.03
1897.2	0.02
1921.4 ^c	0.04
1937.4 ^c	0.06
2927.2	
2936.0	
2941.2	
2969.3	
3047.5 ^g	
3059.4 ^g	
3074.6 ^g	
3089.1	
3119.5	
Σ3131–2921	1.65

^a Intensities relative to that of the combined 739.0 and 740.8 cm⁻¹ bands. ^b Values uncertain since this band is near the low-frequency limit of the MCT-B detector. ^c Position of strongest band or bands in a “complex” of features. ^d Unusually broad feature. ^e Integrated area of all the bands falling in this spectral range; area dominated by the 1438.8 and 1444.1 cm⁻¹ bands. ^f This feature is most likely due largely to contaminant H₂O. ^g Major features in the CH stretching region.

pentadienyl ring have been measured and the resulting band positions and relative strengths have been tabulated. The PAHs reported here are fluoranthene, benzo[*a*]fluoranthene, benzo[*b*]-

TABLE 3: Infrared Frequencies (cm⁻¹) and Intensities for Neutral Benzo[*b*]fluoranthene

frequency in Ar	relative intensity ^a
503.3	0.12
543.6	0.05
563.4	0.02
591.9	0.02
617.9	0.11
627.4	0.02
688.6	0.01
735.7	0.32
744.1	1.00
753.1	0.06
762.6	0.04
777.4	0.68
803.5	0.01
857.8	0.03
892.5, 897.8	0.16
935.8	0.02
946.8	0.03
962.5	0.01
1003.8	0.03
1014.5	0.03
1037.2 ^b	0.08
1105.4	0.03
1139.0	0.03
1150.9	0.08
1156.8, 1158.9	0.04
1175.5	0.01
1216.4	0.06
1234.4 ^b	0.05
1241.7	0.02
1275.3	0.01
1314.2	0.01
1336.4	0.01
1361.5	0.04
1377.5	0.21
1389.1	0.01
1425.3	0.09
1430.7	0.01
1442.6	0.31
1448.3	0.01
1456.3	0.20
1464.6	0.11
1472.9	0.03
1490.4	0.04
1527.7, 1535.2	0.18
1599.6	0.04
1605.2	0.02
1611.9	0.01
1689.4	0.01
1721.5	0.05
1748.4	0.01
1768.0	0.01
1782.9	0.01
1791.3	0.01
1801.7 ^b	0.02
1831.3	0.01
1838.8	0.01
1891.8	0.01
1904.4, 1909.4	0.02
1918.0, 1922.0	0.05
1939.8, 1946.8 ^b	0.07
2974.0	
3016.2	
3034.0	
3054.3	
3065.9 ^c	
3073.5 ^c	
3083.2 ^c	
Σ3113–2970	1.60

^a Intensities relative to the strongest band at 744.1 cm⁻¹. ^b Position of strongest bands in a “complex” of features. ^c Major features in the CH stretching region.

fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, and benzo[*ghi*]fluoranthene.

As a class, these molecules have many spectral characteristics in common with each other and with the spectra of other matrix isolated PAHs. The strongest bands are associated with CH out-of-plane bending modes in the 900–600 cm⁻¹ range.

TABLE 4: Infrared Frequencies (cm⁻¹) and Intensities for Neutral Benzo[*j*]fluoranthene

frequency in Ar	relative intensity ^a
508.3	0.14
547.0	0.06
553.0	0.06
604.4	0.01
628.1	0.02
638.4	0.07
693.5	0.04
706.8	0.01
738.7	0.36
750.1	0.09
769.2	0.68
791.9	0.07
805.7	0.01
815.5	1.00
826.1	0.05
831.7	0.01
857.6	0.03
936.4	0.02
978.4	0.01
1014.0	0.01
1028.8	0.07
1047.1	0.05
1071.5	0.02
1131.3	0.01
1139.6	0.11
1174.7	0.05
1192.3	0.06
1212.6	0.03
1224.9	0.01
1289.7	0.05
1325.8	0.04
1353.7	0.01
1373.3	0.03
1391.8	0.03
1411.8	0.02
1429.5	0.61
1452.9	0.24
1473.6	0.09
1488.0	0.18
1529.0	0.07
1561.4	0.04
1582.1	0.01
1589.3	0.06
1616.5	0.04
1673.2	0.01
1692.5	0.01
1756.3	0.02
1762.4, 1766.2	0.01
1798.8	0.03
1809.2	0.02
1828.4	0.01
1892.5	0.02
1924.6	0.02
1941.3	0.01
2926.5	
2934.1	
2940.7	
2988	
3028.7	
3051.9 ^b	
3066.1 ^b	
3078.2	
3091.5	
3109.5	
Σ3130–2920	1.59

^a Intensities relative to the strongest band at 815.5 cm⁻¹. ^b Major features in the CH stretching region.

Additional strong bands are the CH stretching modes are seen in the 3150–3000 cm⁻¹ region. Weaker features due to various CC modes and CH in-plane bending modes are seen between 1650 and 1000 cm⁻¹. The spectra also contain large numbers of weak bands, particularly between 1950 and 1650 cm⁻¹, that are due to overtone/composition modes.

The spectra of PAHs containing the cyclopentadienyl ring show some characteristic differences from PAHs that contain only benzenoid rings. The fluoranthenes typically exhibit a

TABLE 5: Infrared Frequencies (cm⁻¹) and Intensities for Neutral Benzo[*k*]fluoranthene

frequency in Ar	relative intensity ^a
554.3	0.09
585.0	0.02
601.3	0.11
620.9	0.05
684.7	0.02
743.6, 745.9	1.00
773.6	0.80
803.9	0.01
823.7	0.90
873.4	0.02
883.5	0.54
950.0 ^b	0.08
967.2	0.01
998.6	0.01
1022.7	0.08
1037.6	0.03
1057.2	0.04
1099.8 ^b	0.16
1151.2	0.02
1191.9	0.03
1206.6	0.09
1228.3	0.04
1238.1	0.03
1247.1, 1250.1	0.19
1265.5, 1266.7	0.08
1336.5, 1342.2	0.10
1374.5	0.04
1408.4	0.08
1429.9	0.22
1439.6	0.02
1451.4	0.84
1464.8	0.01
1475.5	0.02
1489.7	0.25
1505.8	0.13
1586.0	0.01
1614.7	0.13
1692.0	0.01
1756.1 ^b	0.17
1770.0	0.01
1779.1	0.01
1784.2	0.01
1791.5	0.02
1799.6, 1801.2	0.01
1920.1	0.02
1924.8	0.02
1941.8, 1944.8	0.04
2940.6	
2961	
3005.0	
3022.6	
3039.6	
3056.6	
3069.3 ^c	
3096.5	
3107.2	
Σ3122–2935	2.53

^a Intensities relative to that of the combined 743.6 and 745.9 cm⁻¹ bands. ^b Position of strongest bands in a “complex” of features. ^c Major feature in the CH stretching region.

moderately larger number of absorption bands compared to pure benzenoid PAHs of comparable size, particularly in the 1550–1350 cm⁻¹ range where the bands are both more numerous and stronger. Normalized to their strongest out-of-plane bending modes, the fluoranthenes typically produce 2.5–5 times as much absorption in this, the aromatic CC stretching region, as do most of the traditional benzenoid PAHs. This presumably arises from the incorporation of the cyclopentadienyl ring for which there is no infrared inactive CC stretch.

In the cases of fluoranthene, benzo[*b*]fluoranthene, and benzo[*k*]fluoranthene, it was possible to make comparisons with earlier matrix isolation and gas-phase laboratory data. The comparisons that could be made were somewhat limited by the lower

TABLE 6: Infrared Frequencies (cm⁻¹) and Intensities for Neutral Benzo[ghi]Fluoranthene

frequency in Ar	relative intensity ^a
501.1	0.09
597.3	0.12
659.9	0.01
667.1	0.13
745.1	0.02
761.3, 762.7	0.57
828.1	1.00
861.7, 864.5	0.03
931.4	0.02
963.8	0.01
971.5	0.01
1016.7	0.03
1131.6, 1134.0	0.06
1161.0	0.01
1184.6	0.04
1212.8, 1214.3	0.06
1372.4 ^b	0.10
1413.3	0.11
1420.3	0.01
1424.6 ^b	0.21
1451.7	0.01
1464.0, 1466.5	0.03
1472.0	0.01
1485.9	0.01
1503.8, 1508.8, 1514.1	0.13
1653.5	0.02
1664.1, 1669.2	0.01
1729.7	0.01
1773.0	0.01
1803.9, 1807.6	0.02
1865.2	0.02
1894.1, 1898.6	0.02
1923.9	0.04
2946.0	
2993.4	
3009.5	
3028.1	
3062.7 ^c	
3084.8	
Σ3102–2942	1.23

^a Intensities relative to the strongest band at 828.1 cm⁻¹. ^b Position of strongest bands in a "complex" of features. ^c Major features in the CH stretching region.

resolution, spectral coverage, and sensitivity of the earlier work. Nonetheless, where comparisons can be made, the agreement between the various data sets was generally very good.

Finally, comparisons between the infrared spectra presented here and the emission band family characteristic of high UV interstellar environments show that PAHs that contain five-sided rings provide a better quantitative match to the ratio of CC and

CH in-plane bending mode strengths relative to CH stretching and CH out-of-plane bending mode strengths than do neutral PAHs containing only six-sided rings. However, they still fail to provide as good a match as can be obtained using the spectra of PAH cations.

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