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Publisher: Taylor & Francis

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## Petroleum Science and Technology

Publication details, including instructions for authors and subscription information:  
<http://www.tandfonline.com/loi/lpet20>

### X-Ray Raman Spectroscopy—A New Tool to Study Local Structure of Aromatic Hydrocarbons and Asphaltenes

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Version of record first published: 15 Aug 2007.

To cite this article: Uwe Bergmann, Henning Groenzin, Oliver C. Mullins, Pieter Glatzel, John Fetzer & S. P. Cramer (2004): X-Ray Raman Spectroscopy—A New Tool to Study Local Structure of Aromatic Hydrocarbons and Asphaltenes, *Petroleum Science and Technology*, 22:7-8, 863-875

To link to this article: <http://dx.doi.org/10.1081/LFT-120038722>

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## X-Ray Raman Spectroscopy—A New Tool to Study Local Structure of Aromatic Hydrocarbons and Asphaltenes

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### ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are essential components in numerous natural and man made organic compounds. In asphaltenes, knowledge of the electronic structure of both its aromatic and aliphatic components is of crucial importance, when trying to understand and predict its macroscopic properties.

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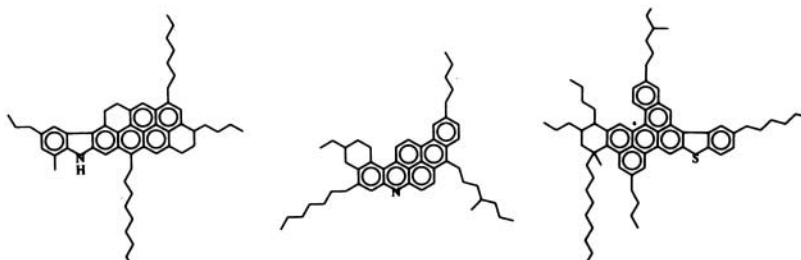
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Theoretical studies of complex PAHs have led to simple rules to describe their  $\pi$  electron distribution, but systematic experimental support is still needed. A novel approach to directly probe carbon type in PAHs is described here, namely the technique of X-ray Raman spectroscopy (XRS). Conventional X-ray absorption spectroscopy (XAS) has been used for many years for element specific characterization of local structure and chemistry. However, in the soft X-ray region (relevant for light elements) its application to numerous carbonaceous systems including asphaltenes encounters problems. Most of the difficulties, including surface sensitivity and restricted sample environments, stem from the submicron path lengths of soft X-rays and/or electrons. XRS provides a means for obtaining the information content of soft X-ray absorption spectra while maintaining the experimental benefits of hard X-ray techniques ( $\sim$ mm path length). In the XRS process an incident photon is inelastically scattered and part of its energy is transferred to excite an inner shell electron into an unoccupied state. Under the dipole approximation, the resulting features are identical to the corresponding XAS spectrum. In the past, the extremely low cross-section of XRS has made this technique impractical, but intense new X-ray facilities and improvements in X-ray optics have helped to advance this unique spectroscopic tool. We have applied XRS to a series of PAHs and several asphaltenes. The results directly support the simple ideas contained in the "sextet-double bond" description of PAHs. Furthermore, we show that XRS can probe the geometry of aromatic ring systems in asphaltenes, as well as its ratio of aromatic and aliphatic constituents.

## INTRODUCTION AND MOTIVATION

Asphaltenes are complex mixtures of aromatic and aliphatic hydrocarbons that are present as a solid suspension in crude oils and coals (Chilingarian and Yen, 1978; Mullins and Sheu, 1998; Sheu and Mullins, 1995; Speight, 1980). Understanding the chemical and physical properties of petroleum asphaltenes is becoming increasingly important due to their inordinate effect on exploitation of deep-sea oil reserves. In this market, where well costs are approaching \$100 million, asphaltene flocculation with concomitant plugging of deep-water sub-sea facilities must be avoided. The complex chemistry of asphaltenes has to be understood on a fundamental level in order to optimize the use of crude oil. However, the molecular structure of complex carbonaceous materials such as asphaltene has eluded satisfactory understanding (Fig 1).





**Figure 1.** Typical proposed structures relevant to asphaltenes (Mullins and Sheu, 1998).

Even the order of magnitude of molecular weight of petroleum asphaltenes has been controversial for 20 years, although that now appears to be solved (Groenzin et al., 1999).

Recent work has demonstrated the strong connection between molecular structure and physical properties of asphaltenes (Buenrostro-Gonzalez et al., 2001). The size of the fused ring moieties is found to scale with the length of alkane chains in asphaltenes and this governing principle determines the size of the fundamental asphaltene micelle in crude oil. The overall molecular structure governs the oil–water interfacial activity for asphaltenes, which is universally observed for crude oil–water emulsions. Clearly, molecular structure is strongly related to important asphaltene properties.

The structures of the fused aromatic ring systems in asphaltenes have been probed by various techniques, including  $^{13}\text{C}$ -NMR, fluorescence depolarization, STM, and high-resolution mass spectroscopy. A consensus is building that the overall size of the fused ring systems consists of 4–10 rings, although some controversy exists here. What is still very much in doubt is the geometry of these ring systems. Are the ring systems similar to pentacene structures, coronene structures, aromatized steroid structures, or others? How do they alter under varying conditions such as pressure and temperature? None of these questions can be answered with the techniques mentioned above. On the other hand, carbon K-edge XAS offers an excellent probe of these structures.

The sensitivity of the near edge of XAS, known as NEXAFS (Near edge X-rays absorption spectroscopy) or XANES (X-ray absorption near edge structure), to local structure and geometry has been known for many years (Stöhr, 1992). For petroleum asphaltenes so far sulfur (George and Gorbaty, 1989) and nitrogen XANES studies (Mitra-Kirtley et al., 1993) provided the most definitive description of the corresponding



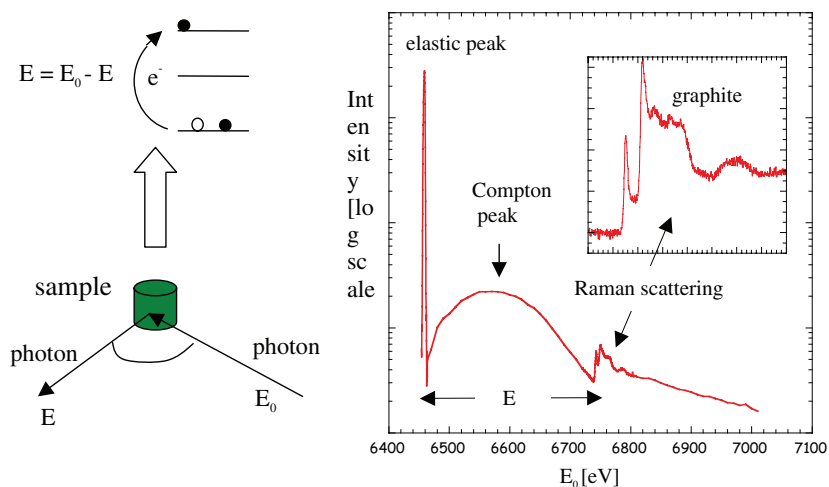
heteroatom moieties. Unfortunately, carbon K-edge XANES in these materials suffers from several problems.

First, if measured in the more bulk sensitive fluorescence mode, the high concentration of carbon (about 90% of the mass fraction) gives rise to saturation effects which strongly distort spectral features needed to quantify the structural properties. Second, if measured by electron yield, the results are from the first 10 nm, and asphaltenes are known to suffer surface oxidation. Third, related compounds such as kerogens (source material for crude oils) occur in rock matrices. Fluorescence detected XANES would not work for bulk analysis of these samples, because the x-ray absorption length is shorter than the length scale of the heterogeneity. Finally, at X-ray energies around 285 eV, carbon XANES have to be conducted under good vacuum conditions, which restricts sample handling and inhibits studies under various chemically relevant conditions. All of these problems can be avoided with a hard X-ray probe. XRS is performed at 6–10 keV where the penetration is of order 1 mm, and is therefore ideally suited to study these systems.

## 2. TECHNIQUE AND INSTRUMENTATION

Carbon K-edge XANES and inner-shell electron energy loss spectroscopy (ISEELS) have been successfully employed to gain detailed structural and chemical information about hydrocarbons for several years (Stöhr, 1992). Characteristic near-edge features such as  $1s \rightarrow \pi^*$  and  $1s \rightarrow \sigma^*$  resonances contain information about the type of bonds (Francis et al., 1994; Yokoyama et al., 1990) and the intramolecular bond lengths (Hitchcock et al., 1984; Sette et al., 1984). Furthermore the peaks can be used to unambiguously determine the orientation of aromatic hydrocarbons on, e.g., metal surfaces (Yannoulis et al., 1987a, b). In recent years *ab initio* calculations have been used to interpret detailed XANES features taken at high resolution, as shown in studies on polycyclic aromatic hydrocarbons (Oji et al., 1997, 1998) or dimethyl phthalate isomers (Urquhart et al., 1997). XANES has also been extensively applied to study polymers, here the combination of the technique with X-ray microscopy has proven very powerful (Urquhart et al., 1999). As the interplay between experiments and theoretical calculations continues to enhance the understanding of hydrocarbons, a true bulk technique with XANES information would give access to a large class of systems, where traditional XANES techniques have strong limitations. Large PAHs as well as asphaltenes and coals with their complex structures and sensitivity to surface oxidation fall in this category.





**Figure 2.** Left: in the XRS process a hard X-ray photon is inelastically scattered providing a small fraction of its energy to excite a core electron into an empty state. Right: inelastic scattering spectrum from graphite. Plotted is intensity versus incident X-ray energy with analyzer energy fixed at 6460 eV.

In XRS, a photon with energy  $E_0$  is inelastically scattered with energy  $E'$  and the lost energy results in the excitation of a core electron (Fig. 2). By measuring the energies of both the incident and scattered photon one obtains the energy transfer  $\Delta E = E_0 - E'$ , corresponding to the excitation energy. Varying  $\Delta E$  by changing the incident energy at a fixed analyzer setting  $E'$  results in a spectrum with mainly three components.

First, a strong quasi-elastic peak at  $\Delta E = 0$  (its width reflects the instrumental energy resolution), then a broad Compton peak and finally the XRS spectrum showing typical XANES features. The schematic setup of an XRS experiment is shown in Fig. 3. The insertion device at a third generation synchrotron source produces an intense X-ray beam with a bandwidth of  $\sim 100$  eV. The beam passes then through a tunable monochromator, used to vary the incident energy  $E_0$ . After passing through focusing optics (not shown in the figure) the beam impinges on the sample and X-rays are scattered essentially in all directions. An analyzer tuned to a fixed energy selects only scattered photons with energy  $E'$ . The spectrum as shown in Fig. 2 is obtained by varying  $E_0$  at fixed  $E'$ .



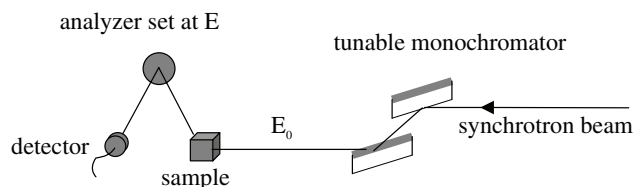


Figure 3. Schematic setup of XRS experiment.

The XRS phenomenon was already noted early last century (DuMond, 1933; Smekal, 1923; Sommerfeld, 1936) and since the 1960s (Mizuno and Ohmura, 1967; Suzuki, 1967) the close connection between XRS and XANES has been established. For a randomly oriented sample, the transition probability for XRS,  $w$ , is described by (Tohji and Udagawa (1989):

$$w = \{(4\pi^3 e^4 h)/(m^2 v_i v_j)\} (1 + \cos^2 \theta) |\langle f | \exp(iqr) | i \rangle|^2 \times \delta(E_f - E_0 - h(v_i - v_j)),$$

where  $\langle f |$  and  $| i \rangle$  are the final and initial state wave functions,  $v_i$  and  $v_j$  are incident and scattered X-ray frequencies,  $\theta$  is the scattering angle, and  $q$  is the momentum transfer. When  $qr \ll 1$ , the dipole approximation is valid and (also using  $|k_i| \cong |k_j|$ ) the above equation becomes (Tohji and Udagawa, 1989):

$$w = \{(64\pi^5 e^4 h)/(m^2 c^2)\} (1 + \cos^2 \theta) \sin^2(\theta/2) |\langle i | r | f \rangle|^2,$$

where the matrix element is the same as for dipole X-ray absorption (Mizuno and Ohmura, 1967). When  $q$  is large, the appearance of the spectrum can change (Krisch et al., 1997), but the work shown here is to a good approximation in the dipole regime. With the advent of tunable synchrotron radiation in the 1980s it has become possible to use the X-ray Raman effect to do spectroscopy. Nevertheless, besides demonstration experiments, there have been only a few applications of XRS so far (Bergmann et al., 2000, 2002; Bowron et al., 2000; Watanabe et al., 1996). Bright new synchrotron sources might change this and, as shown in a recent review (Bergmann et al., 2002), the technique is now beyond demonstration experiments. XRS might become a routine tool in the future.

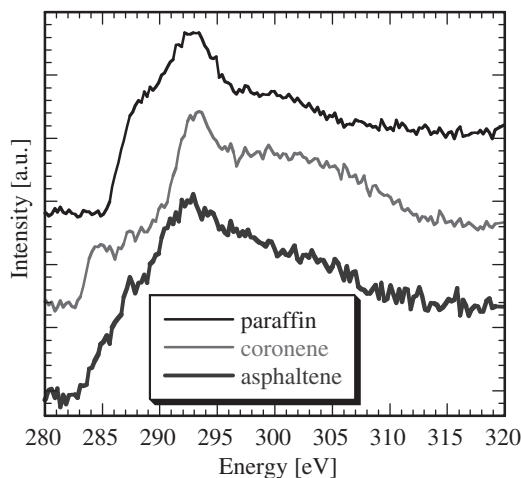
To perform XRS efficiently a very bright X-ray source, a high-resolution incident beam monochromator, and an efficient high-resolution analyzer is required. For the analyzer, two conditions have to be fulfilled simultaneously: good energy resolution and large angular acceptance. We



have built such a device based on 8 curved Johann (Johann, 1931) type Si Bragg crystals operating on intersecting Rowland circles. The instrument is currently the most efficient of its kind, capturing a solid angle of 0.5% of  $4\pi$  sr at an estimated energy resolution of  $<0.4$  eV when used for XRS studies (Bergmann and Cramer, 1998). The experimental energy resolution in XRS is given by the convolution of monochromator and analyzer resolution, and depending on the beamline we achieved a resolution of 1–2 eV. As will be seen in the following, the improvement in energy resolution from 2 to 1.1 eV is critical for a more quantitative analysis, in particular of the  $1s \rightarrow \pi^*$  feature.

### 3. RESULTS AND DISCUSSION

Our first XRS experiment was performed at wiggler beamline X-25 at the National Synchrotron Light Source (Bergmann et al., 2000) and was a study of petroleum asphaltene prepared from a Kuwait crude oil (UG8) using *n*-heptane precipitation (Mitra-Kirtley et al., 1993). The XRS energy resolution in this experiment was  $\sim 2$  eV and Fig. 4 shows spectra of paraffin, coronene, asphaltene.



**Figure 4.** Comparison of carbon XANES in XRS mode obtained for paraffin (top), coronene (middle), and asphaltene (bottom). Spectra have been background corrected and normalized to yield the same edge jump.





The paraffin spectrum shows a sharp edge with a shoulder at  $\sim 288$  eV and the main  $1s \rightarrow \sigma^*$  resonance at about 293 eV. In contrast, the coronene shows a  $1s \rightarrow \sigma^*$  resonance at about the same energy, as well as a feature at  $\sim 285$  eV. Based on assignments of other unsaturated carbon compounds (Bianconi, 1988), this corresponds to a  $1s \rightarrow \pi^*$  transition. The asphaltene exhibits a more diffuse spectrum, which is not surprising considering the complex mixture of molecules involved in this sample. Nevertheless, low energy structure can be distinguished in this spectrum that clearly represents  $1s \rightarrow \pi^*$  intensity. The intensity of this feature can be used to estimate the aromatic fraction of the carbon in this asphaltene, assuming that the model compounds represent accurate spectral models for the saturated and aromatic components of asphaltene.

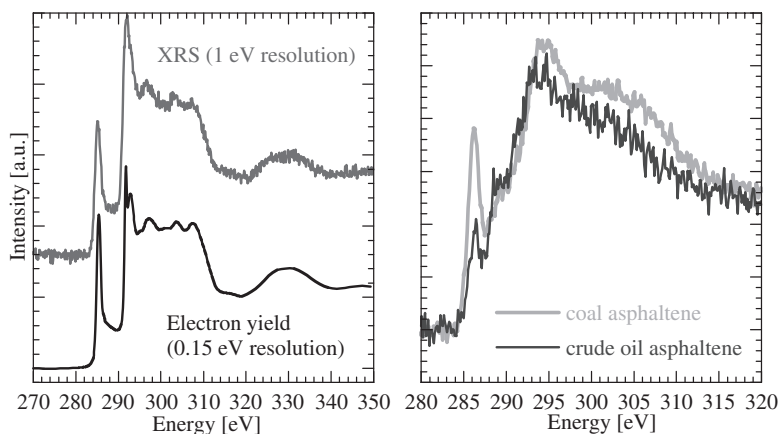
In this regard, we note that coronene has seven aromatic rings, and it has the type of structure expected for the aromatic asphaltene component. A fit to the entire XANES region (282–320 eV) suggests a mixture of 50% aromatic and 50% saturated carbon. The study also shows that better statistics and better energy resolution is necessary for a more quantitative analysis, and the following spectra were obtained at beamline ID-18 at the APS.

Figure 5 left shows an XRS graphite spectrum with 1.1 eV FWHM compared to a conventional XANES spectrum taken in electron yield mode with 0.15 eV resolution (Anders et al., 1997). The resemblance of the two spectra is remarkable and many fine structure features are resolved even at this energy resolution. Figure 5 right shows two asphaltene spectra, crude oil<sup>a</sup> (blue) and coal (green). Comparison of the crude oil asphaltene spectrum with that in Fig. 4 indicates how important good energy resolution is, the small  $1s \rightarrow \pi^*$  feature only seen as a shoulder in Fig. 4 is now resolved. Figure 5 also shows that petroleum and coal asphaltene are different, a fact utilized to elucidate asphaltene structure in other studies. To interpret the structural information contained in these asphaltene spectra, we performed XRS studies of aromatic and aliphatic model compounds. In the following we will concentrate on the PAHs.

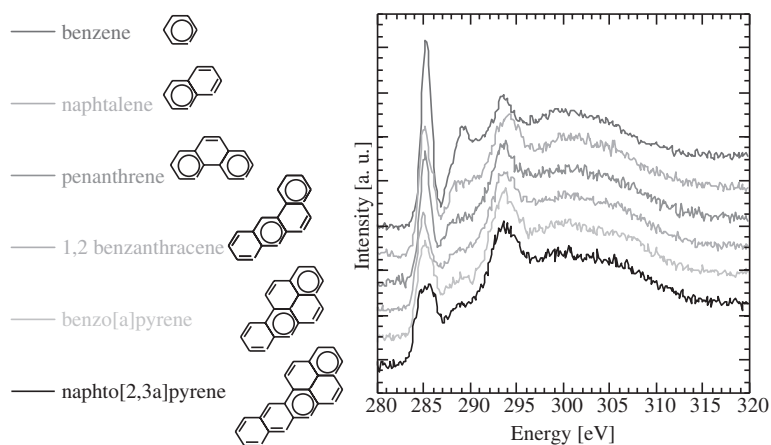
Figure 6 shows a series of PAH spectra with increasing number of rings. A correlation between the number of aromatic rings and the  $1s \rightarrow \pi^*$  peak intensity and width is apparent. This resonance is very large in benzene and much different than that found for crude oil asphaltene. This is a clear indication that the existence of a substantial

<sup>a</sup>Asphaltene from two crude oil sources (Ven #20 and KUH) were measured, they showed identical spectra.





**Figure 5.** Left: comparison of graphite XANES taken in electron yield (bottom) and in XRS mode (top). Right: XRS XANES spectra of two different asphaltenes taken with 1 eV resolution.



**Figure 6.** XRS spectra of compounds with increasing number of aromatic rings. PAHs are shown in the sextet-double bond picture.

fraction of benzene rings in petroleum asphaltene is ruled out. This has been the subject of conflicting papers, and confirms recent optical fluorescence measurements (Ralston et al., 1996). In fact larger, asymmetric ring systems tend to produce a smaller  $1s \rightarrow \pi^*$  transition which is more similar to the petroleum asphaltene. We also find that the crude



oil asphaltene spectrum fits very well to a combination of 45% coal asphaltene and 55% octacosane. When applying two-component fits with PAHs and models of saturated carbon, typically 50% PAH and 50% saturated carbon gives the best fits. This confirms the lower resolution results and indicates that coal asphaltene does not contain a large fraction of saturated carbon.

To address the question of which types of PAHs are predominantly present in asphaltenes, a comparison of the  $1s \rightarrow \pi^*$  peak width (the most isolated spectral feature) is useful. Figure 6 shows a selection of PAH spectra is shown indicating a clear variation in  $1s \rightarrow \pi^*$  peak widths. This finding has been quantified in a recent study, where the number of rings, and type of ring system was studied (Bergmann et al., 2003).

The  $\pi$  electron distribution within such PAHs can be described as consisting of isolated sextets (benzene ring) and of isolated double bonds (see also Fig. 6) (Aihara, 1999; Clar, 1964, 1972; Dias, 1985a, b; Garret, 1986; Ruiz-Morales, 2002). In the 12 different PAHs we studied the ratio of carbons involved in double bonds vs. carbons involved in sextets varied from 0 (benzene and triphenylene) to 2 (tetracene). A linear correlation between this ratio and the  $1s \rightarrow \pi^*$  line width was found. The line widths varied over a large range from 1.1 eV (experimental resolution) for benzene to 3.5 eV for tetracene, indicating a robust correlation. A confirmation of this finding and even larger set of compounds would have important implications on the validity of a recently proposed theoretical model (Ruiz-Morales, 2002). With respect to both coal and petroleum asphaltenes, which show a  $1s \rightarrow \pi^*$  line width of  $\sim 1.3$  eV, the finding strongly suggests that these systems have predominantly rings with a small double bond to sextet ratio. This high degree of sextet carbon (indicating stable compounds) is expected, since asphaltenes are produced in processes involving thermal maturations.

The role of heteroatoms within the sextet-double bond description needs to be clarified. Asphaltenes contain roughly one or two heteroatoms on average per ring system. It would be advantageous to perform XRS experiments on classes of heteroatom containing molecules and compare the results with theory. For instance, one could test the predictions of the predominance of stable heteroatomic aromatic molecules in asphaltenes with theoretical predictions (Garcia-Cruz et al., 2003).

#### 4. CONCLUSIONS

We discuss here the application of a new technique, X-ray Raman spectroscopy (XRS), to address fundamental questions about the



structure of PAHs and asphaltenes. The work has become possible by combining high-resolution X-ray optics with intense X-rays produced at third generation synchrotron facilities. XRS is a hard X-ray version of low energy XANES and ISEELS, and combines the advantages of a 6–10 keV probe with the unique information obtained from the low Z XANES technique. Structural insights about PAHs and asphaltenes can be directly obtained from this powerful local probe. XRS investigation of complex carbonaceous materials is shown to be complementary to other techniques, thus providing invaluable help in the fundamental understanding of these economically important materials.

### ACKNOWLEDGMENTS

This research was partially supported by the National Institutes of Health, grants 44891-5, GM 44380, and GM-48145, and by the Department of Energy, Office of Biological and Environmental Research (SPC). The National Synchrotron Light Source and the Advanced Photon Source are supported by the Department of Energy, Office of Basic Energy Sciences. BioCAT is a National Institutes of Health-supported Research Center RR-08630.

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Received January 27, 2003

Accepted May 17, 2003



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