

Fourier Transform Infrared Spectroscopy (FTIR) 1.8.1

The vibrational motions of the chemically bound constituents of matter have frequencies in the infrared regime. The oscillations induced by certain vibrational modes provide a means for matter to couple with an impinging beam of infrared electromagnetic radiation and to exchange energy with it when the frequencies are in resonance. In the infrared experiment, the intensity of a beam of infrared radiation is measured before (I_0) and after (I) it interacts with the sample as a function of light frequency, $\{\omega_j\}$. A plot of I/I_0 versus frequency is the “infrared spectrum.” The identities, surrounding environments, and concentrations of the chemical bonds that are present can be determined.

Information	Vibrational frequencies of chemical bonds
Element Range	All, but not element specific
Destructive	No
Chemical bonding information	Yes, identification of functional groups
Depth profiling	No, not under standard conditions
Depth Probed	Sample dependent, from μm 's to 10 nm
Detection limits	Ranges from undetectable to $< 10^{13}$ bonds/cc. Sub-monolayer sometimes
Quantification	Standards usually needed
Reproducibility	0.1% variation over months
Lateral resolution	0.5 cm to 20 μm
Imaging/mapping	Available, but not routinely used
Sample requirements	Solid, liquid, or gas in all forms; vacuum not required
Main use	Qualitative and quantitative determination of chemical species, both trace and bulk, for solids and thin films. Stress, structural inhomogeneity
Instrument cost	\$50,000–\$150,000 for FTIR; \$20,000 or more for non-FT spectrophotometers
Instrument size	Ranges from desktop to (2 × 2 m)

8.1 FTIR

Fourier Transform Infrared Spectroscopy

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Introduction

The physical principles underlying infrared spectroscopy have been appreciated for more than a century. As one of the few techniques that can provide information about the chemical bonding in a material, it is particularly useful for the nondestructive analysis of solids and thin films, for which there are few alternative methods. Liquids and gases are also commonly studied, more often in conjunction with other techniques. Chemical bonds vary widely in their sensitivity to probing by infrared techniques. For example, carbon-sulfur bonds often give no infrared signal, and so cannot be detected at any concentration, while silicon-oxygen bonds can produce signals intense enough to be detected when probing submonolayer quantities, or on the order of 10^{13} bonds/cc. Thus, the potential utility of infrared spectrophotometry (IR) is a function of the chemical bond of interest, rather than being applicable as a generic probe. For quantitative analysis, modern instrumentation can provide a measurement repeatability of better than 0.1%. Accuracy and precision, however, are more commonly on the order of 5.0% (3σ), relative. The limitations arise from sample-to-sample variations that modify the optical quality of the material. This causes slight, complex distortions of the spectrum that are dif-

difficult to eliminate. Sensitivity of the sample to environmental influences that modify the chemical bonding and the need to calibrate the infrared spectral data to reference methods—such as neutron activation, gravimetry, and wet chemistry—also tend to degrade slightly the measurement for quantitative work.

The goal of the basic infrared experiment is to determine changes in the intensity of a beam of infrared radiation as a function of wavelength or frequency (2.5–50 μm or 4000–200 cm^{-1} , respectively) after it interacts with the sample. The centerpiece of most equipment configurations is the infrared spectrophotometer. Its function is to disperse the light from a broadband infrared source and to measure its intensity at each frequency. The ratio of the intensity before and after the light interacts with the sample is determined. The plot of this ratio versus frequency is the *infrared spectrum*.

As technology has progressed over the last 50 years, the infrared spectrophotometer has passed through two major stages of development. These phases have significantly impacted how infrared spectroscopy has been used to study materials. Driven in part by the needs of the petroleum industry, the first commercial infrared spectrophotometers became available in the 1940s. The instruments developed at that time are referred to as *spatially dispersive* (sometimes shortened to *dispersive*) instruments because ruled gratings were used to disperse spatially the broadband light into its spectral components. Many such instruments are still being built today. While somewhat limited in their ability to provide quantitative data, these dispersive instruments are valued for providing qualitative chemical identification of materials at a low cost. The 1970s witnessed the second phase of development. A new (albeit much more expensive) type of spectrophotometer, which incorporated a Michelson interferometer as the dispersing element, gained increasing acceptance. All frequencies emitted by the interferometer follow the same optical path, but differ in the time at which they are emitted. Thus these systems are referred to as being *temporally dispersive*. Since the intensity-time output of the interferometer must be subjected to a Fourier transform to convert it to the familiar infrared spectrum (intensity-frequency), these new units were termed Fourier Transform Infrared spectrophotometers, (FTIR). Signal-to-noise ratios that are higher by orders of magnitude, much better resolution, superior wavelength accuracy, and significantly shorter data acquisition times are gained by switching to an interferometer. This had been recognized for several decades, but commercialization of the equipment had to await the arrival of local computer systems with significant amounts of cheap memory, advances in equipment interfacing technology, and developments in fast Fourier-transform algorithms and circuitry.

Beyond the complexities of the dispersive element, the equipment requirements of infrared instrumentation are quite simple. The optical path is normally under a purge of dry nitrogen at atmospheric pressure; thus, no complicated vacuum pumps, chambers, or seals are needed. The infrared light source can be cooled by water. No high-voltage connections are required. A variety of detectors are avail-

able, with deuterated tri-glycene sulfate (DTGS) detectors offering a good signal-to-noise ratio and linearity when operated at room temperature. For more demanding applications, the mercury cadmium telluride (HgCdTe, or mer-cad telluride) detector, cooled by liquid nitrogen, can be used for a factor-of-ten gain in sensitivity.

With the advent of FTIR instrumentation, IR has experienced a dramatic increase in applications since the 1970s, especially in the area of quantitative analysis. FTIR spectrophotometry has grown to dominate the field of infrared spectroscopy. Experiments in microanalysis, surface chemistry, and ultra-thin films are now much more routine. The same is true for interfaces, if the infrared characteristics of the exterior layers are suitable. While infrared methods still are rarely used to profile composition as a function of depth, microprobing techniques available with FTIR technology permit the examination of microparticles and *xy*-profiling with a spatial resolution down to 20 μm . Concurrent with opening the field to new areas of research, the high level of computer integration, coupled with robust and nondestructive equipment configurations, has accelerated the move of the instrument out of the laboratory. Examples are in VLSI, computer-disk, and chemicals manufacturing, where it is used as a tool for thin-film, surface coating, and bulk monitors.

Unambiguous chemical identification usually requires the use of other techniques in conjunction with IR. For gases and liquids, Mass Spectrometry (MS) and Nuclear Magnetic Resonance Spectrometry (NMR) are routinely employed. The former, requiring only trace quantities of material, determines the masses of the molecule and of characteristic fragments, which can be used to deduce the most likely structure. MS data is sometimes supplemented with infrared results to distinguish certain chemical configurations that might produce similar fragment patterns. NMR generally requires a few milliliters of sample, more than needed by either the FTIR or MS techniques, and can identify chemical bonds that are associated with certain elements, bonds that are adjacent to each other, and their relative concentrations. Solids can also be studied by these methods. For MS, the sensitivity remains high, but the method is destructive because the solid must somehow be vaporized. While nondestructive, the sensitivity of NMR spectrometry is typically much lower for direct measurements on solids; otherwise, the solid may be taken into solution and analyzed. For thin films, both the MS and NMR methods are destructive. Complementary data for surfaces, interfaces, and thin films can be obtained by techniques like X-ray photoelectron spectroscopy, static secondary ion mass spectrometry, and electron energy loss spectrometry. These methods probe only the top few nanometers of the material. Depending upon the sample and the experimental configuration, IR may be used as either a surface or a bulk probe for thin films. For surface analysis, FTIR is about a factor of 10 less sensitive than these alternative methods. Raman spectroscopy is an optical technique that is complementary to infrared methods and also detects the vibrational motion of chemical bonds. While able to achieve submicron spatial resolution, the sensitivity of the

Raman technique is usually more than an order of magnitude less than that of FTIR.

As a surface probe, FTIR works best when the goal is to study a thin layer of material on a dissimilar substrate. Lubricating oil on a metal surface and thin oxide layers on semiconductor surfaces are examples. FTIR techniques become more difficult to apply when the goal is to examine a surface or layer on a similar substrate. An example would be the study of thin skins or surface layers formed during the curing cycles used for photoresist or other organic thin films deposited from the liquid phase. If the curing causes major changes in the bulk and the surface, FTIR methods usually cannot discriminate between them, because the beam probes deeply into the bulk material. The limitations as a surface probe often are dictated by the type of substrate being used. A metal or high refractive-index substrate will reflect enough light to permit sensitive probing of the surface region. A low refractive index substrate, in contrast, will permit the beam to probe deeply into the bulk, degrading the sensitivity to the surface.

The discussions presented in this article pertain to applications of FTIR, because most of the recent developments in the field have been attendant to FTIR technology. In many respects, FTIR is a "science of accessories". A myriad of sample holders, designed to permit the infrared light to interact with a given type of sample in an appropriate manner, are interfaced to the spectrophotometer. A large variety of "hyphenated" techniques, such as GC-FTIR (gas chromatography-FTIR) and TGA-FTIR (thermo-gravimetric analysis-FTIR), also are used. In these cases, the effluent emitted by the GC, TGA, or other unit is directed into the FTIR system for time-dependent study. Hyphenated methods will not be discussed further here. Still, common to all of these methods is the goal of obtaining and analyzing an infrared spectrum.

Basic Principles

Infrared Spectrum

Define I_0 to be the intensity of the light incident upon the sample and I to be the intensity of the beam after it has interacted with the sample. The goal of the basic infrared experiment is to determine the intensity ratio I/I_0 as a function of the frequency of the light (w). A plot of this ratio versus the frequency is the infrared spectrum. The infrared spectrum is commonly plotted in one of three formats: as transmittance, reflectance, or absorbance. If one is measuring the fraction of light transmitted through the sample, this ratio is defined as

$$T_w = \left(\frac{I_r}{I_0} \right)_w \quad (1)$$

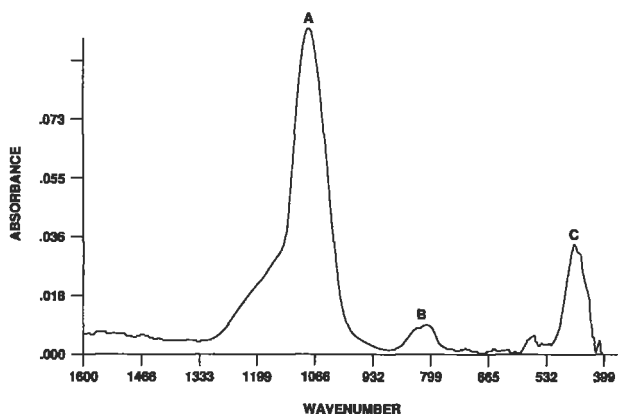


Figure 1 The FTIR spectrum of the oxide of silicon (thin film deposited by CVD). Primary features: (a), asymmetric stretching mode of vibration; (b), bending mode of vibration; (c), rocking mode of vibration.

where T_w is the transmittance of the sample at frequency w , and I_t is the intensity of the transmitted light. Similarly, if one is measuring the light reflected from the surface of the sample, then the ratio is equated to R_w , or the reflectance of the spectrum, with I_t being replaced with the intensity of the reflected light I_r . The third format, absorbance, is related to transmittance by the Beer-Lambert Law:

$$A_w = -\log T_w = (\epsilon_w) (bc) \quad (2)$$

where c is the concentration of chemical bonds responsible for the absorption of infrared radiation, b is the sample thickness, and ϵ_w is the frequency-dependent absorptivity, a proportionality constant that must be experimentally determined at each w by measuring the absorbance of samples with known values of bc . As a first-order approximation the Beer-Lambert Law provides a simple foundation for quantitating FTIR spectra. For this reason, it is easier to obtain quantitative results if one collects an absorbance spectrum, as opposed to a reflectance spectrum. Prior to the introduction of FTIR spectrophotometers, infrared spectra were usually published in the transmittance format, because the goal of the experiment was to obtain qualitative information. With the growing use of FTIR technology, a quantitative result is more often the goal. Today the absorbance format dominates, because to first order it is a linear function of concentration.

Qualitative and Quantitative Analysis

Figure 1 shows a segment of the FTIR absorbance spectrum of a thin film of the oxide of silicon deposited by chemical vapor deposition techniques. In this film, sil-

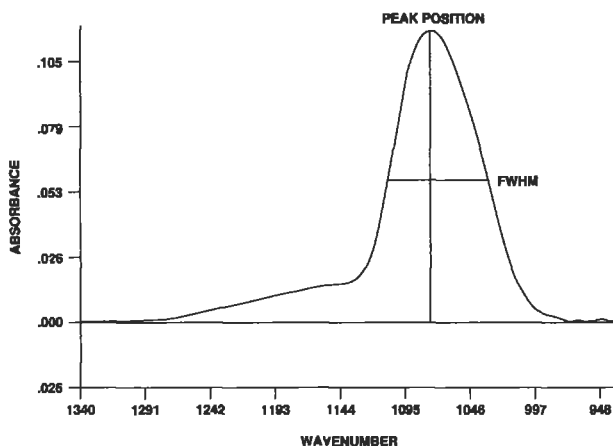


Figure 2 Spectral parameters typically used in band shape analysis of an FTIR spectrum: peak position, integrated peak area, and FWHM.

icon is tetrahedrally coordinated with four bridging oxygen atoms. Even though the bond angles are distorted slightly to produce the random glassy structure, this spectrum is quite similar to that obtained from crystalline quartz, because most features in the FTIR spectrum are the result of nearest neighbor interactions. In crystalline materials the many vibrational modes can be classified by the symmetry of their motions and, while not rigorous, these assignments can be applied to the glassy material, as well. Thus the peak near 1065 cm^{-1} arises from the asymmetric stretching motions of the Si and O atoms relative to each other. The band near 815 cm^{-1} arises from bending motions, while the one near 420 cm^{-1} comes from a collective rocking motion. These are not the only vibrational modes for the glass, but they are the only ones that generate electric dipoles that are effective in coupling with the electromagnetic field. For example, the glass also has a symmetric stretching mode, but since it generates no net dipole, no absorption band appears in the FTIR spectrum. For more quantitative work, the fundamental theory of infrared spectroscopy delineates a band shape analysis illustrated in Figure 2. Three characteristics are commonly examined: peak position, integrated peak intensity, and peak width.

Peak position is most commonly exploited for qualitative identification, because each chemical functional group displays peaks at a unique set of characteristic frequencies. The starting point for such a functional-group analysis is a table or computer database of peak positions and some relative intensity information. This provides a fingerprint that can be used to identify chemical groups. Thus the three peaks just described for the oxide of silicon can be used to identify that material. Typical of organic materials, C–H bonds have stretching modes around 3200 cm^{-1} ; C = O, around 1700 cm^{-1} . Thus, the composition of oils may be qualitatively identified by classifying these and other peak positions observed in the spectrum. In

addition, some bands have positions that are sensitive to physicochemical properties. As a result, applied and internal pressures, stresses, and bond strain due to swelling can be studied.

The Beer-Lambert Law of Equation (2) is a simplification of the analysis of the second-band shape characteristic, the integrated peak intensity. If a band arises from a particular vibrational mode, then to the first order the integrated intensity is proportional to the concentration of absorbing bonds. When one assumes that the area is proportional to the peak intensity, Equation (2) applies.

In solids and liquids, peak width—the third characteristic—is a function of the homogeneity of the chemical bonding. For the most part, factors like defects and bond strain are the major sources of band width, usually expressed as the full width at half maximum (FWHM). This is due to the small changes these factors cause in the strengths of the chemical bonds. Small shifts in bond strengths cause small shifts in peak positions. The net result is a broadening of the absorption band. The effect of curing a material can be observed by peak-width analysis. As one anneals defects the bands become narrower and more intense (to conserve area, if no bonds are created or destroyed). Beyond the standard analysis, higher order band shape properties may also be examined, such as peak asymmetry. For example, the apparent shoulder on the high-frequency side of the band in Figure 2 may be due to a second band that overlaps the more prominent feature.

For many applications, quantitative band shape analysis is difficult to apply. Bands may be numerous or may overlap, the optical transmission properties of the film or host matrix may distort features, and features may be indistinct. If one can prepare samples of known properties and collect the FTIR spectra, then it is possible to produce a calibration matrix that can be used to assist in predicting these properties in unknown samples. Statistical, chemometric techniques, such as PLS (partial least-squares) and PCR (principle components of regression), may be applied to this matrix. Chemometric methods permit much larger segments of the spectra to be comprehended in developing an analysis model than is usually the case for simple band shape analyses.

Methodologies and Accessories

A large number of methods and accessories have been developed to permit the infrared source to interact with the sample in appropriate ways. Some of the more common approaches are listed below.

Single-pass transmission

The direct transmission experiment is the most elegant and yields the most quantifiable results. The beam makes a single pass through the sample before reaching the detector. The bands of interest in the absorbance spectrum should have peak absorbances in the range of 0.1–2.0 for routine work, although much weaker or stronger bands can be studied. Various holders, pellet presses, and liquid cells have been

developed to permit samples to be prepared with the appropriate path length. *Diamond anvil cells* permit pliable samples to be squeezed to extremely thin path lengths or to be studied under applied pressures. Long path-length cells are used for samples in the gas phase. Thin films and prepared surfaces can be studied by transmission if the supporting substrate is transparent to the infrared. The highest sensitivity is obtained with double-beam or pseudo-double-beam experimental configurations. An example of the latter is the *interleaf* experiment, where a single beam is used, but a sample and reference are alternately shuttled into and out of the beam path.

Reflection

If the sample is inappropriate for a transmission experiment, for instance if the supporting substrate is opaque, a reflectance configuration will often be employed. Accessories to permit specular, diffuse, variable-angle, and grazing-incidence experiments are available. The angle of incidence can be adjusted to minimize multiple-reflection interferences by working at the Bragg angle for thin films, or to enhance the sensitivity of the probe to surface layers. A subset of this technique, Reflection Absorption (RA) spectroscopy, is capable of detecting submonolayer quantities of materials on metal surfaces. These grazing and RA techniques can enhance surface sensitivities by using geometries that optimize the coupling of the electromagnetic field at the metal surface. In some instances it has been possible to deduce preferred molecular orientations of ordered monolayers.

Attenuated Total Reflection

In this configuration an Attenuated Total Reflection (ATR) crystal is used, illustrated in Figure 3. The infrared beam is directed into the crystal. Exploiting the principles of a waveguide, the change in refractive index at the crystal surface causes the beam to be back-reflected several times as it propagates down the length of the crystal before it finally exits to the detector. If the sample is put into contact with the crystal surface, the beam will interact weakly with the sample at several points. For extremely thin samples, this is a means of increasing the effective path length. Since the propagating beam in the crystal barely penetrates through the surface of the sample adjacent to the crystal, signals at a sample surface can be enhanced, as well. This also helps in the study of opaque samples. Approximately fivefold amplifications in signals are typical over a direct transmission experiment. The quality of the crystal-sample interface is critical, and variability in that interface can make ATR results very difficult to quantify.

Emission

When samples are heated, they emit infrared radiation with a characteristic spectrum. The IR emission of ceramics, coals, and other complicated solids and thin films can be studied. Also, if conditions make it difficult to use an infrared source

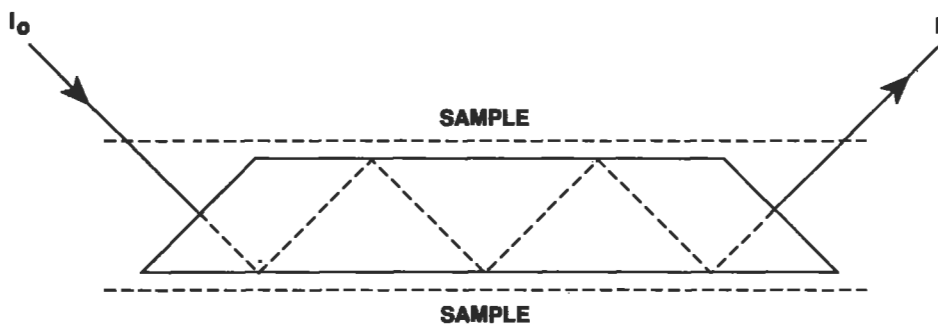


Figure 3 Typical beam path configuration for collecting an FTIR spectrum using an attenuated total reflectance element: I_0 is the incident infrared beam, I is the exiting beam.

(such as an *in situ* measurement of a thin film in the deposition chamber) but permit the controlled heating of a sample, then emission methods provide a means of examining these materials.

Microscopy

Infrared microscopes can focus the beam down to a 20- μm spot size for microprobing in either the transmission or reflection mode. Trace analysis, microparticle analysis, and spatial profiling can be performed routinely.

Interferences and Artifacts

Equipment

Equipment technology and processing software for FTIR are very robust and provide a high degree of reliability. Concerns arise for only the most demanding applications. For quantitative work on an isolated feature in the spectrum, the rule of thumb is that the spectrometer resolution be one-tenth the width of the band. FTIR instruments routinely meet that requirement for solids.

Short- and long-term drift in the spectral output can be caused by several factors: drift in the output of the infrared light source or of the electronics, aging of the beam splitter, and changes in the levels of contaminants (water, CO_2 , etc.) in the optical path. These problems are normally eliminated by rapid, routine calibration procedures.

The two complicating factors that are encountered most frequently are the linearity of detector response and stray light scattering at low signal levels. DTGS

detectors are quite linear and reliable, while MCT detectors can saturate at relatively low light levels. Stray light can make its way to the detector and be erroneously detected as signal, or it can be backscattered into the interferometer and degrade its output. A problem only at very low signal levels or with very reflective surfaces, proper procedures can minimize these effects.

Intrinsic or Matrix

Few cross sections for infrared absorption transitions have been published and typically they are not broadly applicable. The strength of the absorption depends upon changes in the dipole moment of the material during the vibrational motion of the constituent atoms. However, these moments are also very sensitive to environmental factors, such as nearest neighbor effects, that can cause marked changes in the infrared spectrum. For example, carbon-halogen bonds have a stretching mode that may be driven from a being very prominent feature to being an undetectable feature in the spectrum by adding electron-donating or -withdrawing substituents as nearest neighbors. For careful quantitative work, then, model compounds that are closely representative of the material in question are often needed for calibration.

Interface Optical Effects

For thin-film samples, abrupt changes in refractive indices at interfaces give rise to several complicated *multiple reflection* effects. Baselines become distorted into complex, sinusoidal, fringing patterns, and the intensities of absorption bands can be distorted by multiple reflections of the probe beam. These artifacts are difficult to model realistically and at present are probably the greatest limiters for quantitative work in thin films. Note, however, that these interferences are functions of the complex refractive index, thickness, and morphology of the layers. Thus, properly analyzed, useful information beyond that of chemical bonding potentially may be extracted from the FTIR spectra.

Many materials have grain boundaries or other microstructural features on the order of a micrometer or greater. This is on the same scale as the wavelength of the infrared radiation, and so artifacts due to the wavelength-dependent scattering of light at these boundaries can be introduced into the spectra. Thin films, powders, and solids with rough surfaces are the most affected. Again these artifacts are difficult to realistically model, but properly analyzed can provide additional information about the sample.

Conclusions

The principles of infrared spectroscopy can be exploited to extract information on the chemical bonding of an extremely wide variety of materials. The greatest strength of the technique is as a nondestructive, bulk probe of glassy and amor-

phous materials, where few alternate methods exist for obtaining chemical information. For other materials, FTIR is a valuable member in the arsenal of characterization tools. Other methods that are most likely to provide similar information include raman spectroscopy, X-ray photoelectron spectroscopy, NMR, MS, SIMS, and high-resolution electron energy-loss spectroscopy. The nondestructive, noninvasive potential of the infrared technique, and its ease of use, continues to distinguish it from these other methods, with the exception of Raman spectroscopy.

The trends begun with the general introduction of FTIR technology will undoubtedly continue. It is safe to say that the quality of the data being produced far exceeds our ability to analyze it. In fact, for many current applications, the principle limitations are not with the equipment, but rather with the quality of the samples. Thus, the shift from qualitative to quantitative work will proceed, reaching high levels of sophistication to address the optical and matrix interference problems discussed above.

With extensive computerization, the ease of use, and the robustness of equipment, movement of the instrumentation from the research laboratory to the manufacturing environment, for application as *in situ* and at-line monitors, will continue. *In situ* work in the research laboratory will also grow. New environments for application appear every day and improved computer-based data processing techniques make the rapid analysis of large sets of data more commonplace. These developments, coupled with rapid data acquisition times, are making possible the timely evaluation of the results of large-scale experiments. Most likely, much of the new physicochemical information developed by applying FTIR technology will come from trends observed in detailed studies of these large sample data sets.

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