

Points to Consider with Respect to ATR Spectra of Inorganic Compounds

It is widely known that ATR spectra obtained using the ATR measurement method have a different peak intensity ratio than peaks collected using transmission measurement. However, what is not so well known is that a slight shift in peak position may also occur. This shift is a phenomenon seen only with large peaks, and

in the case of organic substances, since the peak shift is small, about 10 cm^{-1} , it is not much of a problem. However, in the case of inorganic compounds, very large disparities may be seen. This Application News introduces points to consider with respect to ATR spectra of inorganic compounds.

■ Peak Shifts in ATR Spectra

In the ATR method, as the penetration depth is proportional to the wavelength, it is a characteristic that peak intensities on the high-wavenumber side become smaller as compared with peaks in transmission spectra. Moreover, the peak positions in ATR spectra may be shifted slightly to the low-wavenumber side as compared with those in transmission spectra. This shift is influenced by the refractive index of the sample, and is especially seen in large peaks. When measurement of organic substances is conducted using a diamond or ZnSe

prism, large peaks may shift about 10 cm^{-1} .

On the other hand, in the case of inorganic compounds, very large peak shifts may occur. Figs.1 and 2 show spectra of silica gel (SiO_2) and calcium carbonate, respectively. As shown in Fig.1, the SiO_2 peak at 1093 cm^{-1} in the transmission spectrum is seen in the vicinity of 1062 cm^{-1} in the ATR spectrum. And, in Fig.2, the peak at 1429 cm^{-1} in the transmission spectrum is seen in the vicinity of 1390 cm^{-1} in the ATR spectrum.

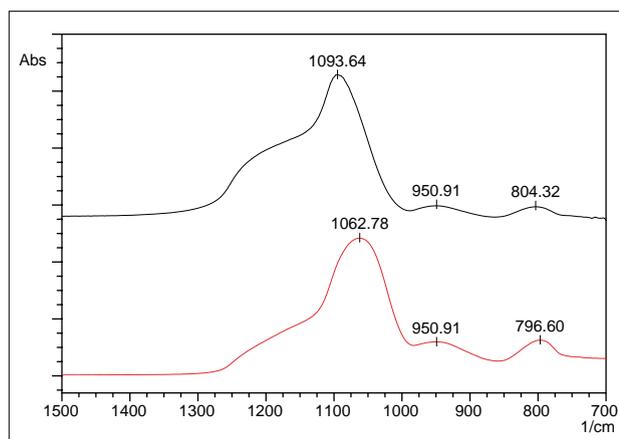


Fig.1 Spectra of Silica Gel (upper : transmission, lower : ATR)

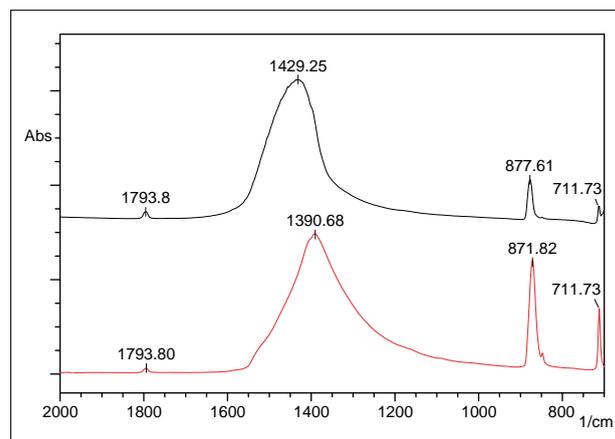


Fig.2 Spectra of Calcium Carbonate
(upper : transmission, lower : ATR)

However, the amount of this peak shift is not constant. Fig.3 shows an ATR spectrum of polystyrene containing calcium carbonate. The peaks at 1417 cm^{-1} and 873 cm^{-1} are due to the calcium carbonate; however, this shift is small when compared to the ATR spectra of Fig.2.

Thus, in ATR spectra of inorganic substances, peak shifts of 30 cm^{-1} or more may be seen in large, broad peaks. However, it is important to note that this amount of shift (peak position) will vary depending on the state of the sample, such as whether it is a pure or mixed substance.

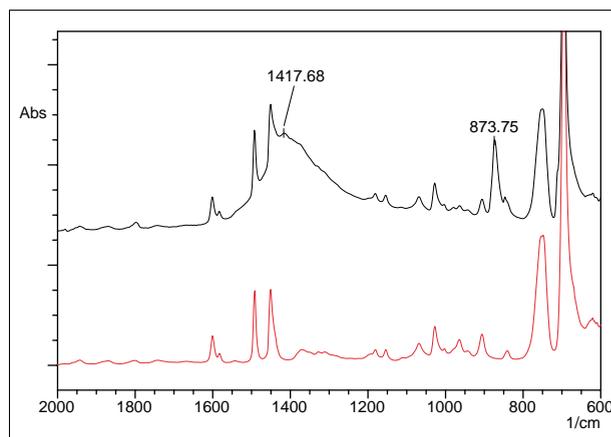


Fig.3 ATR Spectra of Polystyrene with Calcium Carbonate (upper) and Polystyrene (lower)

■ ATR Spectra of Glass

As mentioned above, in ATR spectra of inorganic substances, a large shift in peaks may occur toward the low wavenumbers as compared to peak positions in transmission spectra, and the change in peak position may vary depending on whether the sample is pure or a mixture of substances. Here we introduce some examples of peak shift caused by contact status.

Fig.4 shows ATR spectra which were measured while different levels of force were applied to the prism in the measurement of a glass plate sample. As the applied force increased, the peak intensity increased. For comparison, Fig.5 shows the spectra of Fig.4 with corrected peak intensity in the vicinity of 770 cm^{-1} . The difference in peak shape due to applied force is clearly evident.

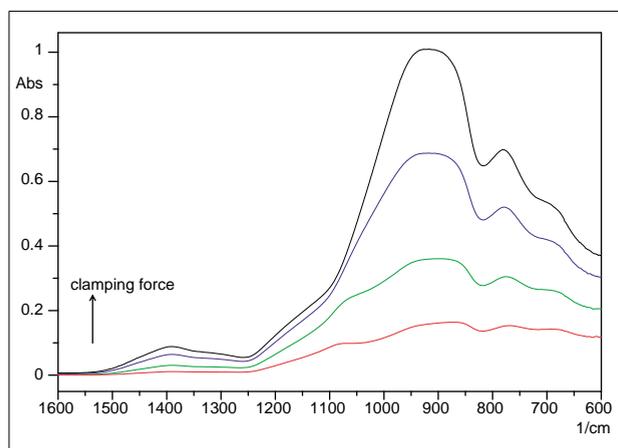


Fig.4 ATR Spectra of Glass

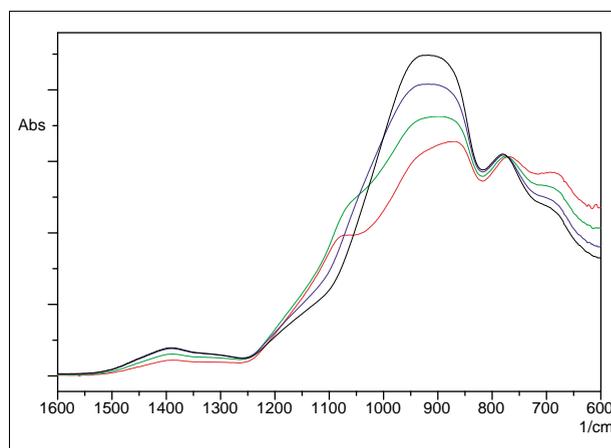


Fig.5 ATR Spectra of Glass (Corrected at 770 cm^{-1})

NOTES:

*This Application News has been produced and edited using information that was available when the data was acquired for each article. This Application News is subject to revision without prior notice.



SHIMADZU CORPORATION. International Marketing Division

3. Kanda-Nishikicho 1-chome, Chiyoda-ku, Tokyo 101-8448, Japan Phone: 81(3)3219-5641 Fax: 81(3)3219-5710
Cable Add.:SHIMADZU TOKYO