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## FT-IR Emission Spectra of Chemisorbed Species, with Application to Species Adsorbed on Alumina

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The principles of infrared emission spectroscopy are briefly reviewed with emphasis on the aspects of its application to the study of chemisorbed species. The main problems of sample preparation, selection of measurement conditions and the most suitable methods of data treatment are discussed.

IR emittance spectra of two typical support materials for supported metal catalysts, alumina and silica, are presented. On the example of a rhenium complex, tetrakis(tricarbonyl- $\mu_3$ -hydroxo-rhenium), formed on alumina support in catalytic amounts (1.5 to 5% Re) it is shown that the four-measurement technique can lead to observation of the adsorbate bands also in the regions of high substrate emission (between 1300 and 400  $\text{cm}^{-1}$ ).

### I. INTRODUCTION

Spectroscopic methods providing information on the structure of adsorbed molecules, and thus on the nature of interaction between adsorbent and adsorbate, are of utmost importance for heterogenous catalysis. As regards vibrational spectroscopy, the relevant are the attenuated total reflection (ATR), IR reflection-absorption spectroscopy (IRRAS), electron energy loss spectroscopy (EELS) and surface enhanced Raman scattering (SERS), but the usual transmission IR technique can be applied as well if the substrate does not absorb very strongly in the spectral region of interest.

The birth of Fourier-transform infrared (FT-IR) spectroscopy with its fast signal accumulation possibilities has opened up a new way towards increased sensitivity in IR spectrometry enabling spectroscopists to deal with spectra recorded under poor energy conditions, *e.g.* very weak emission spectra or spectra in regions of low transmission.

In this paper we intend to review the principles of infrared emission spectroscopy (IRES), give a short overview of the experimental methods that have been suggested for measuring IR emission spectra of molecular species

chemisorbed on different types of surfaces, and also add some of our own recent experience.

## II. BASIC PRINCIPLES OF IRES

The theoretical background of infrared emission spectroscopy has been described in detail in the reviews by Bates<sup>1</sup> and Huong<sup>2</sup>.

Considering the interaction of thermal radiation with condensed phases (solids and liquids), one can start with the basic relationship according to which the portions of radiation absorbed, reflected and transmitted by the sample add up to unity, *i. e.*

$$a + r + t = 1. \quad (1)$$

where  $a$ ,  $r$  and  $t$  are the absorptance, reflectance and transmittance, respectively. According to Kirchoff's law, the emittance,  $e$ , of an object at a given temperature and wavenumber is equal to its absorptance:

$$e(\nu, T) = a(\nu, T) \quad (2)$$

which means that a good absorber is a good emitter as well, and *vice versa*. Consequently, Eq. (1) can be rewritten in the form:

$$e + r + t = 1. \quad (3)$$

This relationship has to be taken into account when designing an emission experiment (choosing the substrate and cell materials) and also when interpreting the spectra obtained, since spectral features due to emission, absorption and reflection can appear in the spectra simultaneously. Thus, in emission experiments, a specular mirror substrate is preferred due to its high reflectivity which means a very low absorptance and, hence, negligible background emittance.

The blackbody, on the other hand, is an ideal thermal emitter. No object can emit more energy at any frequency than a blackbody at the same temperature. The emittance of an object is defined as the radiant power,  $J$ , emitted by that object and is expressed as a fraction of the power emitted by a blackbody at the same temperature:

$$e(\nu, T) = J(\nu, T)/J_{\text{BB}}(\nu, T). \quad (4)$$

Thus, the emittance of a blackbody is unity, and that of any real object (greybody) is less than unity.

The spectral distribution and temperature dependence of the radiant power from a blackbody are described by Planck's law.<sup>1</sup> According to this, the emitted energy at a given frequency increases with increasing temperature, while the maximum in the spectral distribution shifts towards higher frequencies. Stemming from this, high frequency vibrations ( $>2000 \text{ cm}^{-1}$ ) can be more favourably studied at temperatures exceeding 300 K.

When using commercial FT-IR instruments to measure IR emission spectra, the sample is usually mounted at the place of the radiation source or at an optically equivalent spot nearby (although another arrangement has also been proposed)<sup>3</sup>. The detector responds to any deviation from the radiation balance between the sample and the detector. This means that a spectrum is detected if the temperature of the sample is either higher or

lower than that of the detector.<sup>4</sup> The common practice is to heat the sample from the rear using an attached heater block (substrate).

Emission spectra can be presented as radiant power *vs.* wavenumber, *i. e.* single beam spectra on an arbitrary energy scale. However, for quantitative work or more precise intensity comparisons double beam emittance spectra (intensities between 0 and 100%) can be generated by ratioing the emission spectrum of the sample against that of the blackbody at the same temperature.<sup>5,6</sup>

### III. APPLICATION OF FT-IR TO EMISSION SPECTROSCOPY: PRACTICAL ASPECTS

The first but not quite successful attempts to apply IR emission spectroscopy to the study of absorbed species using a grating spectrometer were reported by Eischens and Piiskin<sup>7</sup> in 1955—56. In the 1960's and early 1970's IR emission measurements were published on molten salts<sup>8-11</sup>, fatty acids<sup>12</sup>, minerals<sup>13,14</sup>, greases smeared over metal surfaces<sup>15,16</sup>, and polycrystalline and powdered organic and inorganic compounds<sup>17-19</sup>.

The Fourier-transform technique was first applied to the measurement of infrared emission spectra by Gebbie *et al.*<sup>20</sup> in 1961. It soon became clear that the increased throughput of interferometric spectrometers and the ease and speed of spectrum accumulation made it possible to study very weak radiations like emission of stars and atmospheres of planets.<sup>21-23</sup> Regarding the study of condensed phase materials, FT—IR emission spectroscopy seemed to be very promising, especially in case of thin surface layers such as chemisorbed monomolecular layers on strongly absorbing or opaque substrates. It was believed that sample preparation would be less critical than in transmission or ATR measurements, since even rough surfaces of any shape could be used to measure emission spectra. Systematic studies that followed revealed that, regarding sample preparation, the situation is far from being so favourable, since several conditions have to be fulfilled to get good quality emission spectra.

One of the most important factors determining the quality of emission spectra is sample thickness. Griffiths<sup>24</sup> has shown that characteristic emission spectra can only be obtained from optically thin layers of a sample on a heated specular mirror substrate. If the sample is thick, spectral contrast gets lost and the emission spectrum becomes more like that of a blackbody. When the sample is heated from the rear, the cooler outer layers partially absorb the radiation emitted from the hotter inner layers, especially in the regions of high absorbances. This can lead to apparent splitting of strong emission bands or to inversion at band centers.

Concerning this reduced emission phenomenon, Kember and Sheppard<sup>6</sup> have put forward an alternative explanation involving the selective reflectivity of the sample in the vicinity of strong absorption bands. As a result of a thorough analysis of the problem, Rytter and coworkers<sup>25-26</sup> have concluded that dispersion of the surface reflectivity dominates in these spectral distortions. In order to avoid the problem, they suggest ratioing the sample spectrum against the emission spectrum of a sufficiently thick (opaque) sample as reference instead of that of a blackbody.<sup>25</sup>

Since emission intensity is strongly dependent on the temperature, the sample temperature should be stable during the measurement. Even small

temperature variations or a temperature mismatch between the sample and reference can lead to a sloping and curved background.<sup>27</sup>

Because of their higher speed and sensitivity, liquid nitrogen cooled MCT detectors are preferred in the majority of FT-IR applications. In case of emission work, one must realize that room temperature parts of the spectrometer or any object in the surroundings can contribute to the emission background if the detector is cooled. An efficient way of background elimination is to cool down the whole spectrometer to liquid nitrogen or liquid helium temperature, as it has been done by Durana and coworkers<sup>28,29</sup> and Tobin and coworkers.<sup>30-32</sup> A much simpler and cheaper alternative is to make a four-measurement experiment as suggested by Kember *et al.*<sup>27</sup>: both the sample and the blackbody reference are measured at two temperatures (without any movement of the samples between the two measurements) and the emittance of the sample is calculated as:

$$e = [E_s(T_2) - E_s(T_1)]/[E_{BB}(T_2) - E_{BB}(T_1)], \quad (5)$$

where  $E_s$  and  $E_{BB}$  denote emission of the sample and the blackbody, respectively.

The use of room temperature TGS detectors, though they are 10 to 17 times less sensitive than a cooled MCT detector, has the advantage that there is no need for background elimination<sup>4</sup> unless the interferometer is equipped with a thermostated (heated) Ge/KBr beamsplitter (which may give rise to spurious emission bands at 850 and 1125  $\text{cm}^{-1}$  due to a thin  $\text{GeO}_2$  layer on the beamsplitter surface).<sup>6,27</sup> Correction for beamsplitter emission can be made by the four-measurement method, and there is indication that subtraction of interferograms may lead to better results than subtraction of the spectra themselves.

A number of papers published in the last decade on IR emission spectroscopy deal with surface species on metal substrates.<sup>30-39</sup> It has generally been accepted that polished metal surfaces make the best substrates, thanks to their very low emittance.<sup>19</sup> However, if the sample is very thin (in the order of the thickness of a monomolecular layer), no spectrum can be detected in the direction perpendicular to the sample surface, but increasing emission is observed when the sample is tilted, until grazing angles of incidence are approached.<sup>6,27</sup> An explanation for this behaviour was given by Greenler<sup>40</sup> on the basis of model calculations for the angular distribution of light emitted by dipoles located very close to the reflecting metal surface. Taking into account the dipole radiation pattern and the combination of the direct and reflected rays, his calculations have proven that

(i) the maximum of emitted intensity is expected at viewing angles in the range of 70–80 degrees (measured from the normal to the surface), and  
(ii) only the transition dipole component perpendicular to the metal surface can contribute to the emitted intensity (a condition similar to the so called metal surface selection rule proposed by Pearce and Sheppard<sup>41</sup> for absorption spectra of molecules absorbed on metal surfaces).

For thicker samples ( $> 1$ – $2$  micrometers), emission spectra can be recorded at a normal viewing angle as well, but then another problem may occur. As pointed out by Chase<sup>4</sup>, the radiation returning from the interferometer to the sample may be reflected back into the interferometer by the reflecting substrate. Thus, multiple passing of the interferometer and, hence,

multiple modulation of the beam can occur, which may lead to the appearance of spurious bands in the overtone regions. Therefore, tilting of the sample is recommended, but care must be taken to avoid reflection of outside thermal radiation into the interferometer.

#### IV. IRES STUDIES OF CHEMISORBED SPECIES

Few publications deal with IRES studies of chemisorbed species. As to the type of samples, these works can be divided into two categories: adsorbates on pure metal sheets or on metal single crystal surfaces<sup>28-32</sup> on the one hand, and adsorbates on metal oxides or on oxide supported metal catalysts<sup>33-39,42-49</sup> on the other. The two categories involve different experimental difficulties. In the case of metal supports, the weak emission bands of the small amount of adsorbate may be masked by the background radiation, thus reduction of the latter (*e. g.* by cooling the instrument) can lead to the solution.<sup>28-32</sup>

In the case of metal oxides or oxide supported metal catalysts, the overall emission intensity can be orders of magnitude greater, and the main problem is caused by the emission of the adsorbent or support material which cannot be reduced by cooling since the support is part of the sample and must have the same temperature as the adsorbate. Griffiths<sup>24</sup> has called attention to the problem that in this case the emission of the adsorbate (the species of interest) may be compensated by the absorption of the substrate emission at the same frequencies.

Detection of the emission bands of adsorbates in the spectral regions clear from support emission presents no difficulty, but these regions can be studied in transmission as well. Primet *et al.*<sup>39,42</sup> claim that the IR emission method is capable of yielding information also in the region of lattice vibrations of the support, provided that the sample is thin enough (about 0.1 mg/cm<sup>2</sup>). This spectral region (the region below about 1200 cm<sup>-1</sup>) is of great importance from the catalytic point of view, since bands in this region could give key information on the nature of bonding of adsorbates to the surface. But the situation is not simple even in the case of thin samples: Johnson *et al.*,<sup>47</sup> studying toluene adsorption on metal oxides, observed that the bands of adsorbate above 1000 cm<sup>-1</sup> appeared as emission and below 1000 cm<sup>-1</sup> as absorption bands on the emission background of the support.

In an earlier work carried out in this laboratory,<sup>48,49</sup> we could observe two weak bands in the 600 to 400 cm<sup>-1</sup> region of the emission spectrum of chemisorbed CO on Pt/Al<sub>2</sub>O<sub>3</sub> which could possibly belong to the metal-adsorbate modes.

Other workers<sup>43-45</sup> suggested the use of much thicker samples (0.5 mm or 15 mg/cm<sup>2</sup>). Kember and Sheppard<sup>43</sup> have shown that in this case the adsorbate bands can appear either in emission or in absorption, depending on the actual temperature distribution within the sample. Temperature inhomogeneities depending on the gas pressure in the cell make the equilibrium of emission and absorption processes hard to control.

The sample cells used in this type of studies should operate like catalytic microreactors, so that the samples can be studied under real catalytic conditions. Important aspects of microreactor design and most of the problems inherent in emission spectroscopic measurements of supported catalysts are

discussed by van Woerkom *et al.*<sup>45</sup> According to the authors, the four-measurement technique is not applicable in the case of adsorbed species because emissivity is not independent of temperature.

#### V. EXPERIMENTAL

IR emission spectra were recorded on a Digilab FTS-20C spectrometer with the source unit modified (by inserting an additional mirror) to accept a home-made external emission accessory. The accessory allows temperature control and sample positioning in the vertical plane using a 3-D translation stage. The sample mount is a heatable copper block with exchangeable disk shaped sample holders, 13 mm in diameter. Sample holders can be covered with aluminum foil to eliminate cleaning. The samples were obtained from ethanol suspension by evaporation of the solvent, or by pressing layers (*cca.* 20 mg/cm<sup>2</sup>) on the Al-foil support. The sample holder covered with soot was used for reference blackbody.

All emission measurements were made at 8 cm<sup>-1</sup> resolution accumulating 2000 or more scans using an ambient temperature high sensitivity DTGS detector.

The diffuse reflectance spectra recorded for comparison purposes were measured on a Nicolet 170sx FT-IR spectrometer at 4 cm<sup>-1</sup> resolution using a custom made DR accessory (incorporating two off-axis parabolic mirrors and transmitting about 17% of the radiation when KBr powder is used as sample).

#### VI. RESULTS AND DISCUSSION

The IR emission spectra of two typical support materials for supported metal catalysts, alumina (Al<sub>2</sub>O<sub>3</sub>) and silica (SiO<sub>2</sub>), are shown in Figure 1 in the region between 2200 and 400 cm<sup>-1</sup>. The emittance of both oxides is quite high at low wavenumbers (80–90% of the emittance of our blackbody), and that of silica is more structured in the whole region. The upward slope to low wavenumbers in both spectra might be due to a small temperature mismatch between the samples and the reference blackbody. (Common features in the two spectra not belonging to the oxides include a small bump at 1260 cm<sup>-1</sup> and a broad feature centered at 1620 cm<sup>-1</sup>. The former may belong to bidentate carbonate impurity, whereas the latter is most probably due to moisture. Uncompensated atmospheric water vapor and carbon dioxide also appear in the spectra.)

To check the overall effects to be expected when a surface layer of another substance is added to the sample, a fair amount of silicone grease was spread over the surface of the pressed silica sample. Silicone grease was chosen because of its negligible vapor pressure, ease of handling, and its very strong emission bands just in the region of substrate emissions (see Figure 2A for the emission spectrum of a thin film of silicone grease on a polished copper plate). The emission spectrum of this sample recorded at 343 K was ratioed against that of the blackbody, then the double beam emittance spectrum of the silica disc was subtracted from it. The resulting spectrum is shown in Figure 2B. (Ratioing the two spectra instead of subtracting leads to a very similar result, with a slightly different baseline profile.) It is surprising at first sight that there is strong emission in the 2000 to 1300 cm<sup>-1</sup> region, and that only weak emission remained in the region below 1300 cm<sup>-1</sup> showing strange details. A closer inspection reveals that the strong emission bands appearing above 1300 cm<sup>-1</sup> are not artefacts at all, but greatly enhanced overtone and combination bands, the traces of which can be seen also in the emission spectrum of pure silicone grease

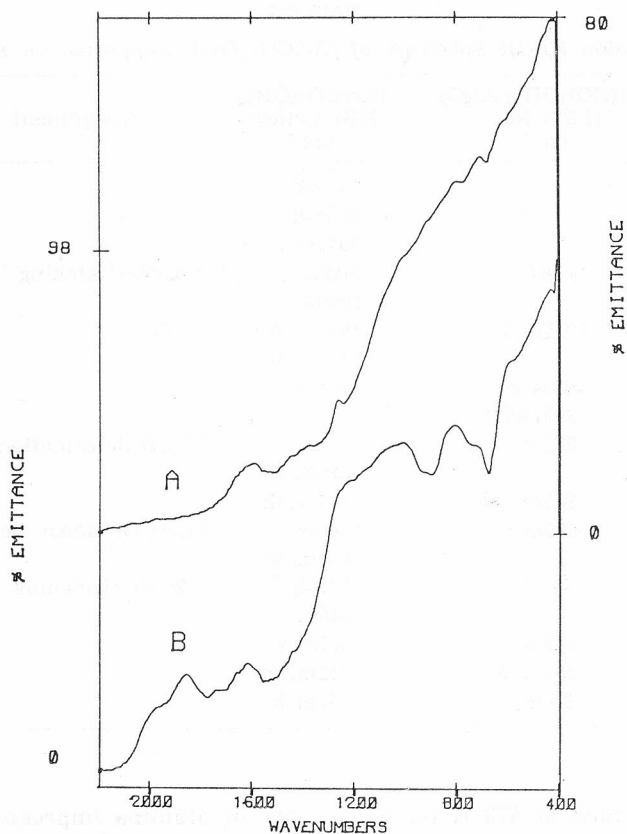


Figure 1. Emission spectra of thin pellets on Al-foil support at 341 K ratioed against blackbody:

- A — Al<sub>2</sub>O<sub>3</sub> (Alon-C, Degussa)  
 B — SiO<sub>2</sub> (Aerosil, Degussa)

(Figure 2A). In the region below 1300 cm<sup>-1</sup>, however, where the substrate emission is high, the absorption and emission of silicone grease are at near-equilibrium. In the regions 1300 to 950 and 870 to 750 cm<sup>-1</sup> absorption seems to dominate, but some of the peaks still point in the direction of emission (e.g. 1265 and 1020 cm<sup>-1</sup>). From this we have drawn the conclusion that, in the region of substrate emission, one has to look for absorption as well as emission bands in order to locate the adsorbate vibrations.

The above experience was utilized when studying a rhenium complex, tetrakis(tricarbonyl- $\mu_3$ -hydroxo-rhenium), formed on the surface of powdered alumina in catalytic amounts (1.5 to 5% of Re). The tetrameric molecule of this rhenium compound (which is very hard to obtain in pure form) is known to have a cube-like structure, shown in Figure 3. Its IR absorption frequencies are known from Ref. [50] and listed in Table I. The reaction leading to the formation of this compound

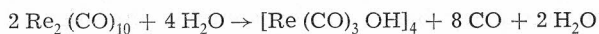




TABLE I  
Emission FT-IR Spectrum of  $[\text{Re}(\text{CO})_3\text{OH}]_4$  Supported on  $\text{Al}_2\text{O}_3$

$[\text{Re}(\text{CO})_3\text{OH}]_4/\text{Al}_2\text{O}_3$ (1.5% Re) $\text{cm}^{-1}$	$[\text{Re}(\text{CO})_3\text{OH}]_4$ KBr pellet* $\text{cm}^{-1}$	Assignment
	2065sh	
	2055sh	
	2045sh	
2038s	2038s	$\nu_s$ (CO) stretching
	1960sh	
1925vs, b	1940vs, b	$\nu_a$ (CO)
	1912vs, b	
1883s, sh	1895vs, b	
890vw(?)		
870w	873m	$\delta$ (OH) deformation
	812m, s	
801m	804w, sh	
653m, s	660m	$\delta$ (ReCO) linear bending
	650m, sh	
545sh	555sh	$\nu$ (ReC) stretching
	540m	
518m	517m, s	
500m, w	512m, sh	
470m, s	457m, b	

\* Ref. 50.

can be performed at 473 K on the surface of alumina impregnated with the solution of the starting material. The tetramer, once formed, is stable up to 670 K, but it cannot be separated from the alumina support without being destroyed. The product was studied by IR transmission spectroscopy, and the carbonyl stretching bands near  $2000\text{ cm}^{-1}$  could be easily detected, but no information could be obtained in the region of the substrate absorption below  $1200\text{ cm}^{-1}$ ;<sup>51</sup> thus, IR emission spectroscopy and, following the suggestion of a referee, diffuse reflection spectroscopy were evoked.

The diffuse reflection (DR) spectra of alumina and of the Re complex on alumina were measured as mixtures with KBr (pure alumina has so high absorbance that no diffusely reflected signal is transmitted to the detector). Both single beam spectra were ratioed against the DR spectrum of pure KBr, and the % reflectance intensity scales obtained in this way were transformed to Kubelka-Munk units. The spectrum of the sample was then subtracted from that of the support material (using appropriate scaling). The resulting difference spectrum is shown in Figure 4: the CO stretching bands of the Re complex were obtained with high SNR at 2030 and  $1910/1885\text{ cm}^{-1}$ , but the spectrum is completely useless in the region of high absorption of the support below  $1000\text{ cm}^{-1}$ . The noise level proportional to the subtracted signals in the low wavenumber part of the spectrum exceeds the intensity of the otherwise very strong carbonyl bands, thus leaving no hope of observing the weaker, low frequency bands of the complex investigated.



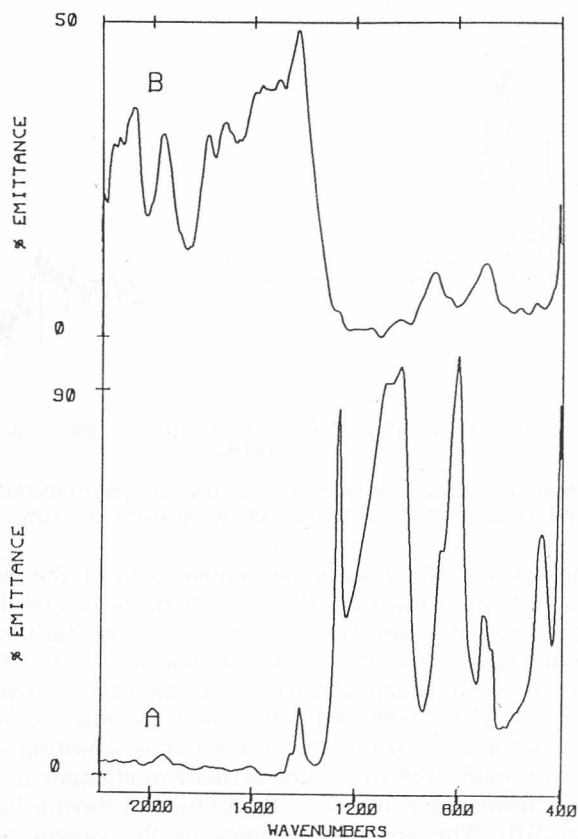


Figure 2. Emission spectra of silicone grease at 343 K ratioed against blackbody. A — Thin layer on polished copper plate. B — A fair amount of grease spread over the surface of the pressed SiO<sub>2</sub> pellet.

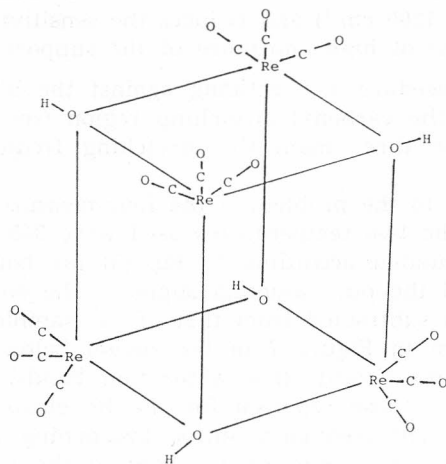


Figure 3. Structure of tetrakis(tricarbonyl- $\mu_3$ -hydroxo-rhenium).<sup>50</sup>

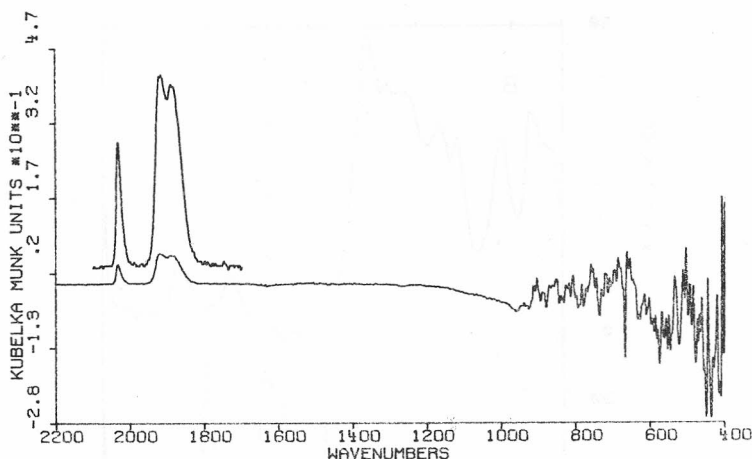


Figure 4. Difference of diffuse reflection spectra of  $[\text{Re}(\text{CO})\text{S}13\text{OH}]_4$  on alumina (1.5% Re) and of alumina (both samples were 0.5% mixtures with KBr).

The emission spectra of the alumina support and of the rhenium complex on alumina (5% Re) are shown in Figure 5 (curves A and B, respectively). The direct ratio of the two spectra gave the trace in Figure 5C. Beside the carbonyl stretching bands, no other spectral feature of the Re complex can be discerned. Some small sharp features pointing downwards in the ratioed spectrum (Figure 5C: 1590, 1380 and 1260  $\text{cm}^{-1}$ ) are due to »impurity« bands in the reference alumina spectrum; the broad bands, pointing upwards around 960 and 570  $\text{cm}^{-1}$  probably indicate some structural changes in alumina during impregnation with *n*-hexane solution of  $\text{Re}_2(\text{CO})_{10}$  and during further treatment to form  $[\text{Re}(\text{CO})_3\text{OH}]_4$ . The spectral changes in the region below 1200  $\text{cm}^{-1}$  cannot be ascribed unambiguously to the presence of the rhenium complex.

In fact, the direct ratioing of the above two single beam spectra (C and B in Figure 5) is not reasonable, since it enhances noise in the regions of low emittance (above 1200  $\text{cm}^{-1}$ ) and reduces the sensitivity to small intensity changes in the regions of high emittance of the support.

The standard procedure, *i. e.* ratioing against the blackbody, leads to a higher S/N ratio in the carbonyl stretching region (see Figure 6), allowing one to determine the three main CO stretching frequencies with greater confidence.

A better solution to the problem is the four-measurement experiment as defined by Eq. (5). The two temperatures used were 345 and 373 K, and the emittances were calculated according to Eq. (5) for both the sample (containing 1.5% Re) and the pure alumina support. The emittance spectrum of the support was then subtracted from that of the sample yielding the difference spectrum shown in Figure 7 in the region below 1400  $\text{cm}^{-1}$ . Several new bands pointing downwards (*i. e.* absorption bands) appeared at wavenumbers very close to those reported for the Re cluster by Herberhold *et al.*<sup>50</sup> (see Table I). Slight frequency shifts, broadening and intensity redistributions of the bands as compared to those of the isolated  $[\text{Re}(\text{CO})_3\text{OH}]_4$  molecule<sup>50</sup> suggest that the tetrameric molecule is weakly bonded to the

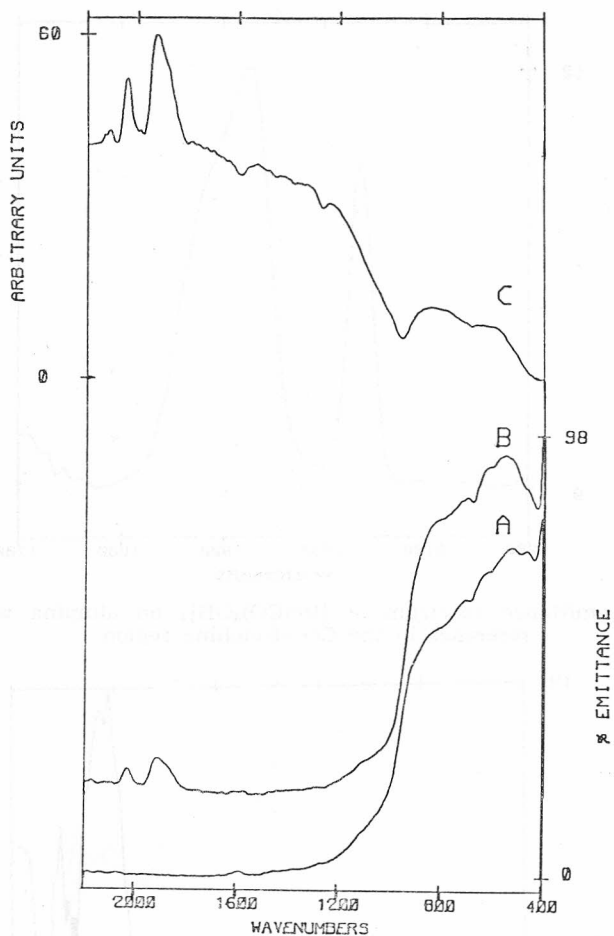


Figure 5. Directly observed emission spectrum of deposited thin layers on polished copper plate at 340 K.

- A —  $\text{Al}_2\text{O}_3$  (Alon-C, Degussa)
- B —  $[\text{Re}(\text{CO})_3\text{OH}]_4$  on  $\text{Al}_2\text{O}_3$  (5% Re)
- C — ratio spectrum of B/A

surface of the alumina support. Additional spectral features that were observed can be attributed, likewise as before, to impurities or changes of emission band shapes of the support. It is difficult to speculate on the origin of the strong band pointing downwards near  $670\text{ cm}^{-1}$ , because of the coincidence with the absorption of atmospheric  $\text{CO}_2$ .

Thus, on the basis of the new emission IR data it seems most likely that the rhenium complex formed on alumina as support has a cube-like tetrameric structure similar to that ascribed to the pure compound.

In a broader sense, the near-success of this study makes us believe that FT-IR emission spectroscopy is worthy of efforts, and might live up to our

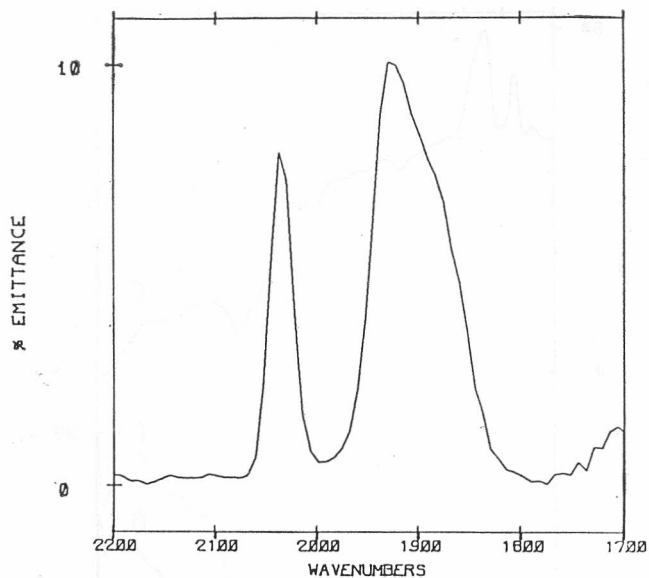


Figure 6. The emittance spectrum of  $[\text{Re}(\text{CO})_3\text{OH}]_4$  on alumina with blackbody reference in the CO stretching region.

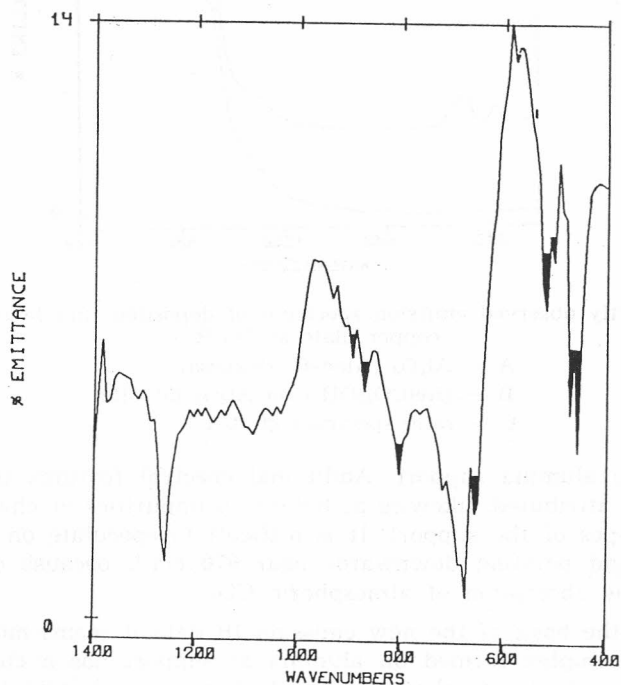


Figure 7. Emission spectrum of  $[\text{Re}(\text{CO})_3\text{OH}]_4$  supported on  $\text{Al}_2\text{O}_3$  using the four-measurement experiment at two different temperatures (347 and 337 K) followed by subtraction of the corresponding alumina spectrum.

expectations in the field of structural studies of chemisorbed molecules on supported metal catalysts in a wide frequency range including the spectral region of adsorbate-substrate vibrations.

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### SAŽETAK

#### **FT-IR emisijski spektri kemisorbiranih vrsta, s primjenom na vrste adsorbirane na aluminij-oksidu**

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Ukratko su prikazana načela infracrvene emisijske spektroskopije s naglaskom na aspekte njezine primjene na studij kemisorbiranih vrsta. Razmatraju se glavni problemi pripreve uzoraka, izbora mjernih uvjeta i najprikladnije metode obradbe podataka.

Prikazani su infracrveni emisijski spektri dvaju tipičnih materijala-nosača za metalne katalizatore, aluminij i silicij oksida. Na primjeru renijeva kompleksa, tetrakis(trikarbonil- $\mu_3$ -hidrokso-renija), stvorenog na aluminij-oksidu kao nosaču u katalitičkim uvjetima (1,5 do 5% Re) pokazalo se da tehnika četiriju mjerenja može rezultirati vrpčama sorbata u područjima visoke emisije supstrata (između 1300 i 400  $\text{cm}^{-1}$ ).