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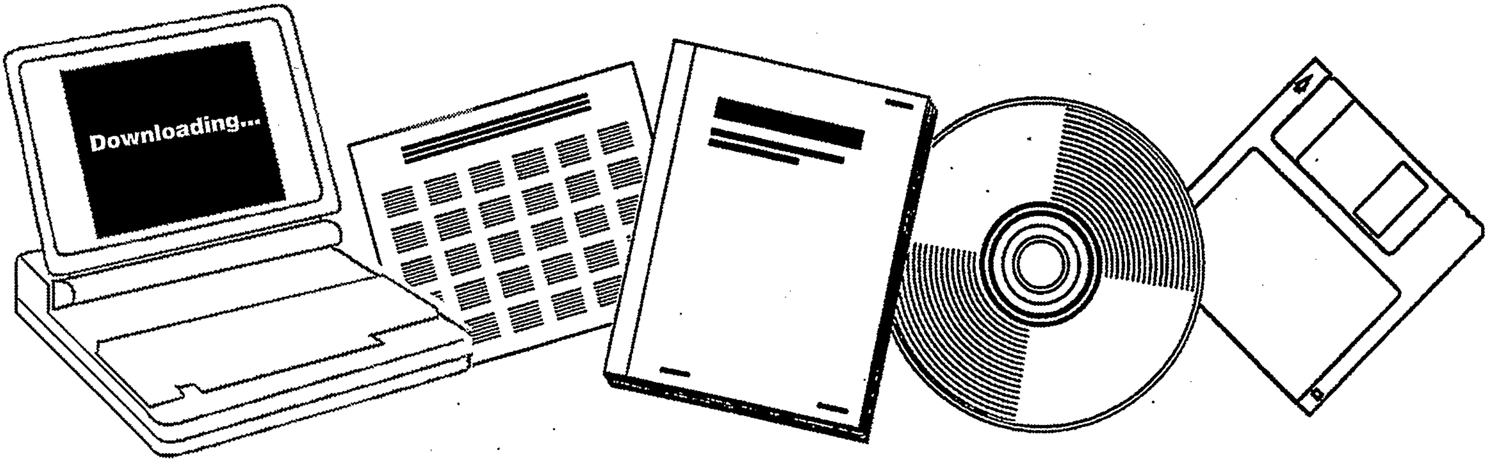
FTIR STUDIES OF HYDROCARBON SYNTHESIS ON PD/ZSM5 CATALYSTS. QUARTERLY PROGRESS REPORT

NOTRE DAME UNIV., IN. DEPT. OF CHEMICAL
ENGINEERING

15 FEB 1985



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DEPARTMENT OF ENERGY

Quarterly Progress Report

February 15, 1985

Project 84PC70788-2

FTIR Studies of Hydrocarbon Synthesis on Pd/ZSM5 Catalysts

directed by

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DISCLAIMER

Brief summary of progress.

During the past quarter two tasks were accomplished: i) a high pressure infrared reactor was built, tested, and modified accordingly, and ii) the Pd/ZSM5 catalyst was prepared and characterized, and the low pressure spectrum of CO on this and other catalysts was obtained.

Summary of progress.

Equipment. Our initial task has been the construction of an infrared reactor capable of high pressure and high temperature operation and capability for concentration and temperature programming. Our initial design was based on the use of saphire windows brazed into metal sleeves welded to the reactor body. This design, shown in fig. 1, had been successfully used in our group in high temperature-low pressure studies(1,2). Unfortunately the windows were not capable of standing the high temperature and pressure conditions although they were sized for high pressure operation. Leaks developed consistenly through the saphire-metal joint and the design was modified to the new version, which uses CaF_2 windows attached to the reactor by a retainer compressed by a graphite foil inert gasket. It is expected that this new design, now under construction, using a conventional seal, will be able to widthstand high pressures and temperatures. The rest of the high pressure components including the flow controllers for concentration programming have operated successfully.

Another task that was initiated was the construction of a high pressure small volume flow reactor which could be operated in parallel to the IR reactor, but at steady state conditions and for longer periods of time to study the catalyst stability. This reactor is now partially completed and it will be tested soon.

Catalyst preparation. While building and testing the high pressure equipment studies of the effect of catalyst preparation were conducted by varying the method of incorporating the metal into the support and using several supports. The H-ZSM5 catalyst, supplied to us by AMOCO Res. Dev. Lab., was first conditioned in the H-ZSM5 or Na-ZSM5 form by contacting it with 0.2M NH_4Cl or NaCl solutions for four hours at 60°C. After conditioning, the supports were thoroughly washed with water and dried overnight at 100°C. Commercial high surface area silica was used in the preparation of the Pd/SiO_2 catalyst.

Pd was incorporated into the supports by wet impregnation and ion exchange. However the wet impregnation technique produced catalysts with the highest methanation activity(3), consequently, this technique was used in subsequent preparations. It was also found that the best activity results were obtained using an organic Pd acetylacetonate solution in methyl chloride. The solution was contacted with the support for 16 hours at room temperature under constant stirring. The solvent was then evaporated by heating it at 40°C for 2 hours. The solids thus obtained were dried overnight at 100°C and stored in N_2. The catalysts were calcined in flowing N_2 for two hours at 400°C and then reduced in H_2 for four hours at 250°C.

Infrared Results. The infrared spectra of CO adsorbed in the Pd supported catalysts were obtained at low pressure using a reactor-cell similar to the one shown in fig. 1a. The catalysts were pressed in the form of a thin wafer which was placed in the reactor catalyst holder. Spectra was collected after exposure to a 5% CO in He stream at room temperature and then flushing the reactor with He. 10 single scan spectra were coadded and ratioed out against a reference spectrum collected in a pure He stream.

The infrared spectra of CO on Pt/SiO_2 and Pd/SiO_2 are shown in fig. 2.

CO adsorbed on Pt has a linear bonded structure with adsorbance at 2075 cm^{-1}. CO adsorbed on Pd has two bands: a linear CO structure with a band located at 2090 cm^{-1}, and a more intense band at 1980 cm^{-1}, corresponding to the bridge bonded structure.

The infrared spectrum of CO adsorbed on the Pd-ZSM5 catalyst, shown in Fig.3, appears much different than the spectrum of Pd supported on silica previously discussed. In the ZSM5 support, the bridge bonded species is the main band with the linear structure reduced to a small shoulder in the spectrum. Furthermore, the frequency of the bridge bonded structure is significantly shifted to a lower value at 1867 cm^{-1}. The other band shown in fig. 3 at 2353 cm^{-1} corresponds to CO_2 since this particular spectrum was collected during reaction with oxygen. The spectrum in the absence of oxygen, retains it bridge bond characteristic as shown in fig. 4. The conclusions to be drawn from this preliminary data is that, indeed as previously shown for the CO methanation reaction (3), the ZSM5 zeolite provides a metal suppport interaction which affects the state of the Pd surface and shifts the CO bond to a lower frequency. As expected CO in the presence of low pressure H_2 yields mainly methane(3).

Future work aim at reproducing the previous data at high pressure to ascertain the hypothesis of this work concerning the dual function mechanism on the Pd-ZSM5 catalyst comprising methanol formation on Pd followed by methanol to gasoline conversion on the ZSM5 catalysts.

References

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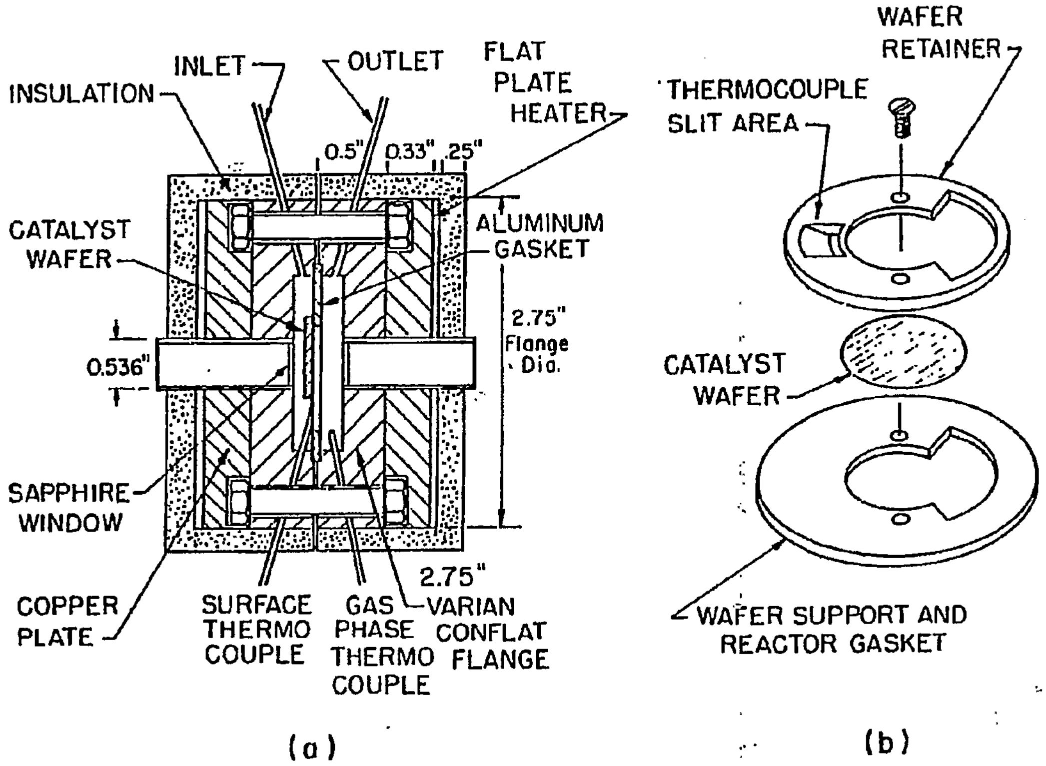
3. Saha and E. E. Wolf, Applied Catalysis, <u>13</u>, 101 (1984).


INSULATION
INLET
OUTLET
FLAT PLATE HEATER
0.5"
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CATALYST WAFER
ALUMINUM GASKET
2.75" Flange Dia.
0.536"
SAPPHIRE WINDOW
COPPER PLATE
SURFACE THERMO COUPLE
GAS PHASE THERMO COUPLE
2.75" VARIAN CONFLAT FLANGE
(a)
WAFER RETAINER
THERMOCOUPLE SLIT AREA
CATALYST WAFER
WAFER SUPPORT AND REACTOR GASKET
(b)

Figure 1

FTIR SPECTRA OF CO
ABSORBED ON Pt/SiO_2 AND Pd/SiO_2

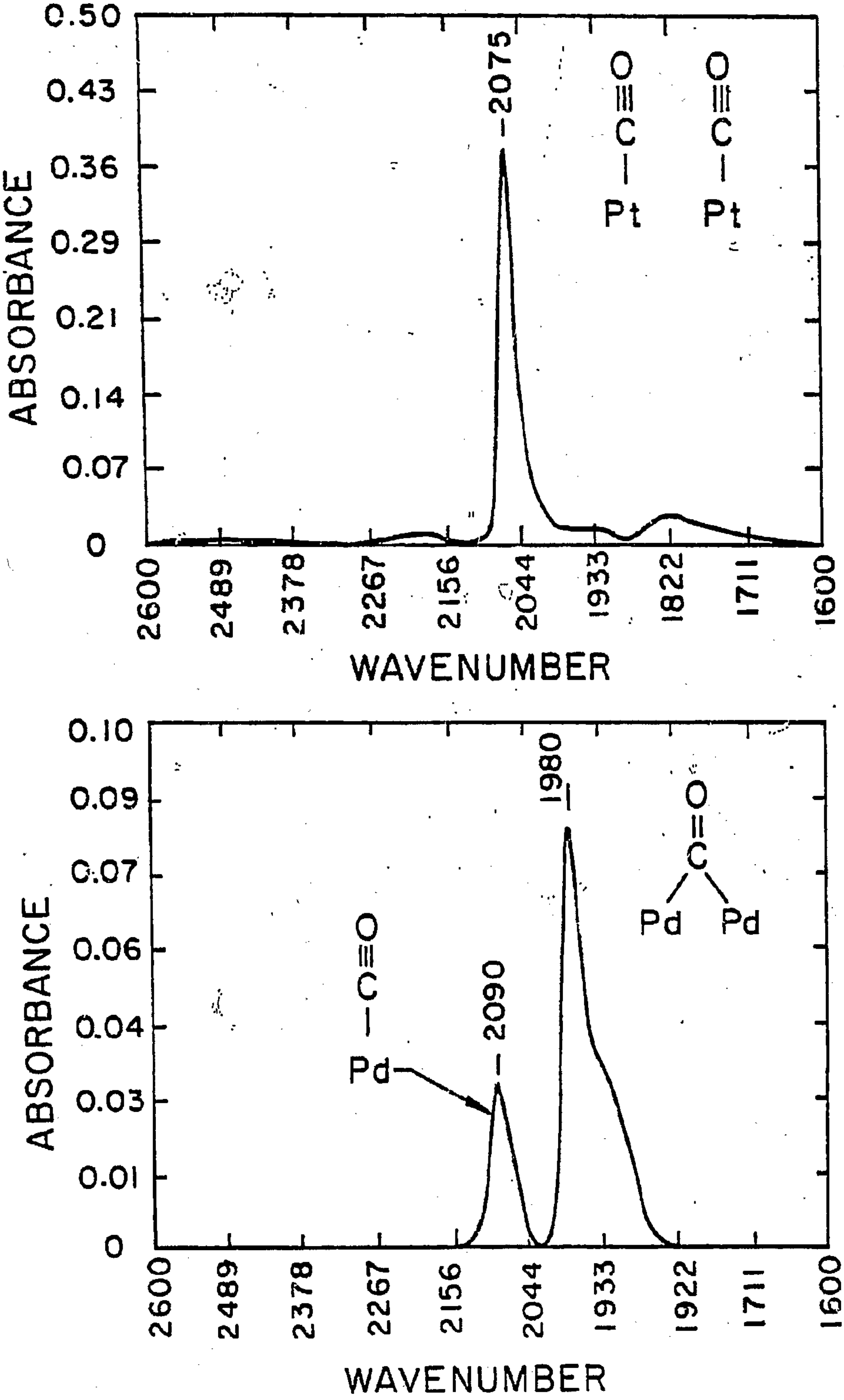
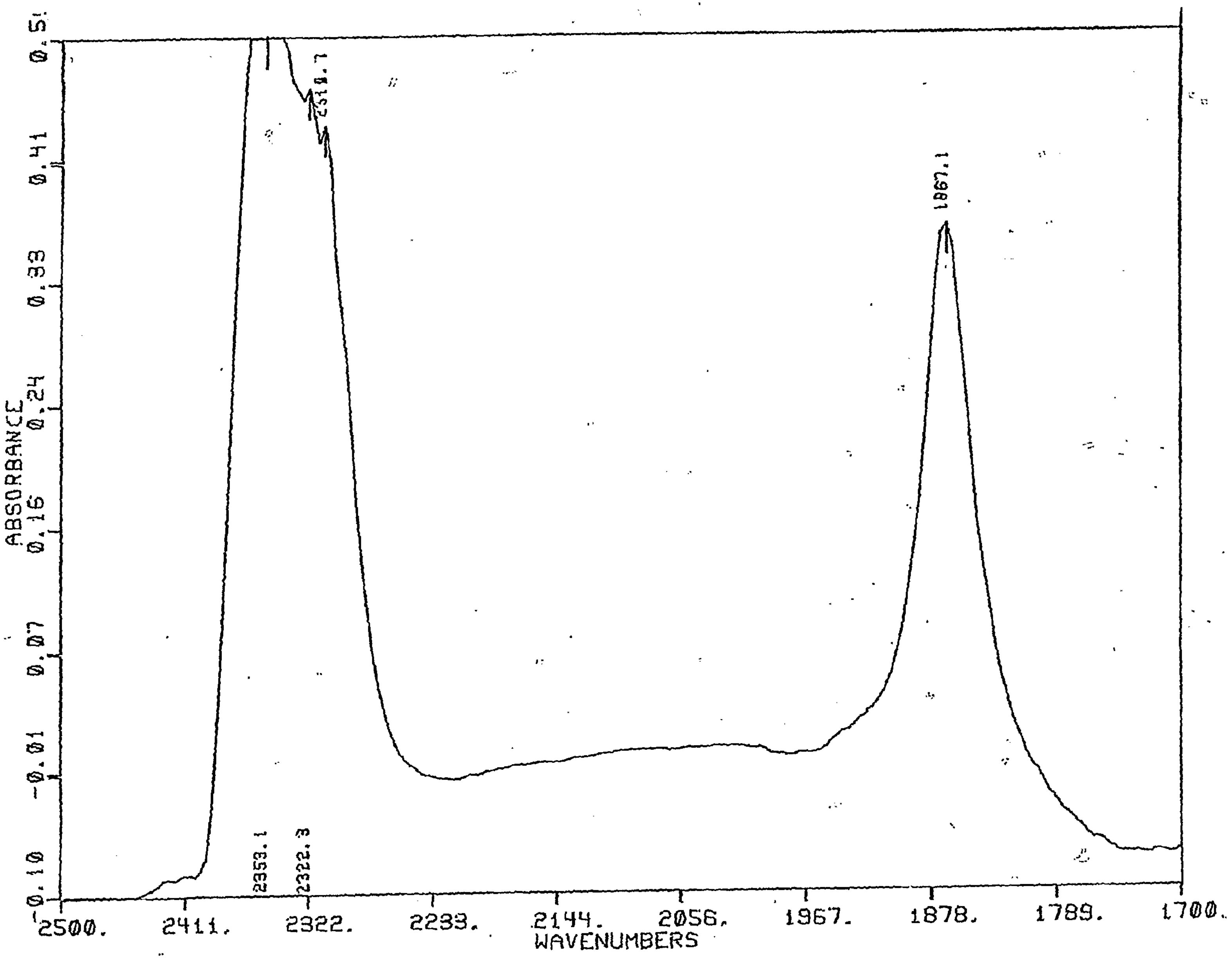


Fig. 2



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CO OXIDATION ON PD-ZSM5 ZEOLITE

Fig. 3

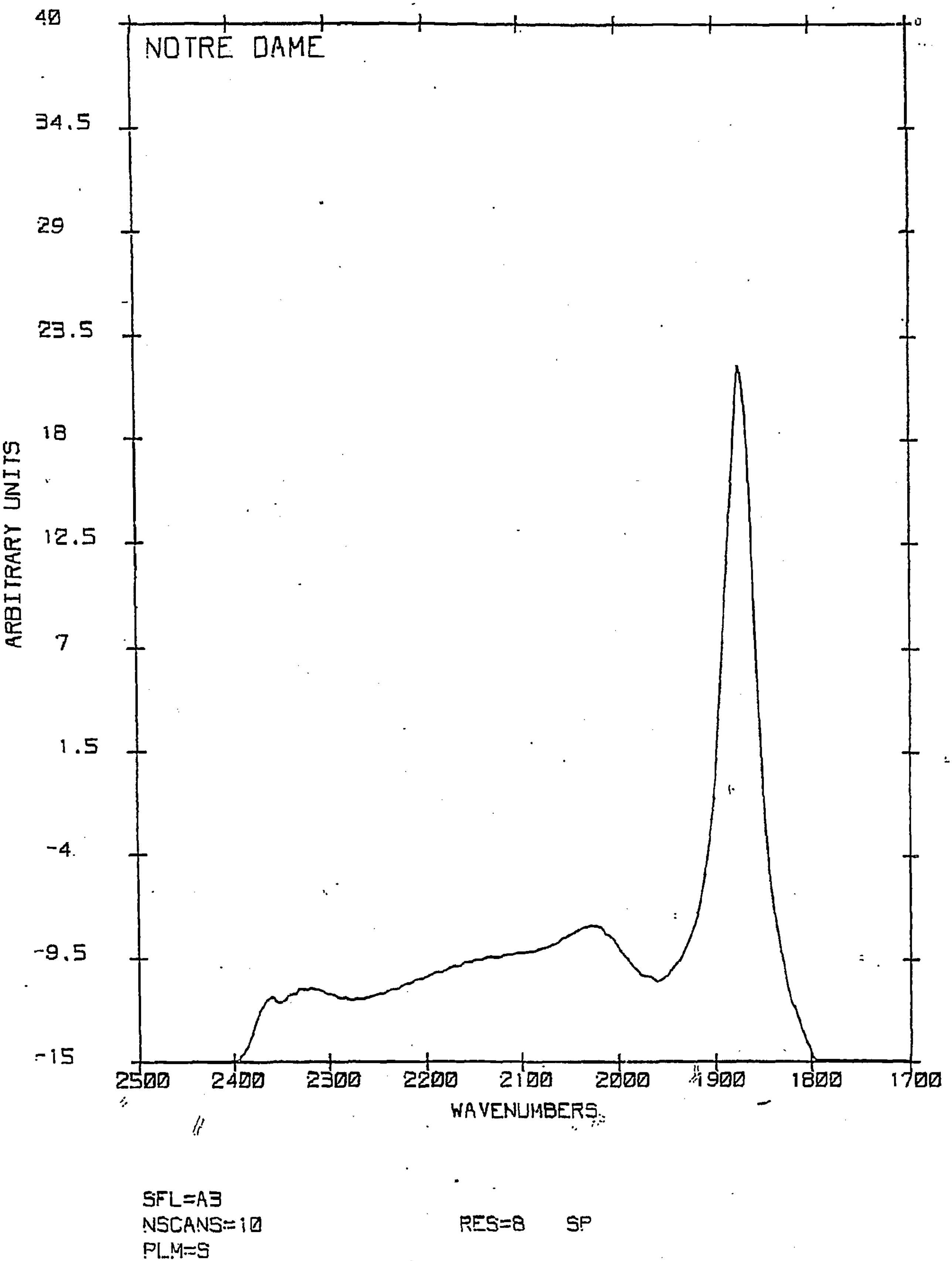
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Fig. 4

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