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ORGANOMETALLIC PHOTOCHEMISTRY AT THE SOLID/GAS INTERFACE. PHOTO--ETC(U)
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High surface area SiO_2 (400 m^2/g) functionalized first with $\equiv$SiH by reaction with $(EtO)_3SiH$ and then reacted with $Co_2(CO)_8$ yields Ⓢ$\equiv SiCo(CO)_4$ (Ⓢ = SiO_2). Photochemistry of Ⓢ$\equiv SiCo(CO)_4$ exposed to various gases has been studied by using Fourier transform infrared photoacoustic spectroscopy, FTIR/PAS. Near-uv irradiation under ^{13}CO yields Ⓢ$\equiv SiCo(CO)_n(^{13}CO)_{4-n}$ and the reaction can be reversed by irradiation under CO. Irradiation under O_2 yields loss of metal carbonyl signals and CO and CO_2 are observed as gas phase products. Experiments with $^{18}O_2$ and with ^{13}CO-enriched Ⓢ$\equiv SiCo(CO)_4$ show that CO_2 originates from CO initially bound to Co and O_2 in the gas phase. Ligand substitution by gas phase PF_3, ethylene, propylene, isobutylene, or propyne can be detected when Ⓢ$\equiv SiCo(CO)_4$ is irradiated in the presence of the gas. All photochemistry is consistent with loss of CO as the primary chemical result of photoexcitation of Ⓢ$\equiv SiCo(CO)_4$. The FTIR/PAS technique is useful on sample sizes of ~1 mg and gives infrared spectra of comparable quality to transmission infrared of KBr/ Ⓢ$\equiv SiCo(CO)_4$ pellets. The FTIR/PAS technique requires no pretreatment or manipulation of the sample and the monitoring of surface and gas phase products can be done <u>in situ</u>.

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TECHNICAL REPORT NO. 26

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ORGANOMETALLIC PHOTOCHEMISTRY AT THE SOLID/GAS INTERFACE. PHOTOCHEMISTRY OF SURFACE-CONFINED COBALT TETRACARBONYL MONITORED BY FOURIER TRANSFORM INFRARED PHOTOACOUSTIC SPECTROSCOPY.

by

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May 11, 1981 11 11 May 81

Organometallic Photochemistry at the Solid/Gas Interface. Photochemistry of Surface-Confined Cobalt Tetracarbonyl Monitored by Fourier Transform Infrared Photoacoustic Spectroscopy

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Organometallic Photochemistry at the Solid/Gas Interface. Photochemistry of Surface-Confined Cobalt Tetracarbonyl Monitored by Fourier Transform Infrared Photoacoustic Spectroscopy

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We wish to report the photochemistry of surface-confined -Co(CO)$_4^-$ fragments exposed to reactive gases. Such photochemistry is of importance in establishing primary events following excitation of the molecular entity attached to the surface and is of relevance to the photoactivation of surface-confined catalysts.[1,2] *We apply, for the first time, the technique* of Fourier transform infrared photoacoustic spectroscopy (FTIR/PAS)[3] to monitor the photoreactions of a species on the surface including <u>in situ</u> monitoring of reactions involving a gas phase species. Without any sample manipulation or preparation, this technique has allowed characterization of the photochemistry of surface species with the molecular level specificity generally possible when infrared absorption spectroscopy is used to monitor reactions of metal carbonyls in homogeneous solution. The results herein establish FTIR/PAS as a technique of unequalled capability in monitoring such surface chemistry.[4]

The system studied is Ⓢ$\geq$SiCo(CO)$_4$ where Ⓢ— represents a high surface area silica (~400 m^2/g from Alfa). The synthetic procedure follows from known reaction chemistry and was carried out according to the representation in (1) and (2).[5] The functionalization of metal oxides such

$$\text{surface-OH} \xrightarrow[(\text{EtO})_3\text{SiH}]{25^\circ\text{C}} \text{surface-O}{\geq}\text{SiH} \tag{1}$$

$$\text{surface-O}{\geq}\text{SiH} \xrightarrow[\text{Co}_2(\text{CO})_8]{25^\circ\text{C}} \text{Ⓢ}{\geq}\text{SiCo(CO)}_4 \tag{2}$$

as SiO_2 using $(RO)_3SiR'$ reagents[6] and reaction of $Co_2(CO)_8$ with R_3SiH to give $R_3SiCo(CO)_4$ are both well-known.[7] The reaction to prepare Ⓢ—SiH is established by transmission infrared of KBr/Ⓢ—SiH (10/1 by weight) pellets showing a feature at ~2250 cm^{-1} associated with the Si-H stretch; no feature in this region is observed for the SiO_2 prior to treatment with $(EtO)_3SiH$. Absorption is also observed in the C-H region reflecting the fact that some residual EtO— groups remain. Reaction of Ⓢ—SiH with $Co_2(CO)_8$ results in additional infrared absorptions in the metal carbonyl region at ~2110 (rel. o.d. = 0.3); 2050 (rel. o.d. = 0.5); and ~2020 (rel. o.d. = 1.0) cm^{-1}. The number of bands and their relative intensities accord well with bands expected for Ⓢ—$SiCo(CO)_4$ based on species such as $(EtO)_3SiCo(CO)_4$.[1,7] From a combination of infrared and elemental analyses the coverage of —$SiCo(CO)_4$ is sub-monolayer (~10^{-11} mol/cm^2), and there is generally considerable —SiH remaining after reaction with $Co_2(CO)_8$.

Figure 1 includes a typical FTIR/PAS characterization of ~1 mg of Ⓢ—SiH/—$SiCo(CO)_4$. The relative FTIR/PAS signals are proportional to infrared absorbances found for Ⓢ—$SiCo(CO)_4$ in KBr. For both forms of infrared the metal carbonyl signals are broader and less well-resolved than the spectral features for species such as $R_3SiCo(CO)_4$ in alkane solution.[1,7] The FTIR/PAS of the Ⓢ—SiH/—$SiCo(CO)_4$ is just as good in terms of signal-to-noise as the FTIR/absorption and does not require palleting or other pretreatment of the sample. Quantities of sample required for FTIR/PAS are as small, or smaller, as typically used to prepare 1 cm diameter KBr/Ⓢ—SiH/—$SiCo(CO)_4$ pellets.

The unique capabilities of the FTIR/PAS are revealed in the photochemical studies. Typically, a ~1 mg sample of Ⓢ—SiH/—$SiCo(CO)_4$ is placed in the FTIR/PAS cell and irradiated at 25°C with the 300-400 nm output from a 150 W Xe lamp focused to ~1 cm^2; the input optical power to the sample is ~100 mW/cm^2. The undisturbed sample can then be characterized by FTIR/PAS.[8] The first significant experiment concerns the results from irradiation of $\textcircled{S}{\geq}\mathrm{SiH}/{\geq}\mathrm{SiCo(CO)_4}$ when the cell contains 1 atm of ^{13}CO (90% ^{13}C). Figure 1 includes the FTIR/PAS spectrum that results after an irradiation of 15 min under ^{13}CO, pumping out all gases, and then introducing Ar for acoustic coupling. The spectra before and after irradiation under ^{13}CO establish the photochemistry represented by (3), a result that would be expected if (4) represents the primary chemical event following photo-

$$\textcircled{S}{\geq}\mathrm{SiCo(CO)_4} + {}^{13}\mathrm{CO} \xrightarrow{h\nu} \textcircled{S}{\geq}\mathrm{SiCo(CO)_n(^{13}CO)_{4-n}} \tag{3}$$

$$\textcircled{S}{\geq}\mathrm{SiCo(CO)_4} \xrightarrow{h\nu} \textcircled{S}{\geq}\mathrm{SiCo(CO)_3} + \mathrm{CO} \tag{4}$$

excitation. When irradiation is carried out for short periods of time, spectral changes are consistent with the sequential replacement of bound CO by ^{13}CO. The FTIR/PAS monitoring can be carried out without pumping out the cell, using the reactive gas as the acoustic coupler. When the gases are not pumped out the ^{13}CO is detected and ^{12}CO is detected as a gas phase photoproduct, as expected. Additionally, small amounts of CO_2 and $^{13}CO_2$ are detected as photoproducts (cf. below). Irradiation of $\textcircled{S}{\geq}\mathrm{Si(CO)_n(^{13}CO)_{4-n}}$ for $n \simeq 0$ under 1 atm CO results in the regeneration of $\textcircled{S}{\geq}\mathrm{SiCo(CO)_4}$ with ~80% recovery of the FTIR/PAS signal for the carbonyl species. Chemically, these results establish CO loss as the principal result of photoexcitation of the $\textcircled{S}{\geq}\mathrm{SiCo(CO)_4}$. This finding parallels the conclusion drawn from studies of $R_3SiCo(CO)_4$ in homogeneous solution and $\textcircled{S}{\geq}\mathrm{SiCo(CO)_4}$ suspended in solution.[1] In particular, the FTIR/PAS shows little or no importance for photoinduced cleavage of the Si-Co bond that would lead to $Co(CO)_4$ or to the dimer $Co_2(CO)_8$. With the FTIR/PAS technique, the data are much more easily obtained and without sample manipulation, compared to conventional infrared methods.

Additional photochemical results are consistent with the dissociative loss of CO from the surface. First, irradiation of the Ⓢ$-\mathrm{SiCo(CO)_4}$ under vacuum leads to disappearance of all metal carbonyl species. This disappearance is dramatically suppressed under CO, as expected. Under 1 atm Ar, irradiation leads to some decomposition, but the rate eventually declines, presumably due to the accumulation of CO in the cell. When decomposition is detected, CO and CO_2 are observed as gas phase photoproducts. Irradiation of the Ⓢ$-\mathrm{SiCo(CO)_4}$ under 1 atm O_2 leads to more rapid decline of the metal carbonyl signals, and a larger signal for gas phase CO_2 is observed, compared to reaction under Ar, Figure 2. Thus, O_2 is a reactive gas and presumably interacts with the photogenerated, coordinatively unsaturated $-\mathrm{SiCo(CO)_n}$ species to lead to the oxidation of CO to CO_2. We estimate the CO/CO_2 product ratio to be ~3/1 when the irradiation is carried out under 1 atm O_2. Irradiation of Ⓢ$-\mathrm{SiCo(CO)_4}$ under $^{18}O_2$ leads to the formation of $C^{18}O^{16}O$ and irradiation of ^{13}CO-enriched Ⓢ$-\mathrm{Si(CO)_4}$ under $^{18}O_2$ leads to $^{13}C^{18}O^{16}O$. These results establish the source of CO_2 to be CO originally bound to Co and O_2 in the gas phase. The Co product is likely some form of Co-oxide; PAS in the visible region is consistent with this conclusion.[9]

FTIR/PAS can also be used to monitor photosubstitution of the Ⓢ$-\mathrm{SiCo(CO)_4}$ using gas phase entering groups such as PF_3 and olefins, Figure 3. At 25°C, the chemistry represented by (5) is detectable. The main

$$Ⓢ\!-\!\mathrm{SiCo(CO)_4} + \mathrm{PF_3} \xrightarrow{h\nu} Ⓢ\!-\!\mathrm{SiCo(CO)_n(PF_3)_{4-n}} \qquad (5)$$

infrared feature is at ~2000 cm^{-1} and is associated with Ⓢ$-\mathrm{SiCo(CO)_3PF_3}$ with the PF_3 occupying an axial position trans to the $-\mathrm{Si}-$, as found for $R_3SiCo(CO)_3P(OPh)_3$ prepared by photosubstitution.[1,10] Irradiation of Ⓢ$-\mathrm{SiCo(CO)_n(PF_3)_{4-n}}$ under 1 atm CO leads to the regeneration of a large fraction of the Ⓢ$-\mathrm{SiCo(CO)_4}$. Irradiation of Ⓢ$-\mathrm{SiCo(CO)_4}$ under ethylene or propylene at 25°C yields loss of all metal carbonyls; $Et_3SiCo(CO)_3$(alkene) was shown previously to decompose at 25°C.[1] But irradiation of the

Ⓢ$>$SiCo(CO)$_4$ at -50°C under ethylene, propylene, isobutylene, or propyne and monitored by FTIR/PAS at that temperature, leads to the generation of new surface metal carbonyl species, Figure 3. The signal at ~1990 cm^{-1} would logically be attributed to Ⓢ$>$SiCo(CO)$_3$(alkene), where the alkene is trans to the $->$Si$-$, paralleling solution studies. A signal that grows in at ~2050 cm^{-1} for ethylene, propylene, or propyne, but not isobutylene, is unidentified at this time. Such a signal could be due to another isomer of the Ⓢ$>$SiCo(CO)$_3$(alkene) where the alkene is cis to the $->$Si$-$, or the peak could be due to multiple substitution. This point is currently under investigation, but it does appear that the species associated with the ~2050 cm^{-1} peak is a primary product, since it appears even at short irradiation times. Interestingly, the ~2050 cm^{-1} peak does not appear in low temperature irradiations of Ph$_3$SiCo(CO)$_4$ in solutions containing 1-pentene or ethylene, but the Ph$_3$Si— group may offer more steric restriction than the Ⓢ$>$Si$-$.

To summarize, we have established the primary photoreaction of Ⓢ$>$SiCo(CO)$_4$ to be loss of CO. This can be exploited to study the oxidation of CO by O$_2$, to prepare inert or labile substitution products, and to elaborate the mechanism of the reactions of immobilized, photogenerated, coordinatively unsaturated intermediates. The technique of FTIR/PAS is shown to be a molecular specific tool having unique capabilities for the study of photoreactions of the surface species on high surface area supports.

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4. There are a number of techniques useful for obtaining vibrational spectra of surface species, cf. "Vibrational Spectroscopies for Adsorbed Species", A. T. Bell, M.L. Hair, Eds., ACS Symposium Series, 1980, 137, American Chemical Society, Washington, D.C. The FTIR/PAS would appear to offer advantages when monitoring both surface and gas phase reaction products in situ.

5. In a typical procedure, ~1 g of high surface area SiO_2 having some -OH available is suspended in ~25 ml of alkane solvent containing excess $(EtO)_3SiH$ at 25°C under N_2. The solution is stirred for 24 h and then filtered to collect a solid. After repeated washing the solid exhibits an infrared signal at ~2250 cm^{-1} associated with Si-H. Infrared transmission experiments indicate that there is ~6.1 mol per cent $\geqslant$SiH.[1b] The powder is then reacted with excess $Co_2(CO)_8$ in alkane solution under N_2 at 25°C for 24 h. After repeated washing, the solid still exhibits an infrared peak at ~2250 cm^{-1} (~3.4 mol per cent SiH) and signals at 2110, 2050, and ~2020 cm^{-1} characteristic of $\geqslant SiCo(CO)_4$ (~1.9 mol percent).[1b] Reaction of the powder with $Co_2(CO)_8$ also leads to some decomposition of the $Co_2(CO)_8$ to leave a Co-oxide/hydroxide on the surface.[1b] Samples were exposed to vacuum for 20 min at 25°C prior to any experimentation to remove any O_2 or H_2O from the surface.

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8. FTIR/PAS spectra were obtained using a Nicolet 7199 FTIR with a gas microphone photoacoustic detector of our own design that allows control of the sample environment. The details are to be published independently by JBK and RHS. Data collection for 8 cm^{-1} resolution spectra typically take 4 min. The acoustic coupling gas in all cases was 1 atm Ar (<1 ppm H_2O, O_2) except when monitoring gas phase products as in photolyses under O_2.

9. The Co-oxide product is detected as an absorber in the visible at ~620 nm.[1b] Monitoring a sample by FTIR/PAS and by PAS in the visible shows the decline of metal carbonyl to be accompanied by the growth of the ~620 nm feature attributed to Co-oxide.

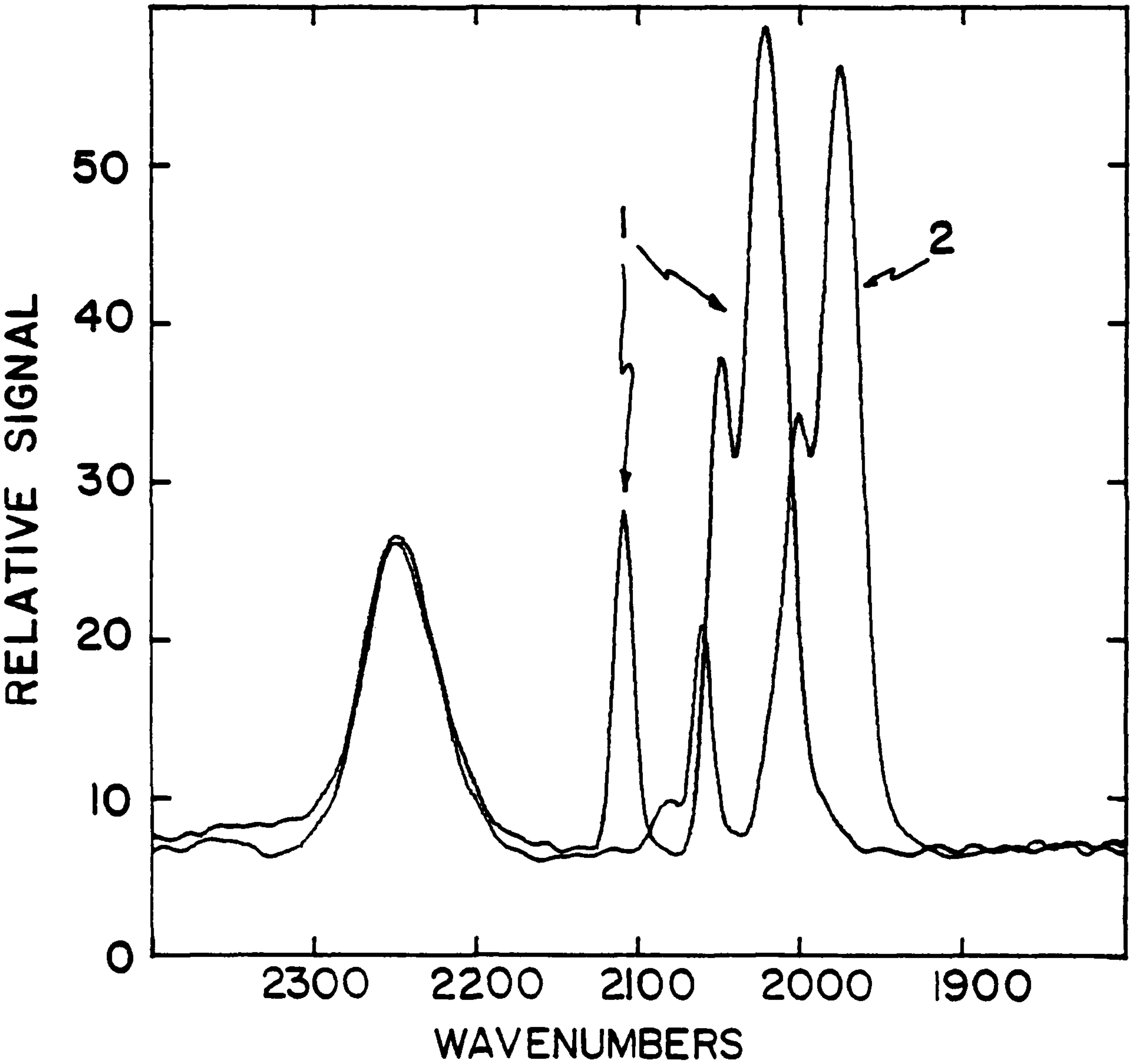
10. Many metal carbonyls undergo photosubstitution under PF_3, Geoffroy, G.L.; Wrighton, M.S. "Organometallic Photochemistry", Academic Press: New York, 1979, including Co carbonyls related to those under study here: Udovich, C.A.; Clark, R.J. Inorg. Chem., 1969, 8, 938.

Figure Captions

Figure 1. FTIR/PAS spectrum before, curve 1, and after, curve 2, 20 min near-uv irradiation of Ⓢ—SiCo(CO)$_4$ under 1 atm ^{13}CO. In each case the acoustic coupling gas is 1 atm Ar. The spectral changes are consistent with the photochemical generation of Ⓢ—SiCo(^{13}CO)$_4$. No ^{13}CO exchange occurs in the dark at 25°C on the timescale of this experimentation.

Figure 2. FTIR/PAS spectrum before, curve 1, and after, curve 2, 20 min near-uv irradiation of Ⓢ—SiCo(CO)$_4$ under 1 atm O_2. For spectra 1 and 2 the acoustic coupling gas is the 1 atm O_2. Spectrum 2 shows gaseous CO and CO_2 photoproducts. Spectrum 3 is after evacuating the sample chamber to remove all gases and introducing O_2 at 1 atm as the acoustic coupling gas.

Figure 3. (A) Curve 1 is the initial FTIR/PAS spectrum of a sample of Ⓢ—SiCo(CO)$_4$ and curve 2 is the spectrum obtained after near-uv irradiation, of the sample characterized in 1, for 10 min under 1 atm PF_3. The product is Ⓢ—SiCo(CO)$_n$(PF_3)$_{4-n}$. Curve 3 is the spectrum that results when the sample characterized in 2 is irradiated under 1 atm of CO to regenerate Ⓢ—SiCo(CO)$_4$. These spectra are recorded using 1 atm Ar as the coupling gas. (B) Spectral changes accompanying the near-uv irradiation of Ⓢ—SiCo(CO)$_4$, curve 1, at low temperature, ~-50°C, under ~100 torr isobutylene for 10 min to form Ⓢ—SiCo(CO)$_3$(isobutylene), curve 2.



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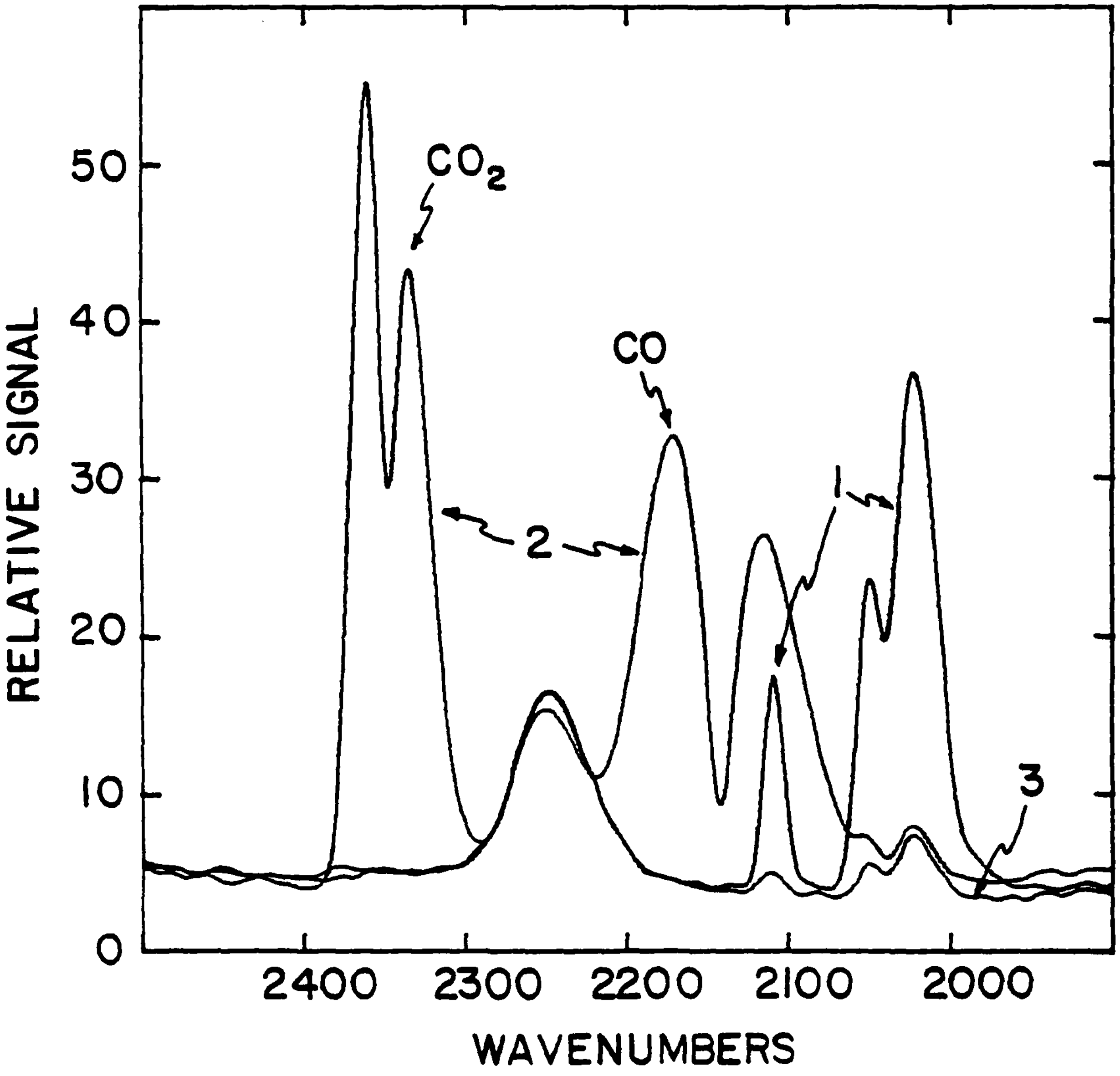

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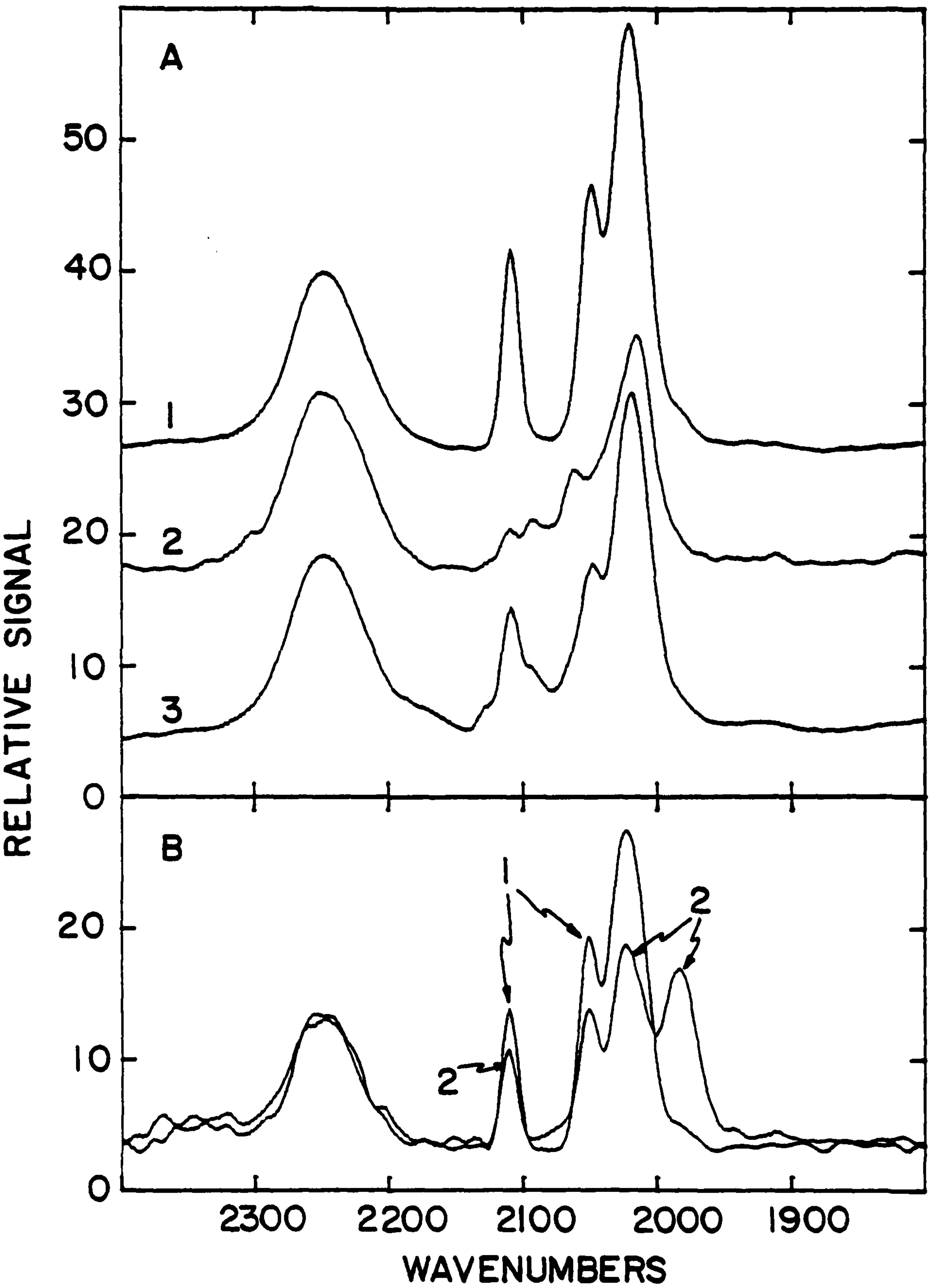
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