

## Toluene Oxidation over Metal Oxides in Relation to Oxide Vibrations

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Received December 6, 1983; revised May 9, 1986

The rate of the selective oxidation of toluene to benzaldehyde over metal oxides has been related to the frequencies of the metal-oxide ion vibrations. Literature data as well as new experimental data are used. It appears that a twin-peaked curve describes the relation. This result is interpreted in terms of a hypothesis on specific energy transfer by vibrational resonance in catalytic reactions. © 1986 Academic Press, Inc.

### INTRODUCTION

This work is based on and motivated by a hypothesis formulated a few years ago (1-3) that one of the factors governing the catalytic activity of a catalyst is the phenomenon of vibrational resonance. The proposal is that resonance can occur between surface vibrations of the catalyst and proper molecular vibrations of the reactant. This idea was in fact put forward much earlier by Myers (4), and from a more quantitative standpoint, the phenomenon of catalysis was interpreted as a resonance effect by Marshadev in a series of papers, e.g., Refs. (5, 6). Following the work of Marshadev, Scheve and co-workers applied the principle of resonance to electron transfer catalysis (7). The latter investigation was undoubtedly influenced by the view prevailing at that time that heterogeneous catalysis was strongly related to the semiconducting properties of the solid phase catalysts.

As a chemical reaction is generally accompanied by changes in the interatomic distances of the reacting species, the reaction coordinate must somehow be expressed in terms of the vibration modes of the species in question (8). Furthermore, the vibration which comes into resonance with the catalyst vibrators must be a very specific one, viz., the vibration (or combi-

nation of vibration modes) which causes the reactant to change its structure towards that of the transition state of the reaction.

In order to focus attention on this aspect of the resonance theory, we have chosen to study a reaction for which the rate-determining step is reasonably well known and defined, viz., the oxidation of toluene to benzaldehyde over metal oxide catalysts (9). As the rate-determining step involves a hydrogen atom displacement (transfer) from the methyl group to the surface of the oxide catalyst (9), it is reasonably easy to deduce which of the toluene normal vibrations will constitute the reaction coordinate. It must be that vibration which distorts the CH<sub>3</sub>-group toward the planar intermediate R-CH<sub>2</sub> (see Fig. 1). The most likely one is the methyl rocking vibration. This appears at 1040 cm<sup>-1</sup> in the infrared spectrum of the free molecule (10).

It must be stressed that the choice of a *hydrogen* transfer is not very crucial. It may very well be a hydride transfer or a proton transfer, depending on the redox character of the metal oxide catalyst. In this connection it should also be pointed out that the metal oxides to be considered must be capable of changing the oxidation state of the metal atoms (or possibly acting as electron-accepting semiconductors). This follows from the generally accepted

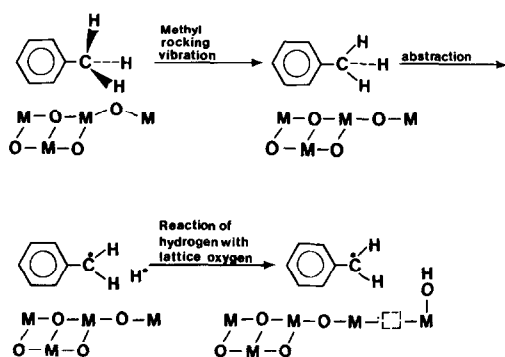


FIG. 1. Sketch of the first steps of toluene oxidation over metal oxides.

Mars-van Krevelen mechanism of this type of catalytic oxidation (11).

#### METHOD

##### *Analysis of Rate Data from Literature*

In order to demonstrate the possible action of a resonance effect we have used the same method of presentation as before (1, 2), viz., plotting the catalytic activity (actually the rate of reaction) against a characteristic wavenumber of the catalyst system. For want of surface vibration data, we have provisionally used the bulk vibration frequencies of the catalyst oxides. From the model outlined above one would expect one or more maxima in such a plot. These maxima should be observed at those wavenumbers for which resonance can take place.

We have used the data from the comprehensive work of Germain and Laugier (12) in such a plot (Fig. 2). The activity is defined as total rate of reaction ( $\text{mmol h}^{-1} \text{m}^{-2}$ ) times the initial selectivity for benzaldehyde formation (12). In Fig. 2 one finds a distinct maximum at about  $520 \text{ cm}^{-1}$  and an indication of a possible maximum at a wavenumber close to  $1040 \text{ cm}^{-1}$ . Note that the second harmonic of a vibration around  $520 \text{ cm}^{-1}$  should appear at about  $1040 \text{ cm}^{-1}$ .

##### *Selection of Frequencies*

Some comments must be made on the selection of frequencies of the M—O vibra-

tions. The vibrations of three-dimensional, repetitive AB patterns have been treated by Born and Huang (13). The detailed solutions, possibly disregarding the most simple cases, are, however, not easily available. Furthermore, the different stoichiometries and symmetry properties of the oxides under discussion, and the more or less hindered mobility of the adsorbate on the surface, make it difficult to designate the vibration which is most prone to interact with the adsorbed molecule.

What one can do, however, without any detailed calculation for each of the oxides, is to distinguish between the vibrations which are predominantly M—O stretches and those that are predominantly M—O—M deformation modes. The former category will comprise the higher wavenumber modes, the latter the lower wavenumber modes. Consequently, an M—O stretching vibration will transfer

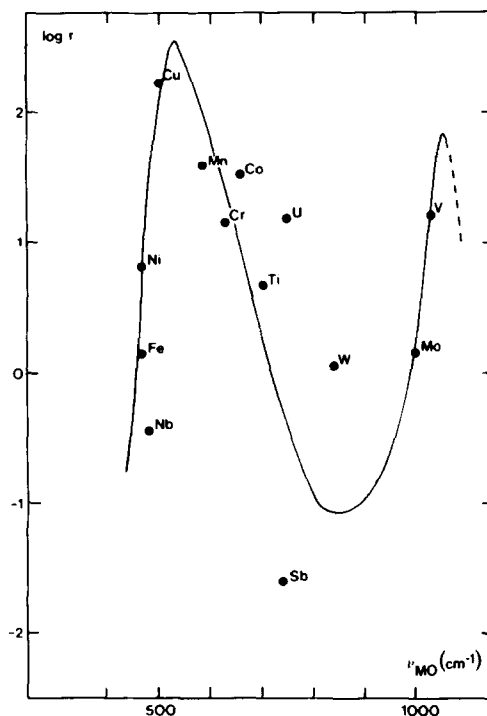


FIG. 2. Plot of literature data (12) on the total rate of reaction ( $A$  in  $\text{mmol h}^{-1} \text{m}^{-2}$ ) times the initial selectivity for benzaldehyde formation versus the wavenumbers of M—O vibrations (cf. Table 1).

more energy per quantum and thus be more effective in transferring resonance energy to the reactant.

As another requirement one must add the intensity of the infrared absorption. A high intensity means a strong variation of the dipole of the vibration system during the vibration. This should make coupling between the two vibrators, the metal oxide and the reactant toluene more probable and facilitate energy transfer.

Thus the selective principle for the wavenumber range of Fig. 2 was to choose those vibrations from literature quotations (14–20) that have high wavenumbers and are designated as “strong.” It should be noted that there is a large variation in the literature concerning the wavenumbers of vibrations for one and the same oxide. This is, no doubt, caused by different preparation techniques and different methods of recording the spectra.

Table 1 gives a detailed description of the sources of the frequency data. In the case of  $\text{WO}_3$ , one may choose to use the strong  $\text{WO}_3$  bands around  $850\text{ cm}^{-1}$  or the much weaker ones at around  $1020\text{ cm}^{-1}$  that clearly involve  $\text{W}=\text{O}$  stretching (19).

### Infrared Emission Spectra

Inspection of the literature indicates that the wavenumbers given for the  $\text{M}-\text{O}$  vibrations of particular metal oxides vary to an extent that is not related to calibration of the spectrometers only. The differences probably depend on the methods of preparing the samples. The investigation of Hunt *et al.* (21) on  $\text{NiO}$  is very striking. These authors find that the 490- and the 405- $\text{cm}^{-1}$  bands vary in relative intensity for different forms of the  $\text{NiO}$  crystallites. The 490- $\text{cm}^{-1}$  absorption band is best described as a surface vibration mode (21), while the other band corresponds to bulk vibration modes.

A similar situation applies, to a greater or lesser degree, to the other oxides. Moreover, the catalytic effect depends on the surface vibration modes, assuming that our model holds. Thus one would like to be able

TABLE 1

Source of Literature Data for the Metal Oxide  $\text{M}-\text{O}$  Stretching Wavenumbers

Oxide	$\bar{\nu}$ $\text{M}-\text{O}$ stretch ( $\text{cm}^{-1}$ )	Ref.
$\text{Nb}_2\text{O}_5$	478 <sup>a</sup>	(14)
$\text{Fe}_2\text{O}_3$	468	(14)
$\text{NiO}$	465	(14)
	745	(16)
$\text{CuO}$	500	(14)
$\text{Co}_3\text{O}_4$	655	(14)
$\text{Mn}_2\text{O}_3$	583	(15)
$\text{Cr}_2\text{O}_3$	625	(14)
$\text{Sb}_2\text{O}_4$	740 <sup>b</sup>	(20)
$\text{WO}_3$	815, 832, 820, 870, 900, 905 <sup>c</sup>	(19)
$\text{MoO}_3$	995	(18)
$\text{V}_2\text{O}_5$	1022	(17)
$\text{TiO}_2$	695	(14)

<sup>a</sup> The  $\alpha$ - $\text{Nb}_2\text{O}_5$  form has been selected as, thermodynamically, it is the most stable one, occurring at the temperature used in the reaction of toluene oxidation.

<sup>b</sup>  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$  are both reported at  $740\text{ cm}^{-1}$ .

<sup>c</sup> Different modifications.

to differentiate between surface and bulk modes.

It seems that infrared emission spectroscopy is a proper technique for this purpose. The emission originates to a larger extent near the surface of the specimen (24) and therefore any band that is strong as regards emission but weaker in transmission spectra can be ascribed to vibrations from the surface region of the particle.

The infrared emission spectroscopy (IRES) technique has been described in the literature (22, 23). We have designed a cell based on the construction used by Primet *et al.* (22), but with some improvements. By introducing a water cooling system to prevent adverse effects on the epoxy resin and the grease holding the window, it is possible to heat the furnace to  $400^\circ\text{C}$ , i.e., a temperature convenient for measuring the activity of the catalysts. The use of a planar joint instead of the hemispherical one used by Primet *et al.* (22) makes it much easier to handle the cell when working under vacuum. The cell is described in detail by Jonsson *et al.* (24).

TABLE 2

IR Transmission Data for the Absorption Bands ( $\text{cm}^{-1}$ ) of the Oxides Used in the Catalysis Experiments of Andersson (26)

TiO <sub>2</sub>	730 s,b 515 s 400 m 325 m	ZrO <sub>2</sub>	750 s 500 b,m 454 w 415 m
V <sub>2</sub> O <sub>5</sub>	1022 s 820 s,b 589 s,b 480 s,b 380 m 328 w	Nb <sub>2</sub> O <sub>5</sub> <sup>a</sup>	805 w,s 629 w 597 m 469 s 450 sh 994 s
Cr <sub>2</sub> O <sub>3</sub>	636 s,b 577 s 444 w 412 m	MoO <sub>3</sub>	864 s,b 819 sh 592 s,b 490 sh 373 s 350 sh
Mn <sub>2</sub> O <sub>3</sub>	660 sh 575 m 526 m 474 m 326 sh	SnO <sub>2</sub>	615 m 470 m
Fe <sub>2</sub> O <sub>3</sub> ( $\alpha$ )	600 sh 542 s,b 470 s,b 385 m 332 s	Sb <sub>2</sub> O <sub>4</sub>	775 sh 744 m 684 sh 649 w 602 m
Co <sub>3</sub> O <sub>4</sub>	668 s 635 sh 580 s 534 m 390 s	Ta <sub>2</sub> O <sub>5</sub> <sup>a</sup>	931 sh 799 sh 543 b
NiO	800 w,b 557 sh 470 s,b 442 sh	WO <sub>3</sub>	840 s,b 774 s 389 sh 369 s 326 sh
CuO	550 s 535 s 485 sh	Bi <sub>2</sub> O <sub>3</sub>	544 w 507 m 434 m 375 sh
ZnO	443 s,b 327 sh		
ThO <sub>2</sub> <sup>a</sup>	478 w 322 w		
U <sub>3</sub> O <sub>8</sub> <sup>a</sup>	825 sh 745 s 636 w 538 m 435 m		

Note. s = strong, m = medium, w = weak, sh = shoulder, b = broad.

<sup>a</sup> Bands are poorly defined.

The metal oxides were prepared as described above and were identified by X-ray powder diffraction. The samples were shaken in a vibration mill and 2 mg of the oxide was stirred with ethanol and spread out on the cell furnace. The thickness of the metal oxide layer was estimated to be  $0.2 \text{ mg cm}^{-2}$ . Evacuation of the IRES cell, inlet of oxygen and toluene were carried out at room temperature.

IRES spectra were recorded at  $107 \pm 1^\circ\text{C}$  on a Perkin-Elmer 580B infrared spectrophotometer linked with a data station. Each spectrum is the sum of 10 spectral scans and the background was subtracted in each case. As the background, a spectrum of the stainless-steel furnace was recorded without any oxide sample. The resulting spectrum was multiplied by a factor ranging from 6 to 10 and smoothed using the Savitsky/Golay function with a smoothing window of 19 points. The resolution in the region  $2000\text{--}200 \text{ cm}^{-1}$  is estimated to be  $13 \text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

The data of the vibration frequencies of Table 1 originate from various sources and they do not relate to the preparations actually used by Germain and Laugier (12). Therefore we have prepared a series of metal oxides, mainly following the methods of Germain and Laugier (12), except for V<sub>2</sub>O<sub>5</sub>, where we employed the method of Miyamoto *et al.* (25). The infrared absorption spectra have been measured by means of the KBr dispersion technique and the results are given in Table 2. Using these oxide preparations, Andersson (26) has made a detailed kinetic investigation of the oxidation of toluene. From his data and those presented in Table 2, we can reconstruct the rate versus wavenumber plot. The result is given in Fig. 3. Once again a twin-peaked pattern is found. Incidentally, the value deduced for the rate for U<sub>3</sub>O<sub>8</sub> from Germain and Laugier (12) appears to be too high.

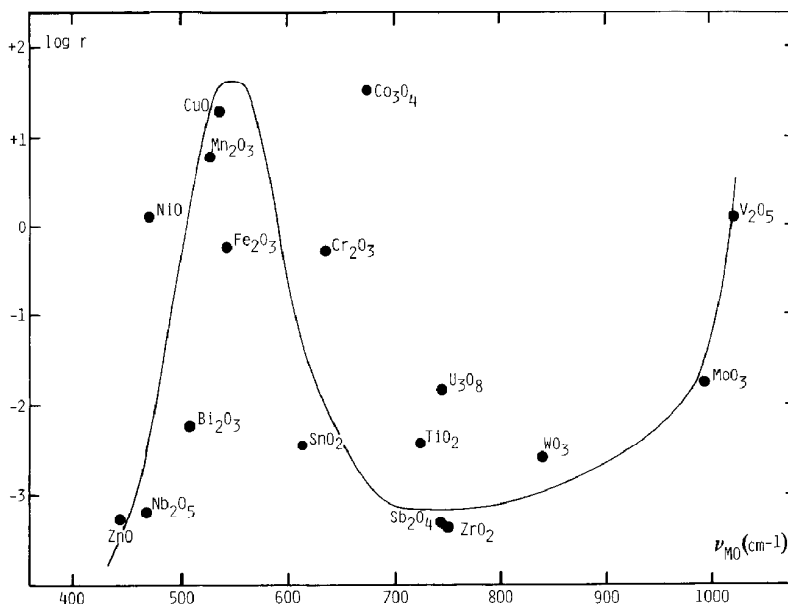


FIG. 3. Plot of the experimental data of rate of benzaldehyde formation (26) against the M—O wavenumbers of Table 2.

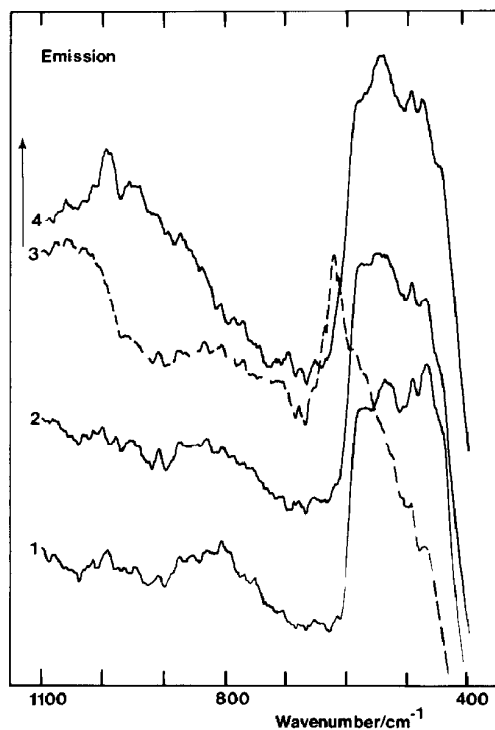


FIG. 4. Emission spectra of copper(II) oxide. (1) CuO under vacuum. (2) CuO contacted with toluene and heated 200°C/30 min. (3) Same as (2) but heated 300°C/30 min. (4) After inlet of 200 Torr O<sub>2</sub> and heating 350°C/2 h.

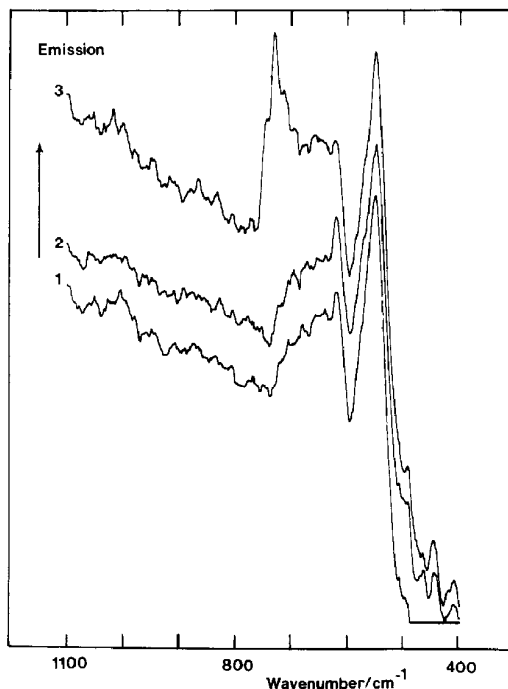


FIG. 5. Emission spectra of Cr<sub>2</sub>O<sub>3</sub>. (1) Vacuum. (2) Contacted with 200 Torr O<sub>2</sub> and heated 300°C/30 min. (3) Same as (2) but after admission of toluene and heated 250°C/30 min.

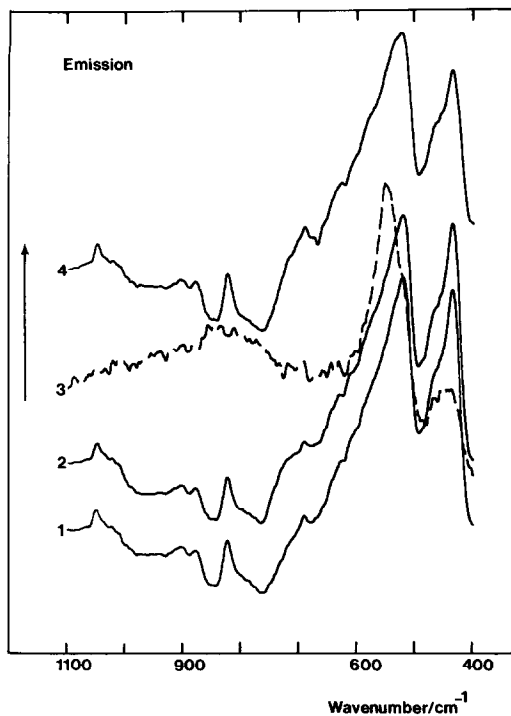


FIG. 6. Emission spectra of  $\text{Fe}_2\text{O}_3$ . (1)  $\text{Fe}_2\text{O}_3$  under vacuum. (2) After exposure to toluene. (3) Same as (2) but heated  $400^\circ\text{C}/1$  h. (4) Same as (3) but after admission of 200 Torr  $\text{O}_2$  and heated  $400^\circ\text{C}/1$  h.

### Choice of Frequencies

The same principle was used as before, i.e., the strongest band expected to correspond to a M—O stretching vibration mode was selected. In addition, the requirement was maintained that the band with the highest wavenumber was selected if there should be more than one strong M—O stretching band.

To test the method, we measured the IR emission spectra of  $\text{V}_2\text{O}_5$  (not shown here, see Ref. (27)),  $\text{Co}_3\text{O}_4$  (see Ref. (24)),  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{Sb}_2\text{O}_4$ . The oxides were measured under vacuum, and then after admission of toluene, after thorough reaction with adsorbed toluene, and after reoxidation with oxygen, respectively. In Figs. 4–7 we present typical spectra. In Fig. 8 we have used the same activity data (from the work of Andersson (26)) as in Fig. 3 and the

frequencies giving the highest emission intensity for the above-mentioned oxides. For  $\text{Co}_3\text{O}_4$  (24) a somewhat split, strong emission band is observed with peaks at  $540$  and  $560\text{ cm}^{-1}$ . These bands are actually affected by the adsorption of toluene, thus indicating some coupling. For all the other oxides we have retained the wavenumbers from the absorption spectra.

One may note that the points are shifted for  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{Co}_3\text{O}_4$ . This means that the left part of the curve is narrower which, in our view, strengthens the interpretation of a resonance between the M—O vibrations (first overtone) and the C—CH<sub>3</sub> rocking vibration.

As indicated above, the resonance-active vibrations are more easily seen in the emission spectra since they are intimately related to surface states. However, as the quality of the spectra was not very high, we have desisted from pursuing this type of work further with our present equipment.

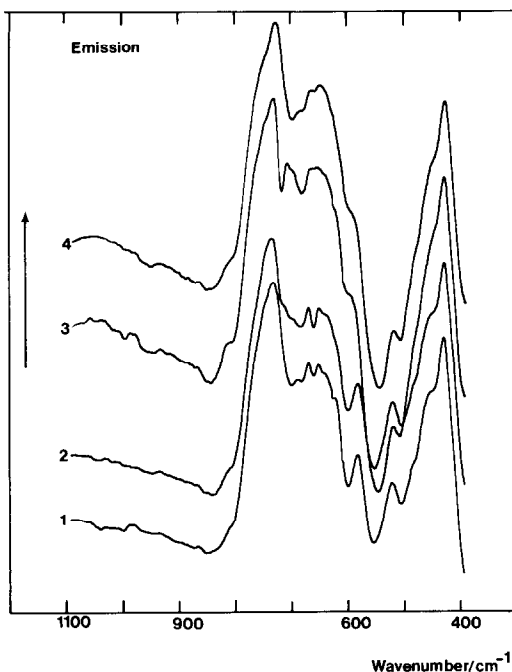


FIG. 7. Emission spectra of  $\text{Sb}_2\text{O}_4$ . (1) Vacuum. (2) The oxide contacted with toluene. (3) Same as (2) but heated  $400^\circ\text{C}/1$  h. (4) After admission of 200 Torr  $\text{O}_2$  and heated  $400^\circ\text{C}/1$  h.

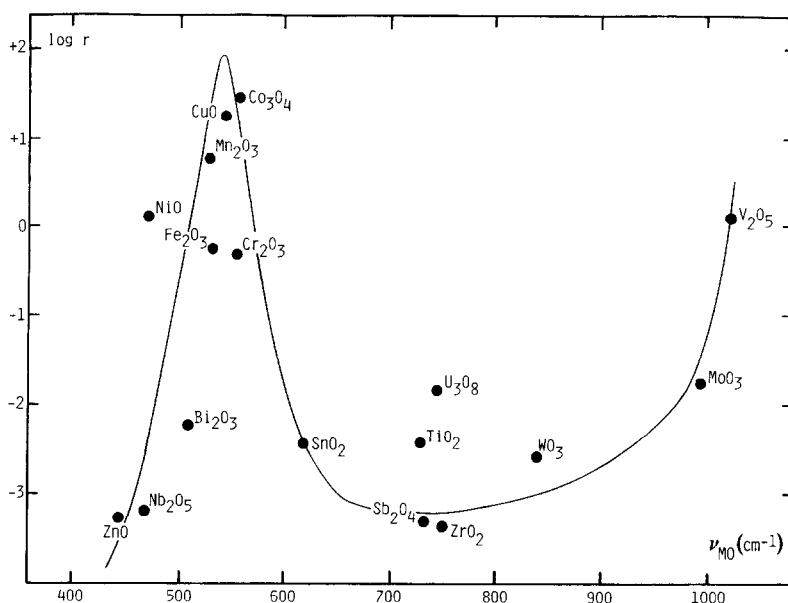


Fig. 8. Adjustment of the data in Fig. 3 from the observations on emission spectra (see text).

One should note that a consideration of the Boltzmann distribution of energy level occupations would favor the low frequency bands. A strict comparison between emission and transmission data is not possible here, because of differences in resolution.

The gathered information shows that the rate of the catalytic oxidation when plotted against the wavenumber of the "most likely" metal-oxygen vibration of the catalyst forms a twin-peaked curve. Andersson (26) also investigated other metal oxides, e.g.,  $\text{SiO}_2$ ,  $\text{Sc}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ , and  $\text{PbO}$ , but found a zero activity for these oxides. This zero activity of the oxides is caused by their inability to change oxidation state or to act as semiconductors, or due to the fact that they may lack vibration bands in the relevant region ( $\text{PbO}$ ).

One can also note that  $\text{Sb}_2\text{O}_4$  and  $\text{U}_3\text{O}_8$  with frequencies around  $750\text{ cm}^{-1}$  are not very good catalysts for the present type of reaction. However, they are well known as oxidation catalysts for the oxidation of, say, propene. It is obviously not the capacity for redox changes that is lacking in the present case for these oxides. Indeed, one

can expand the analysis by noting that the transformation of a propene molecule into an allylic structure necessitates the twisting of the double bond-single bond C—C—C arrangement, and that vibration is associated with absorption at  $755\text{ cm}^{-1}$  (28).

To sum up, we think we have shown that the hypothesis of vibrational resonance can be successfully applied to the oxidation of toluene over metal oxides.

#### ACKNOWLEDGMENT

This work has been sponsored by the Swedish Board for Technical Development (STU).

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