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NOTE

Comments on CO Oxidation Cataluminescence Spectra

A recent paper by Breysse *et al.* (*1*) dealing with "cataluminescence" associated with CO oxidation over reduced and unreduced thoria is of substantial interest for the understanding of the catalytic mechanism of CO oxidation and the mechanism of luminescence from gas–solid interactions. For unreduced thoria, the authors suggested a luminescence mechanism similar to that originally proposed by Wolkenstein (*2*), in which oxygen chemisorbs dissociatively on the surface of thoria and interacts with electrons while the CO chemisorbs on the surface and interacts with holes in the valence band of thoria. They also suggested that, when CO oxidation occurs, CO_2 becomes weakly bound on the surface as a neutral species and that the CO_2 formed is bound to a "virtual" exciton which does not preexist. CO_2 desorption is then accompanied by exciton recombination followed by the emission of a photon with the corresponding recombination energy. The luminescence spectrum obtained for thoria with a gaseous mixture of 2 $CO:O_2$ resembles O_2 adsorboluminescence on thoria and has a small shoulder at 590 nm and a broader peak at 630 nm, whereas the cataluminescence spectra for a 6 $CO:O_2$ ratio show three peaks, at 520, 565, and 610 nm. Thus, these three peaks appear to be associated with the presence of excess CO.

Harvey and Hallett (*3*) presented fluorescence spectra of thoria samples which were annealed in CO at 1400°C and subsequently cooled to 25°C. Upon illumination with 320-nm uv light, they obtained an emission peak at 565 nm and a shoulder indicating a possible second peak at 520 nm. They mentioned that they did not know the origin of these peaks. We would like to point out a correspondence between two of the cataluminescence peaks observed by Breysse *et al.* when a CO-rich mixture was used and the unexplained 520- and 565-nm peaks observed by Harvey and Hallett on CO-annealed thoria. (The third CO-rich cataluminescence peak at 610 nm lies just beyond the spectral range measured by Harvey and Hallett, so that a comparison cannot be made with existing fluorescence data.) This correspondence between peaks in the CO-rich cataluminescence spectra and the CO-annealed thoria fluorescence spectra suggests the possibility that adsorbed CO may play a role in the luminescence. In this regard, we further note that the three peaks in question correspond to lines in the Angström band of CO, with some broadening, which is consistent with emission occurring on the solid surface by an adsorbed excited CO species. The Angström band of gaseous CO involves transitions between the first excited $^1\Sigma^+$ state and the first excited $^1\Pi$ state:

$$B\,^1\Sigma^+ \rightarrow A\,^1\Pi.$$

The Angström band transitions are shown in Table 1. The CO rich cataluminescence peaks of Breysse *et al.* can be identified as the v' equal to 0 to v'' equal to 4, 3, and 2 transitions. Similarly, we could identify the emission peaks of Harvey and Hallett as

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TABLE 1

Angström Band Transitions of CO

Transitions v'	Transitions v''	Wavelength (Å)	Frank–Condon factor[a]
0	5	$\lambda_5 = 6620$	0.087[b]
0	4	$\lambda_4 = 6080$	0.134
0	3	$\lambda_3 = 5610$	0.183
0	2	$\lambda_2 = 5198$	0.211
0	1	$\lambda_1 = 4835$	0.182[c]
0	0	$\lambda_0 = 4511$	0.089[c]

[a] See Ref. (*4*).

[b] Line situated near peak of 1.67-eV thoria absorption band (7).

[c] Line situated near peak of 2.08-eV thoria absorption band (7).

v' equal to 0 to v'' equal to 3 and 2 transitions. The lack of other prominent peaks can be explained by smaller Frank–Condon factors and adsorption bands in thoria.

It would be interesting to verify experimentally that the emission is in fact due to adsorbed CO. This could be done by repeating the experiment of Harvey and Hallett without annealing thoria in CO. If the 565- and 520-nm peaks are absent and appear only after subsequent annealing in CO, then one could conclude that these peaks are probably due to adsorbed CO. On the other hand, if the spectral peaks are present even on samples not exposed to CO, then the 565- and 520-nm peaks must be associated with thoria itself rather than CO.

Despite the fact that, on the basis of the empirical evidence, CO Angström band emission seems quite plausible, it would in fact be rather surprising if the transitions belong to the Angström band since it would mean that a very large amount of energy went into the excitation of CO molecules. The $B^1\Sigma^+$ states lie above 10.78 eV, and the $A^1\Pi$ states lie above 8.07 eV. Since only 5.45 eV is released for each CO_2 formed, at least two CO_2 molecules must be formed to give enough energy to excite one CO to the $B^1\Sigma^+$ state. Only then could the Angström band emission $B^1\Sigma^+ \rightarrow A^1\Pi + h\nu$ occur. Thus, Angström band emission would imply that the mechanism of cataluminescence involves a more elaborate energy transfer process than that suggested by Breysse *et al.* A similar energy transfer process would be needed to explain broadened Angström band emission lines being present in the fluorescence spectrum of Harvey and Hallett since at least three photons at the excitation wavelength of 320 nm would be required to provide enough energy to excite a CO molecule to the $B^1\Sigma^+$ state.

It would be very interesting to try to experimentally confirm the presence of $B^1\Sigma^+$ and $A^1\Pi$ states of adsorbed CO by observing ultraviolet emission lines belonging to the fourth positive band $A^1\Pi \rightarrow X^1\Sigma^+$. Specifically, one might look for the $v' = 0 \rightarrow v'' = 2$ transitions at 1653 Å, as well as the $v' = 0 \rightarrow v'' = 1$ and 3 transitions. Another possible search is for the Birge–Hopfield band $B^1\Sigma^+ \rightarrow X^1\Sigma^+$, which has emission lines at 1210 to 1150 Å. Observing such emission in conjunction with a fluorescence experiment like that of Harvey and Hallett or a cataluminescence experiment would provide solid evidence for $B^1\Sigma^+$ or $A^1\Pi$ excited states on the surface and clear proof of an interesting energy transfer mechanism. It would be rather dramatic to detect even a small flux of photons with energies much higher than those of incident 320-nm photons. Other processes involving the production of higher energy photons have in fact been observed in a laser experiment on anthracene (*5*, *6*) where excitons play a crucial role and in connection with the Auger effect in solids (*7*).

Unfortunately, both the fourth positive band and the Birge–Hopfield band lie well above the absorption edge for thoria, so that it is quite likely that much of the ultraviolet emission from surface CO would be absorbed by the solid or that radiationless energy transfer to the solid would take place. In either case, energy would go into the production of hot electrons or holes in the solid. Thus any experiment to detect radiative deexcitation of the $B^1\Sigma^+$ or $A^1\Pi$ states on the surface could easily yield a null result and consequently should have the highest possible sensitivity. Specifically, such an experiment should be capable of detecting fourth positive band intensities significantly lower than the Angström band emission. Since hot electrons or holes may end up making transitions across the gap, emission somewhat above 5 eV may be observed.

In other experiments, Childs, Harvey, and Hallett (*8*), Bates (*9*), and Linares (*10*) have observed an absorption peak near 4.03 eV in thoria samples which were not annealed in CO. Such peaks below the absorption edge might be associated with various excitations including excitons and impurity levels. Linares found a positive correlation with impurities, as did Childs, Harvey, and Hallett, who attribute the peak to a hole center.

We would argue that the level (or levels) responsible for the 4.03-eV peak may play a role in the fluorescence and cataluminescence experiments discussed above. We note that the 320-nm (3.88-eV) excitation wavelength in Harvey and Hallett's fluorescence experiment is only about 0.15 eV away from the maximum of the 4.03 peak, which has a width of about 0.8 eV. (The central position is in fact 4.03±0.07 eV.) Furthermore, of the three excitation wavelengths used by Harvey and Hallett, the 320-nm (3.88-eV) radiation produced the most fluorescence at 565 nm, while the 278-nm (4.46-eV) excitation wavelength produced roughly half as much, and the 255-nm (4.86-eV) excitation wavelength produced very little 565-nm fluorescence. We observe that this dependence on the excitation wavelength correlates rather well with the 0.8-eV width of the 4.03-eV peak, since 4.86 eV is just outside the peak, whereas 4.46 eV is near the half-maximum point.

The 520-nm emission exhibits a similar trend, whereas those emission peaks which were previously understood exhibit a completely different dependence on excitation wavelength. Thus, the 4.03-eV excitation in thoria seems to be very well correlated with the 520- and 565-nm fluorescence peaks. We might then also find that the 4.03-eV levels play a role in the mechanism which leads to CO-rich cataluminescence peaks at 520, 565, and 610 nm. For example, the 4.03-eV levels might be excited after the release of energy during CO oxidation. If the 520-, 565-, and 610-nm peaks under consideration are in fact Angström band peaks, then we could imagine the following cyclic luminescence mechanism: (1) The transitions $A^1\Pi \rightarrow X^1\Sigma^+$ excite hot carriers (8.07 eV) in the solid; (2) hot carriers acquire additional energy via an Auger process (*7*) involving deexcitation of the 4.03-eV levels (Some energy loss in the form of phonon emission may also occur since 8.07 plus 4.03 eV is greater than the 10.78 eV minimum energy needed to excite a $B^1\Sigma^+$ level.); (3) nonradiative hot carrier surface recombination (*11*) occurs, involving energy transfer to CO which results in $X^1\Sigma^+ \rightarrow B^1\Sigma^+$ transitions, with CO acting as an electron-hole recombination center; (4) $B^1\Sigma^+ \rightarrow A^1\Pi$ + Angström band emission occurs. The energy input comes from excitation of the 4.03-eV levels. Of course, other detailed mechanisms can be imagined in which the Auger effect plays a key role in the transfer of energy to adsorbed CO. The Auger effect is an interesting possibility since it has been observed to yield photons of about twice the gap energy in electroluminescence in germanium (*12*).

If the first experiment proposed above shows that the 520-, 565-, and 610-nm peaks are not associated with adsorbed CO, then the correlation with the Angström band could only be coincidental. The observed fluorescence peaks would then have to be attributed to transitions involving additional levels in the solid, and the occurrence of the same peaks in the CO-rich cataluminescence spectrum would seem to require that transitions to these levels are enhanced by the presence of adsorbed CO or that other transitions are suppressed. For example, CO might play a role in the transfer of energy from the CO oxidation process to the 4.03-eV level or in inhibiting some competing energy loss mechanism. If adsorbed oxygen atoms acted as electron-hole recombination centers, then excess CO might simply decrease the concentration of surface recombination centers and thus permit more energy to go into excitation of levels in the solid. The energy could be transferred to these levels by free carriers or by excitons.

The luminescence mechanism of Breysse *et al.* suggests that excitons are formed, but it does not explain the details of the observed cataluminescence spectrum, nor does it indicate any role for hole centers or other levels in cataluminescence.

It seems clear from existing data that interesting mechanisms must play a role in the luminescence processes discussed above, so that further experiments such as those suggested here could provide considerable insight into the mechanism of catalytic CO oxidation and cataluminescence.

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