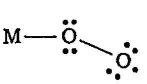
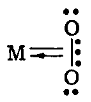
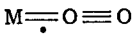
ture, the spectrum obtained from $SnO_2$ is almost the same at room temperature and at −160°C.

In spite of this difference we would like to interpret these spectra on similar lines.

Three different signals occur simultaneously in the ESR spectrum: Signal c, a broad almost symmetric signal with $g = 2.010$; Signal d, a narrow three $g$ value signal with $g_1 = 2.033$, $g_2 = 2.005$, $g_3 = 1.986$; Signal e, a narrow three $g$ value signal with $g_1 = 2.029$, $g_2 = 2.010$, $g_3 = 2.004$.


Angular


Perpendicular


Linear

When a mixture of 1-butene and oxygen is added, the three oxygen signals can be observed again. However, Signal e decreases slowly and finally disappears, while Signal d remains nearly unaltered (Fig. 2). This is an additional proof for the correctness of the interpretation of the spectrum.

Each of the signals, c, d, and e, is supposed to correspond with a special form of adsorbed molecular oxygen. Signal c corresponds with the linear, Signal d with the perpendicular, and Signal e with the angular arrangement. As explained in ref. (*1*) the perpendicular and linear arrangement can only occur with metal ions with empty or partly filled $d$ orbitals. Accordingly $Zn^{2+}$ with the electron configuration [Ar] $3d^{10}$ does not show these bonding structures. However, as $Sn^{4+}$ with the electron configuration [Kr] $4d^{10}$ did show the signals ascribed to these arrangements, we have to conclude, to outer shell bonding ($5d$ orbitals) in this case.

It is further interesting that butene addition removed the signal assigned to a species that is similar to a radical in the classical sense, i.e., with a single electron in an atomic orbital.

### REFERENCE

*1.* CORNAZ, P. F., VAN HOOFF, J. H. C., PLUIJM, F. J., AND SCHUIT, G. C. A., *Discussions Faraday Soc.* **41**, 290 (1966).

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# A Relationship between Infrared Frequencies of Adsorbed Carbon Monoxide and Metal Electron Population

As part of a wider investigation a study has been made of the perturbation of vibrational frequency of the carbon monoxide molecule following adsorption as "linear carbonyl" on face-centered cubic transition metals. A rather uniform increase in frequency with increase in electronic specific heat constant $\gamma_{el}$ of the bulk metal was noted. That the two properties are genuinely interdependent is suggested by expressing observed frequencies as the valence-electron content $E$(CO) of the adsorbed carbon monoxide species using the formula of Gardner and Petrucci (*1*). $E$(CO) is clearly integral for gaseous forms of carbon monoxide but may be nonintegral for adsorbed species. Figure 1 shows that a reasonably linear relationship (not previously reported) is followed between $E$(CO) and $\gamma_{el}$. The latter is a measure of the Fermi electron population of the metal $E$(F) and this property may influence electron transfer at the surface in formation of an adsorbed entity.

Spectroscopic data were taken from literature sources (*1–4*). Results reported using supports for the metal other than silica are omitted since some supports are known to cause displacement of frequencies (*2*, *3*). Since frequencies extrapolated to low coverage are not generally available values used refer to the full-coverage condition. The $\gamma_{el}$ values were taken from the compilation of Gschneidner (*5*). $E$(F), also shown, is derived from the standard Sommerfeld formula without correction for ferromagnetic spin polarization.

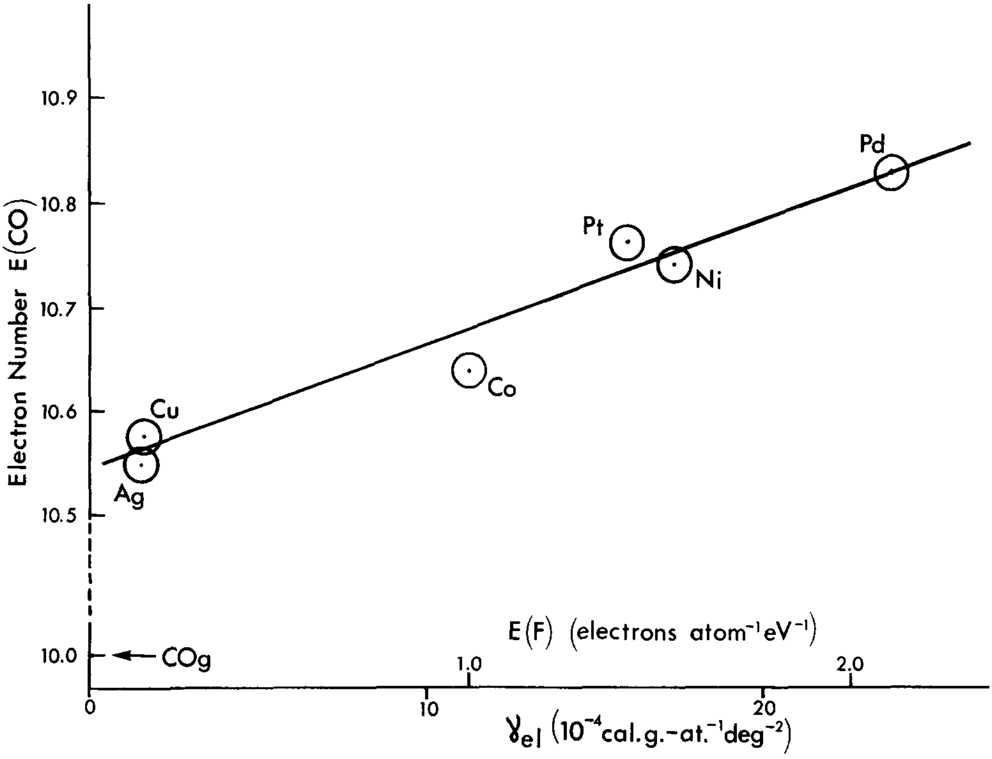

FIG. 1. Relationship of valence-electron number $E$(CO) of adsorbed species to the electronic specific heat constant (Fermi electron population) of the bulk metal.

This result is in seeming agreement with an early analysis by Dowden (*6*) relating strengths of covalent bonds to metal surfaces to the work function and *d*-electron population at the Fermi level. It is questionable, however, whether deductions may be made about the carbon-metal bond from measurements on the carbon–oxygen bond (*7*). Indeed, while heats of adsorption of carbon monoxide on Group VIII metals are closely similar (*8*), surface potentials of the adsorbed layer as measured by one group of workers (*9*) show significant variations for some of the same metals. While the choice of parameters governing energies of adsorption is under continuing discussion (*10*), the relationship reported here shows that the electron content of a representative $\pi$-bonded species, reflected in its vibrational frequency and perhaps also discernible in its surface potential, is directly related to the Fermi-electron population in the metal, at least for metals of the same crystal structure and similar work function [4.41–4.52, ref. (*11*)]. Thus discussion of these properties must be in terms of collective electron properties of the bulk metal rather than the properties of individual atoms [e.g., Sachtler (*12*)].

Measurements are desirable of the infrared spectra of carbon monoxide on early transition metals to test this relationship with other crystal structures. The single result for iron (*13*) gives bands, interpreted as due to carbonyl-type species, at 2020 and 1980 $\text{cm}^{-1}$ [$E$(CO), 11.05 and 11.19]. These results lie well off the points in Fig. 1 and no explanation has been found for this. It may be significant, however, that the relative energies of the *d* sub-bands, which participate in electron "back-donation" in $\pi$-bonds, are known to be quite different in body-centered cubic and face-centered cubic metals (*14*).

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## REFERENCES

*1.* GARDNER, R. A., AND PETRUCCI, R. H., *J. Phys. Chem.* **67**, 1376 (1963).

*2.* EISCHENS, R. P., AND PLISKIN, W. A., *Advan. Catalysis* **10**, 1 (1958).

*3.* O'NEILL, C. E., AND YATES, D. J. C., *J. Phys. Chem.* **65**, 901 (1961).

*4.* HEYNE, H., AND TOMPKINS, F. C., *Discussions Faraday Soc.* **41**, 181 (1966).

*5.* GSCHNEIDNER, K. A., JR., *Solid State Phys.* **16**, 275 (1964).

*6.* DOWDEN, D. A., *J. Chem. Soc.*, p. 242 (1950).

*7.* MILLER, J. R., *Advan. Inorg. Chem. Radiochem.* **4**, 133 (1962).

*8.* BRENNAN, D., AND HAYES, F. H., *Phil. Trans. Roy. Soc.* **A258**, 347 (1965).

*9.* CULVER, R. V., PRITCHARD, J., AND TOMPKINS, F. C., *Proc. 2nd Intern. Congr. Surface Activity* **2**, 243 (Butterworths, London, 1957).

*10.* DOWDEN, D. A., *Discussions Faraday Soc.* **41**, 256 (1966), see discussion remarks.

*11.* BOND, G. C., "Catalysis by Metals," p. 480. Academic Press, New York, 1962.

*12.* SACHTLER, W. M. H., *Trans. 3rd Intern. Vacuum Congress, 1965,* **1**, 41 (Pergamon, London, 1966).

*13.* BLYHOLDER, G., *J. Phys. Chem.* **66**, 1464 (1962).

*14.* GOODENOUGH, J. B., *Phys. Rev.* **120**, 67 (1960).

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