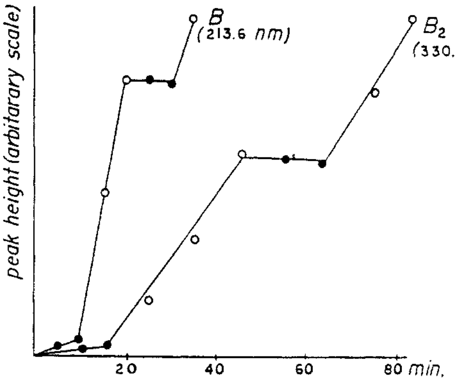

**Figure 3.** Absorption areas vs. time of atomic and dimer species in argon vs. $CH_4$/Ar: (○) in pure Ar matrix; (●) in 10% $CH_4$/Ar matrix.

evaporation of almost any material and the vapor is deposited immediately after each laser pulse (so the sequence is pulse–deposit–pulse–deposit etc., and the light should not perturb the gaseous species traveling to the window).

Using this laser evaporation method combined with UV–vis and IR spectroscopy, we have monitored the behavior of B, $B_2$, Al, $Al_2$, Ga, and In atoms and dimers in the presence of argon (Ar) and $CH_4$. Figure 2 illustrates a spectrum of B and $B_2$ in pure argon.[15] Note that the growth of the B and $B_2$ is almost negligible in the presence of 5% $CH_4$/Ar. However, in pure Ar for the same period of time and evaporation rate B and $B_2$ grows rapidly. The Al system is intermediate; that is, growth is moderately more rapid in Ar than in 5% $CH_4$/Ar. With In and Ga the growth rates are about the same. Figure 3 illustrates this in another way for B and $B_2$. We have used such monitoring techniques successfully before[16,17] and believe in this case they show that B and $B_2$ are efficiently consumed by $CH_4$ while Al species are less so, and Ga and In species are not at all. Thus, taking ratio's of peak areas such as [(area b − a)/area a], we find the values B atom 3.5, $B_2$ 8.0, Al atoms 1.3, Ga atoms 0.8, and In atoms 0.8. A value near 1.0 would indicate no reaction.

Infrared studies of B–$CH_4$ systems were also carried out (Figure 4). New bands at 823, 894, 909, and 971 cm$^{-1}$ ($\delta_{BH}$ or $\delta_{CH}$) and 2007, 2027, 2051, 2118, 2134, and 2500 cm$^{-1}$ ($\delta_{BH}$ bridged and terminal) were observed, clearly showing that reaction products are formed upon deposition of B and $B_2$ with $CH_4$ at 10 K. The IR data suggest that both terminal and bridged B–H species are formed. Also, bands in the 820–971-cm$^{-1}$ region suggest the presence of $H_3C$–B species.[2]

These results demonstrate that ground-state B and $B_2$ react spontaneously with $CH_4$ under matrix conditions. Our earlier results combined with these indicate that ground-state Al atoms react with $CH_4$, albeit less efficiently, but Ga and In do not. Our preliminary results indicate that $C_2$, Si, and $Si_2$ do not react with $CH_4$. We have not been able to monitor C atoms as yet.

We are continuing our studies of B and $B_2$ reactions with other substrates and plan to utilize our laser-evaporation–matrix-isolation apparatus for studies of many other species including metal oxide molecules and heavy metal atoms.

**Figure 4.** Infrared spectrum of B/$B_2$ reaction with $CH_4$ (cm$^{-1}$).

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[13] Friichtenicht (Friichtenicht, J. F. *Rev. Sic. Instrum.* **1974**, *45*, 51–56) first demonstrated that metal atom beams can be produced in this manner. A high-power laser pulse can instantaneously increase the temperature of the target surface within the focused area well above its boiling point. An important advantage of laser evaporation is that heating is localized to a small area and the remainder of the sample and apparatus remain at ambient temperature.

[14] Kang et al. (Kang, H.; Beauchamp, J. L. *J. Phys. Chem.* **1985**, *89*, 3364–3367) have demonstrated that the vapor preferentially exists directly back along the laser beam path. This is due to the hole that is bored acting like a rifle barrel directing the beam. Another advantage is that very little surface oxide is encountered by the beam, so metal oxide vapor as a containment is minimized.

[15] Graham, W. R. M.; Weltner, W. *J. Chem. Phys.* **1976**, *65*, 1516–1521.

[16] Imizu, Y.; Klabunde, K. J. *Inorg. Chem.* **1984**, *23*, 3602–3605.

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## Bonding in the First-Row Transition-Metal Monocarbonyl Molecules

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The molecules MCO, where M is a first-row transition metal, have been of considerable interest as prototypes for CO chemisorption on the metal surfaces. There are now a surprisingly large number of theoretical papers concerning the electronic and bonding properties of these species,[1] particularly NiCO. Much less experimental data have been obtained, mostly from rare-gas matrix

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[1] **TiCo:** Mortola, A. P.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1974**, *96*, 1–10. **FeCO:** Bursten, B. E.; Freier, D. G.; Fenske, R. F. *Inorg. Chem.* **1980**, *19*, 1810–1811. Guenzberger, D.; Saitovitch, E. M. B.; DePaoli, M. A.; Manela, H. *J. Chem. Phys.* **1984**, *80*, 735–744. Daoudi, A.; Suard, M.; Barbier, C. *C. R. Acad. Sci., Ser. 2* **1985**, *301*, 911–914. Sawaryn, A.; Aldridge, L. P.; Blaes, R.; Marathe, V. R.; Trautwein, A. X. *Hyperfine Interact.* **1986**, *29*, 1303–1306. **NiCO:** Cederbaum, L. S.; Domcke, W.; Von Niessen, W.; Brenig, W. *Z. Phys. B* **1975**, *21*, 381–388; Walch, S. P.; Goddard, W. A., III *J. Am. Chem. Soc.* **1976**, *98*, 7908–7917; Clark, D. T.; Cromarty, B. J.; Sgamellotti, A. *Chem. Phys. Lett.* **1978**, *55*, 482–487. Itoh, H.; Kunz, A. B. *Z. Naturforsch. A* **1979**, *34A*, 114–116. Bullett, D. W.; O'Reilly, E. P. *Surf. Sci.* **1979**, *89*, 274–281. Bagus, P. S.; Hermann, K. *Surf. Sci.* **1979**, *89*, 588–595. Rosen, A.; Grundevik, P.; Morovic, T. *Surf. Sci.* **1980**, *95*, 477–495. Rives, A. B.; Weinhold, F. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1980**, *14*, 201–209. Saddei, D.; Freund, H. J.; Hohlmeicher, G. *Chem. Phys.* **1981**, *55*, 339–354. Howard, I. A.; Pratt, G. W.; Johnson, K. H.; Dresselhaus, G. *J. Chem. Phys.* **1981**, *74*, 3415–3419. Rives, A. B.; Fenske, R. F. *J. Chem. Phys.* **1981**, *75*, 1293–1302. McIntosh, D. F.; Ozin, G. A.; Messmer, R. P. *Inorg. Chem.* **1981**, *20*, 3640–3650. Bagus, P. S.; Roos, B. O. *J. Chem. Phys.* **1981**, *75*, 5961–5962. Dunlap, B. I.; Yu, H. L.; Antoniewicz, P. R. *Phys. Rev. A* **1982**, *25*, 7–13. You, X. *Jiegou Huaxue* **1983**, *2*, 183–188. Huzinaga, S.; Klobukowski, M.; Sakai, Y. *J. Phys. Chem.* **1984**, *88*, 4880–4886. Ha, T. K.; Nguyen, M. T. *THEOCHEM* **1984**, *18*, 331–338. Rohlfing, C. M., Hay, P. J. *J. Chem. Phys.* **1985**, *83*, 4641–4649. Kao, C. M.; Messmer, R. P. *Phys. Rev. B* **1985**, *31*, 4835–4847. Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1986**, *84*, 260–267. Carsky, P.; Dedieu, A. *Chem. Phys.* **1986**, *103*, 265–275. **CuCO:** Itoh, H.; Kunz, A. B. *Z. Naturforsch., A* **1979**, *34A*, 114–116. McIntosh, D. F.; Ozin, G. A.; Messmer, R. P. *Inorg. Chem.* **1981**, *20*, 3640–3650. Ha, T. K.; Nguyen, M. T. *THEOCHEM* **1984**, *18*, 331–338. Kuźminskii, M. B.; Bagatufyants, A. A.; Kazanskii, V. B. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1986** (2), 284–288.

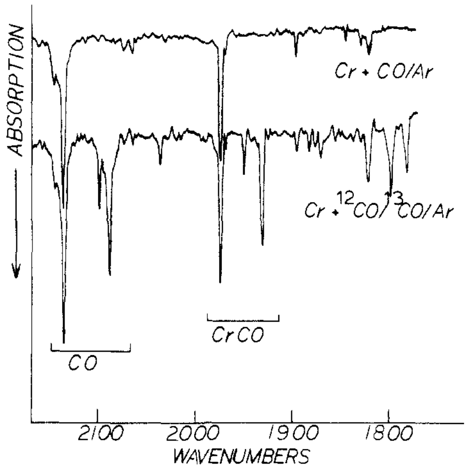

**Figure 1.** Infrared spectra of matrices at 4 K containing (top) Cr atoms and 1:1000 $^{12}CO/Ar$ and (bottom) Cr atoms and approximately 1:1:1000 $^{12}CO$:$^{13}CO/Ar$.

studies, although a few observations have been made in the gas phase.[2]

Within this series of monocarbonyls where the metal mass is relatively large, an excellent indication of the strength of the M–CO bond is the lowering of the CO vibration frequency from that in the free molecule where $\nu_{CO} = 2143$ cm$^{-1}$.[3] (Gas to matrix shifts can be ignored here since they can be expected to amount to only a few reciprocal centimeters.[4]) The first measurements of this kind on NiCO were made by DeKock,[5] and subsequently the CO stretching frequencies of most other members of the series have been measured, largely by Ozin's group.[2] We have recently repeated the work on several transition-metal monocarbonyls in dilute matrices. For CrCO, the correct $\nu_{CO}$ lies at 1977 cm$^{-1}$ as Figure 1 clearly shows. ScCO yielded a broad weak band at 1950 cm$^{-1}$ (shifted appropriately by $^{13}CO$ substitution), but this assignment must be considered as tentative. We have also repeated the Mn + CO studies and observed the IR bands previously reported by Huber et al.[6] But, as also concluded by those authors, none of the band combinations produced in dilute matrices of the metal atoms and mixtures of $^{12}CO$ and $^{13}CO$ is firmly assignable to MnCO. Huber et al. assign $\nu_{CO}$ in MnCO at 1850 cm$^{-1}$,[7] but we could not justify such an assignment since it did not appear as a dominant band in our dilute matrices. In fact, we were concerned about our failure to identify such a band for MnCO and were led to consider the possibility that Mn atoms do not bond to CO.

A plot of all of the presently available $\nu_{CO}$ data is shown in Figure 2. If indeed Mn–CO is nonbonded, then $\nu_{CO} \cong 2140$ cm$^{-1}$, and the familiar "double-humped" graph is now obtained which is traditionally observed for the variation in properties across a row of transition metals. (This graph is a revised version of one given by Ozin and Vander Voet.[7]) This bonding behavior among the MCO molecules is then intuitively appealing.

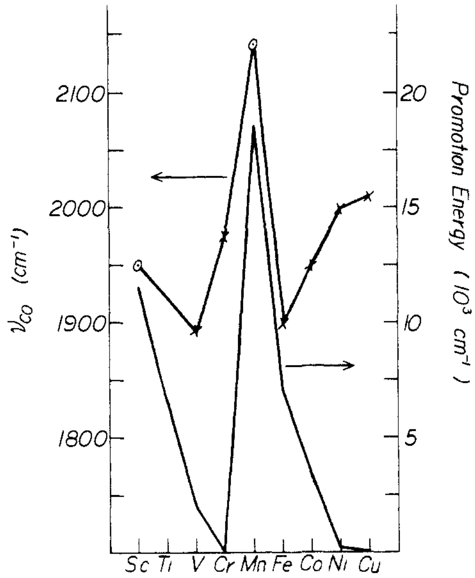

**Figure 2.** Plot of the CO stretching frequencies in the first-row transition-metal monocarbonyl molecules MCO (circled points are tentative). Also shown is the variation of the energy of promotion corresponding to $4s^23d^{n-2} \rightarrow 4s^13d^{n-1}$, where $n$ is the number of valence electrons.[8]

A more rational basis for this proposal is evident when the promotion energy $s^2 \rightarrow sd^{n-1}$ of the first-row metals[8] is also plotted (see Figure 2). A high promotion energy is interpreted as a high barrier to $\sigma$-bond formation and thereby a destabilization of the metal–CO bond. This does not explain the decreasing strength of bonding in going from FeCO to CuCO implied by the $\nu_{CO}$ variation, but that trend can be attributed to repulsion arising from the increasingly filled 3d shell.[9]

We then suggest that theoretical work be attempted on MnCO and expect that it will be found, similar to CuCO, to be essentially nonbonded. The many and extensive calculations on NiCO presumably establish that it is $^1\Sigma$. Correspondingly, but less thoroughly treated, FeCO and CuCO are found to be $^3\Sigma$ and $^2\Sigma$, respectively. The latter was corroborated via ESR by Kasai and Jones.[10] Our attempts to observe FeCO in the same way have not been successful, indicating that the calculated ground state is incorrect or, if correct, the zero-field splitting in the triplet state is >3 cm$^{-1}$.[11] We have been unsuccessful in observing the other monocarbonyls via ESR except for VCO, which yielded a surprising, but quite definite, sextet ground state.[12]

The failure to observe ESR spectra for a (presumed linear) MCO molecule means that either (1) its ground state may be nonmagnetic (i.e., singlet, as calculated for NiCO), (2) if $S \geq {}^1/_2$, it may be orbitally degenerate (possibly this is the case for TiCO where a $^3\Phi$ ground state was predicted[1]), or (3) if $S > {}^1/_2$, the zero-field splitting in the ground state is large (as possibly occurs for $^3\Sigma$ FeCO).

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(9) A referee of this paper has pointed out to us that there are at least three other factors, including overlap, hybridization, and exchange, which moderate the promotional effect upon bonding. He suggests that the correct promoted state of the metal here should be $s^0d^n$, and he derives a curve in Figure 2 which more closely follows the variations in $\nu_{CO}$. However, even in his more refined theory, the high promotional energy of Mn is still the dominant factor, so our suggestion that MnCO is essentially nonbonded remains unaltered.

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