Contribution from Lash Miller Chemistry Laboratories and Erindale College,
University of Toronto, Toronto, Ontario, Canada

Diniobium, Nb_2, and Dimolybdenum, Mo_2. Syntheses, Ultraviolet–Visible Spectra and Molecular Orbital Investigations of Nb_2 and Mo_2. Spectral and Bonding Comparisons with V_2 and Cr_2

W. KLOTZBÜCHER and G. A. OZIN*

Received August 24, 1976 AIC60605D

Diniobium and dimolybdenum are synthesized by Nb atom–argon and Mo atom–argon matrix cocondensation experiments at 10–12 K and identified by quantitative UV–visible spectroscopy. Extended Hückel molecular orbital calculations provide some further insight into the electronic and molecular properties of Nb_2 and Mo_2. Comparisons of the UV–visible spectra and minimum-energy geometries of V_2 vs. Nb_2 and Cr_2 vs. Mo_2 show that the computed bond dissociation energies of the second-row diatomics are consistently higher than those of their first-row congeners. The exceptionally short Nb–Nb and Mo–Mo distances calculated for the minimum energy configurations of Nb_2 and Mo_2, respectively, suggest at least a quadruple bond order for Nb_2 and Mo_2. Formally, a closed-shell configuration would lead to "pentuple and sextuple" bonds for Nb and Mo, respectively.

Introduction

The deliberate synthesis and characterization of small, "naked" transition metal clusters began only about 2 years ago.[1,2] During the original experiments with Cr atoms,[2] it was discovered that quantitative UV–visible monitoring of the diffusion process in low-temperature matrices provided a means of identifying the various clusters formed in the embryonic stages of the nucleation process. By using these methods, the diatomic molecules Sc_2,[3] Ti_2,[3] V_2,[4] Cu_2,[1,5] and Ag_2[5] have since been identified. Today there is considerable theoretical activity in the field,[6] as it has become evident that a detailed understanding of the molecular and electronic properties and chemical reactivity of naked metal clusters, as a function of cluster size and geometry, is fundamental to the understanding of chemisorption and surface chemical reactions on supported and unsupported transition metal catalysts.

In view of the recent flurry of interest in the use of the vapors of the refractory metals of groups 5B and 6B for both macroscale[7-9] and matrix-scale chemical synthesis,[10] it was considered desirable, from the point of view of metal aggregate formation and product design, to establish the fate of these refractory metals when cocondensed at low temperatures with inert and reactive partners.

In this paper we present our findings for Nb atom–argon and Mo atom–argon cocondensations which provide evidence that both isolated metal atoms and metal dimer molecules can be generated and identified in the presence of each other.

Diniobium and dimolybdenum, the subjects of this study, are particularly interesting on three accounts. First, the gaseous molecules Nb_2 and Mo_2 (or in fact the majority of the diatomic molecules of the refractory metals) have not previously been detected by electronic, infrared, or mass spectroscopy, presumably because the extremely high temperatures required to produce measurable vapor pressures of the dimer molecules (ca. 3000 K) are generally sufficient to cause dissociation to their respective atoms. Second, Nb_2 and Mo_2 have not previously been unambiguously identified in Nb atom–Mo atom matrix cocondensation experiments. Third, the electronic spectra of Nb_2 and Mo_2 would serve to complete the data for the first and second transition series grouping of diatomics, V_2, Nb_2, Cr_2, Mo_2.

Experimental Section

The most crucial aspect of this kind of matrix experiment is to be able to deposit the metal vapor at a constant and accurately known rate. This was achieved by incorporating a quartz crystal microbalance into the furnace–cryostat reaction chamber assembly as described previously.[11] Niobium and molybdenum vapors were generated from specially shaped, thin filaments of Nb or Mo (dimensions roughly 1.25 in. × 0.25 in. × 0.01 in.) by direct resistive heating in a vacuum furnace identical with that also reported earlier.[12] Matrices were deposited onto an NaCl optical window cooled to 10 K by a Displex closed-cycle helium refrigerator. Optical spectra were recorded in the range 200–700 nm on a Unican SP 8000. Numerous metal concentration experiments were attempted in the range M:Ar $\simeq$ 1:10^2 to 1:10^5.

It should be noted here that *quantitative* metal concentration studies for highly refractory metals such as Nb and Mo are fraught with experimental difficulties. To begin with, one finds that reasonable working vapor pressures for Nb and Mo (about 10^{-3} Torr) can only be achieved at temperatures extremely close to their melting points (within 50 °C for Nb and 300 °C for Mo). Under these conditions it proved to be quite troublesome (particularly for Nb) to establish reproducible deposition rates from the *same* metal filament, a prerequisite for a series of accurate metal concentration experiments. This problem was further aggravated by the fact that the vaporization history of Nb and Mo filaments was found to have a controlling influence over their useful working lifetimes. In addition, slight radiation heating of the quartz crystal monitors by the very high-temperature source had to be taken into account. However, it should be noted that no significant heating of the optical window could be observed during deposition. All of these factors had to be considered when assessing the UV–visible spectroscopic results of Nb and Mo in Ar matrices as a function of the *total* metal concentration.

Results and Discussion

With regard to Nb_2 and Mo_2 the existing literature is confusing and in some instances contradictory. The uncertainties associated with the diatomic molecules of these refractory metals can in part be related to the different methods of generating the metal atomic vapors (for example, hollow cathode sputtering,[13,14] triode sputtering,[15] and direct resistive heating[16]), as well as the different techniques for subsequently producing the desired metal aggregate (e.g., matrix annealing[13] and metal concentration experiments[16]).

Besides the intense atomic resonance transitions observed for these metals, other weak spectral features were sometimes observed in the optical spectra of these matrices but could only be tentatively ascribed to polymeric species M_n because of the qualitative nature of the experiments.[13-16] However, by employing quantitative metal atom matrix cocondensation experiments and a simple kinetic theory which enables small metal clusters to be identified in the presence of atomic species[1-5] we have been able to generate Nb_2 and Mo_2 and establish their optical spectra.

Atomic Niobium, Nb. Gruen et al.[13] have used a hollow cathode sputtering device and a 10-K cryostat assembly to vaporize and isolate atomic Nb in various low-temperature matrices. Apart from a single absorption observed by Gruen et al.[13] at 366 nm, which is absent in our optical spectra of Nb atoms in Ar (1:10^4), our data are in close agreement, which is gratifying, as direct resistive heating of a niobium filament was employed for our source of Nb atoms.

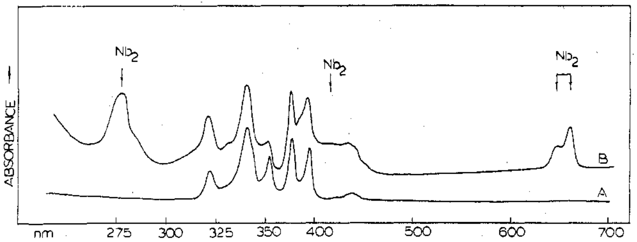

Figure 1. UV-visible spectra: (A) atomic Nb isolated in solid Ar at 10 K at high dilutions (Nb:Ar ≃ 1:10^4); (B) same as spectrum A but at higher concentrations (Nb:Ar ≃ 1:10^3), showing the growth of new absorptions attributable to Nb_2.

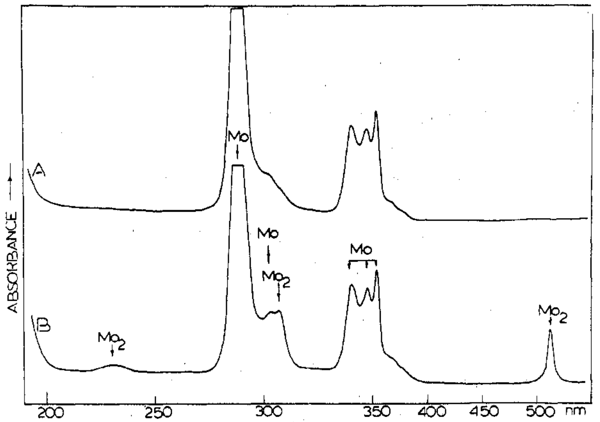

Figure 2. UV-visible spectra: (A) atomic Mo isolated in Ar at 10 K at high dilutions (Mo:Ar ≃ 1:10^4); (B) same as spectrum A but at higher concentrations (Mo:Ar ≃ 1:10^3) showing the growth of new absorptions attributable to Mo_2.

A typical trace of Nb atoms isolated in Ar at a ratio of 1:10^4 is shown in Figure 1A. Note that the regions 700–450 and 320–200 nm are devoid of Nb atomic resonance absorptions and that the medium absorptions observed around 280 and 660 nm by Gruen et al.[13] and ascribed to atomic Nb are absent in our atomic spectra.

Diniobium, Nb_2. By increasing the Nb:Ar concentration ratio in the range 1:10^4 to 1:10^2, three new absorptions were observed to grow in at 660, 420, and 280 nm (Figure 1B) whose absorbances relative to those of a reference Nb atomic resonance line were proportional to the metal concentration. We have previously demonstrated that, under these circumstances,[1-5] trimer and higher aggregates are expected to be still unobservable. On these grounds we can therefore attribute the three new absorptions to the formation of diniobium, Nb_2. It is noteworthy that the group of lines around 500 nm which were observed by Gruen et al.[13] to grow in on annealing Nb/Ar matrices and which were tentatively ascribed to Nb_2 were *not* observed in any of our experiments either on deposition or after matrix annealing. This discrepancy may have arisen from contamination problems associated with the sputtering technique. A final point that should be made is that Gruen et al.[13] did in fact observe both the low- and high-energy transitions of Nb_2 in Ar and Kr matrices but under the conditions used in their experiments felt obliged to assign them to parity-forbidden transitions of atomic Nb.

Atomic Molybdenum, Mo. A typical UV-visible spectrum of Mo atoms isolated in Ar at 10 K (Mo:Ar = 1:10^4) is shown in Figure 2A and the main absorptions are found to correlate extremely well with those reported previously.[14] Note that under the high dilution conditions shown in Figure 2A, the regions 700–360 and 275–200 nm are free of Mo atomic resonance lines.

Dimolybdenum, Mo_2. By increasing the Mo:Ar concentration ratio in the range 1:10^4 to 1:10^2 one observes the growth of three new absorptions at 512, 308, and 232 nm (Figure 2B) whose absorbances relative to a reference Mo atomic resonance line are metal concentration dependent. As previously demonstrated[1-5] the formation of trimer and higher aggregates is negligible under these circumstances, and we can therefore attribute the three new absorptions to the electronic transitions of dimolybdenum, Mo_2.

Table I. Parameters Used in the Extended-Hückel Molecular Orbital Calculations for V_2, Cr_2, Nb_2, and Mo_2

	Orbital	Orbital exponent	H_{ii}, eV
V	3p	3.594	–51.15
	3d	2.994	–5.90
	4s	1.246	–6.85
	4p	1.150	–3.75
Cr	3p	3.817	–56.22
	3d	3.253	–7.00
	4s	1.285	–7.25
	4p	1.200	–3.75
Nb	4p	3.566	–39.50
	4d	3.070	–5.60
	5s	1.351	–6.00
	5p	0.992	–4.00
Mo	4p	3.761	–44.39
	4d	3.105	–7.00
	5s	1.409	–7.09
	5p	0.994	–4.25

It is especially interesting that absorptions around 520 and 305 nm were observed by Gruen et al.[14] to grow in upon annealing Mo/Ar matrices at 20 K. Also, in Ne and Ar matrices heavily doped with Mo, Weltner et al.[16] observed bands in the 510- and 320-nm regions. Similar observations were made in the Mo atom triode sputtering experiments of Schoch et al.[15] No definitive assignment of bands to the dimer could be made by these groups, but it is clear from the results of the present study that they had in fact generated dimolybdenum, Mo_2.

Molecular Orbital Calculations for Nb_2 and Mo_2. To gain a deeper insight into the electronic and molecular properties of diniobium and dimolybdenum and the credibility of our spectral assignments we have performed extended Hückel molecular orbital calculations for Nb_2 and Mo_2. In these calculations the 4p, 4d, 5s, and 5p orbitals of atomic Mo were employed, together with Clementi-Roetti orbital exponents,[17] the Cusachs approximation,[18] and slightly modified Baranovskii values[19] for the coulomb integrals (parameterized to qualitatively fit the observed optical spectrum of Nb_2 and Mo_2). The calculated potential curves for Nb_2 and Mo_2, using the parameters shown in Table I, show an energy minimum for the closed-shell configuration at roughly 2.20 and 2.10 Å, respectively. For these geometries the energy level schemes shown in Figure 3 were calculated[25] and the predicted and observed optical spectra for Nb_2 and Mo_2 in the range of our UV-visible instrument are shown in Table II. Within the framework of the extended-Hückel approach the agreement between the observed and calculated electronic transitions is reasonable. A particularly interesting feature of these Mo_2 calculations is the fact that the Mo–Mo distance is in close agreement with that calculated for Mo_2 by SCF-Xα-SW molecular orbital techniques[20] which also show a minimum energy configuration at 2.12 Å for closed-shell Mo_2.[26] The exceptionally short metal-metal distances calculated for Nb_2 and Mo_2 are noteworthy and are most suggestive of a very high bond order for the metal-metal bond (cf. Mo–Mo bond lengths in the quadruply bonded systems $Mo_2Cl_8^{4-}$ (2.14 Å)[21] and $Mo_2(O_2CCF_3)_4$ (2.09 Å)[22]). In this same vein, it is pertinent to note that, at least for the calculated distances of 2.20 Å for Nb_2 and 2.10 Å for Mo_2, a closed-shell configuration would

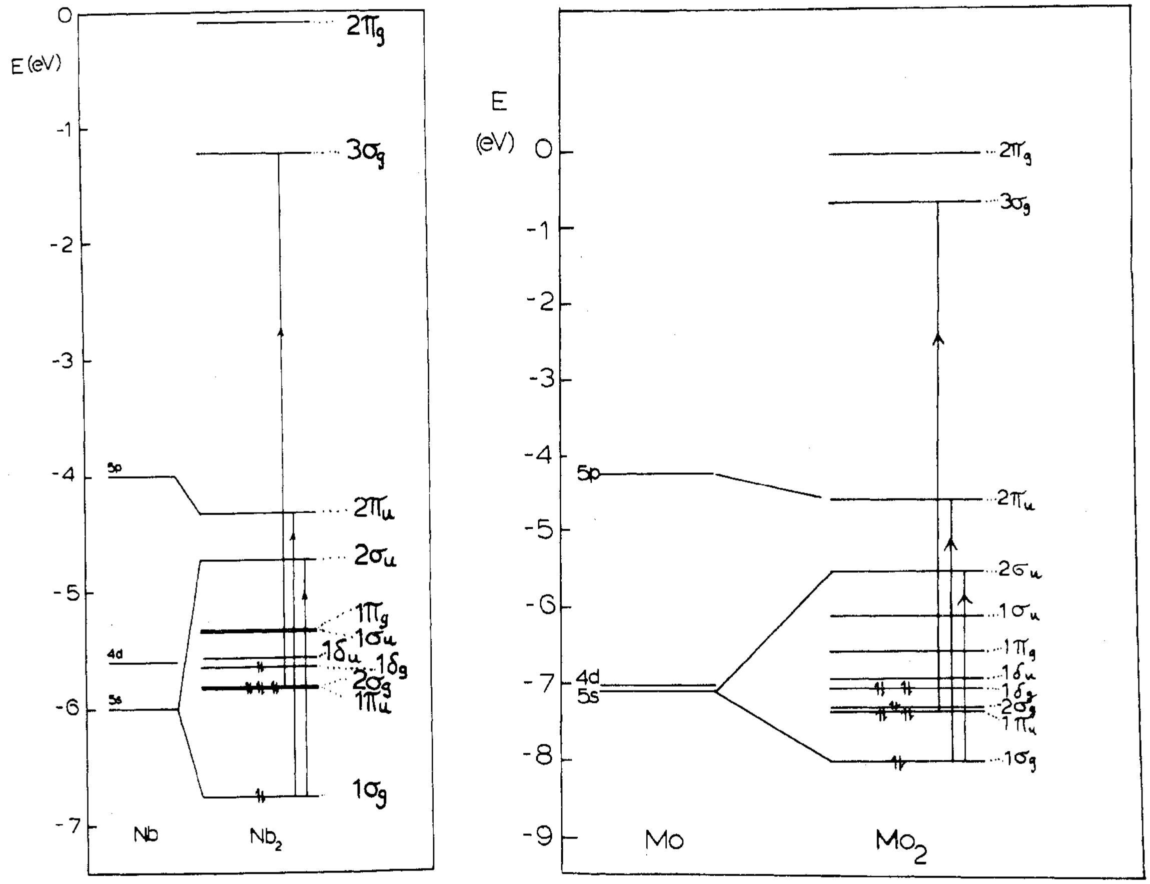

Figure 3. Computed extended-Hückel and molecular orbital energy level schemes for Nb_2 and Mo_2 (see text for notation and parameters used in the calculations).

Table II. Calculated and Observed Optical Spectra for V_2, Cr_2, Nb_2, and Mo_2

		Spectra, nm	
	Assignment	Obsd	Calcd[a]
V_2, $r_e = 1.9$ Å, $D_e = 0.99$ eV	$1\sigma_g \rightarrow 2\sigma_u$	494	521
	$1\sigma_g \rightarrow 1\sigma_u$	558	558
	$1\sigma_g \rightarrow 2\pi_u$	*b*	350
	$2\sigma_g \rightarrow 2\pi_u$	588	607
	$1\pi_u \rightarrow 3\sigma_g$	*b*	350
Cr_2, $r_e = 1.8$ Å, $D_e = 2.65$ eV	$1\sigma_g \rightarrow 2\sigma_u$	456	494
	$1\sigma_g \rightarrow 2\pi_u$	340	309
	$2\sigma_g \rightarrow 2\pi_u$	*b*	389
	$1\pi_u \rightarrow 3\sigma_g$	260	261
Nb_2, $r_e = 2.2$ Å, $D_e = 1.52$ eV	$1\sigma_g \rightarrow 2\sigma_u$	660	612
	$1\sigma_g \rightarrow 2\pi_u$	420	512
	$1\pi_u \rightarrow 3\sigma_g$	280	269
Mo_2, $r_e = 2.1$ Å, $D_e = 3.45$ eV	$1\sigma_g \rightarrow 2\sigma_u$	512	500
	$1\sigma_g \rightarrow 2\pi_u$	308	362
	$2\sigma_g \rightarrow 2\pi_u$	*c*	458
	$1\pi_u \rightarrow 3\sigma_g$	232	186

[a] Only electric-dipole- and spin-allowed electronic transitions in the proximity of the observed transitons are tabulated. [b] Anticipated overlap with atomic absorptions. [c] The predicted $2\sigma_g \rightarrow 2\pi_u$ transition at 458 nm and $1\delta_g \rightarrow 2\pi_u$ at 490 nm either are too weak to be observed or are accidentally coincident with the Mo_2 absorption at 512 nm.

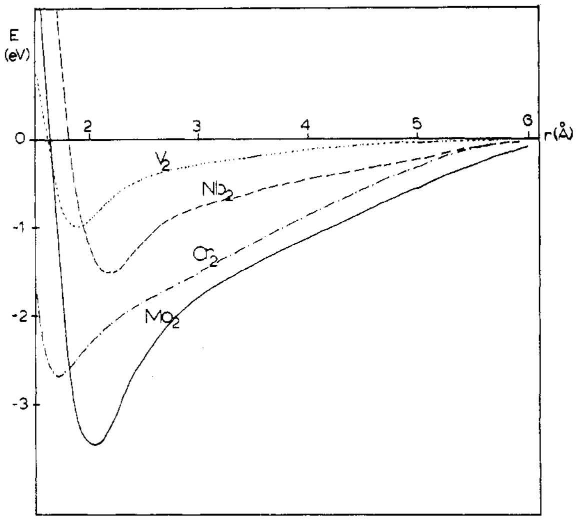

Figure 4. Computed potential energy curves for V_2, Cr_2, Nb_2, and Mo_2 (see text for notation and parameters used in the calculations).

lead to a formally "pentuple and sextuple" bond, respectively![23]

Finally it is interesting to note that the optical spectra for Nb_2 and Mo_2 are qualitatively similar and show the basic pattern of a high-, medium-, and low-energy electronic transition in the spectral range 200–700 nm. Moreover, the spectra of Nb_2 and Mo_2 closely resemble those of their respective first-row congeners V_2[4] and Cr_2[2] and suggest a priori that the electronic configurations and bonding interactions in the V_2–Nb_2 and Cr_2–Mo_2 pairs are somewhat alike. In an attempt to examine trends in the metal–metal bond strengths of M_2 molecules on passing from the first-row to the second-row transition elements, we have computed the molecular orbital energy levels of V_2–Nb_2 and Cr_2–Mo_2 as a function of the internuclear distances (over the range 1.5–6.0 Å) using the optical spectra as a guide for our choice of EHMO parameters. Our results are illustrated in Figure 4 and Table II. Assuming that we are correct in our choice of assignments for the observed electronic transitions of V_2, Cr_2, Nb_2, and Mo_2, we find that the bond dissociation energies of the second-row diatomic molecules are consistently higher than those of their first-row congeners (Table II), analogous to the trend found for first- and second-row transition metal cluster compounds.[24]

Acknowledgment. We gratefully acknowledge the financial assistance of the National Research Council of Canada, the Atkinson Foundation, and Liquid Carbonic. We wish also to acknowledge the extremely helpful correspondence with Dr. J. Norman, Jr., regarding his SCF-Xα-SW calculations for Mo_2.

Registry No. Nb_2, 12596-70-2; Mo_2, 12596-54-2; Nb, 7440-03-1; Mo, 7439-98-7; V_2, 12597-60-3; Cr_2, 12184-82-6.

References and Notes

(1) H. Huber, E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Am. Chem. Soc.*, **97**, 2097 (1975).
(2) E. P. Kündig, M. Moskovits, and G. A. Ozin, *Nature (London)*, **254**, 503 (1975).
(3) R. Busby, W. Klotzbücher, and G. A. Ozin, *J. Am. Chem. Soc.*, **98**, 4013 (1976).
(4) H. Huber, T. A. Ford, W. Klotzbücher, E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Chem. Phys.*, **66**, 524 (1977).
(5) G. A. Ozin, *Appl. Spectrosc.*, **30**, 573 (1976).
(6) R. P. Messmer, S. K. Knudson, K. H. Johnson, J. B. Diamond, and C. Y. Yang, *Phys. Rev. B*, **13**, 1396 (1976), and references therein.
(7) P. S. Skell and M. P. Silvon, paper presented at the Symposium on Atomic Species in Chemical Synthesis, Chicago, Ill., 1975.
(8) M. P. Silvon, E. M. Van Dam, and P. S. Skell, *J. Am. Chem. Soc.*, **96**, 1945 (1974).
(9) P. S. Skell, E. M. Van Dam, and M. P. Silvon, *J. Am. Chem. Soc.*, **96**, 627 (1974).
(10) W. Klotzbücher and G. A. Ozin, in preparation.
(11) M. Moskovits and G. A. Ozin, *J. Appl. Spectrosc.*, **26**, 481 (1972).
(12) E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Mol. Struct.*, **14**, 137 (1972).
(13) D. W. Green and D. M. Gruen, *J. Chem. Phys.*, **57**, 4462 (1973).
(14) D. W. Green and D. M. Gruen, *J. Chem. Phys.*, **60**, 1797 (1974).
(15) F. Schoch and E. Kay, *J. Chem. Phys.*, **59**, 718 (1973).
(16) W. D. Hewett, Jr., J. H. Newton, and W. Weltner, Jr., *J. Phys. Chem.*, **79**, 2640 (1975).
(17) E. Clementi and C. Roetti, "Atomic and Nuclear Data Tables", Vol. 14, Academic Press, New York, N.Y., 1974, p 445.
(18) L. C. Cusachs, *J. Chem. Phys.*, **43**, S157 (1965).
(19) I. Baranovskii and A. B. Nikol'skii, *Teor. Eksp. Khim.*, **3**, 527 (1967).
(20) J. G. Norman, Jr., H. J. Kolari, H. B. Gray, and W. C. Trogler, *Inorg. Chem.*, following paper in this issue.
(21) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 7 (1969).
(22) F. A. Cotton and J. G. Norman, Jr., *J. Coord. Chem.*, **1**, 161 (1971).
(23) Using 4880-Å excitation, preliminary matrix Raman studies of Mo_2 in argon show an intense band at 315 cm^{-1} which we tentatively assign to the fundamental Mo-Mo stretching mode. The frequency of this mode would support the idea of a very high bond order of Mo_2. Dye laser studies are under way to check on the possible interference of resonance Raman and/or fluorescence effects as originally suggested by M. Moskovits (personal communication).
(24) F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975).
(25) In view of Norman's[20] recent SCF-Xα-SW molecular orbital calculations on Mo_2, a closed-shell configuration for Nb_2 $(1\sigma_g^2\,1\pi_u^4\,2\sigma_g^2\,1\delta_g^2)$ and Mo_2 $(1\sigma_g^2\,1\pi_u^4\,2\sigma_g^2\,1\delta_g^4)$ would appear to be a reasonable assignment.
(26) Although our minimum energy geometry (metal-metal bond length) for dimolybdenum is in close agreement with that derived from SCF-Xα-SW calculations,[20] it should be pointed out that less correspondence exists between the respective assignments of the actual electronic spectrum.[20] The main reason for this is that the splitting of the 4d band at the equilibrium Mo-Mo distance calculated by SCF-Xα-SW procedures is about 5 times as large as that derived from extended-Hückel molecular orbital techniques.[20]

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98195, and Contribution No. 5398 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

Electronic Structure of $Mo_2(O_2CH)_4$, Mo_2^{4+}, and Mo_2

JOE G. NORMAN, Jr.,*[1] HAROLD J. KOLARI,[1] HARRY B. GRAY,[2] and WILLIAM C. TROGLER[2]

Received September 1, 1976 AIC60651D

SCF-Xα-SW calculations on $Mo_2(O_2CH)_4$ are used to discuss the metal-metal and metal-ligand bonding in molybdenum(II) carboxylates and interactions between the two. Comparisons are made with similar calculations on HCO_2^-, Mo_2^{4+}, and Mo_2, and previous work on $Mo_2Cl_8^{4-}$ and $Re_2Cl_8^{2-}$. The ordering of the metal-metal orbitals for the carboxylates appears to be the same as for the chloro anions, but the metal-ligand bonding is more covalent, the Mo-Mo bond is stronger, and interactions between the Mo-O π and Mo-Mo bonds are greater in the former. Possible structural implications of these interactions are explored. Mo_2 is found to have a sextuple metal-metal bond, due to the stabilization, relative to Mo_2^{4+} and $Mo_2(O_2CH)_4$, of a 5s-orbital σ-bonding combination which becomes the HOMO. The possibility of such an orbital being occupied in very covalent D_{4h} complexes is discussed. The calculations are in excellent agreement with the UV photoelectron spectrum of $Mo_2(O_2CH)_4$; the observed peaks at 7.7, 9.5, 11.6, and 12.7 eV are assigned mainly to ionization of Mo-Mo δ, Mo-Mo π, Mo-O, and Mo-Mo σ orbitals, respectively. The 80-K electronic spectrum of $Mo_2(O_2CH)_4$ shows peaks at 22.9, 30.8, 33.5, and 4.44 μm^{-1}, with oscillator strengths of 0.0008, 0.03, 0.19, and 0.02, respectively. These are tentatively assigned to forbidden δ → π*, allowed δ → δ*, allowed δ → C-O π*, and allowed π → π* transitions, respectively.

Recently, the nature of the quadruple metal-metal bonds in $Mo_2Cl_8^{4-}$ and $Re_2Cl_8^{2-}$ has been defined in detail using SCF-Xα-SW calculations.[3,4a] A consistent assignment for the electronic spectra of these ions has also been achieved by combining the Xα-SW predictions with polarization data from spectra of single crystals.[3-5] For theoretical studies of strong metal-metal bonding, the chloro anions have the advantage of simple structure. However, they are known only for Mo, Re, and Tc.[6] By far the largest class of compounds of this general structural type (D_{4h} symmetry) is the dinuclear carboxylates, $M_2(O_2CR)_4L_2$, which are well characterized for M = V, Cr, Mo, Re, Ru, Co, Rh, and Cu and a variety of axial ligands L.[7] The occurrence of the same basic structure for so many metals makes these compounds ideal for a theoretical comparison of metal-metal bonding as a function of d^n configuration. We have begun such an investigation with SCF-Xα-SW calculations on molybdenum(II) formate, $Mo_2(O_2CH)_4$. This paper reports the results of these calculations and a proposed assignment for the electronic spectrum of the compound. A preliminary account of the calculations, done with sphere radii ca. 5% smaller than those used here, has appeared.[8] We also present some interesting theoretical results on the species Mo_2^{4+} and Mo_2.

Computational and Experimental Section

Initial Parameters for $Mo_2(O_2CH)_4$. The SCF-Xα-SW method has been thoroughly reviewed.[9] The bond parameters Mo-Mo = 2.09 Å, Mo-O = 2.11 Å, C-O = 1.29 Å, and angle Mo-Mo-O = 92° were taken from the x-ray structure of $Mo_2(O_2CH)_4$;[10] the C-H distance used was 1.08 Å. Coordinates to the nearest 0.000 01 bohr were derived from these parameters using the relation 1 bohr = 0.529 177 Å and the assumption of D_{4h} symmetry. The coordinate system is shown by