Supersonic metal cluster beams of refractory metals: Spectral investigations of ultracold Mo₂

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A novel technique involving pulsed laser vaporization of the bulk metal within a pulsed supersonic nozzle has been shown to successfully produce ultracold bare metal clusters of even the most refractory of metals, tungsten and molybdenum. Clusters of up to 25 atoms may be readily prepared using this technique. Mass-selective resonant two-photon ionization spectra of Mo₂ produced in this fashion show that the dimer is efficiently cooled in the expansion Tₓₓ = 6 K, Tₓ = 5 K, and T₂ = 325 K. We have rotationally resolved the A' 1Σ⁺ - X' 1Σ⁻ (0-0) band for Mo₂ and determined the bond length in the ground and excited states to be 1.940 ± 0.009 and 1.937 ± 0.008 Å, respectively. This confirms and extends the analysis of Efremov et al. [J. Mol. Spectrosc. 73, 40 (1979)] who prepared Mo₂ by flash photolysis of isotopically pure MoCO₂. We have also observed the (1-1), (2-2), and (3-3) sequence bands which together with the ground state data of Efremov et al. determine the vibrational constants 601 = 449.0 ± 0.2 cm⁻¹ and 602 = 2.3 ± 0.2 cm⁻¹ for the A' 1Σ⁺ state. The lifetime of the A' 1Σ⁺ ν = 0 state of Mo₂ has been measured to be 20 ± 3 ns by time-delayed two-photon ionization. The ionization potential of Mo₂ is found to be less than 5.62 eV (compared to 7.10 eV for atomic Mo) indicating a substantially stronger chemical bond in Mo₂ than in Mo₂. A discussion of the electronic structure of Mo₂ and the implications of these findings for bonding in other transition metal dimers is also presented.

I. INTRODUCTION

The electronic structure of metal systems is a topic of great interest in many branches of chemistry and physics, among them homogeneous and heterogeneous catalysis, surface chemistry, inorganic and organo-metallic chemistry, and solid-state physics. Despite the importance of this topic, very little detailed information on the electronic structure of bare metal clusters has emerged from the studies which have been pursued to date. As a result, the study of metal clusters has become an increasingly active field of research as more investigators try their hand with this difficult and important subject.

A detailed understanding of molecular electronic structure derives primarily from the study of molecular spectra. The earliest spectroscopic studies of bare metal clusters utilized hot oven techniques to produce sufficient concentrations of metal dimers for gas-phase work. These studies have contributed a great deal to our understanding of certain classes of metal dimers, in particular the alkali dimers, the group IB dimers, and the group IIA dimers. The vast majority of metals however, particularly those of major importance in catalysis and in much of inorganic chemistry, do not fall into these categories, and with some exceptions have not yet been studied in the gas phase.

Matrix isolation is a well-established technique whereby low temperature environments are used to stabilize high-temperature or reactive species. This method has been extensively utilized to investigate transition metal dimers, and has been extended to the study of transition metal trimers and high clusters as well. The current literature contains examples of useful matrix data involving about 50% of all transition metals. Unfortunately, with this approach the inhomogeneous broadening and perturbations induced by the matrix obscure most of the finer details of spectroscopic structure. Rotational structure is completely lost, precluding the determination of electronic symmetry species and bond length (and in the case of polyatomic molecules, cluster geometry). Often vibrational progressions in excited states are effectively lost as well. Moreover, the magnitudes of the matrix solvent shifts are generally unknown, so the reported electronic transitions may differ with respect to the gas phase by as much as 1000 cm⁻¹. As a result, matrix studies are of somewhat limited utility in guiding our thinking about the nature of the metal-metal bond.

In order to effectively address questions regarding the electronic structure of metal clusters and the nature of metal-metal bonding, particularly in the transition metals, a new experimental approach is required. Hot oven techniques present difficulties in the vaporization of the more refractory metals, such as molybdenum and tungsten, which are formidable in the extreme. In addition, the open d-shell transition metal dimers probably have many low-lying excited electronic states corresponding to the various possible angular momentum couplings of the d electrons. Thermal excitation of these electronic degrees of freedom will greatly complicate the absorption spectra of these dimers, especially at the temperatures required for vaporization. This, in combination with the sequence congestion and extended rotational structure which invariably accompany high temperature spectra, will probably lead to spectra which are too complex to be readily analyzed.

The ideal experimental technique for the spectroscopic study of these interesting molecules should combine the best features of hot oven and matrix spectros-
copy: (1) the molecular species should be in the gas phase, thereby yielding rotational and vibrational information which is usually inaccessible by matrix methods; (2) the approach should permit study of even the most refractory metals, as do matrix isolation techniques; and (3) the internal degrees of freedom should be extensively cooled so that the resulting spectra may be readily interpreted.

Supersonic expansions provide a well-known technique for cooling the internal degrees of freedom of molecules far below the normal boiling point, while maintaining the molecules in the gas phase. In recent work this method has been combined with hot oven technology to produce cold beams of gas phase metal clusters for spectroscopic study. The alkali metal clusters have been extensively investigated using this approach, and dimers of relatively low-boiling metals such as copper may also be conveniently studied. Ultimately, however, this technique is limited to low-boiling materials for which furnaces may be designed.

We have recently been successful in extending these techniques to the high-boiling transition metals by laser vaporization of the bulk metal within a helium supersonic expansion. A localized pulsed heating of the bulk metal by focused laser irradiation is technically superior to the use of a furnace since it is not necessary to heat any part of the apparatus to the extreme temperatures required to vaporize refractory metals. As described below, a newly developed intense pulsed beam source provides the requisite cooling which converts initially hot metal atoms to large concentrations of ultracold clusters. In this approach the helium carrier gas remains at room temperature up to the point of free expansion, resulting in much lower ultimate internal temperatures than oven based expansions of pure hot metal vapor.

The laser vaporization technique has proven to be quite successful in forming metal clusters of the lower boiling metals such as Cu and Al, but are there limits to this new method? As discussed below, we find that comparable cluster intensities of even the most refractory metals may be readily prepared. Tungsten (B. P. = 5933 K), molybdenum (B. P. = 4885 K), iron (B. P. = 3023 K), and nickel (B. P. = 3005 K) are easily vaporized and clusters containing as many as 15 atoms may be routinely prepared. Spectral probes of jet-cooled Mo2 have determined the internal temperatures to be roughly 5 K for the translational and rotational degrees of freedom and 325 K or greater for the unthermalized vibrational degree of freedom. The spectroscopic investigation of the chemically fascinating open d-shell dimers, trimers, and higher clusters is now feasible, unhindered by the complexities of high temperatures.

Among transition metal dimers, the isoelectronic Cr2, Mo2, and W2 dimers are of particular interest concerning the nature of multiple metal–metal bonds. These metals have long been known to form strongly bound dinuclear complexes involving what are thought to be metal–metal quadrupole bonds. The compounds Cr2(CH3)64+, Mo2Cl4+, and W2(CH3)64+ e.g., exhibit extremely short metal–metal bonds (1.98, 2.14, and 2.26 Å in length, respectively). The ground electronic states of the Cr and Mo atoms consist of the high spin d5½ ½ configuration. Pairing all 12 valence electrons of the dimer using simple molecular orbital theory would lead to a singlet ground state with six bonding interactions consisting of one so one do, two dz2, and two dxy bonds. The resulting sextuply bonded diatomic molecules may be expected to exhibit bond lengths even shorter than those of their quadruply bonded complexes mentioned above.

Ab initio calculations of the electronic structures of Cr2 and Mo2 are difficult due to the large number of valence electrons in these systems, and the large number of basis functions required to adequately represent the d orbitals. In addition, the large number of nearly degenerate electronic states obtained using simple Hartree–Fock SCF calculations dictates that extensive configuration interaction be included. Nevertheless, several recent ab initio calculations agree in favor of a sixfold bond order in Mo2. Agreement is not found, however, when these same methods are applied to Cr2, where predictions range from a weak bond 3.06 Å in length to a sextuple bond as short as 1.80 Å.

The only existing gas phase data concerning the group VIB dimers is that of Efremov et al., who produced Mo2 and Cr2 by flash photolysis of the respective metal hexacarboxyls. Their rotational analysis of Mo2 determined the bond length to be 1.92 Å, in close agreement with ab initio predictions. Their rotational analysis of Cr2 gave a bond length of 1.68 Å, however, which is inconsistent with all ab initio calculations. For this reason this experimental result has been largely disregarded. These flash photolysis experiments are hampered by high internal temperatures which characterize the nascent molecules. In addition, there is some uncertainty in identifying the true spectral carrier in the absence of complete spectroscopic data obtained with isotopic labeling. Since these group VIB diatomic molecules are of considerable current interest in determining the extent of d electron participation in metal–metal bonds, we have chosen to reinvestigate these species using the advantages of this new laser vaporization scheme.

In Sec. II of this paper we present a detailed description of the new metal cluster beam source. In Sec. III the gas phase spectra of Mo2 are reexamined using a mass-selective multicolor two-photon ionization detection scheme. A parallel investigation of Cr2 has been published elsewhere. In Sec. IV a discussion of the chemical bond in the group VIB dimers and the implications for other transition metal dimers is presented. In Sec. V a summary of our results and conclusions is given.

II. EXPERIMENTAL
A. Photoionization spectroscopy in a molecular beam
An overview of the experimental apparatus is shown in Fig. 1. The main chamber contains the pulsed supersonic nozzle which can be translated along the
three orthogonal directions to allow precise positioning of the molecular beam. Access of the vaporization laser beam to the metal target rod, located in the nozzle, is obtained through an open channel with a window mounted 52 cm away on the side chamber flange. The molecular beam is collimated with a 5 mm diameter skimmer after which it enters the "A" chamber and subsequently, the photionization region of a time-of-flight mass spectrometer (TOFMS). Reduction of background signal is achieved by lowering the effective base pressure with a liquid nitrogen cryoshield surrounding the ionization region of the TOFMS. A detailed description of the mass spectrometer has been given previously. Critical applications which require extremely well-collimated molecular beams or very low base pressures utilize the "B" chamber to house the TOFMS. In this case, an additional skimmer (1.5 mm diameter) is mounted in the "A" chamber to further collimate the molecular beam.

Detection of metal clusters is achieved with mass analysis provided by the TOFMS. The spectral signature of a particular cluster is measured by scanning a Quanta-Ray Nd: YAG pulsed dye laser (0.5 cm width, 5 nm FWHM) resonant with the electronic state under investigation. A second color of sufficient energy to ionize the electronically excited molecule is provided by a Nd: YAG harmonic or excimer laser radiation (Lumonics TE-860-2). In most chemically bound systems studied to date, this resonant two-photon ionization (R2PI) scheme results predominantly in the production of parent ions. Fluences of the second color are adjusted to minimize background signals arising from single color multiphoton ionization with a resonant or near resonant intermediate state. Typical fluences are on the order of 1 mJ/cm².

Data collection is entirely under computer control. For each laser shot, a complete mass spectrum and additional analog data from laser power monitors are processed. Signals are normalized for laser power fluctuations and stored on floppy disks for subsequent analysis. In this fashion, simultaneous monitoring of many individual isotopic species can be performed.

Rotationally resolved $^{98}$Mo$_2$ spectra were recorded using a Quanta-Ray Nd: YAG pumped dye laser with pressure tuned intracavity etalon (0.08 cm⁻¹ bandwidth). Typical fluences of 15 $\mu$J/cm² were employed to avoid saturation of the Mo$_2$ A - X transition. Electronically excited Mo$_2$ molecules resonantly pumped by the scanning laser were photoionized by absorption of a Nd: YAG fourth harmonic photon at 266 nm. Frequency calibration was provided by monitoring the fringes from a 7 GHz free spectral range quartz etalon.

B. Generation of ultracold metal clusters

Metal atoms are generated by laser vaporization using the Q-switched Nd: YAG second harmonic (532 nm) at the focus of a one meter focal length lens. The metal target, consisting of a 0.125 inch diameter metal rod, is rotated by mechanical connection to a synchronous motor-driven micrometer screw (40 turns per inch, one revolution per minute). This prevents the laser from drilling deep irregular holes in the metal, and proves to be a key factor in producing stable metal cluster concentrations. The optimum laser fluence required to maximize the cluster intensities varies according to the properties of the metal under investigation. For refractory metals such as Mo, W, or Nb, there is a broad operating region between 15 - 30 mJ/pulse which produces the most extensive cluster distributions. Owing to the finite aperture provided by the nozzle faceplate, however, we estimate that only 7 - 15 mJ/pulse is actually incident on the target rod.

The vaporization laser produces a plasma of metal ions within the throat of a pulsed supersonic nozzle as shown in Fig. 4(b). Very intense supersonic gas pulses are employed to recombine and cool the laser-produced plasma. Details of the valve mechanism designed to deliver He gas pulses through an unrestricted 1 mm orifice with backing pressure up to 10 atm are presented in Sec. II.C. Firing of the vaporization laser is synchronized with the supersonic valve such that the plasma is produced at the peak of the helium density above the metal target rod. As the vapor cools in the high density helium, clustering of metal atoms within the exit channel becomes to occur. The contact time between the metal vapor and high density He in the exit channel has a profound effect upon the relative concentrations of cluster sizes in the resulting beam. In fact, the length of the exit channel (distance between the metal rod and point of free expansion) provides a convenient means to control the extent of cluster formation. For example, Fig. 2 shows two cluster size distributions resulting from channel lengths of 3 and 30 mm. Further clustering and cooling of the internal degrees of freedom occurs as the gas freely expands into the vacuum. The clustering of metal atoms requires three-body collision processes,

COPPER CLUSTERS

3mm Extension Channel

30mm Extension Channel

NUMBER OF ATOMS IN CLUSTER

FIG. 2. Copper cluster size distributions resulting from the formation of clusters in two different length extension channels. Both (A) and (B) time-of-flight mass spectra were recorded under identical mass focusing conditions of the spectrometer.

Photons were produced with an ArF (193 nm) laser at ~ 1 mJ/cm². The nozzle backing pressure was 10 atm helium. Note that the additional features which occur in the mass spectra are due to copper oxides Cu₂Oₓ.

so the rate of formation of metal clusters falls off quickly as soon as the gas begins to freely expand. In short, clusters are primarily formed in the exit channel where the helium density is sufficiently high to thermalize the metal vapor to near room temperature. The remaining internal energy is then largely removed in the subsequent supersonic free expansion.

The arrival time of the metal beam 57 cm downstream in the ionization region of the mass spectrometer is extremely narrow, having a temporal width of about 10 µs FWHM. The mean Mo atom beam velocity (c = 1.8 × 10⁶ cm/s) may be calculated from the time interval between the vaporization laser pulse and the photoionization laser pulse. This also enables the calculation of the width of the velocity distribution Δv from which one can calculate a translational temperature Ttrans = 6 K using the expression

\[ T_{\text{trans}} = \frac{v^2 m}{5k} \left( \frac{\Delta v}{v} \right)^2, \quad \text{where} \ m = 100 \ \text{amu}. \]

The absolute time of arrival is critically sensitive to the gas pressure behind the nozzle, the ionization region of the mass spectrometer, and channel length used in the expansion. Short channel lengths which give the limited cluster distributions shown in Fig. 2(a) give rise to a wide range of cluster arrival times with the lighter, faster moving atomic species arriving as much as 80 µs before the metal dimer. Longer channel lengths tend to completely entrap the metal within the He beam. In the latter case, the arrival times occur within 10 µs for all cluster sizes.

As a demonstration of the efficiency of this technique for generating clusters of even the most refractory metals, Fig. 3 illustrates results obtained for W, Mo, Ni, and Fe. Detection is accomplished by an unfocused 193 nm ArF laser (~ 2 mJ/cm²) which photoionizes the clusters with one or two photon excitation depending on the effective ionization potential for each individual cluster. The detection efficiency is not uniform but depends on the photoionization cross section at 193 nm as well as the mass dependent sensitivity of the TOFMS. The latter results from the inability of the ion focusing optics within the TOFMS to uniformly correct for the forward translational momentum of all clusters. Thus, a range of cluster sizes is detected whose mass dependent transmission function depends on the focusing conditions of the TOFMS.

The most remarkable aspect of this technique for generating metal clusters is that even refractory metals such as W, Mo, Nb, Fe, and Ni form as extensive and intense a cluster distribution as the lower boiling metals like Cu and Ag. These ultracold collision-free beams provide an ideal medium for studying the properties of these interesting metal systems.

C. Supersonic nozzle

The supersonic valve is a magnetically operated double-solenoid conceptually similar to that described in several recently published articles. The valve mechanism shown in Fig. 4(a) is driven by two electromagnetic solenoid coils. A thin disk of ferromagnetic material is positioned between the solenoid pole faces and functions as the magnetic actuator. The plunger (which forms a high pressure seal against

FIG. 3. Time-of-flight mass spectra illustrating cluster size distributions obtained from metal beams of iron, nickel, tungsten, and molybdenum. Photons were produced by an ArF (193 nm) excimer laser with a fluence of ~ 2 mJ/cm². The nozzle backing pressure was 8 atm of helium which expanded through a 1 mm orifice. After laser vaporization clusters were formed in an expansion channel 2.5 cm long and 3 mm in diameter. The mass spectra of Fe, Ni, and W contain additional features due to metal oxides MoOₓ. The features in the molybdenum mass spectrum are broadened by the various isotopic modifications due to the seven naturally occurring molybdenum isotopes.

beam pulse profile levels off to a plateau. In order to minimize the total gas throughput, the current pulse to the solenoid which closes the valve is adjusted to occur as early as possible, provided the limiting gas flow is still reached. Under the optimum conditions just described, the logic pulses which drive the respective solenoids, as shown in Fig. 6, will be temporally overlapped. This occurs because the inductive solenoid circuitry introduces a finite response time to the system, and compensation for this is required. Since the solenoid magnetic field is related to the solenoid current, the fastest valve performance will be achieved when the respective open and close magnetic fields have some degree of temporal overlap.

Measurements of the absolute beam intensity under conditions similar to those described in Fig. 5 have determined that the valve delivers gas pulses linear in backing pressure up to 10 atm. Total gas throughput is found to be 0.52 Torr l/pulse at 7.6 atm. This agrees fairly well with the empirical formula of Liepmann4 for unrestricted gas flow through a 1 mm orifice.

The magnetic actuator and solenoid cores are machined from mild steel because of its relatively high magnetic field saturation. Unfortunately, high saturation flux densities are achieved here only at the expense of using core materials with low resistivities resulting in substantial eddy current losses. Water cooling is therefore necessary to remove heat generated by these eddy currents in the steel core solenoids. Typical pulsed magnetic field strengths of 10000 G are employed to fully open the valve under the operating conditions of Fig. 5.

The helium beam pulse is shown in Fig. 5. Helium photons were created by multiphoton ionization with a 193 nm ArF excimer laser. The He beam profile is mapped out by scanning the time delay between the valve opening and the excimer laser firing. Figure 5 represents a profile obtained with 8 atm of He expanding through a 1.0 mm orifice. Total travel of the actuator (1.0 mm at the peak of the gas pulse) is set by the gap between the solenoid cores.

The conditions for unrestricted gas flow through the expansion orifice are determined by monitoring the gas pulse intensity while lengthening the current pulse width in the solenoid which opens the valve. Unrestricted gas flow through the orifice begins when the resulting

![Graph of helium beam pulse intensity over time](image)

**Fig. 5.** Time of arrival of the skimmed helium beam in the photoionization region of the mass spectrometer. Photons are produced by an ArF laser with a fluence of ~1 mJ/cm². The time of arrival is measured by monitoring the intensity of He⁺ photons (y axis) as a function of the delay between the nozzle and ArF laser trigger pulses (x axis). The distance between the nozzle and mass spectrometer was 57 cm. The nozzle-to-skimmer distance was 30 cm. Expansion conditions were: helium backing pressure = 8 atm, orifice diameter = 1 mm, extension channel length = 3.0 cm.
III. THE SPECTROSCOPY OF Mo₂

The jet-cooled A → X spectrum of Mo₂ near 5180 Å is shown in Fig. 7. The signal intensity corresponds to photonics generated with a scanning dye laser and Nd:YAG 4th harmonic (266 nm). Background signal resulting from the absorption of two 266 nm photons is largely responsible for the baseline noise. The spectrum is dominated by a single cold band (0-0) and the apparent absence of a progression in the fundamental vibration. Higher sensitivity scans searching for evidence of the (1-0) band revealed no feature with greater than 0.5% of the (0-0) intensity. To the red of the origin three sequences (1-1), (2-2), and (3-3) are observed. The presence of these sequence bands indicates that predissociation of higher vibrational levels cannot be responsible for the absence of a cold vibrational progression. This electronic transition must therefore connect almost identical potential curves, at least in the region of the potential energy minimum, since only Δυ = 0 transitions are observed. The free-jet spectrum is in good agreement with the previous absorption and emission spectra of Efremov et al., although it is difficult to determine from their photographic plates to what detection limits the (1-0) band is absent.

The intensities of the Δυ = 0 sequence bands are directly related to the vibrational populations in the ground electronic state if one assumes similar Franck-Condon factors. Consequently, this intensity information can be used to estimate the vibrational temperature of dimers in the beam. For the sequence band intensities in Table I, a non-Boltzmann distribution is found with the v = 0 and v = 1 levels representative of a 325 K vibrational temperature, and with the higher vibrational levels populated according to a

![Diagram](https://example.com/diagram)

**FIG. 7.** Resonant two-photon ionization spectra of Mo₂. The intensity of Mo₂ photonics is plotted as a function of the frequency of a scanning dye laser where zero frequency is approximately 5180±10 Å. Photonics of Mo₂ were created by absorption of one Nd:YAG fourth harmonic photon (266 nm) and one photon of a tunable dye laser. Laser fluences were ~1 mJ/cm² and 15 μJ/cm², respectively. The nozzle backing pressure was 8 atm of helium.
higher temperature. It is difficult to imagine why the higher vibrations would be cooled less efficiently than the lower ones in the supersonic expansion. Quite possibly the non-Boltzmann behavior is the result of a bimodal population formed during the clustering process.

A higher resolution spectrum of the (0–0) band for $^{92}$Mo$_2$ with resolved rotational structure is shown in Fig. 8. Much of the spectral complexity has been removed by the cooling of the rotational degree of freedom in the free jet expansion. The simple structure and apparent missing Q branch is characteristic of a $\Sigma$–$\Sigma$ transition. Since the $^{92}$Mo$_2$ molecule consists of identical nuclei with zero spin, every rotational level in a $\Sigma$ type electronic state is missing. This can be independently determined from the rotational spectrum in the following manner. The ratio of the band gap (distance between the innermost lines of the P and R branch) to the rotational spacing is two if all lines are present and 3/2 if every other line is missing. The spectrum of Fig. 8 is therefore only consistent with missing rotational levels in each electronic state.  

Consideration of electronic selection rules identifies the $A-X$ transition as either $\Sigma^+_g-\Sigma^+_u$ or $\Sigma^-_g-\Sigma^-_u$. The ground state term can be determined by examining the intensities of the innermost lines in the P and R branch. These intensities are given by the well-known Hönig–London factors. If odd rotational levels of the ground state are missing ($\Sigma^+_g$ or $\Sigma^-_g$) the innermost lines correspond to R(0) and P(2) with relative intensity R(0)/P(2) = 0.6. Even rotational levels missing ($\Sigma^+_u$ or $\Sigma^-_u$) would result in the assignment of R(1) and P(1) to the innermost lines. The relative intensity would be R(1)/P(1) = 2, which is not observed. Therefore the ground electronic state must be either $\Sigma^+_g$ or $\Sigma^-_g$. The state multiplicity cannot be determined in the current experiment since the spin splitting, if present, would be too small to be resolved. However, $\Sigma^-_g$ is the most likely assignment in view of the short bond distance measured for the ground electronic state. This conclusion agrees with the Mo$_2$ analysis of Ref. 4(a).

Rotational constants of the $A^1\Sigma^+_g$ and $X^1\Sigma^-_g$ states were determined by a least-squares analysis of combination differences
\[ \Delta F'' = R(J''-1) - P(J''+1) = 4E_v''(J'' + \frac{1}{2}) \]

The above fit was performed by omitting terms involving the rotational centrifugal distortion constant. Within experimental error, these results agree with those from Ref. 4(a) for the $X^1\Sigma^-_g$ state. Both sets of results are presented in Table II.

We have simulated the rotational profile shown in Fig. 8 including Hönig–London factors and found a Boltzmann distribution characterized by a rotational temperature of $T_{rot} = 5$ K. It is well known that free-jet expansions are very efficient in removing the spectral complexity caused by large rotational populations. Unfortunately, the resulting spectra often lack sufficient structure for extremely accurate measurement of spectroscopic constants. The more extensive rotational analysis provided by the flash photolysis experiment of Ref. 4(a) yields much more accurate measurements of the ground state constants. However, the authors were unsure of their rotational assignment which in turn introduces a 3% maximum uncertainty in the measurement of the equilibrium bond length $r_0'$. The free-jet data has determined the bond distance with slightly

<table>
<thead>
<tr>
<th>Transition</th>
<th>Intensity</th>
<th>Observed origin</th>
<th>Observed bandhead</th>
<th>Calculated bandhead</th>
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</thead>
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<tr>
<td>0–0</td>
<td>100</td>
<td>0.0 cm$^{-1}$</td>
<td>0.0 cm$^{-1}$</td>
<td>0.0 cm$^{-1}$</td>
</tr>
<tr>
<td>1–1</td>
<td>13.3</td>
<td>−29.6 cm$^{-1}$</td>
<td>−33.4 cm$^{-1}$</td>
<td>−31.8 cm$^{-1}$</td>
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<tr>
<td>2–2</td>
<td>8.6</td>
<td>−60.4 cm$^{-1}$</td>
<td>−67.3 cm$^{-1}$</td>
<td>−66.0 cm$^{-1}$</td>
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<tr>
<td>3–3</td>
<td>3.8</td>
<td>−93.2 cm$^{-1}$</td>
<td>−101.5 cm$^{-1}$</td>
<td>−103.6 cm$^{-1}$</td>
</tr>
</tbody>
</table>

*This work, accurate to ±0.5 cm$^{-1}$.
Band origins measured relative to 0–0 band origin.
Bandheads measured relative to 0–0 bandhead.
Bandheads calculated relative to 0–0 bandhead.

![Diagram](image_url)
TABLE II. Molecular constants from analysis of the $A^1\Sigma^+$ – $X^1\Sigma^+$ transition of $^6\text{Mo}_2$

<table>
<thead>
<tr>
<th></th>
<th>This work $^a$</th>
<th>Efremov et al. $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_0$</td>
<td>449.0 ± 0.2 cm$^{-1}$</td>
<td>443.4 cm$^{-1}$</td>
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<tr>
<td>$\omega_0\sigma''$</td>
<td>2.3 ± 0.2 cm$^{-1}$</td>
<td>1.51 cm$^{-1}$</td>
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<tr>
<td>$B_0'$</td>
<td>0.097 ± 0.0008 cm$^{-1}$</td>
<td>...</td>
</tr>
<tr>
<td>$B_0''$</td>
<td>0.09745 ± 0.0010 cm$^{-1}$</td>
<td>0.0984 ± 0.0001 cm$^{-1}$</td>
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<tr>
<td>$\alpha_0'$</td>
<td>4.8 × 10$^{-4}$ cm$^{-1}$</td>
<td>...</td>
</tr>
<tr>
<td>$r_0'$</td>
<td>1.939 ± 0.009 Å</td>
<td>...</td>
</tr>
<tr>
<td>$r_0''$</td>
<td>1.940 ± 0.009 Å</td>
<td>1.931 ± 0.002 Å $^c$</td>
</tr>
<tr>
<td>$r_0$</td>
<td>1.938 ± 0.009 Å $^d$</td>
<td>1.929 Å $^d$</td>
</tr>
<tr>
<td>$(r_0'' - r_0')$</td>
<td>0.005 ± 0.003 Å $^f$</td>
<td>...</td>
</tr>
</tbody>
</table>

$^a$Estimated 95% confidence limits.
$^b$Reference 4(a).
$^c$Does not include possibility of 3% error in $r_0''$ (6% in $B_0''$) due to an incorrect rotational assignment.
$^d$Estimated from Pekeris relation (Ref. 25) using $B_0'$, $\omega_0'$, and $\omega_0\sigma''$ as in the table.
$^e$Calculated from $B_0'' = B_0'' + \frac{1}{2} \alpha_0''$.
$^f$See the text and Ref. 27.
$^g$Adjusted for $^6\text{Mo}_2$ from $^6\text{Mo}_2$ data of Ref. 4(b).
$^h$For $^6\text{Mo}_2$.
$^i$For $^8\text{Mo}_2$.

The new vibrational constants found by linear regression of these data are listed in Table II.

The $C-X$ transition of $^6\text{Mo}_2$ near 3140 Å was studied in absorption and emission by Efremov et al. $^4(a)$ Due to the complexity of spectral features observed, the authors gave only a speculative vibrational assignment. We have searched for evidence of the $C-X$ electronic transition using resonant two-photon ionization. Since the C state electronic energy is more than half the ionization continuum, two photons of the scanning dye laser will ionize the molecule. The jet-cooled version of the $C-X$ transition is also very complicated, although a strong feature is observed within ± 0.5 cm$^{-1}$ of the reported (0–0) band. $^4(a)$ Careful investigation of this band with mass resolution reveals huge isotopic shifts on the order of 22 cm$^{-1}$ between $^6\text{Mo}_2$ and $^8\text{Mo}_2$. Based on the spectroscopic constants of Ref. 4(a) only a 0.6 cm$^{-1}$ isotopic shift would have been expected for a vibrationless transition. This band, therefore, cannot be the C state (0–0) band. In fact, this isotopically resolved spectral region reveals no (0–0) band or obvious vibrational progression throughout this complicated spectral region.

Aside from the previously mentioned spectroscopic investigations, the two-color ionization probe can be utilized to measure other molecular properties such as ionization potentials and excited state lifetimes. Further work in this laboratory will focus on the measurement of ionization threshold phenomena with tunable UV lasers. However, even in the absence of such tunable UV lasers, the molecular ionization potential may be bracketed by careful power studies involving various fixed frequency lasers. Proceeding in this fashion, we find $\text{Mo}_4$ is easily ionized by low fluences of 193 nm radiation, under conditions in which no observable Mo (I.P. = 7.1 eV) photoions are produced. This strongly suggests that the $\text{Mo}_4$ ionization potential is less than 6.4 eV, unless this wavelength coincides by chance with a resonance which greatly enhances the two-photon ionization process. This indicates that the bonding of the $\text{Mo}_4$ ion is substantially stronger than that of the corresponding $\text{Mo}_2$ neutral ground electronic state.

Measurements of the excited state $A^1\Sigma^+$ lifetime have been obtained by monitoring the intensity of $\text{Mo}_4$ photoions while varying the time delay between the resonant pump laser and Nd: YAG fourth harmonic (266 nm) ionization laser. Each laser has a temporal width of ~5 ns FWHM. Timing jitter between the two lasers is eliminated with a time-to-digital converter which measures the true time delay between pulses with an accuracy of better than 1 ns. The convolution of the two laser pulses therefore dominates the experimental response function. The data shown in Fig. 9 was fit to an exponential decay without deconvolution of the system response function, giving a decay time of $\tau = 18 ± 3$ ns (estimated 95% confidence limits). Assuming that $1/\tau$
represents the radiative rate, an extrapolation to the corresponding absorption cross section gives $\sigma = 10^{14}$ cm$^2$. This is in fair agreement with laser power saturation measurements of the Mo$_2$ $A^1\Sigma_u^+$ $\rightarrow X^1\Sigma_u^+$ transition which places the optical absorption cross section in the range $10^{14}$-10$^{15}$ cm$^2$.

IV. DISCUSSION

Our results, along with those of Efremov and coworkers, show that the bond length of molybdenum dimer is remarkably short and constant in its three lowest known electronic states: 1.938, 1.927, and 1.91 Å in the $X^1\Sigma_u^+$, $A^1\Sigma_u^+$, and $B^1\Pi_u$ states, respectively. This is all the more remarkable because no other known homonuclear diatomic molecule exhibits such constancy in bond length for a variety of low-lying electronic states. The only comparable set of electronic states in homonuclear molecules are Rydberg states, in which the bond length of the molecule remains essentially unchanged throughout a series of states simply because the excited electron is on average too far from the molecule to affect the chemical bonding. Judging from the bond lengths quoted above, a similar principle must be at work in the case of Mo$_2$.

The electronic configuration of the ground state of the molybdenum atom is (Kr) $4d^55s^1$. According to the Wigner–Wittmer correlation rules, $\Sigma$ two ground state Mo atoms may combine to form $1\Sigma_u^+$, $3\Sigma_u^+$, $5\Sigma_u^+$, $9\Sigma_u^+$, $11\Sigma_u^+$ or $13\Sigma_u^+$ molecular states. According to the rotational analysis presented in Sec. III and that given by Efremov et al., any of these states could be the ground state. A number of ab initio studies are in agreement, however, in predicting a $1\Sigma_u^+$ ground state for Mo$_2$ with a bond length in the range 1.90–2.02 Å. The predominant configuration contributing to this state consists of the formally sextuply bonded arrangement $\psi_4(4d)^5\pi_4(4d)^4\psi_5(4d)^4\psi_6(5s)^2$, where the atomic parentage of the molecular orbitals are given in parentheses. This sextuply bonded configuration explains the extremely short Mo–Mo bond, the high ground state vibrational frequency, and the large dissociation energy of Mo$_2$ quite well, at least in qualitative terms.

What is more difficult to understand is how an electronic transition out of this configuration, in which all twelve valence electrons are formally bonding, can leave the chemical bonding essentially intact. In recent work using a generalized valence bond van der Waals method, Goodgame and Goddard appear to have provided an answer to this question. According to their work, the $X^1\Sigma_u^+$ ground state of Mo$_2$ exhibits a local minimum at 3.09 Å, corresponding to the minimum in the $\psi_6(5s)$ orbital energy. This distance is beyond the range of significant $4d$ overlap and corresponds to the bond length of a Mo$_2$ molecule with a single bond. At shorter bond distances, the $\psi_5(5s)$ orbital energy increases, so that its contribution to the chemical bond becomes negligible. At these shorter bond distances, the $4d$ orbitals give sufficient overlap to hold the molecule together, so that despite a formal bond order of six, it is more appropriate to consider Mo$_2$ as having a tight core of strongly bonding $4d$ electrons (giving a bond order of five) and an outer pair of essentially non-bonding $\psi_6(5s)$ electrons.

The picture that emerges, that of a strongly bound Mo$^{2+}$ core surrounded by a nonbonding pair of $\psi_6(5s)$ electrons, is remarkably similar in concept to the bonding in Rydberg states in which only a single electron is sufficiently removed from the molecule to be considered nonbonding. Any excitation of the $\psi_6(5s)$ electrons leaves the quintuply bonded Mo$^{2+}$ core unchanged, and can only change the chemical bonding significantly if the excitation is to an orbital which has strong bonding or antibonding properties. A calculation of the average distance of an electron from the molybdenum nucleus, $\langle r \rangle$, using Slater type orbitals with effective nuclear charges $Z_{	ext{eff}}$ determined according to Slater's rules, predicts that for the $5s$ orbital in the Mo atom $\langle r \rangle_{5s} = 3.23$ Å, while in the $4d$ orbital $\langle r \rangle_{4d} = 1.79$ Å. In light of the very short bond length of $1.94$ Å determined for Mo$_2$ and these values of $\langle r \rangle$, this picture of the $\psi_6(5s)$ orbital lying essentially outside the strongly bound Mo$^{2+}$ core seems quite reasonable.

With this interpretation in mind, the observed $A^1\Sigma_u^+ - X^1\Sigma_u^+$ and $B^1\Pi_u - X^1\Sigma_u^+$ transitions correspond to excitation of one of the $\psi_6(5s)$ electrons to a $\sigma^*$ and a $\pi_*$ orbital, respectively. As these orbitals are higher in energy than the $\psi_6(5s)$ orbital, it is difficult to imagine them having more electron density between the nuclei than the $\psi_6(5s)$ orbital. These transitions, therefore, correspond to the promotion of a nonbonding electron to a higher energy nonbonding orbital. Quite possibly, these transitions are the lowest members of two Rydberg series, leading to Mo$_2$ ion with the expected configuration of $\psi_6(4d^5\pi_4(4d)^4\psi_5(4d)^4\psi_6(5s)^2(\Sigma^2))$.

The complicated spectral structure which appears near 3141 Å, assigned by Efremov et al. to the $C$
state of Mo$\gamma$, has not succumbed readily to analysis. Very likely this represents an excitation out of an orbital of 4d parentage. Quite possibly several such transitions may occur in this region of the spectrum. Such transitions are not expected to leave the bond length unchanged, and a vibrational progression of considerable length is expected. This is in keeping with the complexity of this region of the spectrum.

Although Mo$\gamma$ is evidently now the best known of the open d-shell transition metal dimers, it is not the only system having a very short bond length which is unchanged upon electronic excitation. The A → X transition of Cr$_2$ is now also quite well characterized, and is essentially equivalent to that of Mo$\gamma$. This system, too, shows an extremely short bond length, corresponding to the $\sigma_g(3d)^2\pi_g(3d)^4\delta_g(3d)^4\sigma_g(4s)^2$, $^{1}\Sigma^+_g$ configuration. Again, the bond lengths in the $X^1\Sigma^+_g$ and $A^1\Sigma^+_g$ states are essentially identical, so a similar interpretation must be invoked in the case of Cr$_2$ as well. The argument is not so compelling for Cr$_2$, however, since the analog of the Mo$\gamma$ $B^1\Pi_u$ state has not yet been observed.

The implications of these findings for the remaining transition metal dimers are somewhat speculative, and for this reason these other systems merit investigation. Factors that inhibit chemical bonding in transition metal dimers include: (1) the energetic expense of promoting a 4s electron to a 3d orbital before a pair of 3d$^2$4s$^2$ ground state atoms can sustain anything stronger than a van der Waals bond; and (2) the additional Coulomb repulsion that is incurred by spin pairing two electrons in a bonding orbital, as opposed to leaving them in different spatial orbitals with unpaired spins. Counteracting these factors is the possibility of forming large numbers of bonds utilizing the 3d electrons. One qualitative statement that can be made with some certainty, however, is that multiple bonds involving the 3d electrons are more likely in the early members of the transition series than in the later ones. According to Slater’s rules, as one moves across the first row of transition metals from scandium to zinc, among those metals of atomic configuration 3d$^m$4s$^2$, each additional 3d electron that is added is effective in shielding the 4s electrons from 85% of the added nuclear charge, but only shields the 3d electrons from 35% of this added charge. The net result is a disproportionate contraction of the 3d shell relative to the 4s shell as one moves from scandium to zinc. Thus, the region of optimal 3d–3d overlap in Ni$_2$(3d$^8$) occurs at smaller internuclear distances than in its Ti$_2$(3d$^2$) counterpart. Because the 4s shell has not contracted proportionately, a larger amount of repulsive energy must be stored in the $\sigma_g(4s)$ orbital by shortening the Ni–Ni bond length, before the optimum 3d–3d overlap is reached. It is quite possible that considerations such as these inhibit 3d bonding in Ni$_2$ but encourage it in Ti$_2$.

V. CONCLUSION

Pulsed laser vaporization of bulk metals within a pulsed supersonic helium expansion has been used to successfully generate intense beams of bare metal clusters. The technique is capable of routinely generating clusters of up to 15 atoms of even the most refractory of metals, including molybdenum and tungsten. This will enable the gas-phase spectroscopic study of many metal cluster species for the first time.

The A → X transition of Mo$\gamma$ has been studied using this new technique, demonstrating that the metal clusters generated by this method are efficiently cooled in the supersonic expansion. This molecule exhibits rotational and translational temperatures of 5 K, and shows a non-Boltzmann vibrational distribution equivalent to a temperature of 325 K or higher. Not only are metal clusters readily produced, but they are efficiently cooled as well using this technique.

The $^{64}$Mo$\gamma$ A → X transition has been isotopically resolved, even though this species represents only 2.5% of the overall dimer population. Rotational analysis confirms that the transition is of either the $^2\Sigma^+_g$ or $^2\Pi^+_g$ type, and yields a bond length of $r'_{\text{Mo}}=1.940 \pm 0.010$ Å and $\omega_{\text{Mo}}=1.937 \pm 0.008$ Å in the A and X states, respectively. This extremely short bond length confirms the picture of a sextuply bonded molecule and strongly suggests that the transition is $A^1\Sigma^+_g \rightarrow X^1\Sigma^+_g$.

The only vibrational bands observed in our work are the (0–0), (1–1), (2–2), and (3–3) sequence bands, which confirm that the bond length is virtually identical in the two states. The sequence shifts along with known ground state vibrational constants determine the vibrational constants of the $A^1\Sigma^+_g$ state to be $\omega_{\text{Mo}}=449.0 \pm 0.2$ cm$^{-1}$, $\omega_{\text{Mo}}=2.3 \pm 0.2$ cm$^{-1}$ for $^{64}$Mo$\gamma$. The sequence shifts of band origins and of bandheads together allow a precise determination of the difference in bond lengths in the A and X states, which is found to be $r'_{\text{Mo}}(X^1\Sigma^+_g) - r'_{\text{Mo}}(A^1\Sigma^+_g)=0.005 \pm 0.002$ Å.

A discussion of the chemical bonding in Mo$\gamma$ has been given which concludes that the $\sigma_g(5s)$ molecular orbital is essentially nonbonding in character. Promotion of electrons from this orbital to higher nonbonding orbitals which are far from the closely bound Mo$\gamma$ core then leave the chemical bond in this molecule essentially unchanged, resulting in virtually identical bond lengths in the $X^1\Sigma^+_g$, $A^1\Sigma^+_g$ and $B^1\Pi_u$ states.

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Hopkins, Langridge-Smith, Morse, and Smalley: Spectra of ultracold Mo$_2$


It should be noted that the homonuclear dimer Mo$_2$ is only one of 28 possible isotopic modifications of Mo$_2$ and has a natural abundance of 2.8%. Without the mass selectivity provided by the time-of-flight mass spectrometer, the rotationally resolved spectrum of Mo$_2$ could not have been obtained.

Ground state spectroscopic constants used in the calculation were taken from Ref. 4(a) for Mo$_2$: $B''_1 = 0.08942$, $B''_2 = 0.08940$, $B''_3 = 0.09759$, $B''_4 = 0.09717$. Since the experimental $\alpha''$ is approximately equal to $6(\omega''_0)(2^{1/2} - 5^{1/2})/\omega''_0$ (Ref. 25), $\alpha''$ is likewise taken to obey this formula. $\alpha''$ and $\omega''_0$ are calculated in the text for the Mo$_2$ molecule. For the purpose of this calculation these constants are mass shifted to Mo$_2$. E. Wigner and E. E. Wilmer, Z. Phys. 51, 659 (1928).
