A density-functional study on the formation of Mo_2^{2+}

Reinaldo Pis Diez[a)]

Centro de Química Inorgánica (CEQUINOR), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Universidad Nacional de La Plata (UNLP), Departamento de Química, Facultad de Ciencias Exactas, UNLP, C.C. 962, B1900AVV La Plata, Argentina

Julio A. Alonso[b)]

Departamento de Física Teórica, Universidad de Valladolid, 47011 Valladolid, Spain

The presence of metastable states in the doubly ionized molybdenum dimer is studied using gradient-corrected scalar-relativistic density-functional theory. Seventeen metastable states are found within an energy range of less than 6.5 eV. All those states show lifetimes large enough to assure experimental detection. The calculation of the second adiabatic ionization potential of the neutral molybdenum dimer seems to confirm that the doubly ionized dimer is produced by the electron-capture process $Mo_2^+ + Ar^+ \rightarrow Mo_2^{2+} + Ar$, in which the ionization potentials of Ar and Mo_2^+ play a crucial role [K. Franzreb, R. C. Sobers, Jr., J. Lörinçik, and P. Williams, J. Chem. Phys. **120**, 7983 (2004)]. Moreover, the present results indicate that other species having ionization potentials between 13.01 and 15.34 eV could be used as projectiles to produce Mo_2^{2+}. It is also shown that Xe^+ ions could not react with Mo_2^+ to produce double ionized dimers. A simple thermodynamic argument is also proposed that seems to increase the possibilities of forming Mo_2^{2+} from Mo_2 by using Ar^+ as projectile ions. © *2005 American Institute of Physics.* [DOI: 10.1063/1.2048536]

I. INTRODUCTION

Very recently, Franzreb *et al.*[1] reported the formation mechanism of Mo_2^{2+}, a metastable molecule discovered since 1986.[2] These authors claimed that the above dication is produced in a two-step process: Mo_2^+ forms first by Ar^+ sputtering of a molybdenum surface and subsequent ion-ion collisions of the type $Mo_2^+ + Ar^+ \rightarrow Mo_2^{2+} + Ar$ produce the dication. On the other hand, when Xe^+ ions are used to sputter the metallic surface no Mo_2^{2+} formation is observed. Then, Franzreb *et al.* suggested that the necessary condition for the above resonant charge-transfer mechanism to be successful is that the second ionization potential of Mo_2 should be as close as possible to the first ionization potential of the projectile. The second ionization potential of Mo_2 is estimated in Ref. 1 to be about 15.6 eV, and the ionization potential of Ar is 15.76 eV, whereas the one of Xe is 12.13 eV.[3] These values clearly support the argument of Franzreb *et al.*

The doubly ionized molybdenum dimer was studied by Liu *et al.*[4] from a theoretical viewpoint using both the tight binding method and the local-density approximation to the density-functional theory. Those authors found Mo_2^{2+} to be a metastable molecule with an extremely long lifetime. Nevertheless, no detailed discussion of the electronic spin multiplicity of Mo_2^{2+} was given in Ref. 4. Moreover, those authors claimed that Co_2^{2+} and Ni_2^{2+} are unstable species according to their results. However, we have later studied the existence of metastable states in Ni_2^{2+},[5] Mn_2^{2+} and Co_2^{2+},[6] and Au_2^{2+} (Ref. 7) using the generalized gradient approximation to the density-functional theory, and our results indicated the existence of a large amount of metastable states for the above molecules in a variety of electronic spin states, in contrast to the results reported by Liu *et al.*[4] In the present contribution we investigate the existence of metastable states in Mo_2^{2+} and analyze those properties that could provide further support to the formation mechanism of the dication proposed by Franzreb *et al.*[1] For completeness, results for neutral Mo_2 and the monocation Mo_2^+ are also reported and compared with other results based both on the density-functional theory[8,9] and post-Hartree-Fock methods.[10,11]

II. METHOD AND COMPUTATIONAL DETAILS

Potential-energy curves of several electronic states of Mo_2^{2+} as a function of the internuclear distance are studied in the present work using the density-functional theory[12–14] as implemented in the Amsterdam Density Functional code.[15–17] Relativistic effects are taken into account through the scalar version of the zero-order regular approximation (ZORA).[18–20] It is important to emphasize that even when the spin-orbit term is included into the original ZORA Hamiltonian, the scalar version mentioned above gets rid of the spin-orbit splitting term. A triple-zeta basis set of Slater-type orbitals including a set of polarization functions especially devised for ZORA calculations is used. The frozen-core approximation up to the $3d$ orbital (included) is utilized. The generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (PBE) (Ref. 21) is used to model the exchange-correlation functional. The use of that exchange-correlation functional is justified in view of the results for neutral and ionized gold dimers reported in Ref. 7.

As the experimental ground state of neutral Mo_2 is known to be a singlet state[22] only closed- and open-shell

[a)]Electronic mail: pis_diez@quimica.unlp.edu.ar
[b)]Electronic mail: jaalonso@fta.uva.es

singlet and triplet states of Mo_2^{2+} are studied in the present work. Potential-energy curves for both closed- and open-shell singlet states are calculated using a broken-symmetry approximation to force the correct dissociation limit. Due to the single-determinantal nature of the Kohn-Sham version of the density-functional theory, the calculation of potential-energy curves for triplet states is impossible beyond the minimum region. For these states only the portion of the curve around the minimum is calculated. This of course prevents us to characterize the corresponding state as a metastable one but at least its existence is guaranteed. All the singlet metastable states found in this work are characterized by their equilibrium bond lengths, the energy difference between the top of the barrier and the metastable minimum (which is termed dissociation energy from now on), and their harmonic vibrational frequencies. For the triplet states found in the present letter only their equilibrium bond lengths and harmonic vibrational frequencies are reported. Total energies at the equilibrium bond length relative to the lowest-energy state are also given.

Lifetimes of both closed- and open-shell singlet metastable states are also calculated to gain insight into the possibility of experimental detection of the metastable states found. The simple, semiclassical WKB approximation[23] is used for this purpose. The lifetime is calculated as

$$\tau = \frac{1}{\nu T}, \tag{1}$$

where ν is the dimer vibrational frequency in s^{-1}, and T is the transmission coefficient, given by

$$T = \exp\left(-\frac{2}{\hbar}\int \{2m[V(r) - E]\}^{1/2} dr\right). \tag{2}$$

In the above equation m is the dimer reduced mass, $V(r)$ is the potential energy as a function of the internuclear distance r, and E is the dimer energy evaluated at the lowest vibrational state. The integral is calculated between the classical turning points of the potential-energy curve.

III. RESULTS AND DISCUSSION

As a first test of the methodology used throughout the present work, the relevant properties of Mo_2 and Mo_2^+ are calculated and compared with experimental results reported by Morse[22] and Simard *et al.*[24] and other theoretical works. Table I shows calculated and experimental properties of Mo_2. It can be seen in that table that the bond distance of the neutral dimer is overestimated no matter how sophisticated the electron correlation treatment is. On the density-functional theory side, the local spin-density approximation plus a generalized gradient approximation (GGA) correction included perturbatively,[8] the B3LYP hybrid exchange-correlation functional,[9] and the PBE generalized gradient approximation used in the present work predict bond distances about $0.03–0.12$ Å larger than the experimental value. Harmonic vibrational frequencies reported in Refs. 8 and 9 are within an acceptable $50–80$-cm^{-1} error in excess, whereas the PBE harmonic vibrational frequency, on the other hand, is only about 40 cm^{-1} lower than the experimental value.

TABLE I. Calculated and experimental equilibrium bond distances (R_e, in angstroms), dissociation energies (D_e, in eV), harmonic vibrational frequencies (ω_e, in cm^{-1}), and adiabatic ionization potentials (IP, in eV) of Mo_2 in its $^1\Sigma_g$ ground state.

Method	R_e	D_e	ω_e	IP
Experimental	1.938[a]	4.48[b]	477[a]	6.95[b]
This work	2.066	3.38	439	7.16[c]
				7.83[d]
				8.91[e]
				9.05[f]
Local spin-density approximation (LSDA)+GGA[g]	1.97	3.40	552	
B3LYP[h]	1.965	⋯	533.5	
CI[i]	2.01	0.86	388	
MRSDCI+Q[j]	1.993	3.9[k]	447.5	6.88

[a]Reference 22.
[b]Reference 24.
[c]This IP corresponds to $Mo_2 \rightarrow Mo_2^+(1 - {}^2\Sigma_g)$.
[d]This IP corresponds to $Mo_2 \rightarrow Mo_2^+({}^2\Delta_g)$.
[e]This IP corresponds to $Mo_2 \rightarrow Mo_2^+({}^2\Pi_u)$.
[f]This IP corresponds to $Mo_2 \rightarrow Mo_2^+(2 - {}^2\Sigma_g)$.
[g]Reference 8.
[h]Reference 9.
[i]Reference 10.
[j]Reference 11.
[k]Estimated value.

The dissociation energy is strongly underestimated in all cases. The adiabatic ionization potential from the neutral dimer to the ground state of Mo_2^+ is in excellent agreement with the experimental value. This is a very encouraging result, as one of the aims of the present work is to calculate ionization potentials. On the other hand, post-Hartree-Fock methods such as configuration interaction (CI) (Ref. 10), multireference CI, and multireference single & double excitation configuration interaction (MRSDCI), including Davidson-type corrections denoted as Q (Ref. 11) predict bond distances larger than the experimental value, too, the error being similar to that of the density-functional theory. The MRSDCI vibrational frequency is 30 cm^{-1} below the experimental value and very similar to the PBE value obtained in this work. The dissociation energy is closer to the experiment than density-functional-theory-based values, but it must be stressed that that value is only an estimation made by the authors. The adiabatic ionization potential calculated

TABLE II. Calculated equilibrium bond distances (R_e, in angstroms), dissociation energies (D_e, in eV), harmonic vibrational frequencies (ω_e, in cm^{-1}), and dissociation products (DP) for Mo_2^+ in its ground state and some low-lying excited states. Experimental results, if available, are also given.

Method	R_e	D_e	ω_e	DP
Experimental		4.62[a]		
This work: $1 - {}^2\Sigma_g$	2.051	3.72	414	$Mo(d^5s^1)+Mo^+(d^5)$
This work: ${}^2\Delta_g$	2.089	4.55	338	$Mo(d^5s^1)+Mo^+(d^4s^1)$
This work: ${}^2\Pi_u$	2.352	3.48	280	$Mo(d^5s^1)+Mo^+(d^4s^1)$
This work: $2 - {}^2\Sigma_g$	2.202	3.34	334	$Mo(d^5s^1)+Mo^+(d^4s^1)$
MRSDCI+Q$- {}^2\Sigma_g$[b]	1.982	3.8[c]	428.6	

[a]Reference 24.
[b]Reference 11.
[c]Estimated value.
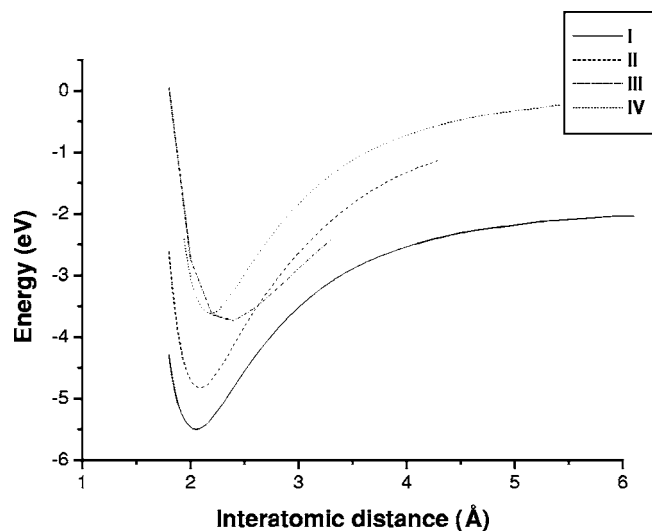
FIG. 1. Potential-energy curves for four stable states of Mo$_2^+$ as functions of the interionic distance. I corresponds to state $1-^2\Sigma_g$, II corresponds to state $^2\Delta_g$, III corresponds to state $^2\Pi_u$, and IV corresponds to state $2-^2\Sigma_g$.

at the MRSDCI level of theory is in complete agreement with experimental data. Interestingly, Balasubramanian and Zhu attribute their discrepancies with experiment to strong correlation effects, to the quality of the basis sets, and to the use of effective core potentials.[11] The relatively poor description of the properties of transition-metal dimers around the minimum is mainly due to the multireference character of the wave function and the quality of the basis set used (see Ref. 25 for a good description of the problems associated to the study of Cr$_2$, a challenging species similar to Mo$_2$). In the Kohn-Sham version of the density-functional theory, the lack of the exact exchange-correlation functional is the main source of error around the minimum, similar to the problem of the multireference character of the wave function mentioned above. If the exact exchange-correlation functional were known, then the exact electron density would be obtained and an exact description around the minimum would be attained. Thus, we suggest that the discrepancies between the present results and experimental data for the challenging Mo$_2$ molecule are mainly due to errors in the description of exchange-correlation effects made by the PBE functional and, to a lesser extent, to the quality of the basis set and the frozen-core approximation used. It should be stressed, however, that our results are in good agreement with the sophisticated multireference CI calculations of Balasubramanian and Zhu.[11]

Table II shows the calculated and experimental properties of Mo$_2^+$. Unfortunately, only the dissociation energy is experimentally known for Mo$_2^+$. It can be seen that both the present results and the MRSDCI ones[11] follow the same trend that was already observed in the neutral dimer. Calculated dissociation energies are underestimated. Considering the errors found in the equilibrium bond distance and the vibrational frequency of the neutral dimer it could be expected that the experimental equilibrium bond distance and vibrational frequency of the ground state of Mo$_2^+$ are about 1.92 Å and 460 cm^{-1}, respectively. Figure 1 shows the potential-energy curves for the four stable states of Mo$_2^+$

studied. It should be mentioned that severe convergence problems prevent us from completing some of the curves far beyond the minimum.

A close inspection to the valence electronic configuration of the ground state of Mo$_2$ and the various states of Mo$_2^+$ reveals that the $3\sigma_g$, $4\sigma_g$, $2\pi_u$, and $1\delta_g$ molecular orbitals can be considered as a sort of active space for building the different electronic states of Mo$_2^{2+}$. It should be noted that even though the calculations are carried out in broken-symmetry mode the electronic configurations are given using the $D_{\infty h}$ point-group notation. Four closed-shell and six open-shell singlets and eight triplets are generated from the active space mentioned above. Table III shows the valence electronic configuration and other relevant properties of those states. Figures 2 and 3 show the potential-energy curves for closed- and open-shell singlet states, respectively. It must be mentioned that the open-shell singlet state 15 is poorly characterized due to severe convergence problems for most of the points calculated to construct the potential-energy curve. It can be seen from the table that calculated lifetimes are sufficiently large in all cases to assure experimental detection of doubly ionized molybdenum dimers.

It can be seen from Table III that the most important enlargements in the equilibrium bond distance with respect to the singly ionized dimer occur when electrons are removed from $3\pi_u$ and $3\sigma_g$ molecular orbitals. On the contrary, electrons on $4\sigma_g$ and $1\delta_g$ molecular orbitals have little effect on the equilibrium bond distance when removed. These facts clearly indicate that the $3\pi_u$ and $3\sigma_g$ molecular orbitals possess a strong bonding character, whereas the $4\sigma_g$ and $1\delta_g$ ones exhibit a weak bonding character. According to the dissociation products identified for closed- and open-shell singlets, the $4\sigma_g$ molecular orbital mainly presents an s atomic orbital-character.

The second adiabatic ionization potential of Mo$_2$ is calculated as Mo$_2^+ \rightarrow$ Mo$_2^{2+}$. The stable and metastable states found for those ions lead to various possible combinations for the "reaction" above. These combinations provide a rather wide range of second adiabatic ionization potentials for Mo$_2$ from 13.01 to 17.58 eV. Table IV shows in detail all the possible adiabatic ionization potentials of Mo$_2^+$. It can be seen from the table that ionization potentials from the Mo$_2^+$ ground state to states 8 and 9 of Mo$_2^{2+}$ compare well with the ionization potential of argon [15.76 eV (Refs. 3 and 26)], suggesting that the formation mechanism of Mo$_2^{2+}$ by a resonant charge-transfer process proposed by Franzreb et al.[1] could be possible. It is worth noticing that some other calculated ionization potentials, such as those from the $^2\Delta_g$ of Mo$_2^+$ to states 11 and 12 of Mo$_2^{2+}$, from the $^2\Pi_u$ of Mo$_2^+$ to state 15 of Mo$_2^{2+}$, and from the $2-^2\Sigma_g$ of Mo$_2^+$ to state 15 of Mo$_2^{2+}$, are also close to the ionization potential of argon. It is expected, however, that the excited states of Mo$_2^+$ exhibit a negligible population at temperatures below 1000 K. On the other hand, the lower second ionization potentials calculated in this work are slightly above 13 eV, which is considerably larger than the ionization potential of xenon [12.13 eV (Ref. 13)]. This fact seems to suggest that Mo$_2^{2+}$ could not be formed by Xe$^+$ bombardment, in agreement with the suggestions made by Franzreb et al.[1] Furthermore and assuming the

TABLE III. Valence electronic configuration of metastable closed-shell and open-shell singlet and triplet states of Mo$_2^{2+}$. Equilibrium bond distances (R_e, in angstroms), dissociation energies with respect to the top of the barrier (D_e, in eV), harmonic vibrational frequencies (ω_e, in cm^{-1}), total energies at R_e relative to the lowest-energy minimum (ΔE, in eV), and the dissociation products (DP) are also given. Lifetimes (τ, in seconds) are given for closed-shell and open-shell singlet metastable states only.

Configuration	R_e	D_e	ω_e	ΔE	$\tau \times 10^{-28}$	DP[a]
$3\pi_u^4 3\sigma_g^2 4\sigma_g^0 1\delta_g^4$ (1)	2.060	1.45	349	0.0	5.28	I+I
$3\pi_u^4 3\sigma_g^2 4\sigma_g^1(\uparrow)1\delta_g^3(\uparrow)$ (2)	2.100	⋯	429	0.85	⋯	
$3\pi_u^4 3\sigma_g^2 4\sigma_g^1(\uparrow)1\delta_g^3(\downarrow)$ (3)	2.120	1.76	287	1.07	10.1	I+II
$3\pi_u^3(\uparrow)3\sigma_g^2 4\sigma_g^1(\downarrow)1\delta_g^4$ (4)	2.484	0.67	185	2.02	3.37	I+II
$3\pi_u^4 3\sigma_g^2 4\sigma_g^2 1\delta_g^2(\uparrow\uparrow)$ (5)	2.120	⋯	350	2.30	⋯	
$3\pi_u^4 3\sigma_g^1(\uparrow)4\sigma_g^1(\downarrow)1\delta_g^4$ (6)	2.280	0.71	228	2.33	2.81	I+II
$3\pi_u^4 3\sigma_g^2 4\sigma_g^2 1\delta_g^2(\uparrow\downarrow)$ (7)	2.200	1.61	170	2.66	15.6	II+II
$3\pi_u^3(\uparrow)3\sigma_g^2 4\sigma_g^1(\uparrow)1\delta_g^4$ (8)	2.163	⋯	360	2.86	⋯	
$3\pi_u^4 3\sigma_g^1(\uparrow)4\sigma_g^1(\uparrow)1\delta_g^4$ (9)	2.102	⋯	278	2.87	⋯	
$3\pi_u^2(\uparrow\downarrow)3\sigma_g^2 4\sigma_g^2 1\delta_g^4$ (10)	2.927	0.57	141	3.37	4.21	II+II
$3\pi_u^3(\uparrow)3\sigma_g^2 4\sigma_g^2 1\delta_g^3(\downarrow)$ (11)	2.593	0.77	133	3.37	6.38	II+II
$3\pi_u^3(\uparrow)3\sigma_g^2 4\sigma_g^2 1\delta_g^3(\uparrow)$ (12)	2.378	⋯	375	3.46	⋯	
$3\pi_u^4 3\sigma_g^1(\uparrow)4\sigma_g^2 1\delta_g^3(\downarrow)$ (13)	2.204	0.36	224	3.77	2.10	II+II
$3\pi_u^4 3\sigma_g^1(\uparrow)4\sigma_g^2 1\delta_g^3(\uparrow)$ (14)	2.139	⋯	447	4.16	⋯	
$3\pi_u^3(\uparrow)3\sigma_g^1(\downarrow)4\sigma_g^2 1\delta_g^4$ (15)	2.501	⋯	⋯	4.62	⋯	II+II
$3\pi_u^2(\uparrow\uparrow)3\sigma_g^2 4\sigma_g^2 1\delta_g^4$ (16)	2.322	⋯	307	5.66	⋯	
$3\pi_u^3(\uparrow)3\sigma_g^1(\uparrow)4\sigma_g^2 1\delta_g^4$ (17)	2.242	⋯	325	6.31	⋯	
$3\pi_u^4 3\sigma_g^0 4\sigma_g^2 1\delta_g^4$ (18)	Repulsive					II+II

[a]State labeled as I is Mo$^+ - {}^6$S($d^5 s^0$). State labeled as II is Mo$^+ - {}^6$D($d^4 s^1$).

validity of the mechanism proposed by Franzreb *et al.*,[1] a variety of projectiles with ionization potentials within the range of 13.01–15.34 eV could be designed to produce Mo$_2^{2+}$.

We finally note that according to very simple thermodynamic arguments the process Mo$_2^+$+Ar$^+ \rightarrow$ Mo$_2^{2+}$+Ar could take place spontaneously if the ionization potential of Mo$_2^+$ is lower than the ionization potential of Ar. The Gibbs free energy for the process under study is given by $\Delta G = \Delta H - T\Delta S$. The entropic term could be considered negligible as the process occurs in the gas phase, thus $\Delta G \approx \Delta H$. Then, ΔH is calculated as the difference between the enthalpies of the simple ionization processes Mo$_2^+ \rightarrow$ Mo$_2^{2+}$ and Ar$\rightarrow$Ar$^+$, and the Gibbs free energy is given by $\Delta G \approx$ IP(Mo$_2^+$)

$-$IP(Ar). Since ΔG is required to be a negative number for an spontaneous process then IP(Mo$_2^+$) < IP(Ar), the condition IP(Mo$_2^+$)=IP(Ar) being useful only when the resonant charge-transfer channel is considered. From this thermodynamic argument all the ionization processes involving the ground state of Mo$_2^+$ and states 1 to 4 and 6 of Mo$_2^{2+}$, could take place if Ar$^+$ ions are used as projectiles.

IV. CONCLUSIONS

The presence of metastable states in the doubly ionized molybdenum dimer, Mo$_2^{2+}$, has been studied using gradient-corrected density-functional theory in a scalar relativistic version. Our calculations predict the presence of 17 meta-
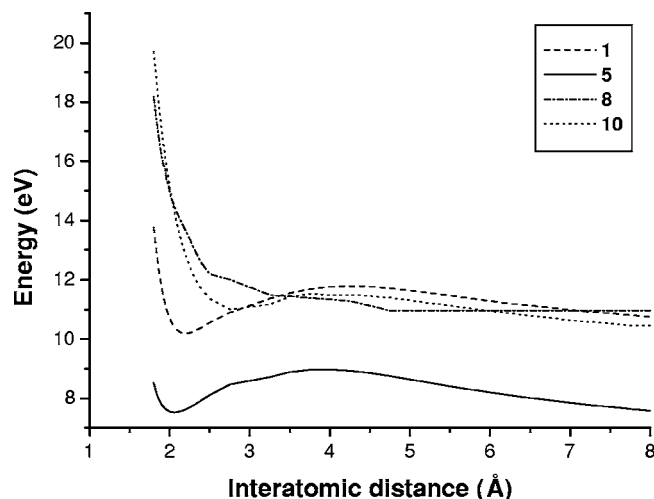

FIG. 2. Potential-energy curves for closed-shell singlet metastable states of Mo$_2^{2+}$ as functions of the interionic distance.
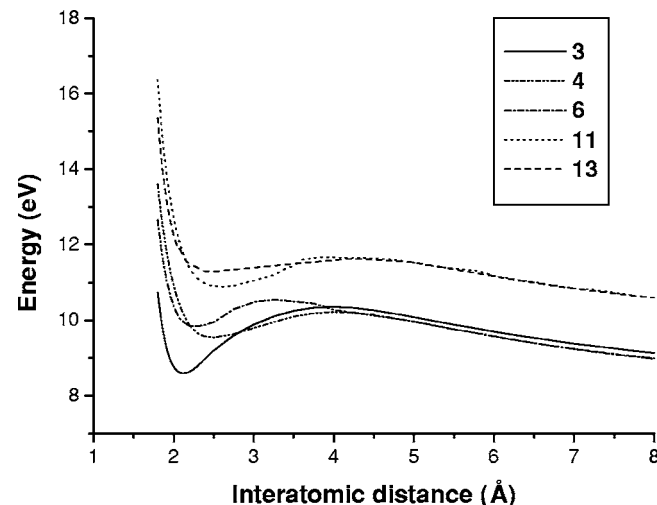

FIG. 3. Potential-energy curves for open-shell singlet metastable states of Mo$_2^{2+}$ as functions of the interionic distance.

TABLE IV. Second adiabatic ionization potentials, in eV, of Mo$_2$ calculated as Mo$_2^+ \rightarrow$ Mo$_2^{2+}$. See Tables II and III for labels used to identify the different states.

Mo$_2^{2+}$ states	Mo$_2^+$−1−$^2\Sigma_g$	Mo$_2^+$−$^2\Delta_g$	Mo$_2^+$−$^2\Pi_u$	Mo$_2^+$−2−$^2\Sigma_g$
1	13.01	⋯	⋯	⋯
2	13.86	13.19	⋯	⋯
3	14.08	13.41	⋯	⋯
4	15.03	⋯	13.29	⋯
5	⋯	14.64	⋯	⋯
6	15.34	⋯	⋯	13.46
7	⋯	15.00	⋯	⋯
8	15.87	⋯	14.13	⋯
9	15.88	⋯	⋯	14.00
10	⋯	⋯	14.64	⋯
11	⋯	15.71	14.64	⋯
12	⋯	15.80	14.73	⋯
13	⋯	16.11	⋯	14.90
14	⋯	16.50	⋯	15.29
15	⋯	⋯	15.89	15.75
16	⋯	⋯	16.93	⋯
17	⋯	⋯	17.58	17.44

stable states within an energy range of less than 6.5 eV. The calculated lifetimes are large enough for all the metastable states indicating that they can be experimentally detected. Due to the amount of states found for Mo$_2^+$ and Mo$_2^{2+}$ the calculated second adiabatic ionization potential of neutral Mo$_2$ exhibits a wide range from 13.01 to 17.58 eV. Some ionization potentials lie within about 0.1 eV of the ionization potential of argon indicating the resonant charge-transfer process Mo$_2^+$+Ar$^+ \rightarrow$ Mo$_2^{2+}$+Ar could be possible. Moreover, the present results suggest that Xe$^+$ could not be used to produce Mo$_2^{2+}$ if the resonant charge-transfer process is assumed to be valid. Finally, a complementary thermodynamic argument is proposed to explain the formation mechanism of Mo$_2^{2+}$. It is shown in that case that the ground state of Mo$_2^+$ could react with ions of Ar$^+$ to form several metastable states of Mo$_2^{2+}$.

ACKNOWLEDGMENTS

[1] K. Franzreb, R. C. Sobers, Jr., J. Lörincik, and P. Williams, J. Chem. Phys. **120**, 7983 (2004).

[2] T. T. Tsong, J. Chem. Phys. **85**, 639 (1986); Surf. Sci. **117**, 593 (1986).

[3] *CRC Handbook of Chemistry and Physics*, 59th ed., edited by R. C. West (CRC, Boca Raton, FL, 1979).

[4] F. Liu, M. R. Press, S. N. Khanna, and P. Jena, Phys. Rev. Lett. **59**, 2562 (1987).

[5] R. Pis Diez and J. A. Alonso, Chem. Phys. Lett. **332**, 481 (2000).

[6] R. Pis Diez, J. A. Alonso, J. M. Matxain, and J. M. Ugalde, Chem. Phys. Lett. **372**, 82 (2003).

[7] R. Pis Diez and J. A. Alonso, J. Mol. Struct.: THEOCHEM **639**, 203 (2003).

[8] R. Pis Diez, Int. J. Quantum Chem. **76**, 105 (2000).

[9] D. Kraus, M. Lorenz, and V. E. Bondybey, PhysChemComm **4**, 44 (2001).

[10] P. M. Atha and I. H. Hillier, Mol. Phys. **45**, 285 (1982).

[11] K. Balasubramanian and X. Zhu, J. Chem. Phys. **117**, 4861 (2002).

[12] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[13] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[14] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).

[15] Computer code ADF2004.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

[16] C. Fonseca Guerra, J. G. Snijders, G. te Velde, and E. J. Baerends, Theor. Chem. Acc. **99**, 391 (1998).

[17] G. te Velde, F. M. Bickelhaupt, S. J. A. van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders, and T. Ziegler, J. Comput. Chem. **22**, 931 (2001).

[18] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **99**, 4597 (1993).

[19] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **101**, 9783 (1994).

[20] E. van Lenthe, A. E. Ehlers, and E. J. Baerends, J. Chem. Phys. **110**, 8943 (1999).

[21] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[22] M. D. Morse, Chem. Rev. (Washington, D.C.) **86**, 1049 (1986).

[23] E. Merzbacher, *Quantum Mechanics* (Wiley, New York, 1967).

[24] B. Simard, M.-A. Lebeault-Dorget, A. Marijnissen and J. J. ter Meulen, J. Chem. Phys. **108**, 9668 (1998).

[25] H. Dachsel, R. J. Harrison, and D. A. Dixon, J. Phys. Chem. A **103**, 152 (1999).

[26] The calculated ionization potential of argon was found to be 15.78 eV in the present work, in excellent agreement with the experimental value given in Ref. 3. This calculation was carried out at the same level of theory used throughout.