Stability of Doubly Charged Transition-Metal Dimers

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The spatial dependence of the interaction potentials in doubly charged dimers of transition-metal atoms has been calculated by use of both the tight-binding and the self-consistent-field linear combination of atomic orbitals–molecular orbitals methods. The study reveals an interesting correlation between the stability of the doubly charged dimers and their electronic structure. Situations have been identified where the charged dimers can exist in metastable states so long that their metastability may be impossible to observe.

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It is well known that the interaction between two like *point* charges is repulsive at *all* distances. However, when charged particles have a finite size, as they almost always do, it is not clear what the interaction between them should be at distances comparable to their size. In this Letter we report results of such investigations by considering the interaction between two positively charged transition-metal atoms. The total energies of doubly charged dimers belonging to the 3*d* (Ti, V, Cr, Fe, Co, and Ni), 4*d* (Nb, Mo, Rh, and Pd), and 5*d* (Ta, W, Ir, and Pt) series have been calculated as functions of their interatomic distance by a simple tight-binding method. The results are augmented by fully self-consistent linear combination of atomic orbitals–molecular orbitals (LCAO-MO) calculations based upon the local density-functional theory.

The results display a unique relationship between the electronic structure and stability of the doubly charged dimers. For example, while the Ni_2^{++} potential is a monotonically decreasing function of distance (repulsive at *all* distances), the interaction between two Cr^+ ions is strongly attractive at small distances, thus causing formation of a long-lived metastable state. The strength of the metastable states increases as one goes from Ni to Cr and then decreases as the *d*-level occupancy is further reduced. Similar trends have been noticed for 4*d* and 5*d* elements. The existence of metastable states indicates that not all doubly charged transition metal dimers would spontaneously dissociate into separate ions. The process may be a delayed one and the corresponding lifetime in some systems may be so large that the metastability of the states may not be observable. In none of the dimers studied do the interionic potentials decrease as $1/r$ for distances less than about 12 a.u.

The physics of charged clusters has been a problem of great current interest[1] ever since it was discovered[2] that the electrostatic repulsion in isolated multiply charged clusters leads them to fragment into smaller sizes. This phenomenon, called "Coulomb explosion," results from a delicate balance between the electrostatic interaction which pulls the charges apart, and the cohesive energy that binds them together. Many experiments[3,4] and model calculations[1,5] have been carried out to study the minimal number of atoms for which a multiply charged cluster is stable. While some of the early experiments[2] suggested a critical size of about 30 atoms for Coulomb explosion, recent experiments[6] have indicated that some of the doubly charged noble-metal trimers may even be stable. Tsong[4] has reported that a doubly charged molybdenum dimer is stable with a binding energy of at least 1.2 eV. Our systematic study of transition-metal dimers reveals that while Co_2^{++}, Ni_2^{++}, Pd_2^{++}, and Pt_2^{++} are *unstable*, others belonging to group V*A* and VI*A* are *metastable*. In particular, the activation barrier for Mo_2^{++} exceeds 2 eV and the probability of its dissociating into two isolated ions is virtually negligible. In the following, we outline our theoretical methods and discuss the results in detail.

One of our studies is based on a semiempirical tight-binding approach[7] where the total energy is expressed as a sum of the electronic term E_e, a semiempirical repulsive term E_R, and the Coulomb energy E_C:

$$E = E_e + E_R + E_C. \tag{1}$$

The electronic term represents energy gained as a result of formation of molecular levels from the atomic levels. Since the main source of binding in transition elements is due to *d* bands, the electronic energy included contribution only from *d* states and was calculated in a tight-binding framework. The repulsive term E_R representing core-core repulsion is taken in a Born-Mayer form,

$$E_R = \tfrac{1}{2} A \sum_{i,j} \exp(-pR_{ij})/R_0, \tag{2}$$

where A and p are constants determined by the use of the bulk equilibrium distance, cohesive energy, and bulk modulus. R_{ij} is the distance between the ions and R_0 is the interparticle distance in the bulk phase. Finally, the Coulomb energy is taken as the energy of point charges located on two ions. Other details of the calculations will be published in a forthcoming paper.

In Fig. 1, we plot the total energies (relative to two

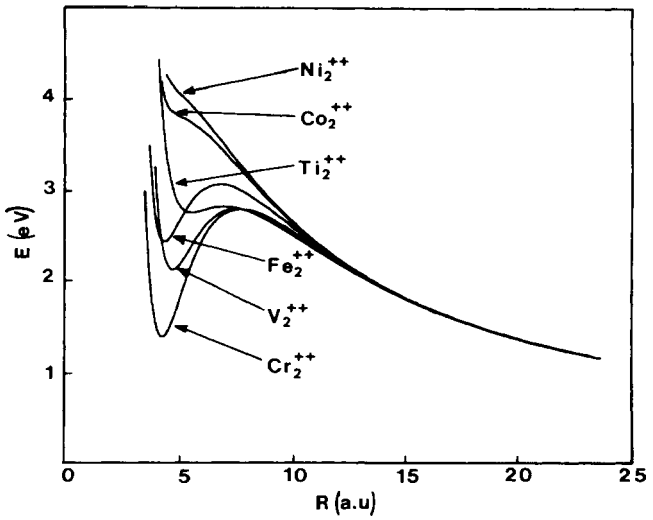

FIG. 1. Interaction energies of Ti_2^{++}, V_2^{++}, Cr_2^{++}, Fe_2^{++}, Co_2^{++}, and Ni_2^{++} as functions of interparticle spacing. The energies are measured with respect to isolated ions.

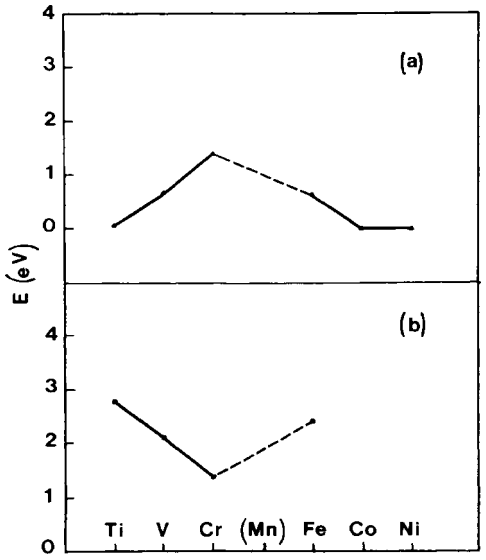

FIG. 2. (a) Activation barrier and (b) the dissociation energy D_e for various $3d$ elements. The dashed lines indicate that no data were obtained for the Mn system.

isolated ions) of doubly charged $3d$ transition-metal dimers (Ti, Cr, Fe, Co, and Ni) as functions of interparticle spacing. It is seen that, in all cases, the total energies of the charged dimers are greater than the sum of energies of separate fragments (separate metal ions) for all separations, indicating that they do *not* form *stable* states. However, as one moves from Ni towards the middle of the series, the energy curve shows the building of a barrier to the fragmentation. Similar trends are observed for elements in the $4d$ and $5d$ series.

In Fig. 2, we plot the activation barriers and the energies of dissociation (defined as the difference in the energies between separated ions and that at the metastable minimum where applicable) for $3d$ elements. Note that there is no activation barrier against spontaneous fragmentation for elements with d^9 (Ni) and d^8 (Co) atomic configurations. The barriers increase as one approaches the middle of the series, peaking at elements with d^5 configuration (Cr, Mo, and W). The barriers then begin to decrease for elements to the left of Cr (Mo, W) as the d occupancy decreases. The dissociation energy shows the opposite trend. The above systematic trend can be understood in a simply bonding-antibonding picture. For example, in Ni_2^{++} there are sixteen d electrons out of which ten occupy the bonding and six the antibonding orbitals. Since antibonding character leads to the destabilization of a system, this effect combined with the Coulomb repulsion between two positive ions make N_2^{++} unstable. In Co_2^{++}, there are two fewer electrons in the antibonding state; consequently, the appearance of a hump in the interaction potential in Fig. 1. This signals the onset of a barrier against fragmentation which becomes a reality in Fe_2^{++} as two more electrons are removed from the antibonding orbit. In Cr_2^{++}, which exhibits the maximum metastability, all the eight d electrons are in the bonding state. Two additional electrons from the bonding state are missing as one proceeds successively from Cr_2^{++} to V_2^{++} to Ti_2^{++}. Since removal of bonding electrons favors an unstable behavior, the barrier for Ti_2^{++} (V_2^{++}) is less than that in V_2^{++} (Cr_2^{++}). This provides convincing evidence that the electronic structure plays a dominant role in the stability of charged dimers.

In the tight-binding calculations, the effects of spin have been ignored. In neutral clusters of Cr_2, for example, the role of spins was found to be important in binding.[8] However, for doubly charged clusters the role of spins is expected to be a subtle effect in view of the large Coulomb repulsion energy. This view is further substantiated later in this paper by explicit comparison between tight-binding and *ab initio* LCAO-MO calculations in Ni_2^{++} and Mo_2^{++}. In Mn, the magnetic interaction also plays a dominant role. Since we were unable to obtain accurate tight-binding parameters for Mn, no calculations of Mn_2^{++} are presented. The dashed lines in Fig. 2, therefore, reflect the absence of any information for Mn.

In Fig. 3, we compare the total energies as functions of distance for Cr_2^{++}, Mo_2^{++}, and W_2^{++} which belong to $3d$, $4d$, and $5d$ series, respectively. It is interesting to note that the deepest potential well exists for Mo_2^{++}. Furthermore, the total energy of Mo_2^{++} does not become less than its metastable minimum until the Mo ions are at least 20 a.u. apart.

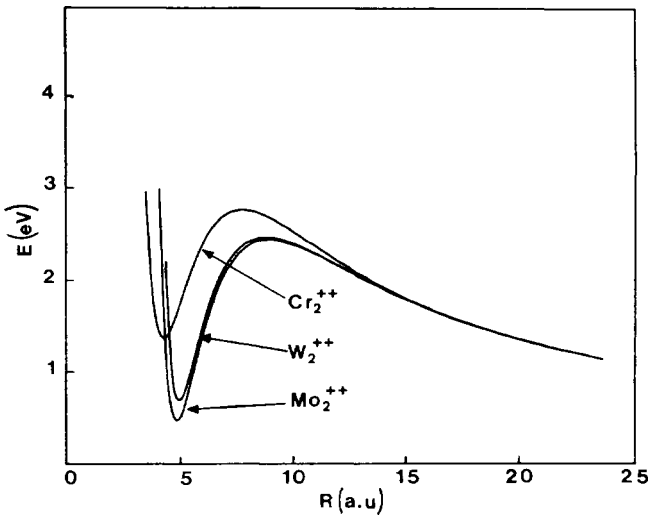

FIG. 3. Interaction energies of Cr_2^{++}, Mo_2^{++}, and W_2^{++} as functions of interparticle separation.

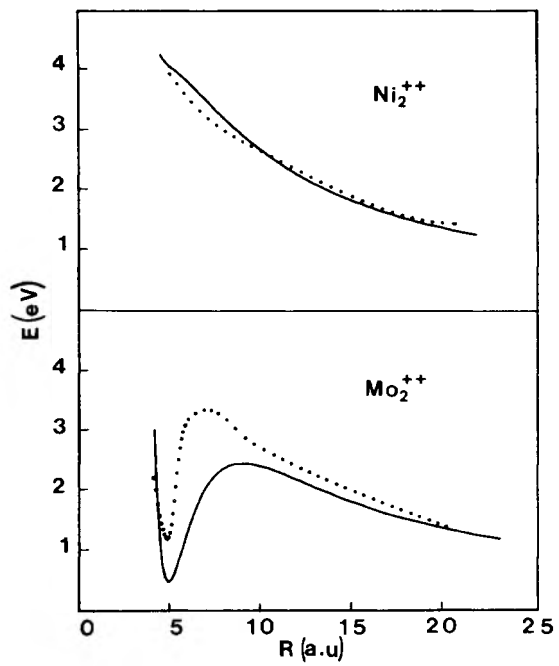

FIG. 4. Binding energy of Mo_2^{++} and Ni_2^{++} as functions of interparticle spacing based on tight-binding (continuous curve) and *ab initio* (dotted curve) techniques.

This unusual feature leads to a very small probability for fragmentation of Mo_2^{++}. We have calculated this probability using the WKB approximation. In this approximation, the transmission coefficient is given by the expression[9]

$$T=\exp\left[\frac{-2}{\hbar}\int\{2m[V(r)-E]\}^{1/2}dr\right]. \quad (3)$$

Here m is the effective mass, $V(r)$ is the interaction potential, r is the distance between the atoms, and E is the energy of the molecule. Each molecule was taken in its lowest vibrational state (having zero-point energy). The lifetime is then given by

$$\tau=1/fT, \quad (4)$$

where f is the vibrational frequency of the molecule. For V_2^{++}, Cr_2^{++}, Fe_2^{++}, Nb_2^{++}, Mo_2^{++}, Ta_2^{++}, W_2^{++}, Rh_2^{++}, and Ir_2^{++} our calculations predict lifetimes greater than 10^{50} s, suggesting that these molecules, once formed in their lowest vibrational states, have exceedingly long lifetimes and, for all practical purposes, can be considered as "stable" molecules.

The validity of our conclusion, of course, solely rests on the reliability of the tight-binding approach especially since the parameters in Eq. (2) are obtained from the bulk data. To clarify this ambiguity, we have carried out *ab initio* calculations based upon LCAO-MO theory within the density-functional framework. We have chosen Ni_2^{++} and Mo_2^{++} as examples since the former is unstable while the latter is stable.

The *ab initio* studies are based on the self-consistent multipolar discrete-variational method.[10] Basically, the method involves a solution of single-particle equations within the local-density framework with numerical free-ion functions. We have used the Von Barth–Hedin form of the spin-dependent exchange-correlation potential and the free-ion functions $3s$, $3p$, $3d$, $4s$, and $4p$ for Ni and $4s$, $4p$, $4d$, $5s$, and $5p$ for Mo as basic sets. The deep-level core functions are frozen. We found that such a freezing does not affect either the one-electron eigenvalues or the binding energy. Further, the above ionic basis sets are augmented with overlapping multipolar functions with $l\leq 2$ for a more accurate representation of the charge distribution.

In Fig. 4, we compare the total energies of Ni_2^{++} and Mo_2^{++} obtained in the LCAO-MO and tight-binding methods. Note that the *ab initio* calculations produce the same behavior as seen in Fig. 1. This comparison gives confidence in the predictions of the tight-binding calculations. By treating the molecules in the reduced $C_{\infty v}$ symmetry, we obtain an antiferromagnetic ground state with $M_s=0$ for Mo_2^{++}. As the interatomic distance shrinks from 7 a.u. (the location of the potential barrier peak) to 4.7 a.u. (the location of the metastable minimum), the spin moment on each site decreases continuously from its free-ion–like value to $3.5\mu_B$. The dissociation barrier, $\Delta=2.15$ eV, and metastable equilibrium bond length, $R_e=4.7$ a.u., are in good agreement with the tight-binding (TB) results ($\Delta=2.0$ eV, $R_e=4.65$ a.u.). This large activation barrier indicates that the Mo_2^{++} has to be raised to an energy of about

2.0 eV before it can dissociate into two separate Mo^+ ions. This is consistent with Tsong's[4] low-temperature field-evaporation experiment where he observed that Mo_2^{++} has a minimum binding energy of 1.20 eV. The discrepancy in the two curves in the 4.5–9.0-a.u. region may be attributed to the fact that (a) the tight-binding approach neglects spin polarization and (b) the self-consistent configuration of the Mo^+ ions in the local spin-density approach is closer to $4d^5 5s^0$, while in the TB calculations, two d electrons (not s electrons) are removed to form Mo_2^{++}. The presence of the more diffuse s electrons allows for greater overlap and shifts the TB energy curve below the local spin-density curve. In Ni_2^{++} both these effects are greatly diminished and the local spin-density and TB potential surfaces are closer at all interionic distances.

A further check on the reliability of the tight-binding results can also be made by comparison of the calculated binding energies and bond lengths of neutral dimers with experiment. For Ni_2 and Mo_2 the calculated binding energies and bond lengths in the tight-binding scheme are 1.2 eV, 2.4 Å, and 5.2 eV, 2.5 Å, respectively. These compare well with experimental values[11] of 1.2 eV, 2.2 Å (for Ni_2) and 4.2 eV, 1.94 Å (for Mo_2). The theoretical value[8] using the self-consistent-field–LCAO method in Mo_2 is in much better agreement with experiment. It is worth pointing out that Tomanek *et al.*[12] have calculated binding energies of neural dimers of Ni, Cu, Pt, Ag, Au, and Rh using the tight-binding approximation. Their results are in very good agreement with experiment. Thus, we believe that the trends exhibited in Fig. 1 are independent of the approximations made in our calculation.

In conclusion, we have carried out a systematic study of the stability of doubly charged transition-metal dimers. The occupancy of the d-electron levels is found to play a dominant role in the fragmentation process. While most of the doubly charged dimers are metastable, there are clusters with nearly filled d-shell that undergo spontaneous fragmentation. In some dimers, the activation barrier against spontaneous fragmentation is so large that the cluster could stay in the metastable state for, essentially, an infinitely long time. In such situations, experiments where time scales are short compared to the lifetime could misinterpret these states to be stable. Experimental verification of our predictions that clusters such as Co_2^{++} and Ni_2^{++} are unstable while doubly charged dimers of group III, IV, and V are metastable are eagerly awaited.

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