CHEMICAL BONDS AND ELECTRONIC STATES OF TRANSITION METAL CONTAINING DIATOMICS

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ABSTRACT. The present work deals with results of all electron ab initio HF-CI calculations on homonuclear transition metal dimers as well as on transition metal-group IV diatomics. The homonuclear dimers considered are those of the iron group, FeZ', CoZ', and NiZ', and of the first platinum metal triad, RuZ', RhZ', and PdZ'. The transition metal-group IV diatomics include the carbides CoC, NiC, RuC, RhC, PdC as well as the molecules PdSi and PdGe. In the homonuclear dimers, the principal bonding orbitals are the outermost $s_d$ molecular orbitals. The d electrons are partly localized and their interactions give rise to "bands" of low-lying electronic states. The d electrons, however, become increasingly important for the chemical bonds in the sequences NiZ', CoZ', FeZ' and PdZ', RhZ', RuZ'. This is revealed by increasing excess of electrons in the bonding relative to the antibonding natural orbitals. The chemical bonds in the heteronuclear dimers are apparently due to the formation of delocalized molecular orbitals involving the d orbitals of the transition metal atoms. However, while the spectra of the low-lying electronic states of the heteronuclear dimers containing the platinum metal atoms are consistent with simple molecular orbital diagrams, those of the molecules NiC and CoC are derivable by coupling of the angular momenta of the ions. Altogether our results indicate that the iron group atoms even as part of the diatomic molecules essentially retain their individuality.

1. INTRODUCTION

The transition metals have many unique properties, which are owing to the partly filled, inner d shells of the transition metal atoms. Thus, the iron group elements exhibit exceptional magnetic properties, and elements of the iron group as well as of the platinum metal triads are active as catalysts in hydrogenation processes and also in the ammonia synthesis. Furthermore, due to the partly filled d shells, the transition metal atoms are able to form stable compounds in many different oxidation states, and therefore the chemistry of these atoms is unique and very rich.
During recent years there has been a growing interest particularly in small molecular systems containing coordinatively unsaturated transition metal atoms. Thus, as is apparent from several pertinent reviews (1-3), especially the "naked" transition metal clusters have been subjects of numerous theoretical and experimental investigations. Studies of such small, well-defined systems contribute to the fundamental scientific knowledge, and this will presumably also facilitate and aid the understanding of larger transition metal containing systems.

The present paper has been devoted to the smallest possible units that contain transition metal atoms, namely the diatomic molecules. We are especially concentrating on two distinct groups of such molecules. The first group contains the homonuclear transition metal dimers composed of atoms belonging to the iron group, Fe, Co, and Ni, or to the first platinum metal triad, Ru, Rh, and Pd. The second group deals with the corresponding transition metal carbides with the exception of the FeC molecule. In addition, we have included the molecules PdSi and PdGe.

For all the molecules considered we have applied all electron ab initio Hartree-Fock (HF) and configuration interaction (CI) calculations to elucidate their electronic structures and the natures of their chemical bonds. Although the molecules all have been treated equivalently in the calculational work, our results reveal qualitative differences, especially in the spectra of the low-lying electronic states.

For the homonuclear transition metal dimers the numbers and the symmetries of the low-lying electronic states are exactly those expected when the angular momenta of the monopositive ions are coupled. However, in going from Ni2 to Co2 to Fe2, the d electrons contribute increasingly to the formation of the chemical bond. The same holds true in going from the iron group dimers to the dimers of the first platinum metal triad.

The growing importance of the d electrons for the bond formation in the homonuclear dimers shows up as excess of electrons in the bonding relative to the antibonding natural orbitals.

With respect to the transition metal carbide molecules, it has become clear that there are qualitative differences between the low-lying electronic states, as to numbers and symmetries, of the iron group carbides and those of the carbides of the first platinum metal triad. Thus, for the molecules NiC and CoC the pattern of the low-lying electronic states is recognized to arise from the coupling of the angular momenta of the monopositive transition metal ions with those of a C- ion in the 4S_u term. For the molecules RhC and RuC, on the other hand, it has been possible to rationalize the low-lying electronic states in terms of simple molecular orbital diagrams.

The PdC molecule as well as the molecules PdSi and PdGe deviate from the molecules RhC and RuC, because the Pd atom as part of these diatomics essentially retains its closed shell (4d)_{10} configuration. The low-lying electronic states in the three Pd-group IV diatomics may be rationalized by means of molecular orbital diagrams, in which the two highest lying occupied orbitals are essentially the valence s and p orbitals of the group IV atoms.

The d electrons of the transition metal atoms appear to participate considerably more to the formation of the chemical bonds in the carbide molecules than in the transition metal dimers. Thus, in the carbide