The Mendeleev periodic table of atoms is one of the most important principles in natural science. However, there is shortage of analog for molecules. Here we propose two periodic tables, one for diatomic molecules and one for triatomic molecules. The form of the molecular periodic tables is analogous to that of Mendeleev periodic table of atoms. In the table, molecules are classified and arranged by their group number $G$, which is the number of valence electrons, and the periodic number $P$, which represents the size of the molecules. The basic molecular properties, including bond length, binding energy, force constant, ionization potential, spin multiplicity, chemical reactivity, and bond angle, change periodically within the tables. The periodicities of diatomic and triatomic molecules are thus revealed. We also demonstrate that the periodicity originates from the shell-like electronic configurations of the molecules. The periodic tables not only contain free molecules, but also the “virtual” molecules present in polyatomic molecules. The periodic tables can be used to classify molecules, to predict unknown molecular properties, to understand the role of virtual molecules in polyatomic molecules, and to initiate new research fields, such as the periodicities of aromatic species, clusters, or nanoparticles. The tables should be of interest not only to scientists in a variety of disciplines, but also to undergraduates studying natural sciences.

1 Introduction

The law of atomic periodicity has long been known as the most significant rule in chemistry. Atoms are classified into different groups in a periodic table according to their electronic configurations. As a result, atomic properties change periodically with the table. Subsequent interesting questions then arise. Does periodicity of molecules exist? Is there a periodic table correlating molecular properties and electronic configurations? There have been many attempts to answer these questions over the past century.

As early as the 1930s, Clark classified diatomic molecules into different groups and periods on the basis of a “period matrix” of the component atoms [1]. However, the matrices are the simple combinations of element symbols, and lack physical insight, since at the time the molecular orbital (MO) theory had not yet been developed. In addition, the correctness of the matrices could not be tested by comparing molecular properties, as both experimental and theoretical data were in very short supply at that time [2].

Starting in the 1970s, Hefferlin composed some fragments of periodic tables, including a table of homonuclear diatomic molecules and tables of oxides and halides. Some properties of these molecules, such as transition moment [3,4], internuclear separation, ionization potential and dissociation potential have been compiled [5]. However, the patterns in the diagrams are not clear, so that the existence of molecular periodicity is uncertain. Kong [6] proposed a simple periodic table almost three decades ago. With the limited experimental data available, he suggested that molecular properties change periodically within the table. However, the molecules contained in the table were free diatomic molecules only, and it did not contain the “virtual” diatomic molecules found in polyatomic molecules. Hefferlin et al. [7,8] have classified molecules by group theory...
and correlated molecular properties by group dynamics. However the causal relationship between molecular structure and molecular properties is not explicit. Very recently, Kamal et al. indicate that for many homonuclear diatomic molecules, their calculated properties have periodic characteristics with the atomic numbers of the consisted atoms. However, their work neither summaries the feature by a periodic table, nor includes heteronuclear diatomic molecules.

Many efforts have been made to classify properties according to the atomic electronic configuration in a molecule. For example, Sidgwick [10] proposed the 18-electron rule to explain the periodicity of organometallic compounds. Haas [11] suggested a principle of element displacement, correlating the pseudohalogens with perfluoroorganic elements. Recently, Castleman et al. [12] correlated the photoelectron spectroscopy of the molecular ions TiO–, ZrO–, and WC– to those of the isoelectronic superatoms O or C obtained by shifting six positions in the atomic periodic table. However, the above correlations refer to the electronic configuration of the central atom, and not to the complete molecular orbitals. These studies therefore relate to the Mendeleev periodicity of atoms only, rather than to molecular periodicity, which we discuss in this paper.

Here we propose two general periodic tables for diatomic and triatomic molecules and their substituted derivatives. The tables are compiled in the light of simple MO theory. It is found that molecular properties change periodically within the tables.

2 Results and discussion

2.1 Classifying molecules by G and P

According to simple MO theory, the electronic configuration of the ground state has shell-like structure. Furthermore, the outermost shell or the valence shell dominates molecular properties. Molecules possessing the same number of valence electrons have similar electronic configurations, and hence have analogous properties. In other words, molecular properties are determined by the number of electrons in their outermost shell. The relationship can be expressed by a table similar to the periodic table of atoms. Firstly, molecules are classified into different groups G. G is the group number, and is defined as the number of electrons in its valence shell. G is thus equal to \( g_1 + g_2 \) or \( g_1 + g_2 + g_3 \) for diatomic or triatomic molecules, respectively, where \( g_1, g_2 \) and \( g_3 \) are the group numbers of the component atoms in the atomic periodic table. For example, the molecules NO and CO\(_2\) are classified into the group \( G = 11 \) of diatomic molecules and the group of \( G = 16 \) of triatomic molecules, respectively.

The molecular periodic table is based on MO theory, which is valid for covalent compounds but not for ionic compounds. A simple criterion, \( \Delta g \), where \( \Delta g = g_1 - g_2 \), is used to discriminate between diatomic molecules. Those molecules with \( \Delta g < 3 \), such as \( N_2 (\Delta g = 0) \) or CO (\( \Delta g = 2 \)), are considered as covalent molecules, and are included in the diatomic periodic table. For ionic molecules, on the other hand, the \( \Delta g \) values are usually larger than 3, for example BF (\( \Delta g = 4 \)). These molecules are excluded from the periodic table. In addition, hydride molecules, molecules containing transition metal atoms, and boron compounds are not included in the table.

Furthermore, molecular properties also depend upon the size of molecules. Molecular size can be expressed roughly by periodic number \( P \), which is the sum of the atomic periods of the component atoms. For diatomic molecules, \( P = p_1 + p_2 \), where \( p_1 \) and \( p_2 \) are the periods of the component atoms in the atomic table. Small diatomic molecules, like CN, N\(_2\), NO or O\(_2\), have the period number \( P = 2 + 2 = 4 \). Larger diatomic molecules like CP, P\(_2\) and PSe belong to the periods \( P = 5, 6, \) and 7, respectively. For triatomic molecules, the period number \( P \) is the sum of \( p_1, p_2 \) and \( p_3 \). The molecule CO\(_2\), for example, thus belongs to the period \( P = 6 \).

2.2 Periodic table of diatomic molecules

Having classified molecules in terms of \( G \) and \( P \), a periodic table for diatomic molecules—known as The Periodic Table of Diatomic Molecules—can be compiled and is shown in Table 1. The table consists of many blocks ranked by different \( G \) and \( P \) numbers. A representative molecule is shown in each block. A few isoelectronic molecules with the same \( G \) and \( P \) numbers are also contained in the blocks. The properties of these molecules are similar to each other. For example, the representative molecule of the block \( G = 10 \) and \( P = 4 \) is N\(_2\). However, the block also contains the isoelectronic molecule CO. The blocks are arranged in order of group number \( G \) from left to right, and period number \( P \) from top to bottom of the table. The blocks in the table are numbered sequentially in terms of \( N \), which is called the molecular number. The form of the molecular periodic table is analogous to that of Mendeleev periodic table. In the short form of the atomic periodic table, there are eight groups of atoms ranked in eight columns. Similarly, there are 16 groups of diatomic molecules listed in 16 columns in the diatomic molecular table.

The molecules listed in the periodic table not only contain free diatomic molecules, but also include “virtual diatomic molecules” contained in polyatomic molecules. Two adjacent atoms bound by a chemical bond in a polyatomic molecule can be roughly considered as a diatomic molecular entity, and are denoted “virtual diatomic molecule” in this work. Five substituted molecules, NN–H, NN–CH\(_3\), NN–NH\(_2\), NN–OH and NN–F, related to the free diatomic molecule NO, are shown in the insert in Table 1 as an example. Each NN– part in NN–H, NN–CH\(_3\), NN–NH\(_2\), NN–OH or NN–F molecules has ten valence electrons itself. In addition, the molecular orbital in the NN– vicinity can be