Molecular Multiplets of Alkaline Atoms

R. A. Hefferlin*

Department of Physics, Southern College, Collegedale, Tennessee 37315

A. V. Sepman and G. V. Zhuvikin†

Department of Physics, St. Petersburg University, St. Petersburg 198904, Russia

Received August 7, 1995⊗

Molecules formed from alkali-metal atoms are classified with the apparatus of group dynamics. The groups *SO*(1,2), *SO*(3), and *SU*(ν) are used in turn. Ionization potentials (*IP*) of diatomic combinations of Li−Cs display symmetry-breaking consistent with the group chain *SU*(ν) → *SU*(1). Known *IP* of triatomic combinations of Li−K are used to predict values of three unknown species: LiLiK, LiNaK, and LiKK have *IP* of 3.9, 3.8, and 3.6 eV, respectively.

I. INTRODUCTION

The concept of molecular multiplets was formulated[1,2] after Barut and Rumer and Fet presented a group-theoretical interpretation for the rows and columns of the periodic table of chemical elements in terms of *SO*(4,2) symmetry.[3−5] From analysis of tabulated molecular data[6] it has been shown that a well-organized collection of molecular multiplets can be treated as the periodic system of molecules.[7] Here we take a multiplet of very closely-related elements, the alkali metals and hydrogen, and elucidate the properties of multiplets of molecules formed from atoms of these elements.

II. MULTIPLETS OF *SO*(1,2) SYMMETRY

The group *SO*(1,2) is a subgroup of the conformal group symmetry of the chemical elements.[2] Generators T_0, T_-, and T_+ of *SO*(1,2) obey the relations

$$[T_0, T_\pm] = \pm T_\pm, [T_+, T_-] = -2T_0$$

The whole set of alkali metals, including hydrogen, can be treated as members of the infinite multiplet of the group. This multiplet is given in Table 1, where n is the principle quantum number of the operator T_0 and takes on values 1, 2, 3 ...

The generators of *SO*(1,2) can be expressed via bosonic creation and annihilation operators of a_n^+ and a_n of

$$T_0 = \sum_{n\geq 1} n a_n^+ a_n$$

$$T_+ = \sum_{n\geq 1} \sqrt{[(n+1)n]}\, a_{n+1}^+ a_n$$

$$T_- = \sum_{n\geq 1} \sqrt{[(n-1)n]}\, a_{n-1}^+ a_n$$

Making use of the ladder operator T_+ and the seniority vector $|HH\rangle$ of the diatomic molecules, the first (0) alkaline diatomic multiplet of *SO*(1,2) can be derived (Table 2). Other multiplets (1), (2), etc. are constructed by using a vector orthogonal to the first binomial ($n = 4$ in the table) as a new seniority vector. Molecular N-atomic multiplets of *SO*(1,2) are derived from the seniority vector $|H_N\rangle$ in a similar way. We can conclude that conformal symmetry produces infinite sets of infinite alkaline multiplets going beyond the finite set of really-existing alkaline molecules.

Table 1

n	vector
1	$\|H\rangle$
2	$\|Li\rangle$
3	$\|Na\rangle$
4	$\|K\rangle$
5	$\|Rb\rangle$
6	$\|Cs\rangle$
7	$\|Fr\rangle$
...	...

Table 2. (0) Multiplet for *SO*(1,2) Symmetry

n	vector
2	$\|HH\rangle$
3	$\|LiH\rangle$
4	$\sqrt{(2.5)}\|LiLi\rangle + \sqrt{(3/5)}\|NaH\rangle$
5	$\sqrt{(3/5)}\|NaLi\rangle + \sqrt{(2/5)}\|KH\rangle$
6	$\sqrt{(9/35)}\|NaNa\rangle + \sqrt{(16/35)}\|KLi\rangle + \sqrt{(10/35)}\|RbH\rangle$
7	$\sqrt{(6/14)}\|KNa\rangle + \sqrt{(5/14)}\|RbLi\rangle + \sqrt{(3/14)}\|CsH\rangle$
8	$\sqrt{(8/42)}\|KK\rangle + \sqrt{(15/42)}\|RbNa\rangle + \sqrt{(12/42)}\|CsLi\rangle + \sqrt{(7/42)}\ FrH\rangle$
...	...

The problem can be avoided if we realize that the set of alkalines is a finite one. Then the noncompact group *SO*(1,2) can be changed to the compact group *SO*(3).

III. MULTIPLETS OF *SO*(3) SYMMETRY

Let ν be the number of different alkali metal atoms under consideration. The group *SO*(3) can be defined with generators[2]

$$U_0 = \sum_{n=1}^{\nu} m a_n^+ a_n$$

$$U_+ = \sum_{n=1}^{\nu} \sqrt{[(u+m+1)(u-m)]}\, a_{n+1}^+ a_n$$

$$U_- = \sum_{N+1}^{\nu} \sqrt{[(u-m+1)(u+m)]}\, a_{n-1}^+ a_n$$

where $u = (\nu - 1)/2$ and $m = n - (\nu + 1)/2$. These

† Contact for technical inquiries.

⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1995.

0095-2338/96/1636-0399$12.00/0

Table 3. Atomic Multiplet $v = 7$, $u = 3$, for n = 1−7

m	vector
−3	|H⟩
−2	|Li⟩
−1	|Na⟩
0	|K⟩
+1	|Rb⟩
+2	|Cs⟩
+3	|Fr⟩

Table 4. Diatomic Alkaline Multiplets $u = 6$

m	vector
−6	|HH⟩
−5	|LiH⟩
−4	$\sqrt{(6/11)}$|LiLi⟩ + $\sqrt{(5/11)}$|NaH⟩
−3	$\sqrt{(9/11)}$|NaLi⟩ + $\sqrt{(2/11)}$|KH⟩
−2	$\sqrt{(15/33)}$|NaNa⟩ + $\sqrt{(16/33)}$|KLi⟩ + $\sqrt{(2/33)}$|RbH⟩
−1	$\sqrt{(50/66)}$|KNa⟩ + $\sqrt{(15/66)}$|RbLi⟩ + $\sqrt{(1/66)}$|CsH⟩
0	$\sqrt{(200/462)}$|KK⟩ + $\sqrt{(225/462)}$|RbNa⟩ + $\sqrt{(36/462)}$|CsLi⟩ + $\sqrt{(1/462)}$|FrH⟩
+1	$\sqrt{(50/66)}$|RbK⟩ + $\sqrt{(15/66)}$|CsNa⟩ + $\sqrt{(1/66)}$|FrLi⟩
+2	$\sqrt{(15/33)}$|RbRb⟩ + $\sqrt{(16/33)}$|CsK⟩ + $\sqrt{(2/33)}$|FrNa⟩
+3	$\sqrt{(9/11)}$|CsRb⟩ + $\sqrt{(2/11)}$|FrK⟩
+4	$\sqrt{(6/11)}$|CsCs⟩ + $\sqrt{(5/11)}$|FrRb⟩
+5	|FrCs⟩
+6	|FrFr⟩

generators obey the commutator relations

$$[U_0, U_\pm] = \pm U_\pm, [U_+, U_-] = 2U_0$$

The quantum number u defines the type of the irreducible representation[8] of the group $SO(3)$. The $SO(3)$ multiplet of alkaline metal atoms, including hydrogen, is given in Table 3.

Diatomic multiplets of $SO(3)$ can be derived from the vector |HH⟩ with the aid of the ladder operator U_+ and the identification of orthogonal seniority vectors. These multiplets correspond to the values $u = 6, 4, 2, 0$. The diatomic multiplet $u = 6$ is given in Table 4.

From the comparison of Tables 2 and 4 one can conclude that largest of the amplitudes in the equivalent linear combinations of molecular states is usually equal to or larger for $SO(3)$ multiplets than for $SO(1,2)$ multiplets.

Both $SO(1,2)$ and $SO(3)$ groups can be treated as subgroups of the large group G, the group of general linear transformations of the atomic space. This group is generated by the whole set of operators $a_i^+ a_j$. Linear spaces of N-atomic molecules are irreducible under this group for any given $N = 1, 2, ...$ and form large molecular multiplets. These multiplets coincide with unitary multiplets of groups $SU(\nu)$ if the initial atomic multiplet is finite.[9]

IV. MULTIPLETS OF $SU(\nu)$ SYMMETRY[10]

Unitary $SU(\nu)$ multiplets are irreducible for any given N in the bosonic representation.[2] Elements of $SU(\nu)$ multiplets are eigenvectors of operators $a_i^+ a_i$ for $i = 1$ to ν. Symmetry breaking for the group $SU(\nu)$ can be taken into account in the group chain

$$SU(\nu) \rightarrow SO(3)$$

where properties of the $SO(3)$ group were described in section III, or in the chain

$$SU(\nu) \rightarrow SU(\nu-1) \rightarrow ... \rightarrow SU(1)$$

Table 5

atom	*IP*, eV	*EA*, eV
Li	5.3918	0.618
Na	5.13912	0.5479
K	4.34070	0.5015
Rb	4.17717	0.4859
Cs	3.89394	0.4716

Table 6

molecules	*IP*, eV
LiLiLi	4.17[a]
LiLiNa	4.1[b]
LiNaNa	4.07[b]
NaNaNa	3.97[c]
LiLiK	?
LiNaK	?
NaNaK	3.7[c]
LiKK	?
NaKK	3.6[c]
KK	3.4[c]

[a] Reference 12. [b] Reference 13. [c] Reference 14.

We now consider that this last chain corresponds to the ordering of the chemical elements in accordance with the way their properties change.[11] As an example, the ionization potential *IP* and electron affinity *AE* are given in Table 5 for alkali metals Li, Na, K, Rb, and Cs. The monotonic change in the listed values can be interpreted as $SU(5)$ symmetry-breaking. If we choose only the chemical elements Li, Na, and K as the atomic multiplet $SU(3)$, then the multiplet of the same atoms' triatomic molecules is given in Table 6. *IP* are given for these triatomic species.[12−14] Making use of linear interpolation, it was possible to predict the unknown *IP* 3.9, 3.8, and 3.6 eV for LiLiK, LiNaK, and LiKK, respectively.

Symmetry breaking $SU(\nu) \rightarrow SU(1)$, with $\nu = 3$ or 4, has been analyzed for diatomic molecules also. *IP* for diatomic molecules is well-fitted with the "mass" formula

$$IP = A + Bm + Cm^3$$

where the coefficients A, B, and C decrease as 1:0.1:0.01 approximately. The fit is worse if other chemical elements, for example, hydrogen, are included in the alkaline multiplet.

REFERENCES AND NOTES

(1) Zhuvikin G. V.; Hefferlin, R. The Periodic System of Diatomic Molecules: A Group-Theoretical Approach. *Vestnik Leningradskovo Universiteta* (Russian) **1983**, *16*, 10−16.
(2) Zhuvikin, G. V.; Hefferlin, R. Symmetry Principles for Periodic Systems of Molecules; Southern College: Tennessee, 1994; Joint Report of the Physics Departments of Southern College and St. Petersburg University (JR-PHYS-SC/SPBU, widely distributed to academic and laboratory libraries) #1, pp 1−84.
(3) Rumer, Y. B.; Fet, A. I. The Group Spin (4) and the Mendeleev System. *Theor. Math. Physics* **1972**, *9*, 1081.
(4) Barut, A. O. In Structure of Matter (Proceedings of the Rutherford Centenary Symposium 1971); Wybourne, B., Ed.; University of Canterbury Press: Canterbury, 1972; pp 126−136.
(5) Fet, A. I. Conformal Symmetry of the Chemical Elements. *Theor. Math. Physics* **1975**, *22*, 227.
(6) Carlson, C. M.; Hefferlin, R. A.; Zhuvikin, G. V. Analysis of Group Theoretical Periodic Systems of Molecules Using Tabulated Data; Southern College: Tennessee, 1995; JR-PHYS-SC/SPBU #2, pp 1−32.
(7) Carlson, C. M.; Cavanaugh, R. J.; Hefferlin, R. A. Periodic systems of Molecule States from the Boson Group Dynamics of $SO(3)\times SU(2)_s$. *J. Chem. Inf. Comput. Sci.* In press.
(8) Lowe, J. P. Quantum Chemistry; Academic Press: New York, 1978; Chapter 13.

(9) Wigner, E. P. Group Theory and its Applications to the Quantum Mechanics of Atomic Spectra; Academic Press: New York, 1972; Chapters 14 and 15.
(10) Lichtenberg, D. B. Unitary Symmetry and Elementary Particles; Academic Press: New York, 1978; Chapters 1, 3−6.
(11) Komarov, V. S.; Lyakhovsky, V. D. Unitary Symmetry of Molecules. *Sov. J. Chem. Phys.* **1990**, *5*, 1501−1519.
(12) Knight, W. D.; Clemenger, K.; de Heer, W. A.; Sauders, W. A.; Chou, M.; Coher, M. L. *Phys. Rev. Lett.* **1984**, *52*, 2141−2143.
(13) Kappes, M. M.; Schumacher, E. *Surf. Sci.* **1985**, *156*, Part 1, 1−7.
(14) Metal Clusters; Moskovits, M., Ed. Wiley Interscience Publications: New York, 1986; Table 6.3.

CI950073F