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Complete SO(3)xSU(2) and SO(2,1) Periodic Systems for Diatomic and Triatomic Molecules

Chris M. Carlson
Physics Department
Southern College of SDA
Collegedale, TN 37315

Abstract

The principles of group theory as applied to periodic systems are reviewed. Complete sets of possible multiplets of state vectors are tabulated for $N = 2$ and $N = 3$ in both $SO(3)xSU(2)$ and $SO(2,1)$ symmetry. Expectation values of ΔH_a, $I.P.$, S_{298}^0, and ω_e for some of these state vectors are plotted on the principle axes of the two groups of interest. The consistent regularity of these plots gives validity to this theory. The structures of the periodic systems for $N = 2$ and $N = 3$ in both $SO(3)xSU(2)$ and $SO(2,1)$ are then described and shown in 3-D figures.

I. Introduction.

Ever since Mendeleev proposed the periodic system of the elements in 1869, the tantalizing prospect of extending its principles to molecules lay before physicists and chemists alike. This goal was realized in 1979 when Hefferlin et al completed a diatomic molecular periodic system which could be generalized to triatomic and larger molecules.[1] Hefferlin used entirely empirical methods in obtaining this system and a subsequent system for triatomic molecules.[2] Empirical methods become increasingly difficult as higher order periodic systems are constructed due to lack of data for any significant number of molecules of a given N-atomic species. Thus, a more theoretical approach is necessary.

The beginning of such an approach in the early twentieth century was the demonstration by Fock that the orthogonal group $O(4)$ describes the structure of energy levels in hydrogen.[3] Inspired by this result, it was shown in 1972, independently by Rumer and Fet, and by Barut, that $O(4)$ can also render a classification scheme for the atoms. Fet went on to demonstrate that the cartesian product of the special orthogonal group $SO(4,2)$ with the special unitary group $SU(2)$ describes the complete periodic system of atoms, including the Madelung rules for neutral atoms.[4] If a second $SU(2)$ group is included, the period doubling of the Mendeleev chart can be closely, although not exactly, described.

In 1983, Zhuvikin and Hefferlin proposed that group theory could be applied to N-atomic molecular periodic systems by means of the repeated multiplication of the atomic symmetry group with itself.[5] This lead to N-atomic molecular periodic systems which are $2N$-dimensional. Then, the theory was revised to include the repeated multiplication of bases of irreducible representations instead of groups, thereby allowing the dimensionality of the periodic system to remain constant for all N-atomic molecules. The idea was revised further

in 1992 when Zhuvikin and Hefferlin proposed that since a given molecule may contain more than one identical atom, bosonic symmetry must be employed.[6]

This paper is a effort to substantiate the validity of this theory. The group theoretical constructs of Zhuvikin and Hefferlin are summarized, and the results of the theory are explained. These results are the complete group-theoretical periodic systems for both diatomic and triatomic molecules, each in terms of two different symmetry groups, namely $SO(3) \times SU(2)$ and $SO(2,1)$. Graphs which demonstrate the clearly periodic nature of the systems are included along with descriptions of the structure of each individual periodic system.

II. Theory

Section 2.1. Group theory applied to the periodic chart of the atoms.

In order to apply the principles of group theory, the atoms are assumed to be particles which have an inherent, internal symmetry described by a group[6] G. These particles can be transformed into one another by the elements[6] of G. Fet showed that choosing G to be the group $SO(4,2) \times SU(2)$, or one of its subgroups from one of three group chains, results in descriptions (in the form of bases for irreducible representations) of portions of the periodic chart of the atoms.[4] These basis states for irreducible representations (or multiplets) exist in a Hilbert representation space $\mathcal{H}(1)$. The orthonormal basis set of vectors which span $\mathcal{H}(1)$ consists of the set of atoms together with a vacuum state.[6] Furthermore, these basis vectors are distinguished by at most four chemical quantum numbers, the specific combination being determined by the subgroup G; They are the chemical principle quantum number n, the chemical angular momentum quantum number ℓ, the z-component of the chemical angular momentum quantum number m, and the z-component of the chemical spin μ. The group G describes the possible values of its associated quantum numbers, within the usual quantum mechanical constraints imposed by the given values of the other quantum numbers.

Atomic multiplets for several choices of G from one particular subgroup chain of $SO(4,2) \times SU(2)$ are now described. A multiplet using the subgroup $SO(3)$ describes all possible values of the m quantum number for artificial choices of n, ℓ, and μ, i.e., m ranges from $-\ell$ to $+\ell$. One such multiplet is {B, N, F} which has $n = 2$, $\ell = 1$, $\mu = -1/2$, and allows m the values -1, 0, 1 (see Fig. 1.). Using $SU(2)$ symmetry, a multiplet is described by specifying n, ℓ, and m, then letting μ be -1/2 or +1/2, e.g., {H, He}. $SO(4)$ multiplets are described by selecting n, and μ, then letting ℓ range from $-(n-1)$ to $+(n-1)$ and letting m

l	m	n=1 -1/2	1/2	n=2 -1/2	1/2	n=3 -1/2	1/2	n=4 -1/2	1/2	n=5 -1/2	1/2	n=6 -1/2	1/2	n=7 -1/2	1/2
$l=0$	$m=0$	H	He	Li	Be	Na	Mg	K	Ca	Rb	Sr	Cs	Ba	Fr	Ra
$l=1$	$m=-1$			B	C	Al	Si	Ga	Ge	In	Sn	Tl	Pb	--	--
	$m=0$			N	O	P	S	As	Se	Sb	Te	Bi	Po	--	--
	$m=1$			F	Ne	Cl	Ar	Br	Kr	I	Xe	At	Rn	--	--
$l=2$	$m=-2$					Sc	Ti	Y	Zr	Lu	Hf	Lr	Ku	--	--
	$m=-1$					V	Cr	Nb	Mo	Ta	W	--	--	--	--
	$m=0$					Mn	Fe	Tc	Ru	Re	Os	--	--	--	--
	$m=1$					Co	Ni	Rh	Pd	Ir	Pt	--	--	--	--
	$m=2$					Cu	Zn	Ag	Cd	Au	Hg	--	--	--	--
$l=3$	$m=-3$							La	Ce	Ac	Th	--	--	--	--
	$m=-2$							Pr	Nd	Pa	U	--	--	--	--
	$m=-1$							Pm	Sm	Np	Pu	--	--	--	--
	$m=0$							Eu	Gd	Am	Cm	--	--	--	--
	$m=1$							Tb	Dy	Bk	Cf	--	--	--	--
	$m=2$							Ho	Er	Es	Fm	--	--	--	--
	$m=3$							Tm	Yb	Md	No	--	--	--	--

Fig. 1. $\mathcal{H}(1)$ for group chain $SO(4,2) \times SU(2) \supset SO(4) \times SU(2) \supset SO(3) \times SU(2)$.

range from $-\ell$ to $+\ell$ for each value of ℓ. An example of an $SO(4)$ multiplet is {Na, Al, P, Cl, Sc, V, Mn, Co, Cu}. A slightly more complicated subgroup is $SO(3) \times SU(2)$ for which multiplets are described by varying m and μ for given n and ℓ, e.g., {Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd}. The preceding subgroups are all taken from one group chain[6] of $SO(4,2) \times SU(2)$. This chain is given by Eq. (1):

$$SO(4,2) \times SU(2) \supset SO(4) \times SU(2) \supset SO(3) \times SU(2) \supset SO(2) \times SU(2) \quad (1)$$

Only one subgroup is examined from a second chain,[6] which is given by Eq. (2):

$$SO(4,2) \times SU(2) \supset SO(2,1) \times SO(3) \times SU(2) \supset SO(2,1) \tag{2}$$

This particular symmetry group is $SO(2,1)$. Multiplets in $SO(2,1)$ are defined by varying n for given values of ℓ, m, and μ. A typical multiplet is {H, Li, Na, K, Rb, Cs, Fr, ...} (see Fig. 2.).

ℓ	m	μ	n=1	n=2	n=3	n=4	n=5	n=6	n=7	
l=0	m=0	mu=-1/2	H	Li	Na	K	Rb	Cs	Fr	SO(2,1)
		mu=1/2	He	Be	Mg	Ca	Sr	Ba	Ra	
	m=-1	mu=-1/2		B	Al	Ga	In	Tl	-	
		mu=1/2		C	Si	Ge	Sn	Pb	-	
l=1	m=0	mu=-1/2		N	P	As	Sb	Bi	-	
		mu=1/2		O	S	Se	Te	Po	-	
	m=1	mu=-1/2		F	Cl	Br	I	At	-	SO(2,1)
		mu=1/2		Ne	Ar	Kr	Xe	Rn	-	
	m=-2	mu=-1/2			Sc	Y	Lu	Lr	-	
		mu=1/2			Ti	Zr	Hf	Ku	-	
	m=-1	mu=-1/2			V	Nb	Ta	-	-	
		mu=1/2			Cr	Mo	W	-	-	
l=2	m=0	mu=-1/2			Mn	Tc	Re	-	-	SO(2,1)xSO(3)xSU(2)
		mu=1/2			Fe	Ru	Os	-	-	
	m=1	mu=-1/2			Co	Rh	Ir	-	-	
		mu=1/2			Ni	Pd	Pt	-	-	
	m=2	mu=-1/2			Cu	Ag	Au	-	-	
		mu=1/2			Zn	Cd	Hg	-	-	
	m=-3	mu=-1/2				La	Ac	-	-	
		mu=1/2				Ce	Th	-	-	
	m=-2	mu=-1/2				Pr	Pa	-	-	
		mu=1/2				Nd	U	-	-	SO(2,1)
	m=-1	mu=-1/2				Pm	Np	-	-	
		mu=1/2				Sm	Pu	-	-	
l=3	m=0	mu=-1/2				Eu	Am	-	-	
		mu=1/2				Gd	Cm	-	-	
	m=1	mu=-1/2				Tb	Bk	-	-	
		mu=1/2				Dy	Cf	-	-	
	m=2	mu=-1/2				Ho	Es	-	-	
		mu=1/2				Er	Fm	-	-	
	m=3	mu=-1/2				Tm	Md	-	-	
		mu=1/2				Yb	No	-	-	

Fig. 2. $\mathcal{H}(1)$ for group chain $SO(4,2) \times SU(2) \supset SO(2,1) \times SO(3) \times SU(2) \supset SO(2,1)$.

Notice that there are infinitely many multiplets in $SO(2,1)$, each of which is infinite in size. This results from the noncompact nature of the group $SO(2,1)$ which implies that there are infinitely many elements. A more detailed, theoretical development of these concepts follows.

Section 2.2. Basis vectors for the Hilbert representation spaces $\mathcal{H}(1)$, $\mathcal{H}(2)$, and $\mathcal{H}(3)$.

Let $\{a_1, a_2, a_3, ..., a_n\}$ be the set of atoms. Then the basis set[6] for $\mathcal{H}(1)$ is $\{|a_1>, |a_2>, |a_3>,..., |a_n>, |0>\}$, where $|0>$ is the so-called vacuum state. This vacuum state is defined to be normalized.[7]

$$<0|0> = 1 \tag{3}$$

The atomic basis vectors are created by means of creation operators which operate on the vacuum state.[6] Also, annihilation operators acting on the vacuum state give the scalar zero.[7]

$$|a_i> = b_{a_i}^+ |0>$$
$$b_{a_i}|0> = 0 \tag{4}$$

Moreover, since there can be more than one atom of a particular species in a given N-atomic molecule, these creation and annihilation operators must conform to bosonic symmetry,[6] i.e., they must obey these commutation relations:

$$[b_{a_i}^+, b_{a_j}^+] = 0$$
$$[b_{a_i}, b_{a_j}] = 0 \tag{5}$$
$$[b_{a_i}, b_{a_j}^+] = \delta_{ij}$$

The result of the annihilation operator acting on a basis vector is the vacuum state if the annihilation operator corresponds to the given basis vector, otherwise it is the scalar zero. This can be shown by means of the third commutator of Eq. (5).

$$b_{a_i}|a_j> \, = \, b_{a_i}b_{a_j}^+|0> \, = \, \delta_{ij}|0> + b_{a_j}^+b_{a_i}|0> \, = \, \delta_{ij}|0> + 0 \, = \, \delta_{ij}|0> \tag{6}$$

Also, this same commutator demonstrates the orthonormality of the basis vectors.

$$<a_i|a_j> \, = \, <0|b_{a_i}b_{a_j}^+|0> \, \doteq \, <0|\delta_{ij}|0> + <0|b_{a_j}^+b_{a_i}|0> \, = \, \delta_{ij}<0|0> \, = \, \delta_{ij} \tag{7}$$

In a similar manner, the basis vectors for the diatomic representation space $\mathcal{H}(2)$ and the triatomic representation space $\mathcal{H}(3)$ are defined using the atomic creation operators.[8]

$$|a_i a_j> \, = \, b_{a_i}^+ b_{a_j}^+|0>$$

$$|a_i a_j a_k> \, = \, b_{a_i}^+ b_{a_j}^+ b_{a_k}^+|0> \tag{8}$$

The orthonormality of these vectors does not come about as easily as it does for the atoms, but a similar method (the repeated use of the commutators) is used to determine the inner product of a given vector with itself. This inner product is the square of the norm. The normalization coefficient is clearly the reciprocal of the norm. The general expressions of these concepts for diatomic and triatomic basis vectors are given in Eq. (9).

$$|a_i a_j|^2 \, = \, <a_i a_j|a_i a_j> \, = \, 1 + \delta_{ij}$$

$$|a_i a_j a_k|^2 \, = \, <a_i a_j a_k|a_i a_j a_k> \, = \, 1 + \delta_{ij} + \delta_{ik} + \delta_{jk} + 2\delta_{ij}\delta_{jk} \tag{9}$$

For those state vectors that have norm greater than one, the normalization coefficient is placed inside the Dirac "ket" notation, e.g., $|1/\sqrt{2}\ BB>$.

Section 2.3. Ladder operators for *SO(3)*x*SU(2)* and *SO(2,1)*.

Ladder operators are the bosonic representation of the differential generators of a given subgroup G of $SO(4,2)$x$SU(2)$. There are two requirements for a valid bosonic representation of a symmetry group G. The first is that the operators exhibit the same closed set of commutation relations as some set of linear combinations of the differential generators. This means that the differential generators and the bosonic operators define abstractly identical Lie algebras. The second stipulation is that, when the one-parameter Lie group is formed from these bosonic operators, the parameter has the same range as that allowed by the Lie group formed from the differential generators.[9] The group $SO(3)$x$SU(2)$ has six ladder operators, three corresponding to $SO(3)$ and three corresponding to $SU(2)$.

The three operators of $SO(3)$ transmute state vectors by changing the value of the m quantum number. In bosonic representation, they have the following form:[8]

$$L_+ = \sum_{m=-\ell}^{+\ell} \sqrt{(\ell+m+1)(\ell-m)}\, b^+_{m+1} b_m$$

$$L_- = \sum_{m=-\ell}^{+\ell} \sqrt{(\ell-m+1)(\ell+m)}\, b^+_{m-1} b_m \qquad (10)$$

$$L_0 = \sum_{m=-\ell}^{+\ell} m b^+_m b_m$$

In these equations, the creation operator b^+_{m+1}, for example, refers to the atom having the same values of the quantum numbers n, ℓ, and μ as the vector on which it is currently operating, except that m is one unit larger. In other words, if L_+ were acting on $|B>$, then b^+_{m+1} would be the creation operator for $|N>$. The L_+ operator transforms a given state vector into a vector with the next highest possible value of m. Analogously, L_- transforms

vectors to ones with the next lowest possible value of m. L_0 operating on a vector returns the value of m times the current vector. Here are some examples:

$$L_+|B> = \sqrt{2}|N>$$

$$L_+|F> = 0$$

$$L_-|F> = \sqrt{2}|N>$$ (11)

$$L_0|B> = -1|B>$$

The ladder operators of $SU(2)$ change the values of the μ in the same sense that those for $SO(3)$ change m. They have the following form:[8]

$$S_+ = \sum_{\mu=-s}^{+s} \sqrt{(\tfrac{3}{2}+\mu)(\tfrac{1}{2}-\mu)}\, b_{\mu+1}^+ b_\mu$$

$$S_- = \sum_{\mu=-s}^{+s} \sqrt{(\tfrac{3}{2}-\mu)(\tfrac{1}{2}+\mu)}\, b_{\mu-1}^+ b_\mu$$ (12)

$$S_0 = \sum_{\mu=-s}^{+s} \mu\, b_{\mu}\cdot b_\mu$$

In these equations, s is the chemical spin quantum number, i.e., $s = \mu_{max}$. The operations of S_+, S_-, and S_0 are analogous to those of L_+, L_-, and L_0, as seen in these examples:

$$S_+|H> = |He>$$

$$S_-|He> = |H>$$ (13)

$$S_-|H> = 0$$

The commutation relations for $SO(3)$ and $SU(2)$ are identical. Therefore, only those for L_+, L_-, and L_0 are given in Eq. (14).

$$[L_0, L_+] = L_+$$

$$[L_0, L_-] = -L_- \tag{14}$$

$$[L_+, L_-] = 2L_0$$

The difference between the representations of these two groups is in the range of the Lie group parameter. The Lie group corresponding to $SO(3)$ allows the parameter to range from $-\pi$ to π, while that for $SU(2)$ allows a range from -2π to 2π.

The operators corresponding to the $SO(2,1)$ subgroup transform vectors by increasing the value of n. Their form[10] is given by Eq. (15):

$$\Gamma_+ = \sum_{n=1}^{\infty} \sqrt{(n+\ell+1)(n-\ell)}\, b_{n+1}^+ b_n$$

$$\Gamma_- = \sum_{n=1}^{\infty} \sqrt{(n-\ell-1)(n+\ell)}\, b_{n-1}^+ b_n \tag{15}$$

$$\Gamma_0 = \sum_{n=1}^{\infty} n b_n^+ b_n$$

These are analogous to the L and S operators except that Γ_+ will never return a zero result, since n, in principle, is unbounded. As stated in section 2.1, this unbounded characteristic of n corresponds to the noncompact nature of $SO(2,1)$. Now, here are some examples:

$$\Gamma_+|H> = \sqrt{2}|Li>$$

$$\Gamma_-|Al> = \sqrt{10}|B> \tag{16}$$

$$\Gamma_0|Na> = 3|Na>$$

The commutation relations for these operators are given in Eq. (17):

$$[\Gamma_0,\Gamma_+] = \Gamma_+$$

$$[\Gamma_0,\Gamma_-] = -\Gamma_- \tag{17}$$

$$[\Gamma_+,\Gamma_-] = -2\Gamma_0$$

The range on the Lie group parameter for the $SO(2,1)$ operators is $-\pi$ to $+\pi$.

The coefficients generated by the raising and lowering operators in this and the previous examples do not have much significance when operating only on atoms, i.e., they are lost when the necessary normalization is done. Their significance arises when operating on diatomic and triatomic molecules. As will be shown, the operations in these cases often result in state vectors which consist of linear combinations of basis vectors. Thus, the normalization coefficient is the inverse of the sum of the norms of the component vectors. Therefore, the individual coefficient for each component is not lost.

Section 2.4. Generation of multiplets using ladder operators.

The specifics of this discussion are limited only to the groups of immediate interest, namely $SO(3)xSU(2)$ and $SO(2,1)$, but the principles set forth apply in general, i.e., they apply to any symmetry group and to the space $\mathcal{H}(N)$ for any value of N. The Hilbert space $\mathcal{H}(N)$ is generally reducible with respect to the symmetry group G. Bases for irreducible

representations (or multiplets) of $\mathcal{H}(N)$ corresponding to G are generated by repeated operation of the ladder operator(s) of G on a chemical seniority vector until a zero result is obtained.[8] By definition, a chemical seniority vector is a state vector which returns the zero result when acted upon once by either the lowering operator(s) or the raising operator(s) of the group. For example, the atomic state vector $|B>$ in $SO(3)xSU(2)$ is a legitimate chemical seniority vector, since $L_-|B> = S_-|B> = 0$. Some results of this process for the atomic case have already been introduced in a qualitative manner in section 2.1.

First, consider $SO(3)xSU(2)$. Operating on the diatomic chemical seniority vector $|1/\sqrt{2}\ BB>$, L_+ increases m from -2 to -1 and produces (after normalization) the vector $|BN>$. Repeating this process results in the vectors $1/\sqrt{3}\{|BF> + \sqrt{2}|1/\sqrt{2}\ NN>\}$, $|NF>$, and $|1/\sqrt{2}\ FF>$, which have $m = 0$, $m = 1$, and $m = 2$ respectively. Note that $L_+|1/\sqrt{2}\ FF> = 0$, which signifies the end of L_+ operations. Now consider the role of S_+, which operates on each of the above mentioned state vectors generated by L_+. This generates the multiplet shown in Fig. 3. (The customary Dirac notation has been eliminated for convenience.) The multiplet has chemical spin multiplicity $S = 3$ and chemical angular momentum $\ell = 2$. Thus, using spectroscopic notation, the multiplet is denoted as ^3D. Also, we can construct a state vector orthogonal to the $1/\sqrt{3}\{|BF> + \sqrt{2}|1/\sqrt{2}\ NN>\}$ vector, which is located at $m = 0$, $\mu = -1$ in ^3D. This orthogonal vector is $1/\sqrt{6}\{2|BF> - \sqrt{2}|1/\sqrt{2}\ NN>\}$. The orthogonality is verified by calculating the inner product of the vectors including the proper norms values for each component. This orthogonal vector is a valid chemical seniority vector which leads to another multiplet, specifically a ^3S. Similarly, there exists a vector orthogonal to $1/\sqrt{2}\{|BO>+|CN>\}$ which is a chemical seniority vector for a ^1P multiplet. For the chemical seniority vector $|1/\sqrt{2}\ BB>$, therefore, the

	mu=-1	mu=0	mu=1
m=-2	sqrt(1/2) BB	BC	sqrt(1/2) CC
m=-1	BN	sqrt(1/2){ BO + CN }	CO
m=0	sqrt(1/3){ BF + NN }	sqrt(1/6){ BNe + 2 NO + CF }	sqrt(1/3){ CNe + OO }
m=1	NF	sqrt(1/2){ NNe + OF }	ONe
m=2	sqrt(1/2) FF	FNe	sqrt(1/2) NeNe

Fig. 3. ^3D multiplet for chemical seniority vector $|1/\sqrt{2}\ BB>$ for $SO(3)\mathrm{x}SU(2)$.

decomposition of the representation space $\mathcal{H}(2)$ has been shown to be the direct sum of three orthogonal multiplets.

$$\mathcal{H}(2) = {}^3D \oplus {}^3S \oplus {}^1P \tag{18}$$

The same process is applied to triatomic chemical seniority vectors such as $|1/\sqrt{6}$ BBB>, resulting in the ^4F multiplet given in Fig. 4.

mu=-3/2	mu=-1/2	mu=1/2	mu=3/2
sqrt(1/6) BBB	sqrt(1/2) BBC	sqrt(1/2) BCC	sqrt(1/6) CCC
sqrt(1/2) BBN	sqrt(1/6){ BBO + 2 BCN }	sqrt(1/6){ 2 BCO + CCN }	sqrt(1/2) CCO
sqrt(1/10){ BBF + 2 BNN }	sqrt(1/30){ BBNe + 2 BCF + 4 BNO + 2 CNN }	sqrt(1/30){ 2 BCNe + CCF + 2 BOO + 4 CNO }	sqrt(1/10){ CCNe + 2 COO }
sqrt(1/15){ 3 BNF + NNN }	sqrt(1/5){ BNNe + BOF + CNF + NNO }	sqrt(1/5){ BONe + CNNe + COF + NOO }	sqrt(1/15){ 3 CONe + OOO }
sqrt(1/10){ BFF + 2 NNF }	sqrt(1/30){ 2 BFNe + CFF + 2 NNNe + 4 NOF }	sqrt(1/30){ BNeNe + 2 CFNe + 4 NONe + 2 OOF }	sqrt(1/10){ CNeNe + 2 OONe }
sqrt(1/2) NFF	sqrt(1/6){ 2 NFNe + OFF }	sqrt(1/6){ NNeNe + 2 OFNe }	sqrt(1/2) ONeNe
sqrt(1/6) FFF	sqrt(1/2) FFNe	sqrt(1/2) FNeNe	sqrt(1/6) NeNeNe

Fig. 4. ^4F multiplet for chemical seniority vector $|1/\sqrt{6}\ BBB>$ for $SO(3)xSU(2)$.

Again, orthogonal chemical seniority vectors are determined and lead to othogonal multiplets, the direct sum of which is $\mathcal{H}(3)$. Thus, for this chemical seniority vector, $\mathcal{H}(3)$ is given by Eq. (19):

$$\mathcal{H}(3) = {}^4F \oplus {}^4P \oplus {}^2D \oplus {}^2P \tag{19}$$

Moving to $SO(2,1)$ symmetry, $|1/\sqrt{2}\ HH>$ is chosen as a chemical seniority vector, since $\mathbf{r}_-|1/\sqrt{2}\ HH> = 0$. Repeated operations of $\mathbf{r}_+$ on this vector result in the multiplet shown in Fig. 5. Note that the number of components in the states is monotonically increasing with n. The number of components does not reach a maximum and then symmetrically decrease, as was the case with $SO(3)xSU(2)$. As mentioned previously, this is due to the noncompact nature of $SO(2,1)$. As before, orthogonal chemical seniority vectors

{l}=0

n=2	sqrt(1/2) HH
n=3	HLi
n=4	sqrt(1/5) {sqrt(3) HNa + LiLi}
n=5	sqrt(1/10) {2 HK + sqrt(6) LiNa}
n=6	sqrt(1/70) {2 sqrt(5) HRb + 4 sqrt(2) LiK + 3 NaNa}
n=7	sqrt(1/28) {sqrt(6) HCs + sqrt(10) LiRb + 2 sqrt(3) NaK}
n=8	sqrt(1/42) {sqrt(7) HFr + 2 sqrt(3) LiCs + sqrt(15) NaRb + 2 KK}

Fig. 5. [0] multiplet for chemical seniority vector $|1/\sqrt{2}\ HH>$ for $SO(2,1)$.

are constructed and produce orthogonal multiplets. For example, the vector orthogonal to $1/\sqrt{5}\{\sqrt{3}\,|HNa> +\sqrt{2}\,|1/\sqrt{2}\ LiLi>\}$ is the vector $1/\sqrt{5}\{\sqrt{2}\,|HNa> -\sqrt{3}\,|1/\sqrt{2}\ LiLi>\}$. These vectors are located at $n = 4$. An additional component is added at $n = 6$, $n = 8$, and so on, allowing a new orthogonal seniority vector at each of these positions. Thus, $\mathcal{H}(2)$ is represented by an infinite number of orthogonal multiplets, each containing an infinite

number state vectors. These orthogonal multiplets are described by the chemical quantum number $\{\ell\}$. This chemical quantum number is similar, but not identical, to the chemical angular momentum quantum number ℓ, hence the notation $\{\ell\}$. The behavior of $\{\ell\}$ with respect to atomic multiplets for $SO(2,1)$ is identical to that of ℓ. For example, there are two multiplets which are located at $\{\ell\} = 0$. Similarly, there are 6, 10, and 14 multiplets at $\{\ell\}$ = 1, 2, and 3 respectively. This correspondence of $\{\ell\}$ to ℓ vanishes when molecules are considered. On the basis of concepts in section 2.5, molecular multiplets correspond to increasing values of $\{\ell\}$. These values depend on the number of identical atoms in the chemical seniority vector. The case for the chemical seniority vector $|1/\sqrt{2}\ HH>$ is expressed in Eq. (20):

$$\mathcal{H}(2) = [0] \oplus [2] \oplus [4] \oplus [6] \oplus \ldots \tag{20}$$

Eq. (20) indicates that $\mathcal{H}(2)$ is decomposed into multiplets located at $\{\ell\} = 0, 2, 4, 6$, etc.

Similarly, this is accomplished for the triatomic seniority vector $|1/\sqrt{6}\ HHH>$, which leads to the following decomposition of $\mathcal{H}(3)$:

$$\mathcal{H}(3) = [0] \oplus [2] \oplus [3] \oplus [4] \oplus [5] \oplus 2[6] \oplus \ldots \tag{21}$$

In the above equation, 2[6] signifies that there exists two multiplets located at $\{\ell\} = 6$. Also, note that there is no [1] in Eq. (21), i.e., there is no multiplet at $\{\ell\} = 1$. Fig. 6 gives the [0] multiplet. This decomposition is somewhat more complex than that for $\mathcal{H}(2)$ in Eq. (20), and further details are given in section 2.5.

$\{l\}=0$

n=3	sqrt(1/6) HHH
n=4	sqrt(1/2) HHLi
n=5	sqrt(1/14) {sqrt(3) HHNa + 2 HLiLi}
n=6	sqrt(1/84) {3 HHK + 3 sqrt(6) HLiNa + sqrt(2) LiLiLi}
n=7	sqrt(1/84) {sqrt(5) HHRb + 4 sqrt(2) HLiK + 3 HNaNa + 2 sqrt(3) LiLiNa}
n=8	sqrt(1/168) {sqrt(6) HHCs + 2 sqrt(10) HLiRb + 4 sqrt(3) HNaK + 4 LiLiK + 3 sqrt(2) LiNaNa}
n=9	sqrt(1/308) {sqrt(7) HHFr + 4 sqrt(3) HLiCs + 2 sqrt(15) HNaRb + 2 sqrt(5) LiLiRb + 4 HKK + 4 sqrt(6) LiNaK + sqrt(3) NaNaNa}

Fig. 6. [0] multiplet for chemical seniority vector $|1/\sqrt{6}$ HHH$>$ for $SO(2,1)$.

Section 2.5. Determination of possible multiplets from Clebsch-Gordan coefficients.

The decomposition of the representation space $\mathcal{H}(N)$ with respect to the group G can be determined by a method other than the use of ladder operators and chemical seniority vectors described in section 2.4. This technique involves the direct product of N number of atomic multiplets, thereby generating N-atomic molecular multiplets. For the purposes of this paper, therefore, there exist two scenarios corresponding to the two symmetry groups of interest, $SO(3)$x$SU(2)$ and $SO(2,1)$.

First, the case for $SO(3) \times SU(2)$ is discussed. Atomic multiplets in $SO(3)$ symmetry are denoted as $[n, s, \mu][\ell]$. The chemical quantum numbers n, s, and μ are grouped together because they have nothing to do with the action of the group once they are chosen. The chemical quantum number ℓ must also be fixed, but its chosen value determines the range of m, the dynamical chemical quantum number of $SO(3)$. Therefore, ℓ is separated from the other chemical quantum numbers. Similarly, atomic multiplets for the spin group $SU(2)$ are denoted as $[n, \ell, m][s]$. Thus, atomic multiplets for $SO(3) \times SU(2)$ symmetry are denoted $[n][\ell][s]$. The decomposition of the N-dimensional Hilbert space $\mathcal{H}(N)$ is given[8] by Eq. (22).

$$\mathcal{H}(N) = \prod_{i=1}^{N} [n_i][\ell_i][s_i] = \sum_{L} \sum_{S} C^{LS} [L][S] \tag{22}$$

In this equation, L and S refer to the possible results of combining the ℓ_i's and s_i's respectively. The notation $[L][S]$ refers to a particular N-atomic multiplet in $SO(3) \times SU(2)$. The constants denoted C^{LS} are integer Clebsch-Gordan coefficients.

Now, consider the symmetry group $SO(2,1)$. In the same manner as before, atomic multiplets for $SO(2,1)$ are denoted $[m, \mu][\{\ell\}]$. While the values of all these chemical quantum numbers must be chosen, the value of $\{\ell\}$ defines the initial value of n, namely it is $\{\ell\} + 1$. The decomposition of the space $\mathcal{H}(N)$ for N-atomic molecules is given[8] in Eq. (23).

$$\mathcal{H}(N) = \prod_{i=1}^{N} [m_i][\mu_i][\{\ell_i\}] = \sum_{\{L\}} C^{\{L\}} [\{L\}] \tag{23}$$

In Eq. (23), $\{L\}$ refers to a possible combination of the $\{\ell\}_i$'s, and $[\{L\}]$ denotes molecular multiplets located at a specific value of $\{L\}$. Presumably, the $C^{\{L\}}$ constants are, as before, integer Clebsch-Gordan coefficients.

The result of these decomposition formulas allows the determination of which multiplets exist for a given chemical seniority vector without calculating the actual state vectors. That is, Eqs. (18 - 21) can not only be viewed as descriptions of the results obtained by ladder operators and chemical seniority vectors, but also as specific cases of Eqs. (22) and (23).

Section 2.6. Observable operators and expectation value identities.

The definitions of the single-particle, two-particle, and three-particle observable operators, $P(1)$, $P(2)$, and $P(3)$ respectively, are given by the following equations.[6]

$$P(1) = \sum_{i=1}^{N} \sum_{j=1}^{N} P(1)_{ij}\, b_{a_i}^+ b_{a_j}$$

$$P(2) = \sum_{i \geq k}^{N} \sum_{j \geq l}^{N} P(2)_{ij,kl}\, b_{a_i}^+ b_{a_k}^+ b_{a_j} b_{a_l} \tag{24}$$

$$P(3) = \sum_{i \geq k \geq m}^{N} \sum_{j \geq l \geq n}^{N} P(3)_{ij,kl,mn}\, b_{a_i}^+ b_{a_k}^+ b_{a_m}^+ b_{a_j} b_{a_l} b_{a_n}$$

In these equations, the set of atoms is denoted $\{a_1, a_2, ..., a_n\}$, and the summation is over all possible atoms. $P(1)_{ij}$ is a two-dimensional matrix, while $P(2)_{ij,kl}$ and $P(3)_{ij,kl,mn}$ are tensors

of rank four and six respectively. By calculating the expectation value of $P(1)$ for an atom a_i, it becomes clear that the diagonal elements of the $P(1)_{ij}$ matrix at least contain data for all properties of the atom a_i.

$$<P(1)>_{a_i} = \frac{<a_i|P(1)|a_i>}{<a_i|a_i>} = P(1)_{ii} \tag{25}$$

Similarly, the diagonal elements of the tensors $P(2)_{ij,kl}$ and $P(3)_{ij,kl,mn}$ contain at least data for diatomic and triatomic molecules.

Clearly it is possible to use the $P(N)$ operator on an N-atomic state vector. However, it is also possible to use the $P(M)$ operator on an N-atomic state vector as long as $M \leq N$. This process, when interference terms are dropped, leads to a set of identities[8] relating the expectation values of certain operators. The identities for $P(1)$ are given in Eq. (26).

$$<a_i|P(1)|a_i> = <a_i|P(1)|a_i>$$

$$<a_ia_j|P(1)|a_ia_j> = <a_i|P(1)|a_i>+<a_j|P(1)|a_j> =$$

$$\tfrac{1}{2}[<a_ia_i|P(1)|a_ia_i>+<a_ja_j|P(1)|a_ja_j>]$$

$$\tag{26}$$

$$<a_ia_ja_k|P(1)|a_ia_ja_k> = <a_i|P(1)|a_i>+<a_j|P(1)|a_j>+<a_k|P(1)|a_k> =$$

$$\tfrac{1}{3}[<a_ia_ia_i|P(1)|a_ia_ia_i>+<a_ja_ja_j|P(1)|a_ja_ja_j>+<a_ka_ka_k|P(1)|a_ka_ka_k>] =$$

$$\tfrac{1}{2}[<a_ia_i|P(1)|a_ia_i>+<a_ja_j|P(1)|a_ja_j>+<a_ka_k|P(1)|a_ka_k>]$$

The last expressions in the second and third equation strings are called diatomic homonuclear approximations because they recasts all observables in terms of homonuclear diatomic

molecules. Similarly, the third expression in the third equation string is called the triatomic homonuclear approximation. The $P(1)$ operator, in the second expression of the second and third equation strings, reflects the attribute of additivity which corresponds to the theory of atoms in molecules.[11]

The identities for $P(2)$ are given in Eq. (27):

$$<a_i a_j|P(2)|a_i a_j> \ = \ <a_i a_j|P(2)|a_i a_j>$$

$$(27)$$

$$<a_i a_j a_k|P(2)|a_i a_j a_k> \ = \ <a_i a_j|P(2)|a_i a_j> + <a_j a_k|P(2)|a_j a_k> + <a_i a_k|P(2)|a_i a_k>$$

Again, there is a suggestion of additivity in the second equation which alludes to the theory of diatomics in molecules.[12] Note that there are fewer identities for $P(2)$ than for $P(1)$. This is due to the restriction of $P(M)$ and N-atomic states mentioned earlier. Consequently, there is only one identity for $P(3)$.

$$<a_i a_j a_k|P(3)|a_i a_j a_k> \ = \ <a_i a_j a_k|P(3)|a_i a_j a_k> \qquad (28)$$

These identities are useful in graphical analysis of multiplets of state vectors. They allow the plots of additional diatomic and triatomic multiplets that would otherwise be impossible because of a lack of data. By using the $P(M)$ operator on an N-atomic state for $M < N$, the N-atomic expectation values are transformed into M-atomic expectation values. While these identities are theoretically legitimate, any physical significance remains to be seen.

III. Computer program and data.

Section 3.1. *GTPS* (Group Theoretical Periodic Systems) computer program.

GTPS is a symbolic manipulation program which is based on the theory set forth in the preceding portions of this paper.[13] Given a suitable chemical seniority vector, *GTPS* generates multiplets of state vectors in a selected symmetry by applying commutation relations and normalization procedures. *GTPS* was used to produce the majority of the multiplets studied. The remainder were calculated by hand and then verified by the program.

Section 3.2. Data sources, errors, confidence levels, and approximations.

In this paper, only four properties are considered, namely heat of atomization (ΔH_a), ionization potential (*I.P.*), gas-phase entropy at 298K (S_{298}^0), and diatomic vibration frequency (ω_e). This analysis depends solely on tabulated data.

Atomic data for *I.P.* were taken from the <u>CRC Handbook of Chemistry and Physics</u>[14] with no errors given. S_{298}^0 data for atoms, diatomic, and triatomic molecules were taken from the JANAF Tables[15] of 1974-1982. Many of the data in these tables have errors given with 95% confidence-limits. The average of these errors is approximately 1% for triatomic molecules[2], and a similar value is assumed for diatomic molecules.

Diatomic data for dissociation potential (referred to as ΔH_a in this paper) were obtained from Huber and Herzberg[16]. Extremely few errors are explicitly given. A few values are indicated as being somewhat uncertain; However, it is commonly accepted in the field to take the errors to be approximately 5% with 95% confidence.

Data for ω_e and *I.P.* of diatomic molecules were also taken from Huber and Herzberg[16]. The description of errors is the same as for diatomic ΔH_a above. Additional

diatomic values for *I.P.* as well as all triatomic *I.P.* data were taken from Gurvich[17]. The average of the given errors for diatomic molecules is less than 4.27%. (If more than one datum was listed, the worst case was selected, hence the "less than" wording.) These errors are with 95% confidence.

Triatomic ΔH_a data were obtained from Sauval[18]. The individual errors for ΔH_a are taken as 10% (15% for a few which Sauval[2] called "doubtful") with 95% confidence.

In an attempt to remedy the problem of a lack of data, rough approximations were made for the *I.P.*, S_{298}^0, and ω_e data of certain diatomic molecules. Given that the *I.P.* of XeF is less than or equal to 10.23 eV, and given that *I.P.* for F is 17.41 eV, *I.P.* values, for which one of the atoms in the diatomic molecule is a rare gas, were taken to be one half the atomic value for the other constituent atom.[16] *I.P.* data for Ne_2, Ar_2, and NeAr were taken to be equal to that for F_2, Cl_2, and FCl respectively.[19] Also, *I.P.* for B_2 is taken to be 8 eV.[19] S_{298}^0 data, for a molecule in which one constituent atom is a rare gas, were taken to be the average of the S_{298}^0 data for molecules with the same constituent atomic row numbers.[20] From observation of the data, some ω_e values which included rare gas atoms were taken to be a percentage of the average ω_e for each unique combination of the row numbers of the constituent atoms. Specifically, the data were taken as 8% of this average, unless the molecule included fluorine with the requisite rare gas, in which case 42% of the average was taken.

IV. Results of the computer experiment.

Section 4.1. Graphical analysis of periodicity in $SO(3)\times SU(2)$ and $SO(2,1)$ multiplets.

Plots of expectation values of observables are constructed for multiplets in both $SO(3)\times SU(2)$ and $SO(2,1)$ symmetry using various observable operators and expectation value identities. Four properties are discussed; They are ΔH_a, $I.P.$, S^0_{298}, and ω_e. The purpose of this discussion is to establish the periodic nature of the plotted surfaces. A complete set of graphs for $SO(3)\times SU(2)$ are located in appendix A. Similarly, a set of all constructed graphs for $SO(2,1)$ are in appendix B.
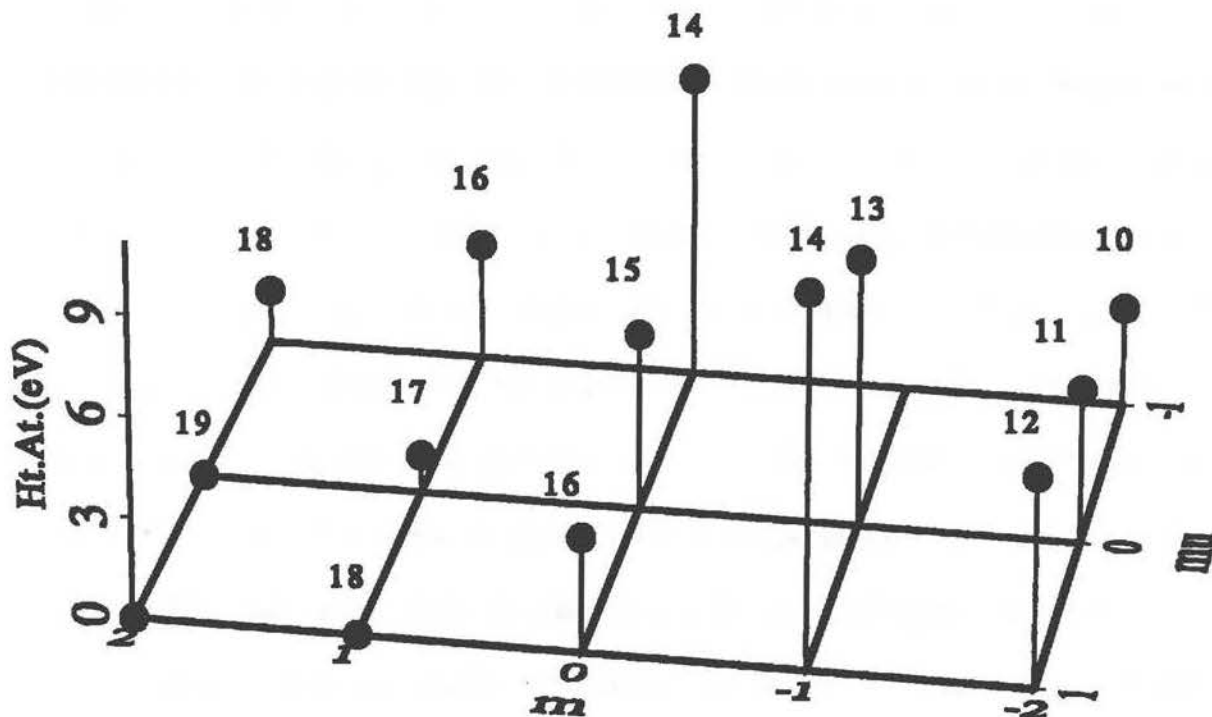
Fig. 7. ΔH_a plot for ^3D with $(R_1, R_2) = (2,2)$ using $P(2)$.

First, consider ΔH_a for $SO(3)\times SU(2)$ symmetry. The ^3D for diatomic molecules (Fig. 7), for which constituent atoms are taken from row two on the periodic chart [denoted $(R_1,R_2) = (2,2)$], is constructed using the $P(2)$ operator. This ^3D has a surface which slopes up at first and then down with decreasing values of both m and μ. The numbers above the

points on this and other plots refer to the number of valence electrons in each state. Previous work by at this institution[5] indicates a tendency for isoelectronic molecules to have invariant data. The fact that this is true, at least to a first approximation, for these plots corroborates the current observation.
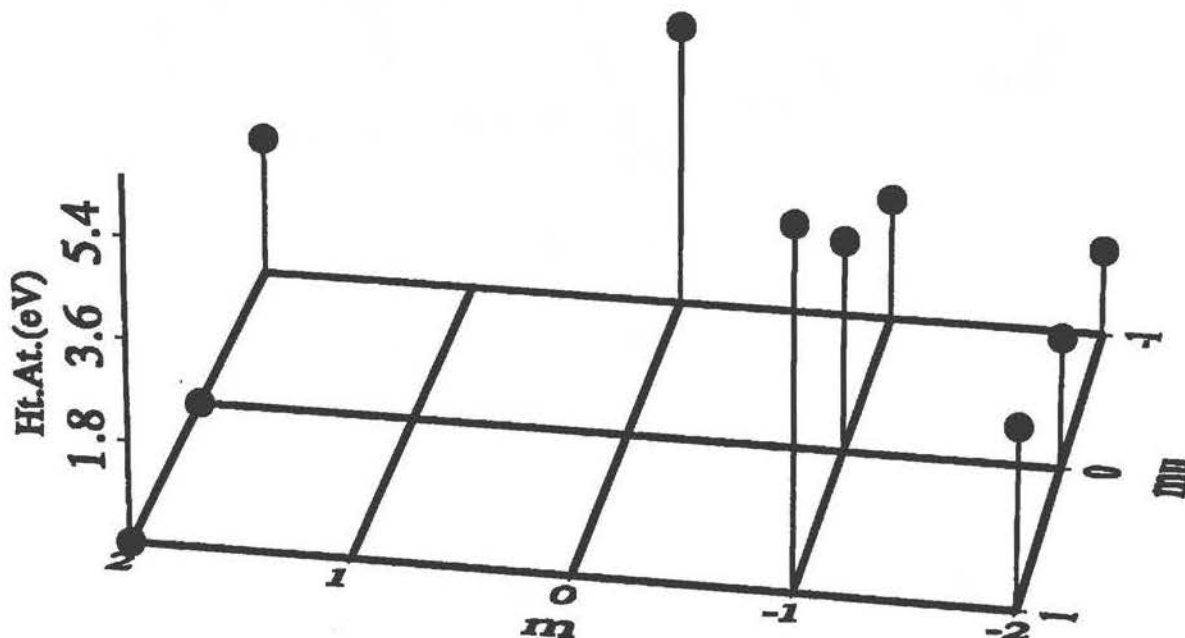
Fig. 8. ΔH_a plot for ^3D with $(R_1, R_2) = (3,3)$ using $P(2)$.

Now, the ^3D multiplet with $(R_1, R_2) = (3,3)$ is considered (Fig. 8). Although there are several points missing (due to lack of data), those points present follow the same shape, i.e., positive followed by negative slope with decreasing m and μ, as the ^3D with $(R_1, R_2) = (2,2)$.
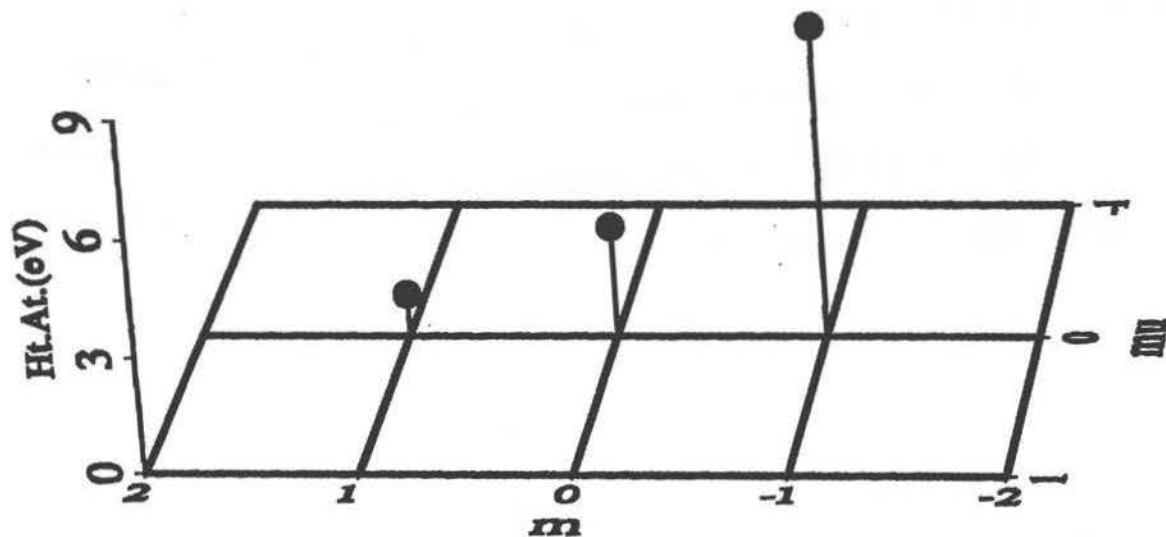
Fig. 9. ΔH_a plot for ^1P multiplet with $(R_1, R_2) = (2,2)$ using $P(2)$.

Furthermore, the orthogonal multiplets ^1P and ^3S, both with $(R_1, R_2) = (2,2)$, show the same trends at the corresponding positions in the ^3D (see Figs. 9 and 10).
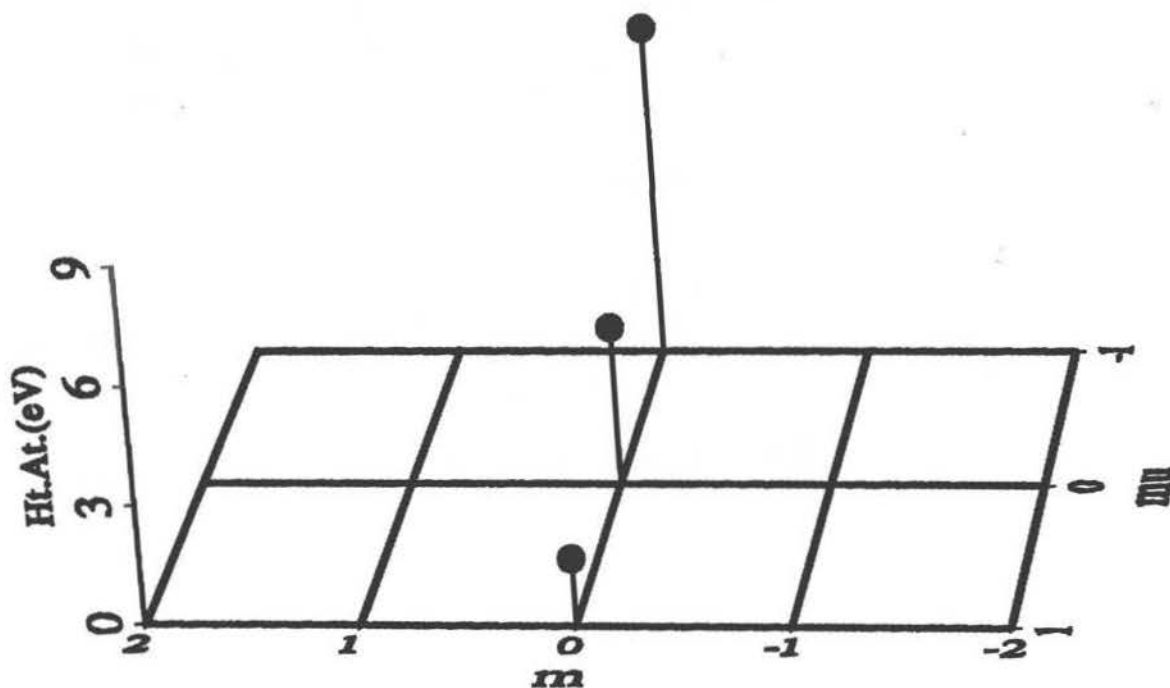
Fig. 10. ΔH_a plot for ^3S multiplet with $(R_1, R_2) = (2,2)$ using $P(2)$.
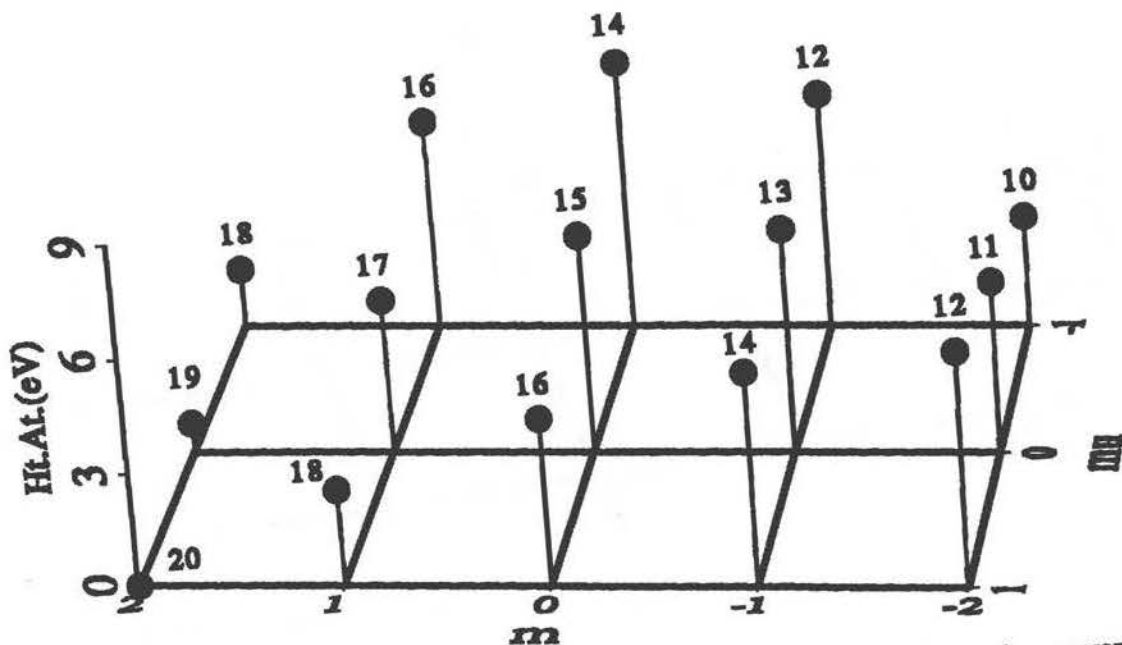
Fig. 11. ΔH_a plot for ^3D multiplet with $(R_1,R_2) = (2,2)$ using $P(1)$ diatomic homonuclear approximation.

Also, using the $P(1)$ operator and the diatomic homonuclear approximation identity given in Eq. (23), a ^3D, ^1P, and ^3S are generated (Figs. 11, 12, and 13). This ^3D surface is a "smoothed out" version of the non-homonuclear ^3D. The ^3S is again similar at the
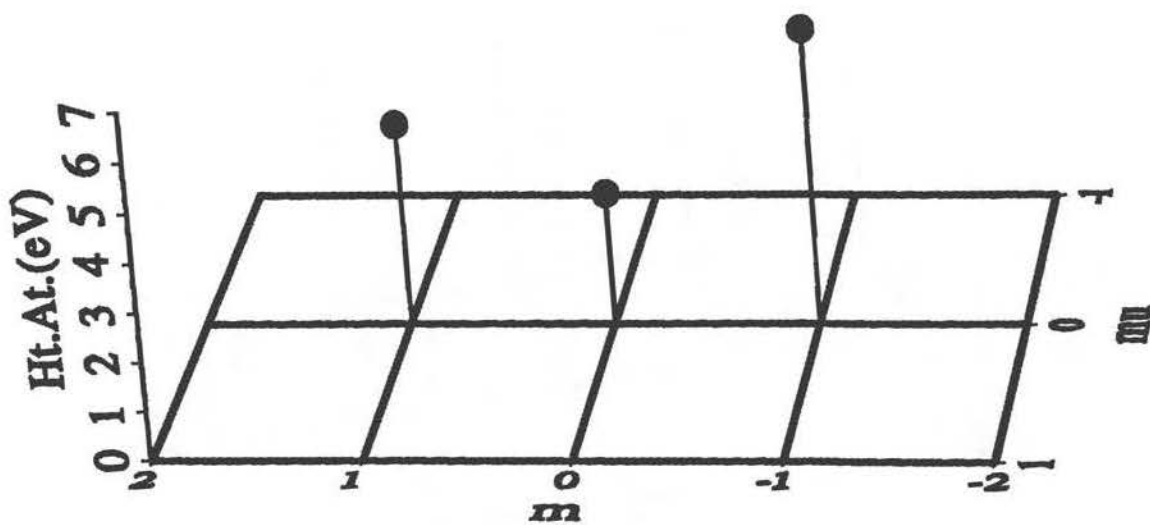
Fig. 12. ΔH_a plot for ^1P multiplet with $(R_1,R_2) = (2,2)$ using $P(1)$ diatomic homonuclear approximation.
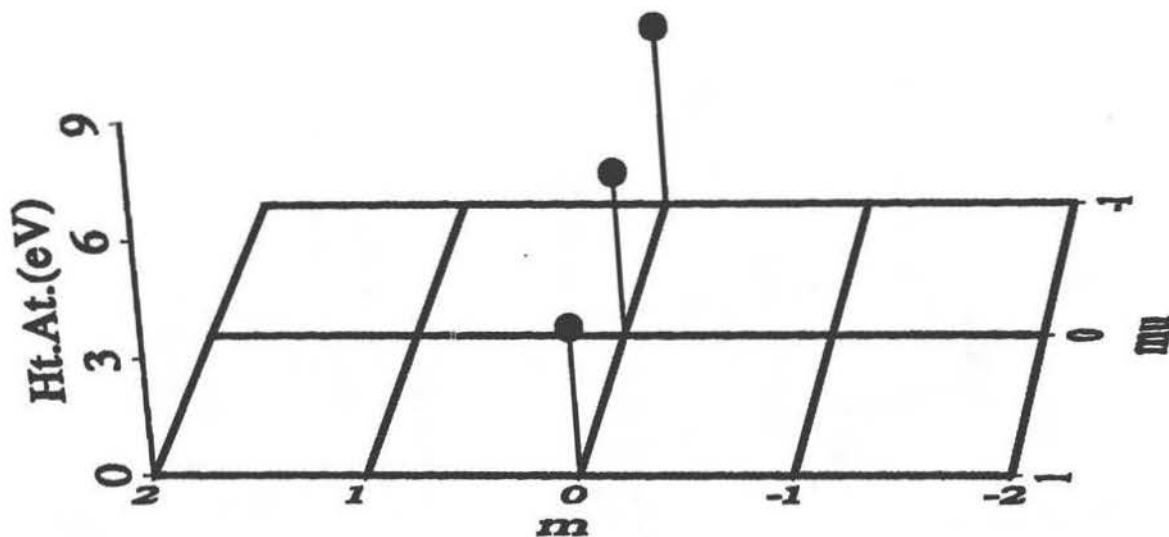
Fig. 13. ΔH_a plot for ^3S multiplet with $(R_1,R_2) = (2,2)$ using $P(1)$ diatomic homonuclear approximation.

corresponding positions in the ^3D, but the ^1P does not conform at the corresponding positions in the ^3D.

Again, the $(R_1,R_2) = (3,3)$ homonuclear plots are similar to the $(R_1,R_2) = (2,2)$ homonuclear plots including the non-conformity of the ^1P (only ^3D shown, Fig. 14).
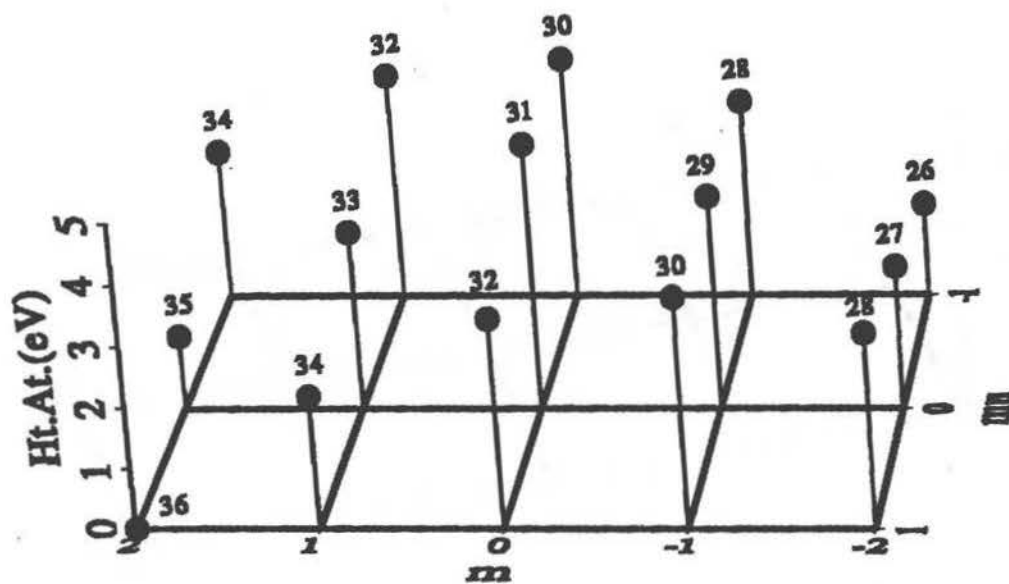
Fig. 14. ΔH_a plot for ^3D multiplet with $(R_1,R_2) = (3,3)$ using $P(1)$ diatomic homonuclear approximation.
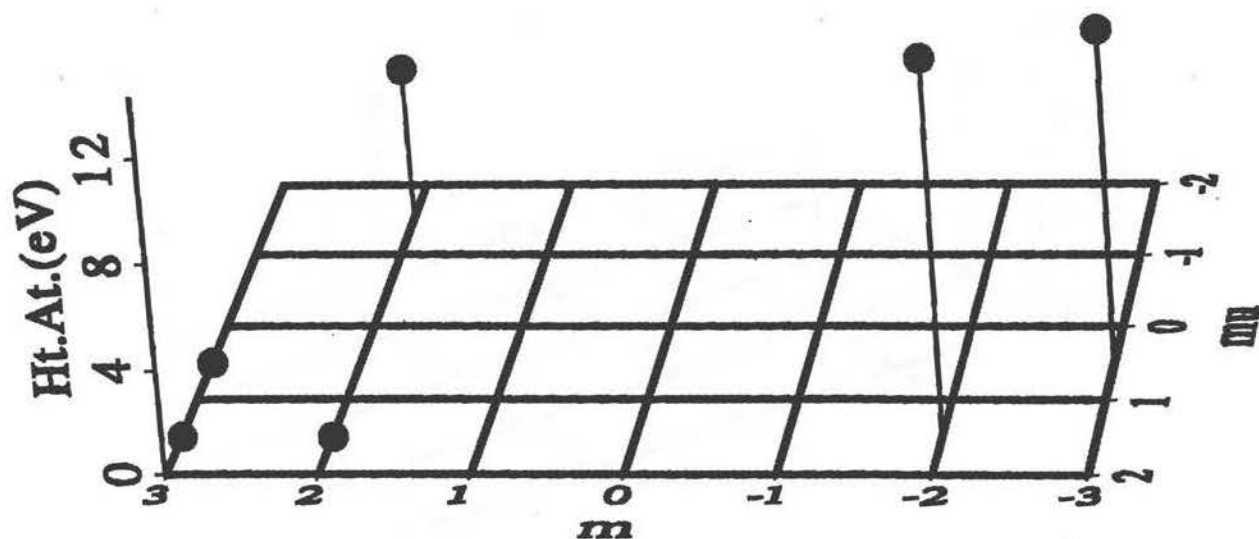
Fig. 15. ΔH_a plot for ^4F multiplet with $(R_1, R_2, R_3) = (2,2,2)$ using $P(3)$.

There is also a ^4F plot for triatomic molecules with $(R_1, R_2, R_3) = (2,2,2)$ using $P(3)$ which has only a few points (Fig. 15). However, these points form a surface which conforms to that of the diatomic ^3D in the region where data exist. The plots of ΔH_a using the $P(1)$ diatomic homonuclear approximation clearly lend themselves to more simple curve fitting more so than those for $P(2)$. However, the $P(2)$ operator maintains complete consistency between multiplets for ΔH_a in $SO(3) \times SU(2)$.

ΔH_a data are also plotted in $SO(2,1)$ symmetry. In general, a graph for $SO(2,1)$ contains more than one multiplet. Since multiplets are one-dimensional in n, they are placed side-by-side in order of increasing $\{\ell\}$. The combination of multiplets in a graph is described by the chemical atomic angular momenta [denoted (ℓ_1, ℓ_2)] and the group numbers (i.e., column numbers on the periodic chart) of the constituent atoms.
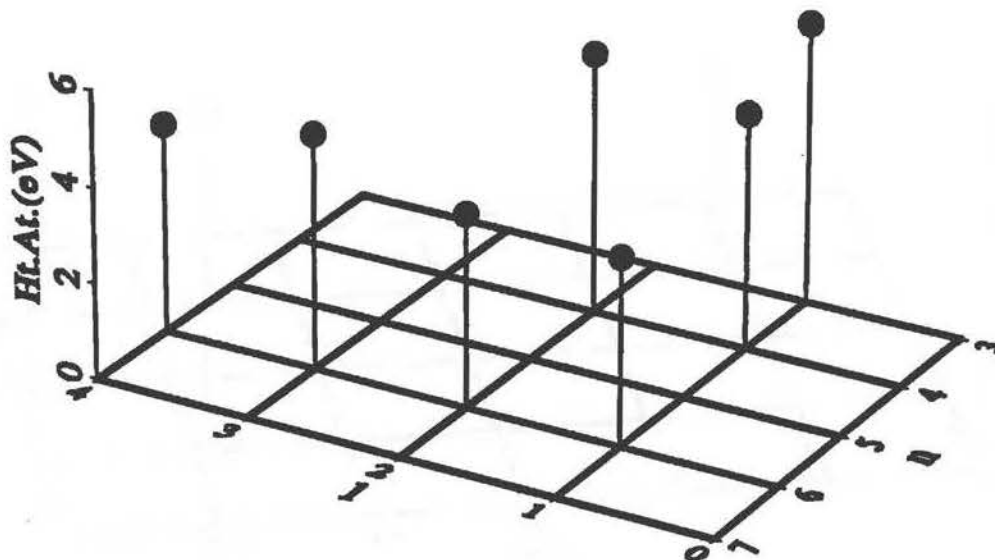
Fig. 16. ΔH_a plot for [1] - [4] multiplets with $(\ell_1, \ell_2) = (0,1)$ and groups $(1,7)$ using $P(2)$.

Only three graphs have been constructed, two of which have similar surfaces, namely (ℓ_1, ℓ_2) = (0,1), groups (1,7) and (ℓ_1, ℓ_2) = (1,1), groups (4,4) (Figs. 16 and 17). The third, (ℓ_1, ℓ_2) = (1,1), groups (7,7), does not have the decreasing slope with increasing n that characterizes the first two (see Fig. 18). However, curve fits for all three graphs would be simple.
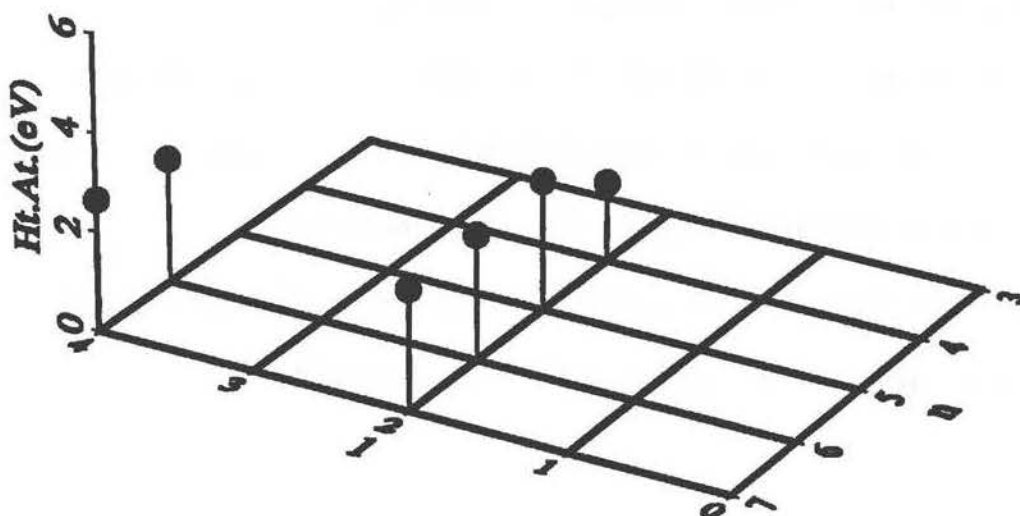
Fig. 17. ΔH_a plot for [2] and [4] multiplets with $(\ell_1, \ell_2) = (1,1)$ and groups $(7,7)$ using $P(2)$.
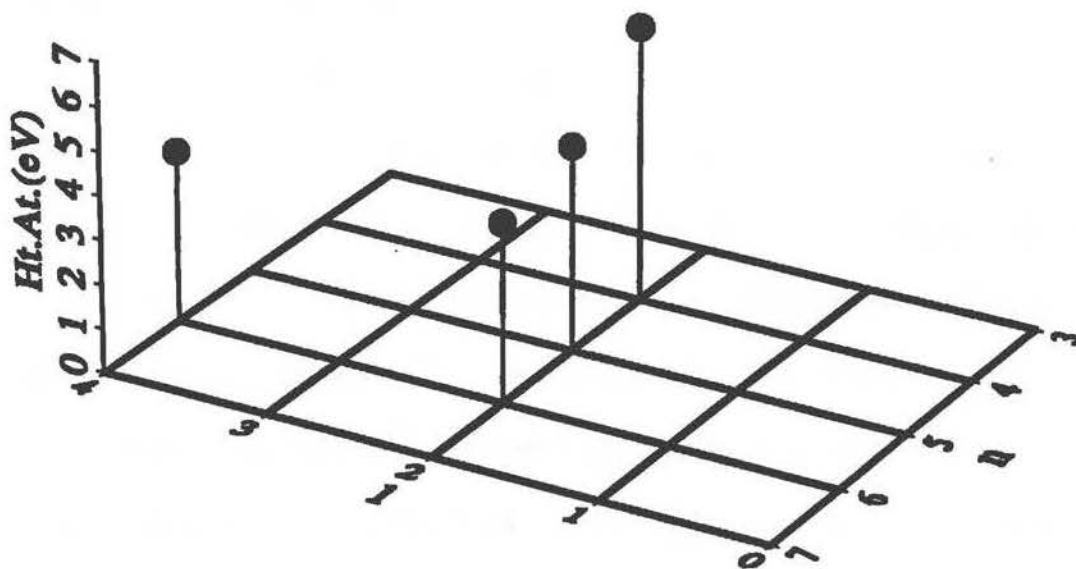
Fig. 18. ΔH_a plot for [2] and [4] multiplets with $(\ell_1, \ell_2) = (1,1)$ and groups (4,4) using $P(2)$.

As alluded to in the previous two paragraphs, an eventual goal of this work is the curve fitting of these surfaces to allow the prediction of missing state-vector expectation values, which, in many cases, will lead to prediction of individual molecular data. As a first step in this process, Tables I for ΔH_a (and Tables II-IV for $I.P.$, S_{298}^0, and ω_e) is prepared and summarizes the relationships between atomic, diatomic, and triatomic multiplets for various observable operators, expectation value identities, choices of row numbers of the constituent atoms for $SO(3)xSU(2)$, as well as choices of chemical angular momentum and group number for the constituent atoms for $SO(2,1)$. These tables also tabulate the location of the graph in the appendices, the number of states in the multiplet for which only actual data were included, as well as the number of states in which some approximate data were included (the specific approximation and the points effected are noted on the individual graphs), the number of data eligible for prediction (no. of missing points), and an *index of fittability* (an integer from 1 to 5). The latter gives a qualitative indication of the ease of a curve fit for the surface.

The tables also indicate an inclusive relationship between surfaces (one surface being a portion of another) by a single, horizontal or vertical line connecting them on the table. Where lines would cross or detour, certain matching symbols are used. Surfaces that are entirely similar are connected using double lines where possible and a different set of matching symbols where lines would cross or detour. See the key on each of Tables I-IV for specific notation. It should be noted that, in a few cases, similarity is indicated although some approximate data are not completely consistent. The uncertainty in these approximations accounts for this discrepancy. As demonstrated by these tables, there are many multiplets for which no plots have yet been made. Nevertheless, there are enough to make some preliminary observations.

An example of how to use these tables is now described using Table II. In this example, all plots are referenced by their appendix number, i.e., the first item listed for each plot in each table. As a general rule, it is best to choose two plots first and then use the tables to determine their relationship. For example, plot $A13$ and $A19$ are completely similar, as are both of these to $A15$, as indicated by the double line connecting them in spite of the fact that $A15$ lies between them on the double line. Furthermore, $A13$ and $A20$ are inclusively similar as indicated by the single line connecting them. $A13$ is also inclusively similar to $A25$. This is indicated by the "*" symbol which is among the set of symbols which show inclusive similarity. This symbol is used since it would be awkward to use a connecting single line. Correspondingly, $A20$ and $A25$ are marked by a "#" symbol which is among the set that describe complete similarity. These tables contain a complete and concise summary of the relationships between plots.
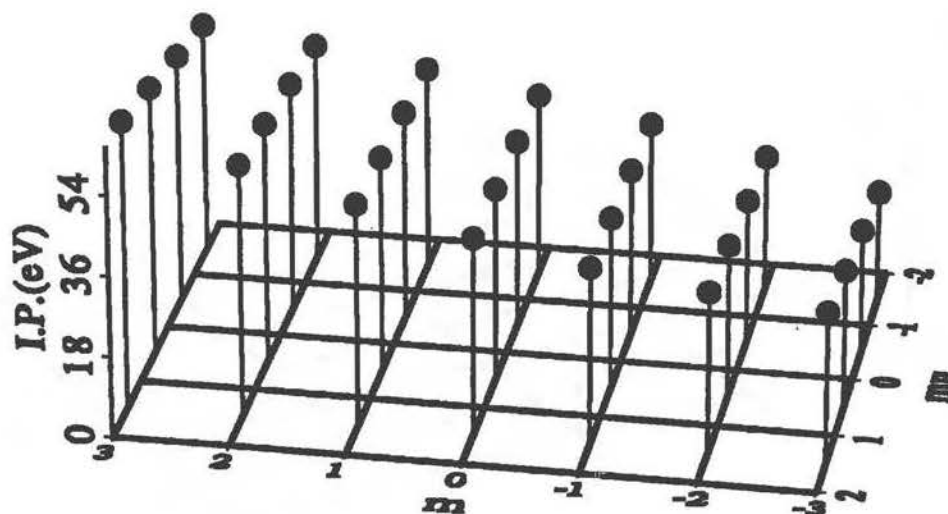
Fig. 19. *I.P.* plot for ^4F multiplet with $(R_1,R_2,R_3) = (2,2,2)$ using $P(1)$.

Table II indicates that for $SO(3) \times SU(2)$, similarity exists for atomic, diatomic, and triatomic multiplets with all operators and identities investigated except $P(2)$ acting on triatomic states. $P(1)$ generates nearly planar surfaces for all N-atomic states considered. An example of this is given in Fig. 19. These conclusions (and others yet to be presented) can be verified by reference to the appropriate graphs (indexed in the corresponding table) in the appendices.

I.P. for $SO(2,1)$ shows surfaces sloping monotonically downward with increasing n values and no inflection points for $P(1)$ acting on atomic states nor $P(2)$ acting on diatomic states. Fig. 20 shows one such case. These were the only operators and identities plotted.
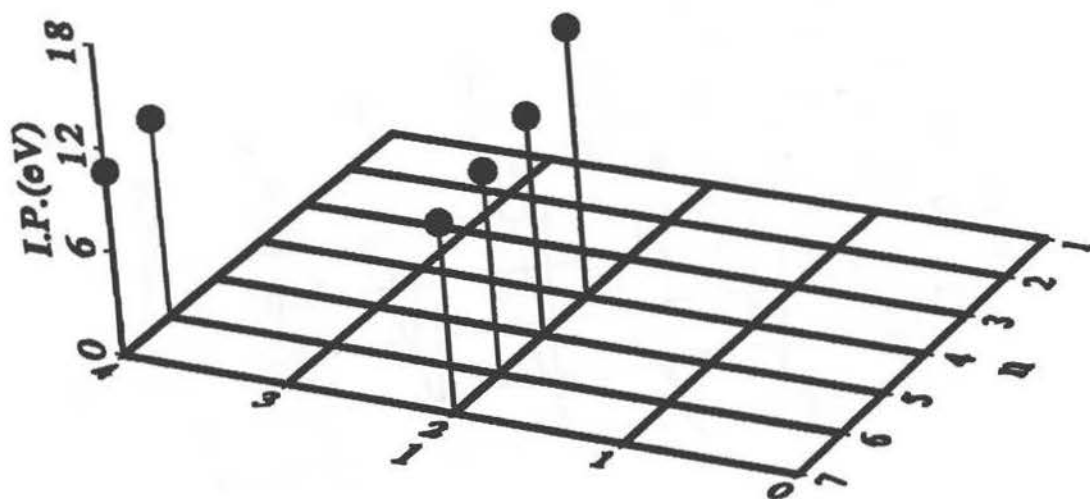
a maximum at the position of maximum m and minimum μ. For decreasing m, each surface converges toward an intermediate value between its maximum and minimum.
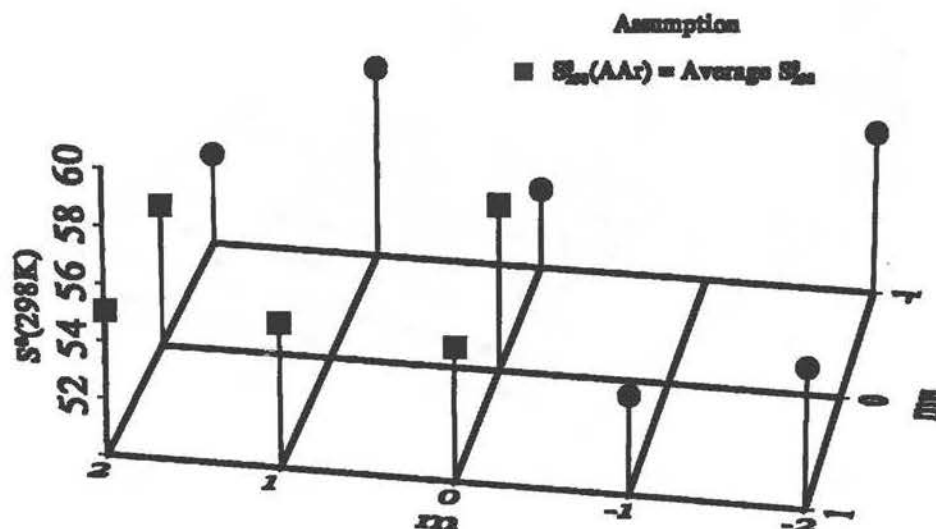
Fig. 22. S_{298}^0 plot for ^3D multiplet with $(R_1, R_2) = (3,3)$ using $P(2)$.

Forming other sets of similar graphs are those for $P(2)$, except for $(R_1, R_2) = (2,3)$, $(\ell_1, \ell_2) = (1,0)$, which are similar but not easily fittable, and those for diatomic homonuclear $P(1)$, which are easily fittable but do not have inclusive similarity for ^1P nor ^3S. An example of this is given in Fig. 22. Another apparent irregularity is the atomic ^2D.

All graphs prepared for S_{298}^0 in $SO(2,1)$ using $P(1)$ on atomic and $P(2)$ on diatomic states have virtually identical surfaces (Fig. 23, e.g.). These surfaces are characterized by positive slope in the direction of increasing n, but also with negative concavity with increasing n.
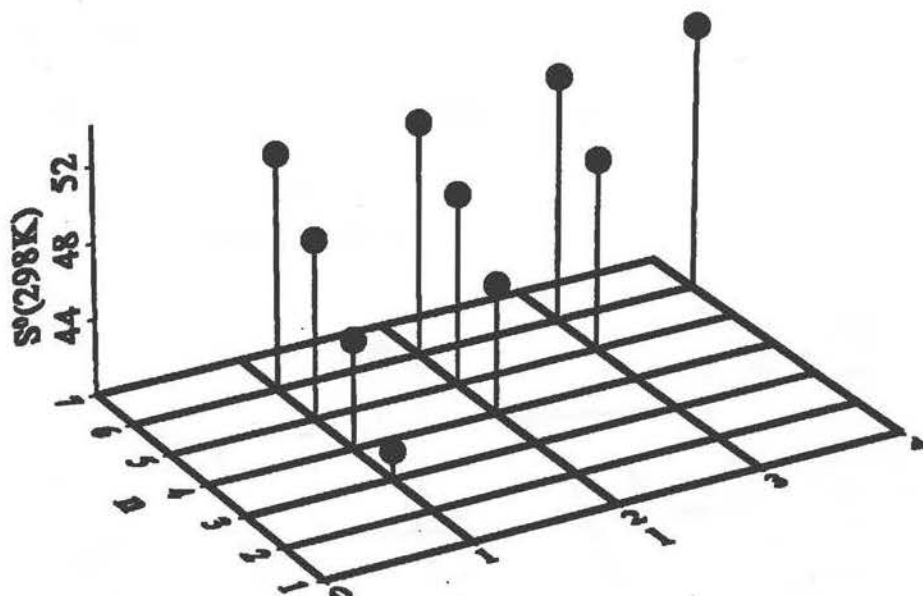
Fig. 23. S_{298}^0 plot for [1] - [4] multiplets with $(\ell_1, \ell_2) = (0,1)$ and groups (1,7) using $P(2)$.

Next, consider ω_e for diatomic multiplets in $SO(3)\times SU(2)$ (see Table IV). This property, by definition, has only values for diatomic molecules. Thus, the only operators and identities used are $P(2)$ and diatomic homonuclear $P(1)$. $P(2)$ surfaces for ^3D multiplets first slope up and then down with decreasing m and μ (e.g., Fig. 24). The ^1P and ^3S
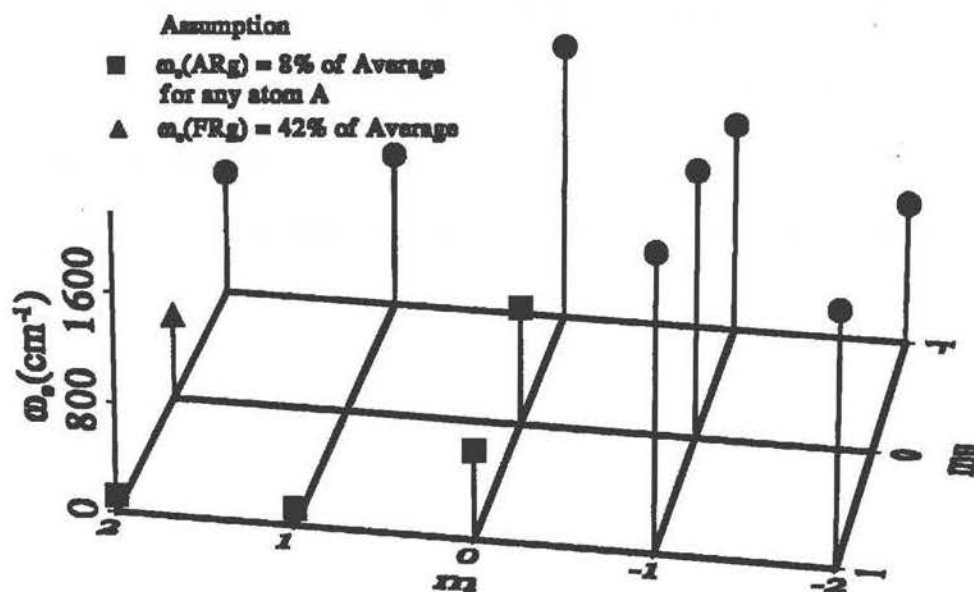
Fig. 24. ω_e plot for ^3D multiplet with $(R_1, R_2) = (2,2)$ using $P(2)$.

multiplets exhibit inclusive similarity to the ^3D multiplets. This is not the case for the ^3P surfaces. The homonuclear $P(1)$ plots have an extremely smooth nature with no inflection points (e.g., Fig. 25). However, the ^1P is not inclusively similar to the ^3D.
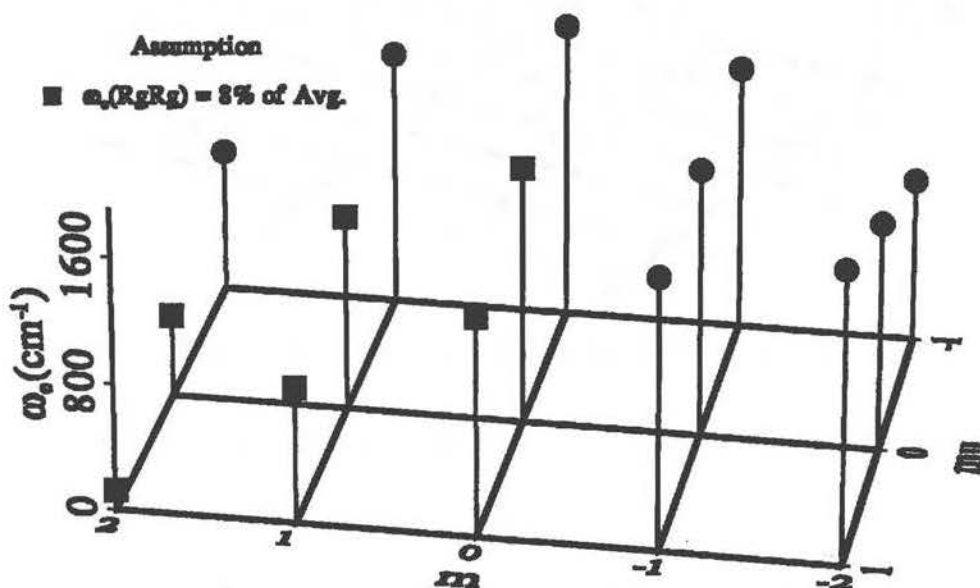
Fig. 25. ω_e plot for ^3D multiplet with $(R_1, R_2) = (2,2)$ using diatomic homonuclear approximation.

It is interesting to note the similar shape of these surfaces and ΔH_a for diatomic states. This suggests a correlation between these properties, namely that vibration frequency is related to bond energy for diatomic molecules, which we would intuitively expect.

The only observable operator used for ω_e in $SO(2,1)$ is $P(2)$. All constructed surfaces have both positive slope and concavity for increasing n (see Fig. 26, e.g.), except the plot for $(\ell_1, \ell_2) = (1,1)$, groups $(7,7)$ which has positive slope but negative concavity for increasing n. They all have no inflection points and would thus be easily fitted.
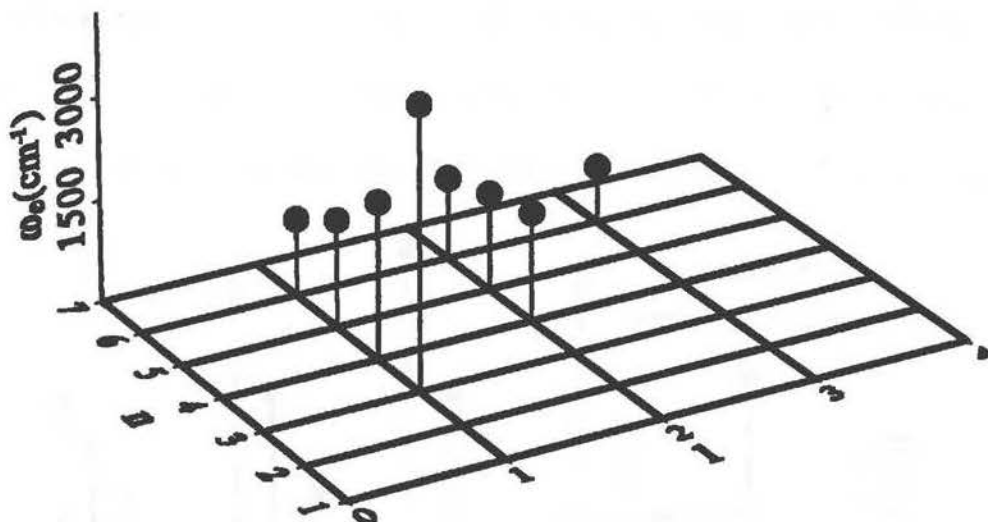
Fig. 26. ω_e plot for [1] - [3] multiplets for $(\ell_1, \ell_2) = (0,1)$ and groups (1,7) using $P(2)$.

As a final note about the periodicity of the multiplets, Tables I-IV clearly indicate that, for a majority of the cases, $SO(3) \times SU(2)$ demonstrates periodicity with respect to the row numbers of the constituent atoms (indicated by the horizontal double lines and corresponding symbols), and $SO(2,1)$ demonstrates similarity with respect to the group numbers (indicated in the same manner). In spite of some cases in both symmetries where consistency between inclusive multiplets is lost, the periodicity, as just described, remains.

Section 4.2. Structure of periodic systems for $SO(3) \times SU(2)$ and $SO(2,1)$.

The structure of atomic, diatomic, and triatomic periodic systems is determined by the location of the constituent multiplets with respect to a coordinate system. In the case of systems using $SO(3) \times SU(2)$ symmetry, these coordinates are the values of the n and ℓ chemical quantum numbers for the states which constitute a given multiplet. As for systems in $SO(2,1)$ symmetry, values of the n and $\{\ell\}$ chemical quantum numbers are used. In all

the periodic systems discussed, it is assumed that all atoms exist for $n \leq 7$ and $\ell \leq 3$, i.e., some but not all atoms are assumed to exist for $Z \leq 156$.
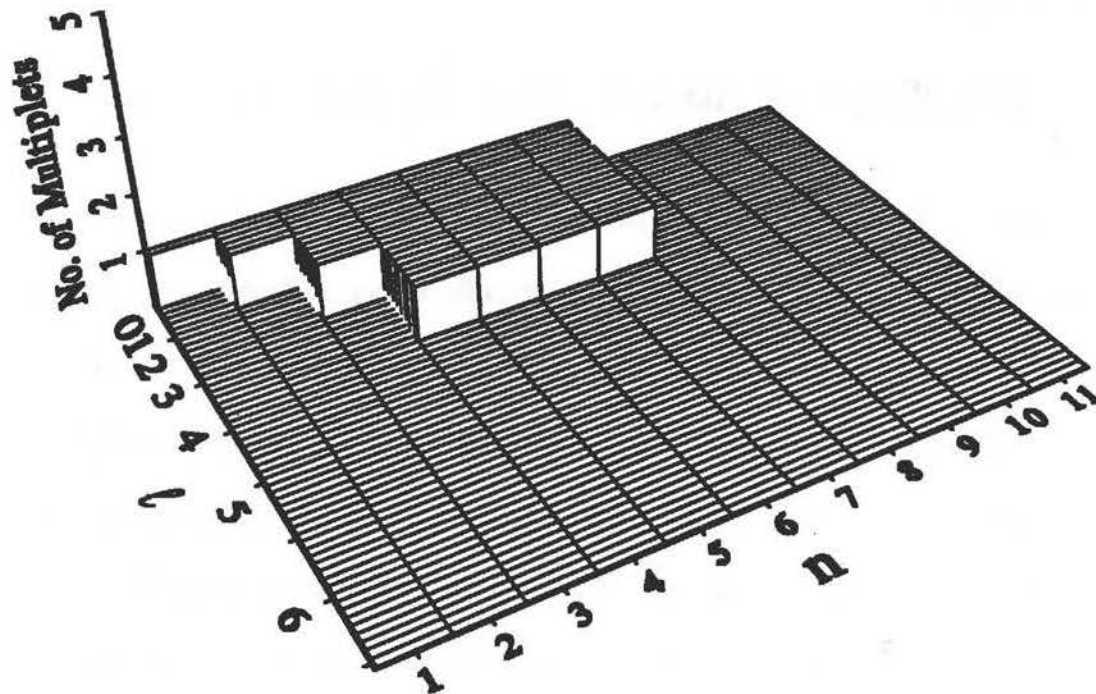
Fig. 27. Atomic periodic system in $SO(3)$x$SU(2)$ symmetry.

For the group $SO(3)$x$SU(2)$, the atomic periodic system consists only of multiplets with chemical spin multiplicity $S = 2$. By referring back to Fig. 1, it can be easily seen that there exits one and only one multiplet for each allowed combination of n and ℓ. This is illustrated further by Fig. 27. In this figure, note that the number of sections in each multiplet corresponds to the chemical angular momentum multiplicity. Also, any two atomic multiplets, denoted $[n_i][\ell_i][s_i]$ and $[n_j][\ell_j][s_j]$, are *substitutable* if $\ell_i = \ell_j$ and $s_i = s_j$. When this is the case, it is denoted as $[n_i][\ell_i][s_i] \leftrightarrow [n_j][\ell_j][s_j]$. This means that the structure of the state vectors within the two multiplets are isomorphic, and to obtain one from the other, one must merely substitute the corresponding atomic symbol at each position in each state vector.

The molecular periodic systems for $SO(3) \times SU(2)$ symmetry are derived by means of this substitutability principle. Equivalence classes of N-atomic molecular multiplets are defined in Eq. (29):

$$\left[\!\left[\, [L_x][S_x] \,\right]\!\right] = \left\{\, [L_y][S_y] \,\middle|\, \forall\, i \in \mathbf{I}\left([n_{x_i}][\ell_{x_i}][s_{x_i}] \leftrightarrow [n_{y_i}][\ell_{y_i}][s_{y_i}] \right) \right\} \qquad (29)$$

In this equation, $\mathbf{I} = \{1, 2, \ldots, N\}$ is an index set. These equivalence classes require members to consist of direct products of substitutable atomic multiplets. An important further constraint is that each member of a given equivalence class must contain an equal number of identical atomic multiplets in its direct product. For example, multiplets for the chemical seniority vectors $|1/\sqrt{6}\ BBB\rangle$ and $|1/\sqrt{6}\ AlAlAl\rangle$ belong to the same class, but $|1/\sqrt{2}\ BBAl\rangle$ and $|BAlGa\rangle$ do not. For diatomic multiplets, there are 76 different equivalence classes. There exist 954 equivalence classes for triatomic multiplets. The results of this process make it necessary to determine only one multiplet for each of the equivalence classes in order to discern the structure of the N-atomic molecular periodic system. Complete sets of diatomic and triatomic multiplets for $SO(3) \times SU(2)$ periodic systems are included in Appendices C and D respectively.

The diatomic molecular periodic system for $SO(3) \times SU(2)$ consists of roughly equal numbers of triplet and singlet chemical spin multiplets. Therefore, the periodic system is divided into two coordinate systems, one for each chemical spin state. These are given in Figs. 28 and 29. As was the case for the atomic system, the number of sections shown on each multiplet corresponds to the chemical angular momentum multiplicity. Note that the first triplet
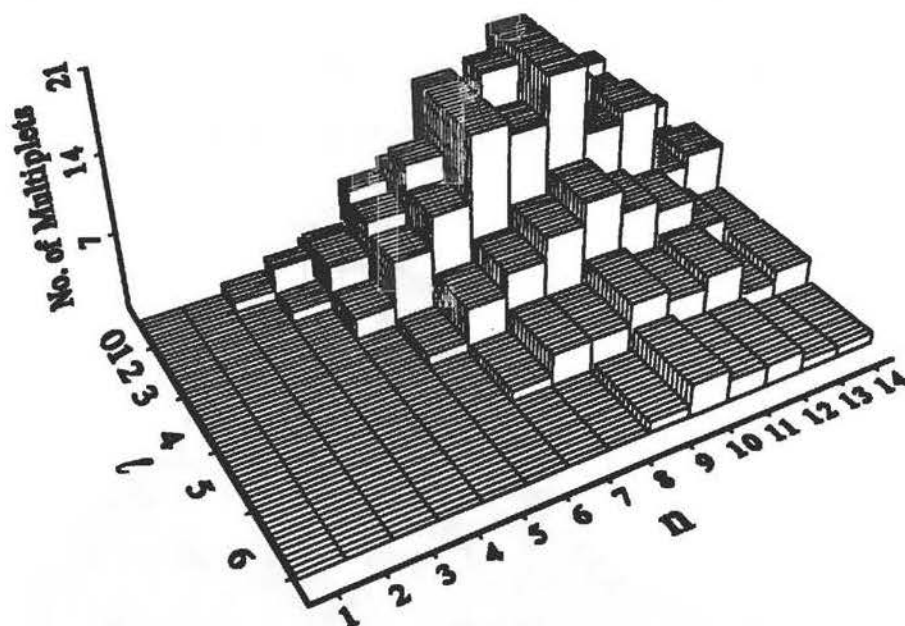
Fig. 28. Diatomic singlet periodic system in $SO(3)\mathrm{x}SU(2)$ symmetry.

multiplets occur along the line in the n-ℓ plane given by $\ell = n - 2$. The most abundant state of chemical angular momentum is $\ell = 2$, i.e., the ^3D state. Furthermore, the single position
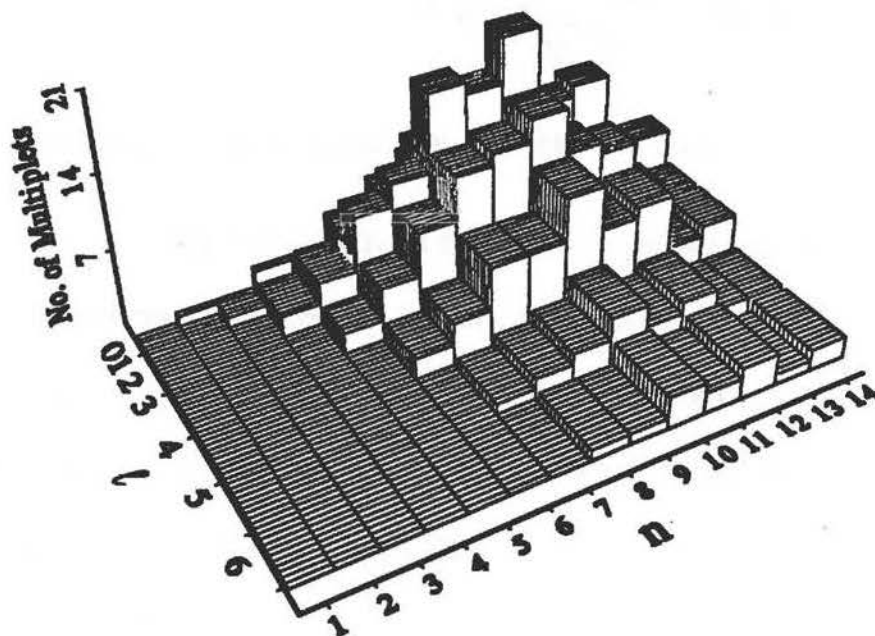
Fig. 29. Diatomic triplet periodic system in $SO(3)\mathrm{x}SU(2)$ symmetry.

with the largest number (21) of multiplets is $\ell = 2$ and $n = 10$. The system of singlets is similar to that of the triplets, but there are no ^1S multiplets at $n = 2$ and no ^1I multiplets at $n = 8$. Also, the $\ell = 1, 2,$ and 3 states for $n = 10$ have the same number of multiplets.
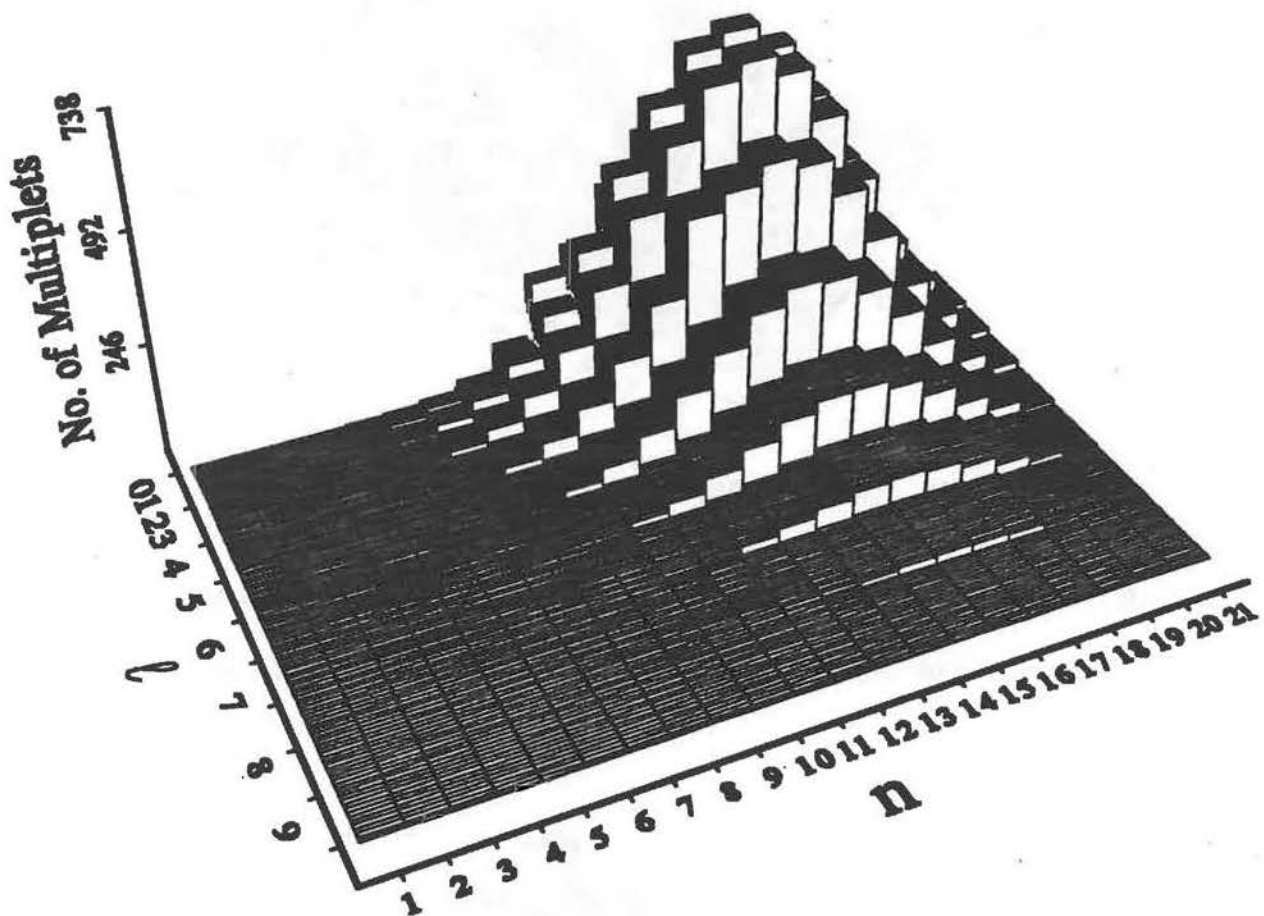
Fig. 30. Triatomic doublet periodic system in $SO(3)\mathrm{x}SU(2)$ symmetry.

The diagrams for the triatomic systems of $SO(3)\mathrm{x}SU(2)$ are constructed in the same manner as those for the diatomic system. Again, the periodic system is divided into two coordinate systems, one for doublet and one for quartet states (Figs. 31, 32). The first quartet multiplets occur along the line $\ell = n - 3$. The number of multiplets at the extreme allowable values of the coordinates is relatively small. Thus, these are difficult to
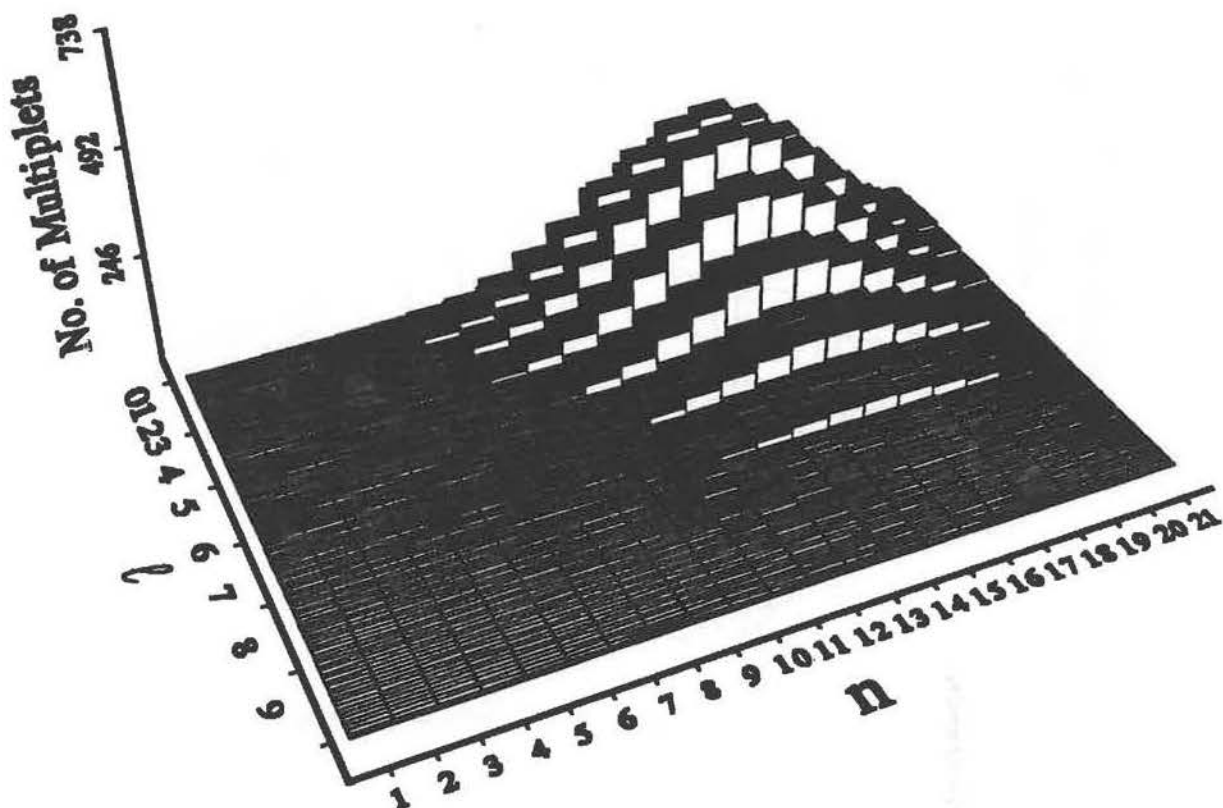
Fig. 31. Triatomic quartet periodic system in $SO(3)$x$SU(2)$ symmetry.

see on the the figures. The number of quartets multiplets is only slightly greater than half of the number of doublets. For each value of ℓ, the position with the maximum number of multiplets in both cases (doublets and quartets) is $n = 15$. Note the smooth nature of these triatomic plots which appear to be somewhat Gaussian.

The atomic periodic system in $SO(2,1)$ symmetry is given in Fig. 32. Note that multiplets begin at given values of n and $\{\ell\}$, and contain infinitely many subsequent values of n (only $n \leq 11$ shown). Multiplets begin along a diagonal line in the n-$\{\ell\}$ plane, namely $\{\ell\} = n - 1$. The number of atomic multiplets is linearly increasing for increasing values of n and $\{\ell\}$ along this diagonal. Verification of this is given by reference back to Fig. 2.

Substitutable atomic multiplets are denoted $[m_i][\mu_i][\{\ell_i\}] \leftrightarrow [m_j][\mu_j][\{\ell_j\}]$ when $\{\ell_i\} = \{\ell_j\}$.
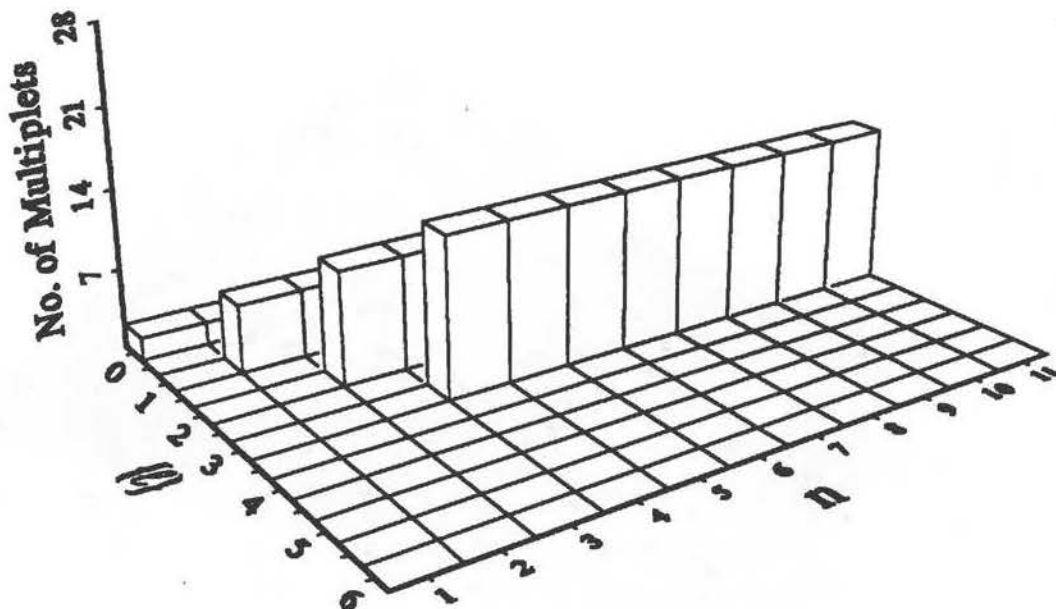
Fig. 32. Atomic periodic system in $SO(2,1)$ symmetry.

Molecular periodic systems for $SO(2,1)$ are constructed by means of this substitutability principle. The definition of equivalence classes of N-atomic molecular multiplets is given in Eq. (30).

$$\llbracket [\{L_x\}] \rrbracket = \left\{ [\{L_y\}] \mid \forall\, i \in \mathbf{I}\left([m_{x_i}][\mu_{x_i}][\{\ell_{x_i}\}] \leftrightarrow [m_{y_i}][\mu_{y_i}][\{\ell_{y_i}\}] \right) \right\} \qquad (30)$$

As in the $SO(3) \times SU(2)$ case, each member of a given equivalence class must also contain the same number of identical atomic multiplets in its direct product as do the other members. This guarantees that all molecular multiplets from a given equivalence class are substitutable. There are 62 unique equivalence classes for diatomic multiplets, and 411 for triatomic multiplets. Appendices E and F contain complete sets of multiplets (up to substitutability) for diatomic and triatomic periodic systems in $SO(2,1)$ symmetry.
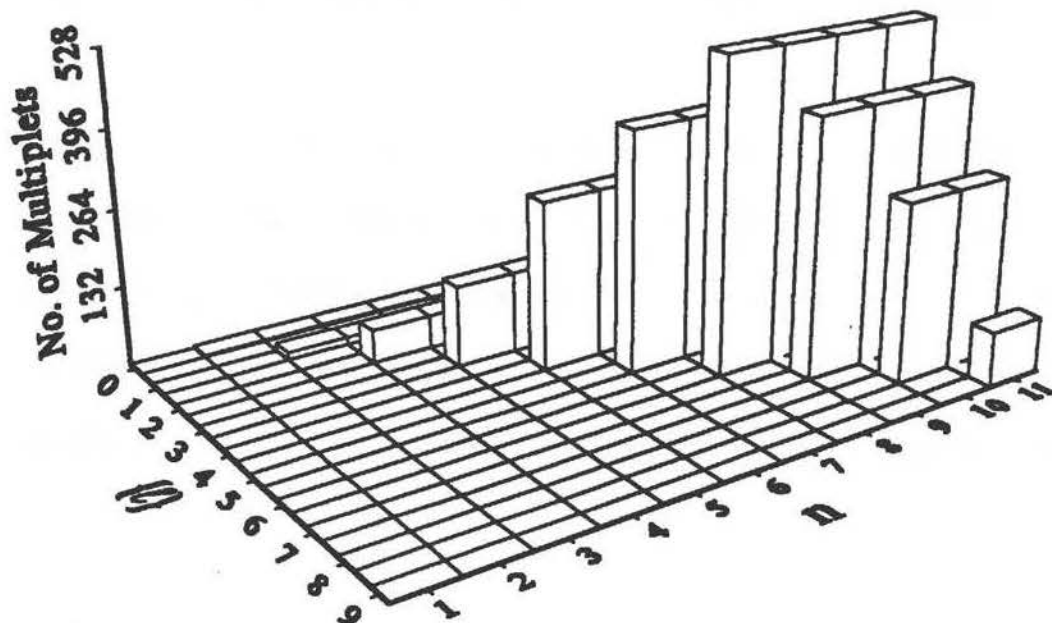
Fig. 33. Diatomic periodic system in $SO(2,1)$ symmetry.

The periodic system for diatomic molecules in $SO(2,1)$ symmetry is depicted in Fig.

33. Diatomic multiplets begin along the line in the n-$\{\ell\}$ plane given by $\{\ell\} = n - 2$. The
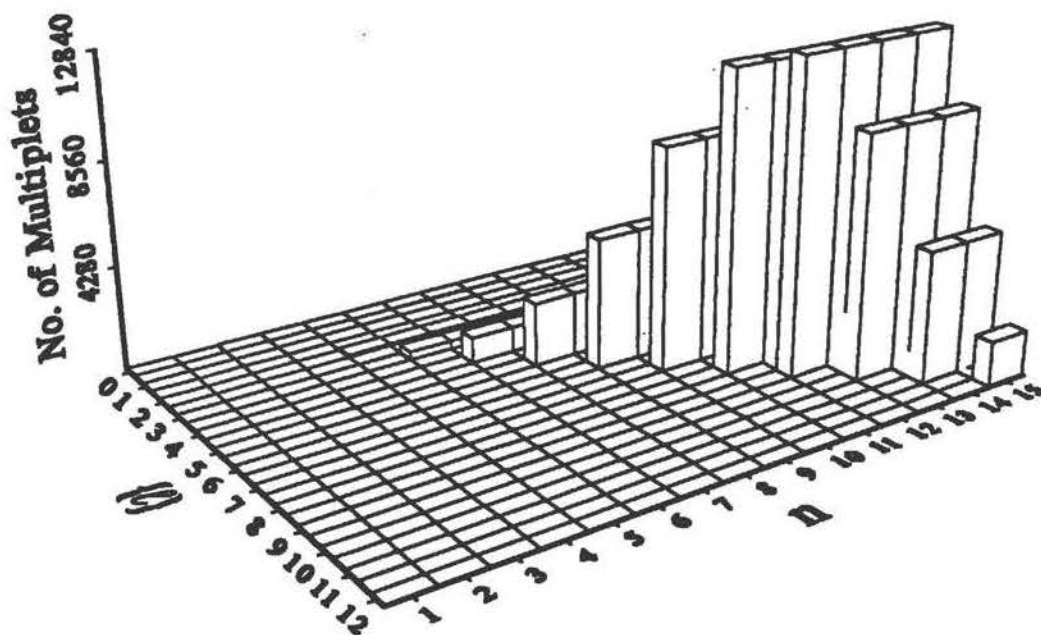
Fig. 34. Triatomic periodic system in $SO(2,1)$ symmetry.

number of multiplets is maximum at $\{\ell\} = 6$ and monotonically decreases in both directions from this point.

The triatomic molecular periodic system for $SO(2,1)$ contains multiplets that begin along the line $\{\ell\} = n - 3$. The overall shape of the system is similar to that for diatomic molecules (See Fig. 34). The number of multiplets for a given $\{\ell\}$ increases monotonically with $\{\ell\}$ until a maximum is reached at $\{\ell\} = 9$ and then monotonically decreases. Because of the relatively small number of multiplets at $\{\ell\} = 0$, 1, and 2, these multiplets are difficult to discern in Fig. 34.

V. Conclusion.

As the result of the theory proposed by Zhuvikin and Hefferlin, the group-theoretical molecular periodic systems for diatomic and triatomic molecules have been completed for two subgroups of the group $SO(4,2) \times SU(2)$, the symmetry group of the atomic periodic chart. These subgroups are $SO(3) \times SU(2)$ and $SO(2,1)$. Each subgroup leads to a set of multiplets which constitutes its respective periodic system. These molecular periodic systems have the property that their structure is 3-dimensional. This is also true for all N-atomic periodic systems, whereas some previously devised systems were $2N$-dimensional.

Expectation value plots for states within multiplets in each symmetry demonstrate periodicity. Multiplets in $SO(3) \times SU(2)$ symmetry have been shown to demonstrate periodicity primarily with respect to the row numbers on the atomic periodic chart of the constituent atoms, while periodicity in $SO(2,1)$ is with respect to the group (column) numbers. Details are given in Tables I-IV. It is this periodicity which will allow the curve fitting subsequent data prediction possible.

The future of this project, other than curve fitting and predicting data from the plots already obtained, falls in three areas. First, there still remain many multiplets for which plots are to be constructed and their periodicity verified more generally. Secondly, the investigation into different subgroups of $SO(4,2) \times SU(2)$ and even different subgroups of other groups which more accurately describe the periodic system of atoms can be made. Lastly, the principles set forth in Section 2 are completely general. Therefore, while the possibility of verification of results with actual data decreases for higher order molecular systems, the structure of such systems is, in principle, determinable.

Appendix A:

Plots of ΔH_a, $I.P.$, S_{298}^0, and ω_e for $SO(3)\mathrm{x}SU(2)$ symmetry group

SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Triplet D
Heat of Atomization (eV)
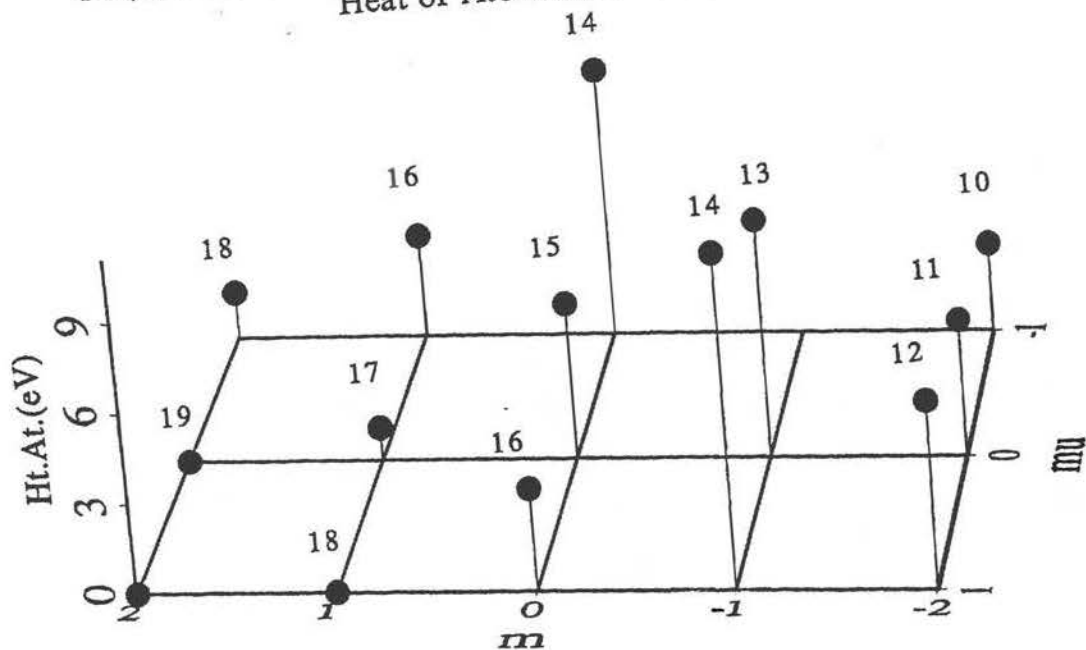
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Singlet P
Heat of Atomization (eV)
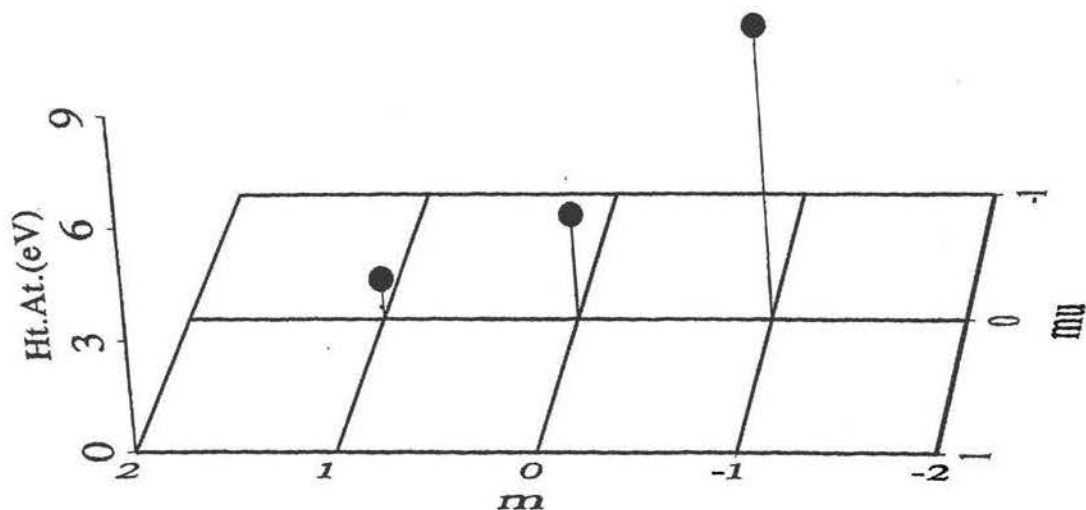
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Triplet S
Heat of Atomization (eV)

A3
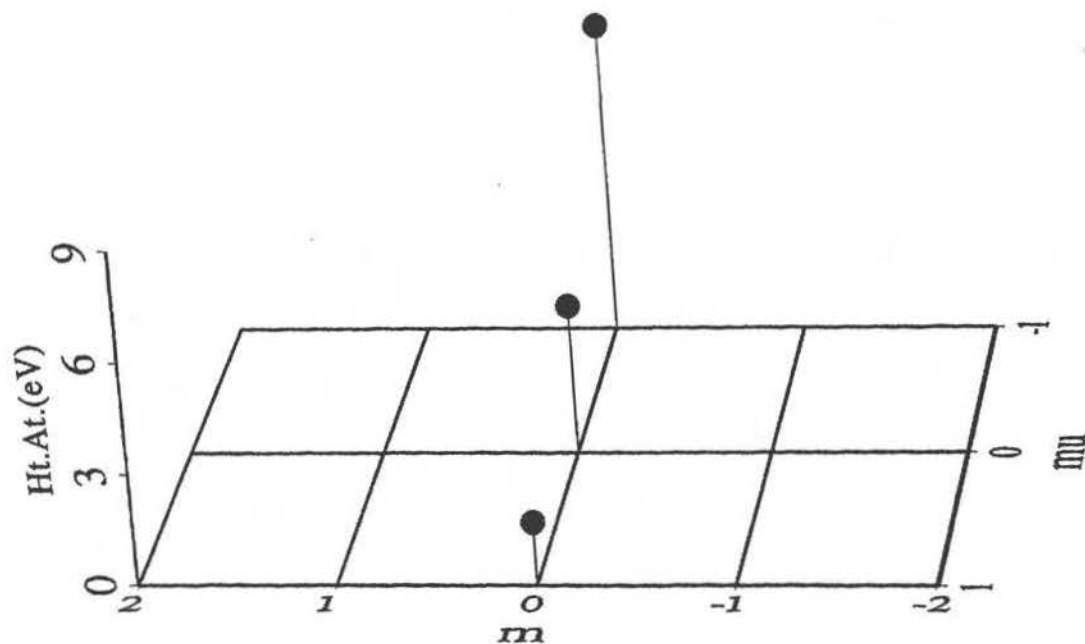
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(3,3) Triplet D
Heat of Atomization (eV)

A4
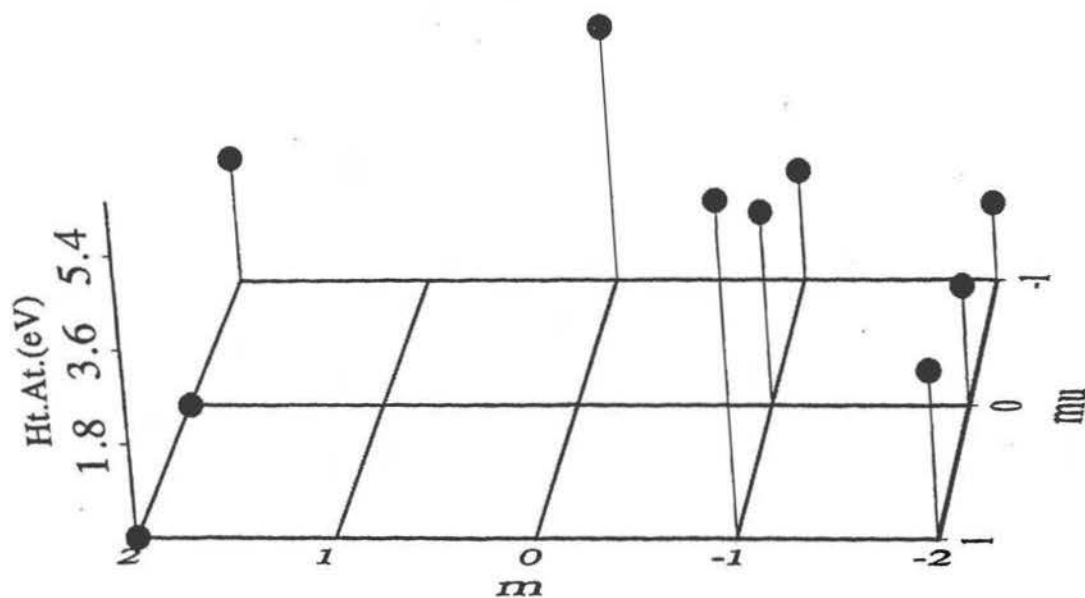
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(3,3) Triplet S
Heat of Atomization (eV)

A5
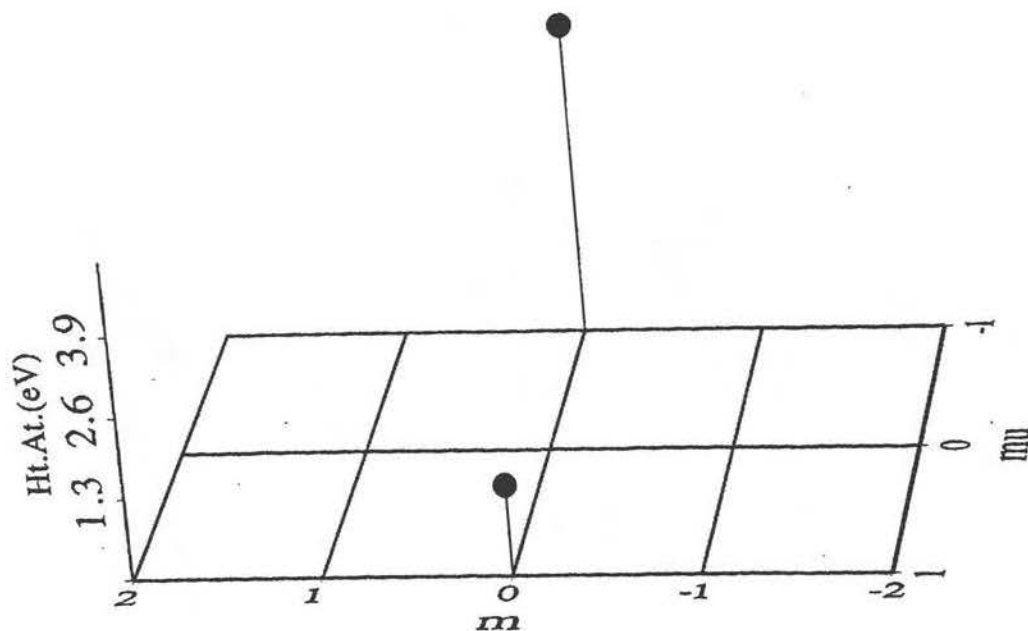
SO(3)xSU(2) Triatomic Molecules (R₁,R₂,R₃)=(2,2,2) Quartet F
Heat of Atomization (eV)

A6
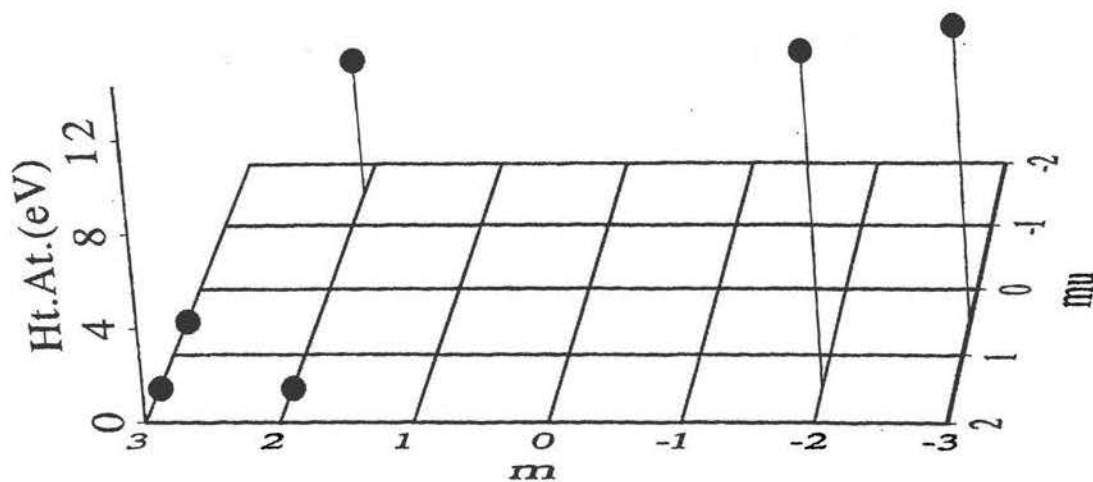
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Triplet D
Heat of Atomization (eV) Homonuclear Approximation

A7
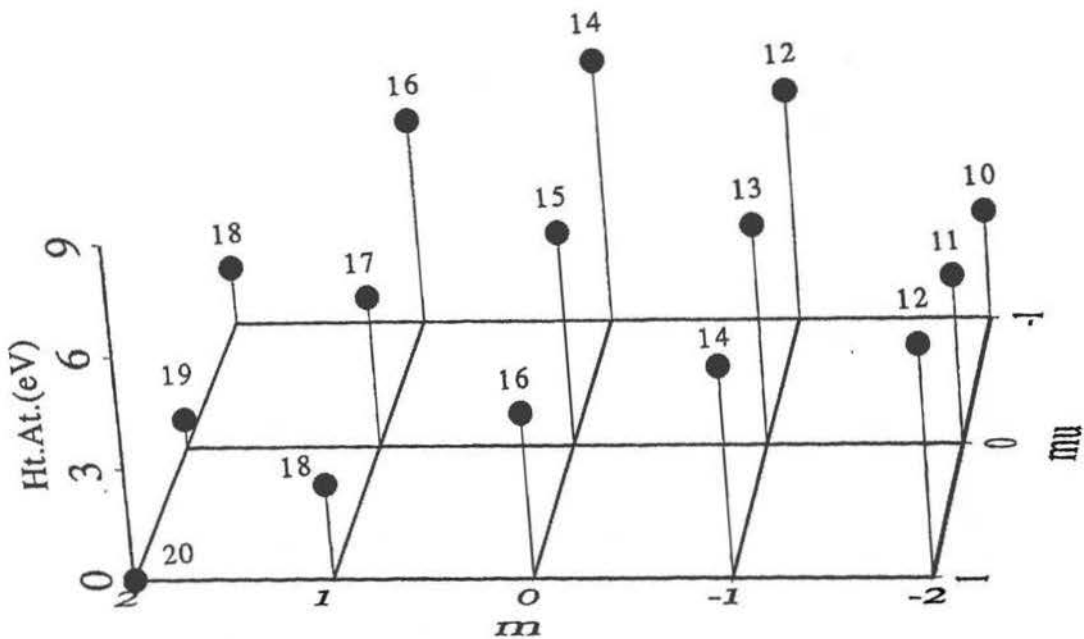
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Singlet P
Heat of Atomization (eV) Homonuclear Approximation

A8
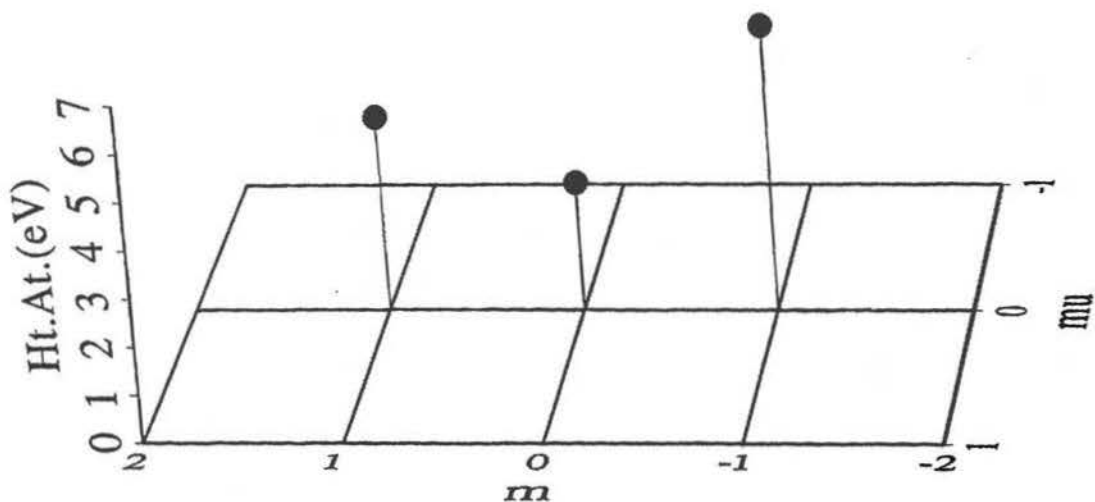
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Triplet S
Heat of Atomization (eV) Homonuclear Approximation

A9
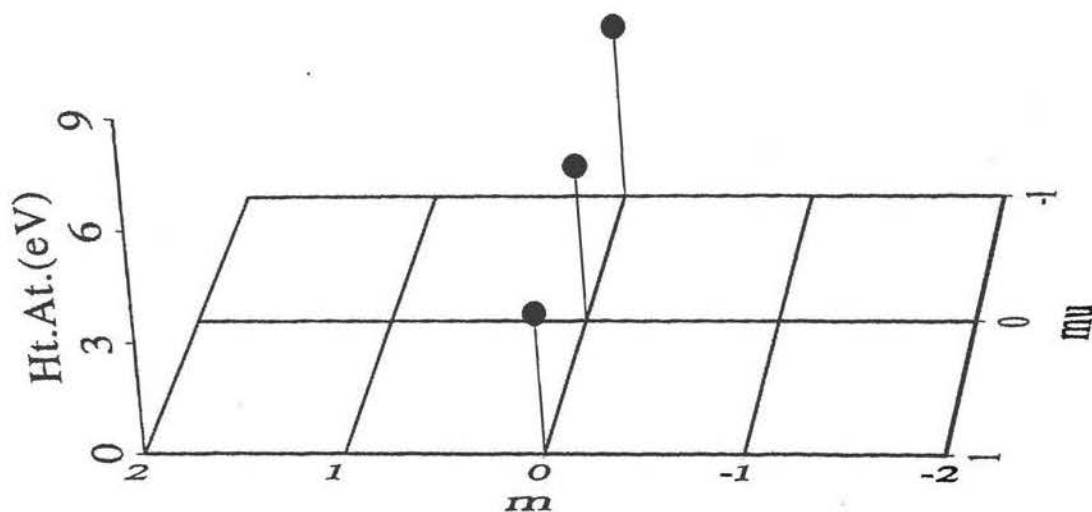
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(3,3) Triplet D
Heat of Atomization (eV) Homonuclear Approximation

A10
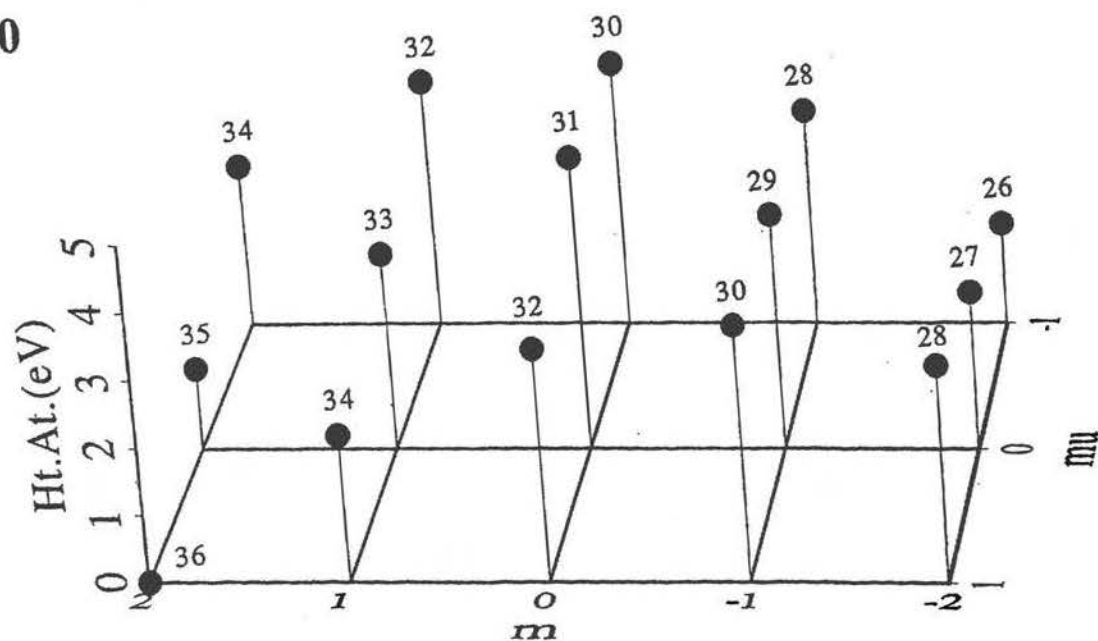
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(3,3)$ Singlet P
Heat of Atomization (eV) Homonuclear Approximation

A11
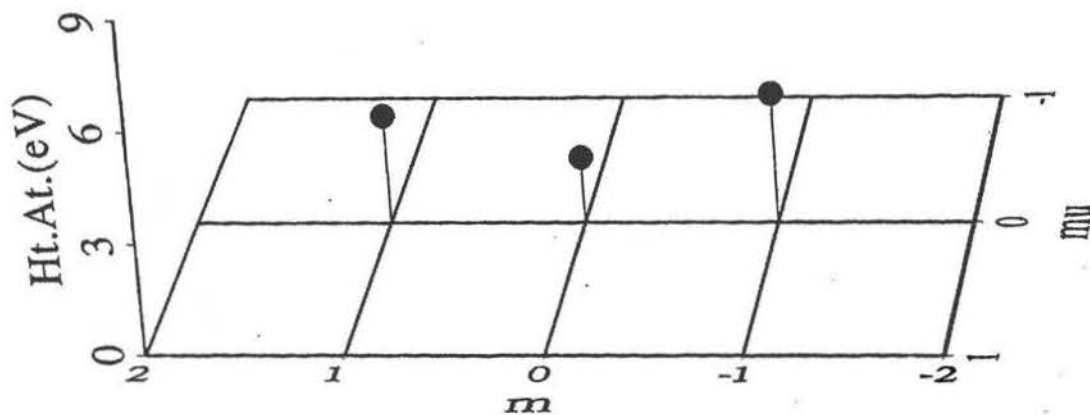
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(3,3)$ Triplet S
Heat of Atomization (eV) Homonuclear Approximation

A12
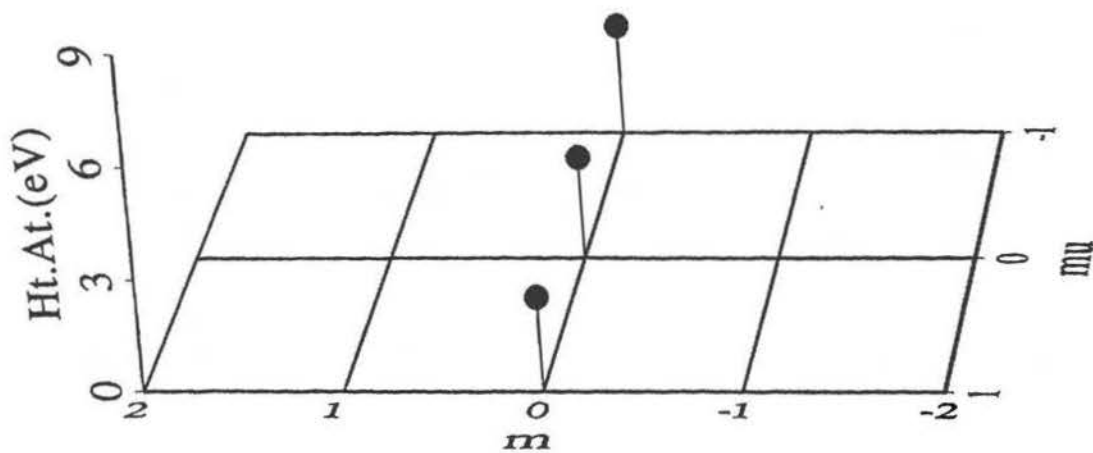
SO(3)xSU(2) Atoms (R)=(2) Doublet P
Ionization Potential (eV)

A13
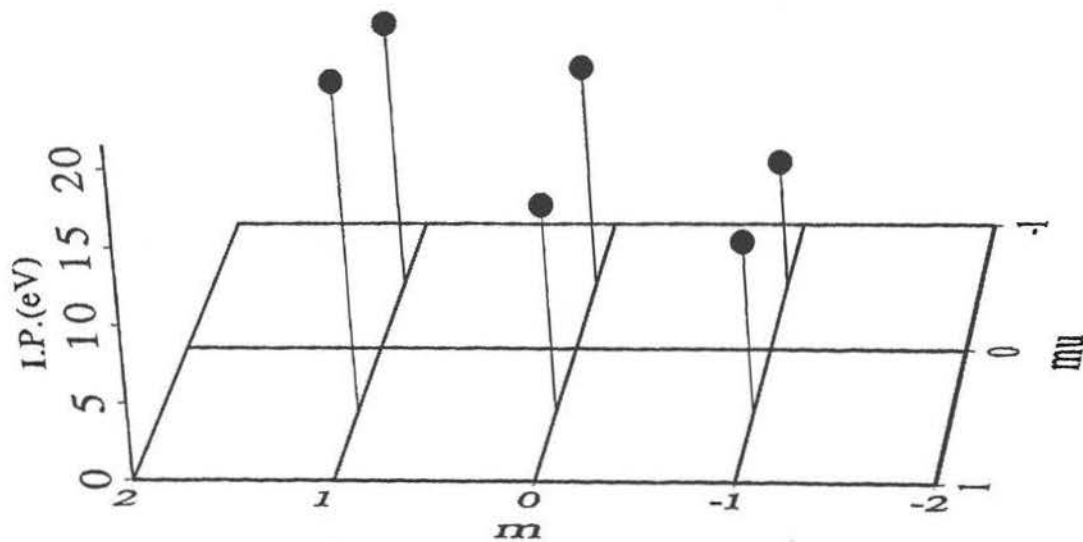
SO(3)xSU(2) Atoms (R)=(3) Doublet D
Ionization Potential (eV)

A14
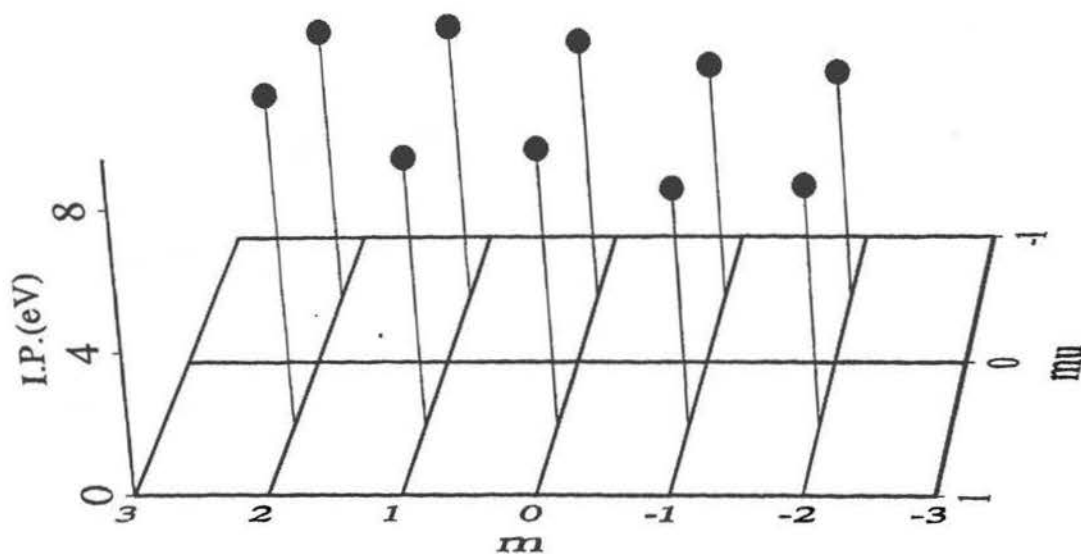
SO(3)xSU(2) Atoms (R)=(3) Doublet P
Ionization Potential (eV)

A15
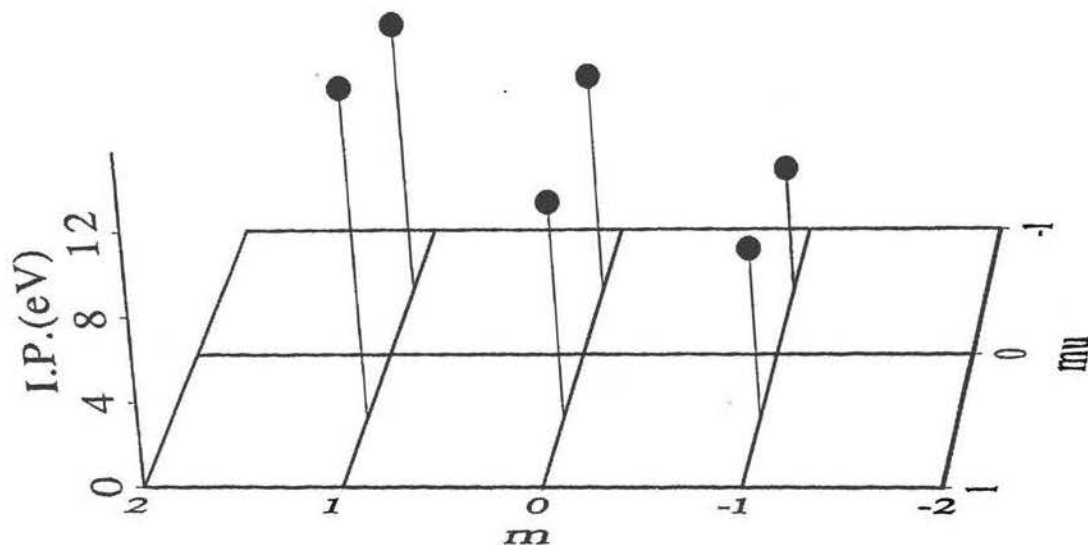
SO(3)xSU(2) Atoms (R)=(4) Doublet F
Ionization Potential (eV)

A16

57
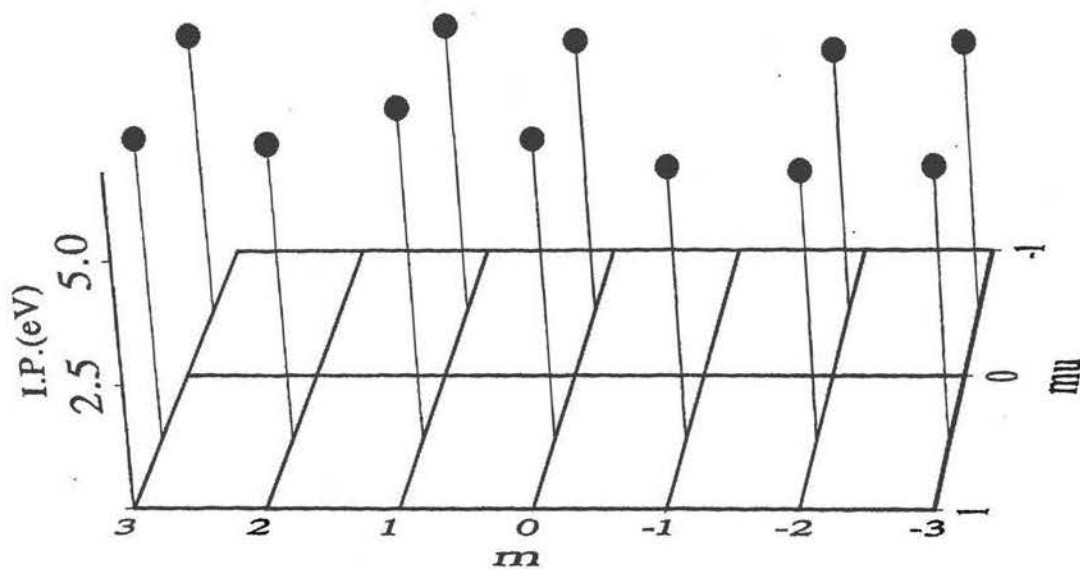
SO(3)xSU(2) Atoms (R)=(4) Doublet D
Ionization Potential (eV)

A17
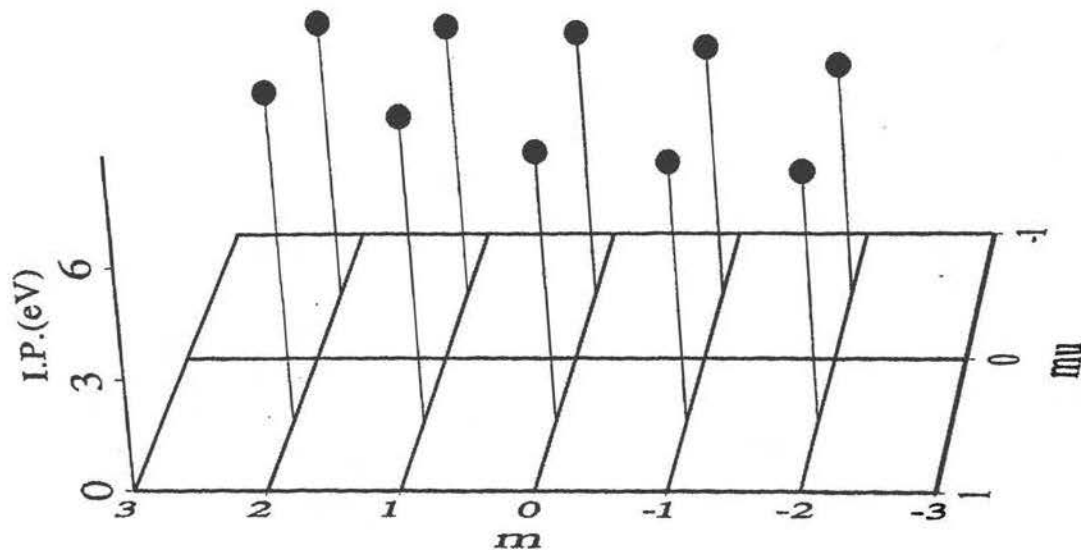
SO(3)xSU(2) Atoms (R)=(5) Doublet D
Ionization Potential (eV)

A18
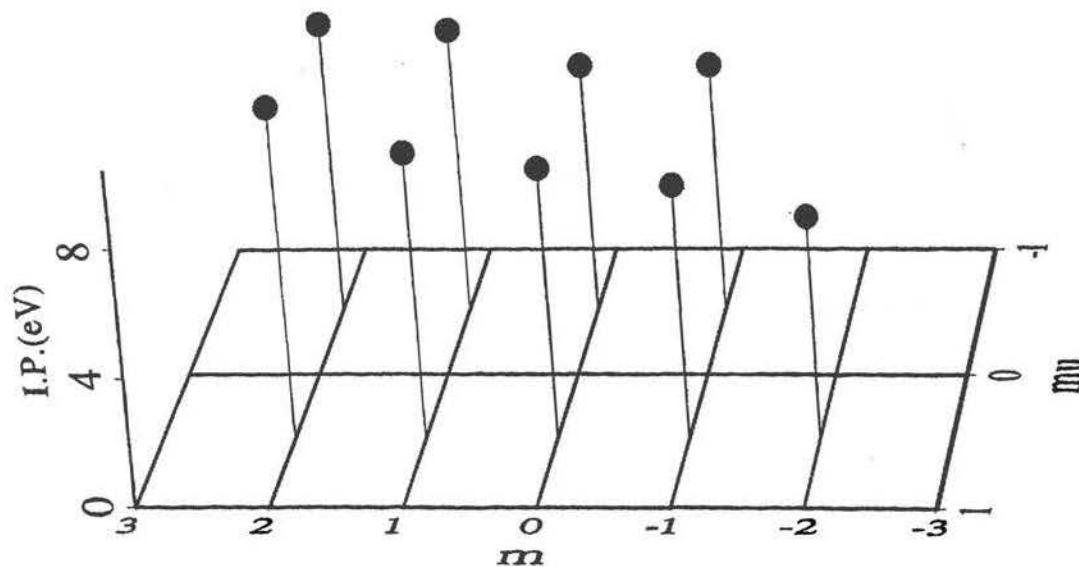
SO(3)xSU(2) Atoms (R)=(6) Doublet P
Ionization Potential (eV)

A19
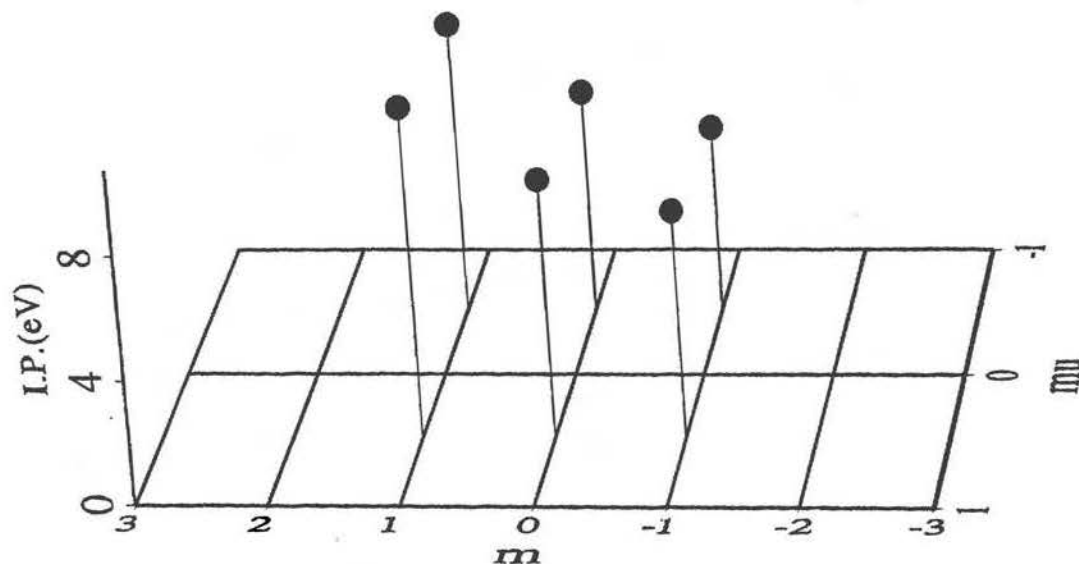
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Triplet D
Ionization Potential (eV)

A20
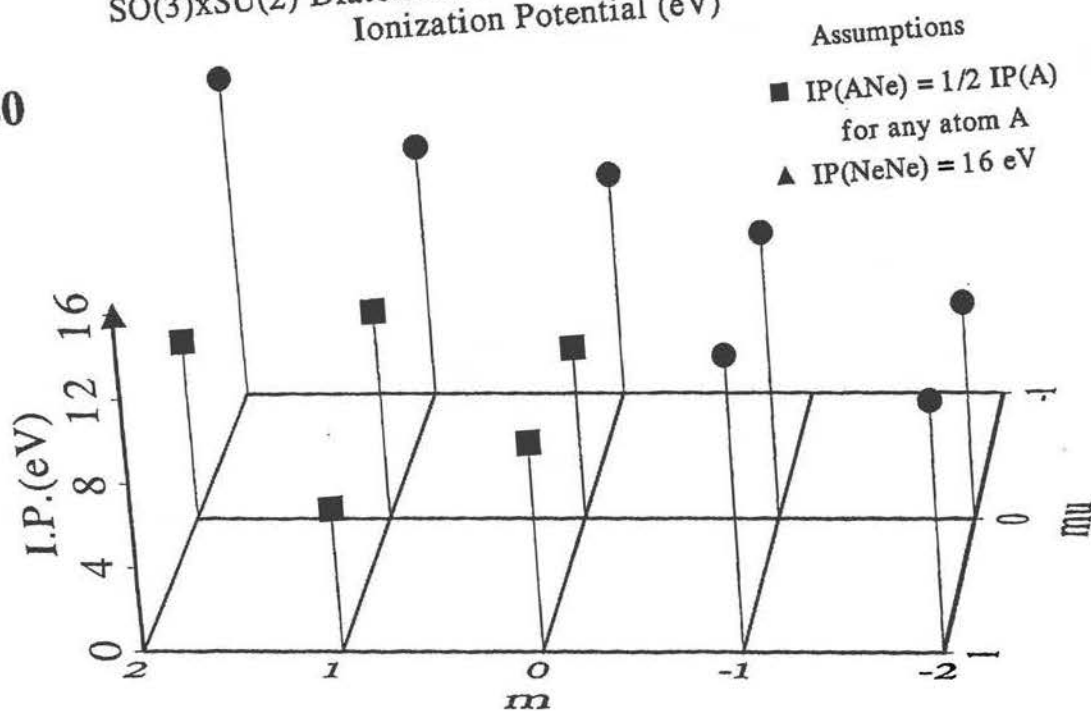
Assumptions

■ IP(ANe) = 1/2 IP(A) for any atom A
▲ IP(NeNe) = 16 eV

SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,2)$ Triplet S
Ionization Potential (eV)

A21

Assumption

■ IP(ANe) = 1/2 IP(A)
for any atom A

I.P.(eV)

12

8

4

0

2   1   0   -1   -2

m

mu

-1   0   1

SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(3,3)$ Triplet D
Ionization Potential (eV)

A22

Assumptions

■ I.P.(AAr) = 1/2 I.P.(A)
for any atom A

▲ I.P.(ClCl) = I.P.(ArAr)

I.P.(eV)

12

9

6

3

0

2   1   0   -1   -2

m

mu

-1   0   1
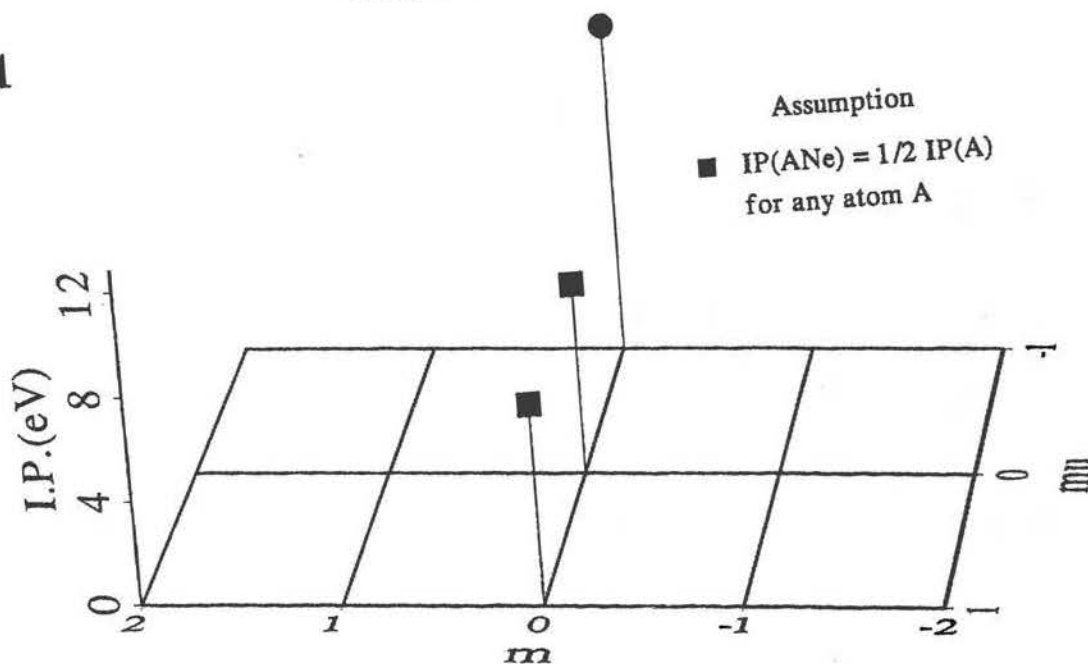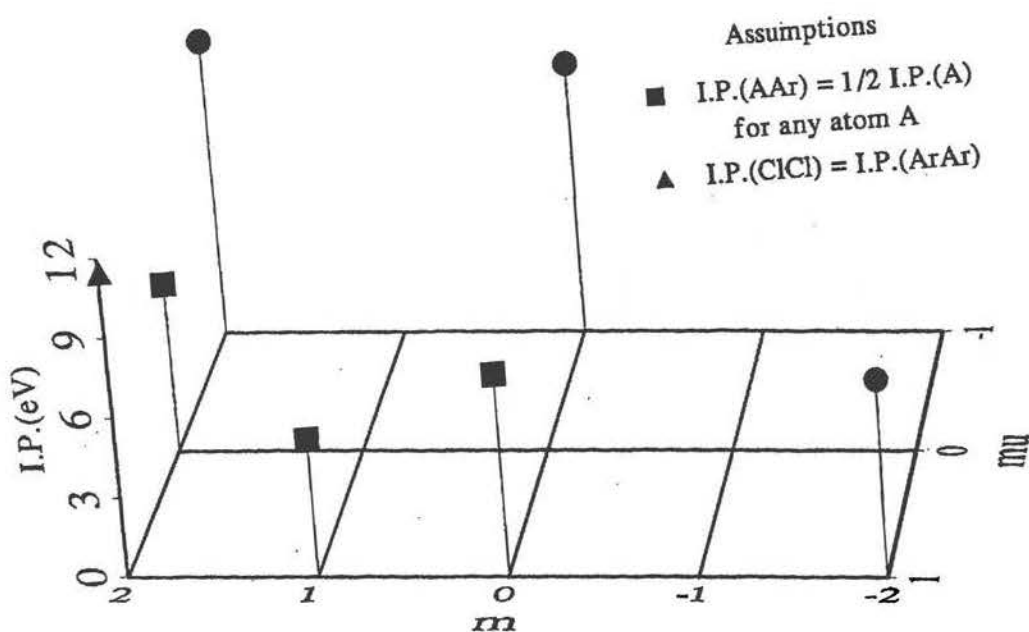
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,3)$ $(l_1,l_2)=(1,1)$ ^3D
Ionization Potential (eV)

A23
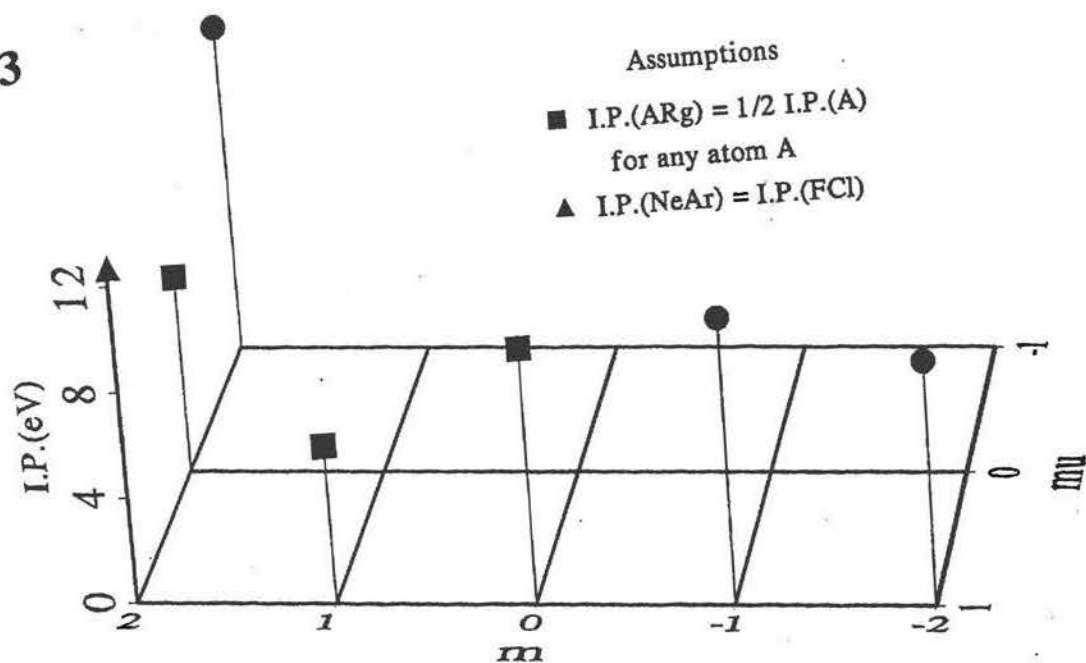
Assumptions

■ I.P.(ARg) = 1/2 I.P.(A)
for any atom A
▲ I.P.(NeAr) = I.P.(FCl)

SO(3)xSU(2) Triatomic Molecules $(R_1,R_2,R_3)=(2,2,2)$ Quartet F
Ionization Potential (eV)

A24

SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Triplet D
Ionization Potential (eV) Homonuclear Approximation

A25

Assumptions

● I.P. of B₂ = 8eV
▲ I.P. of Ne₂ = 16 eV
■ Both of the Above
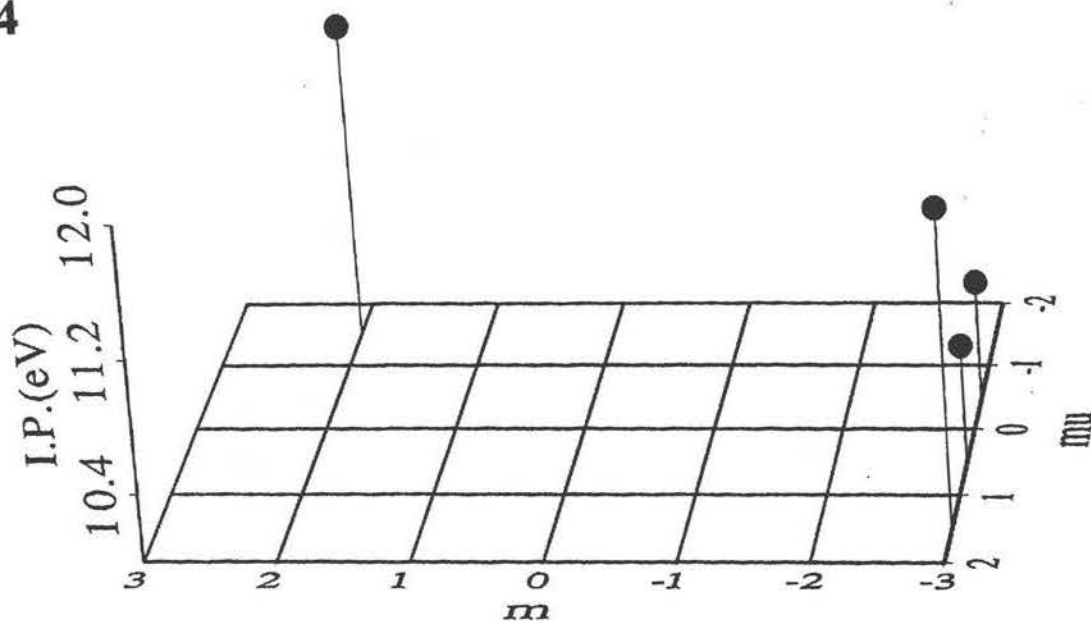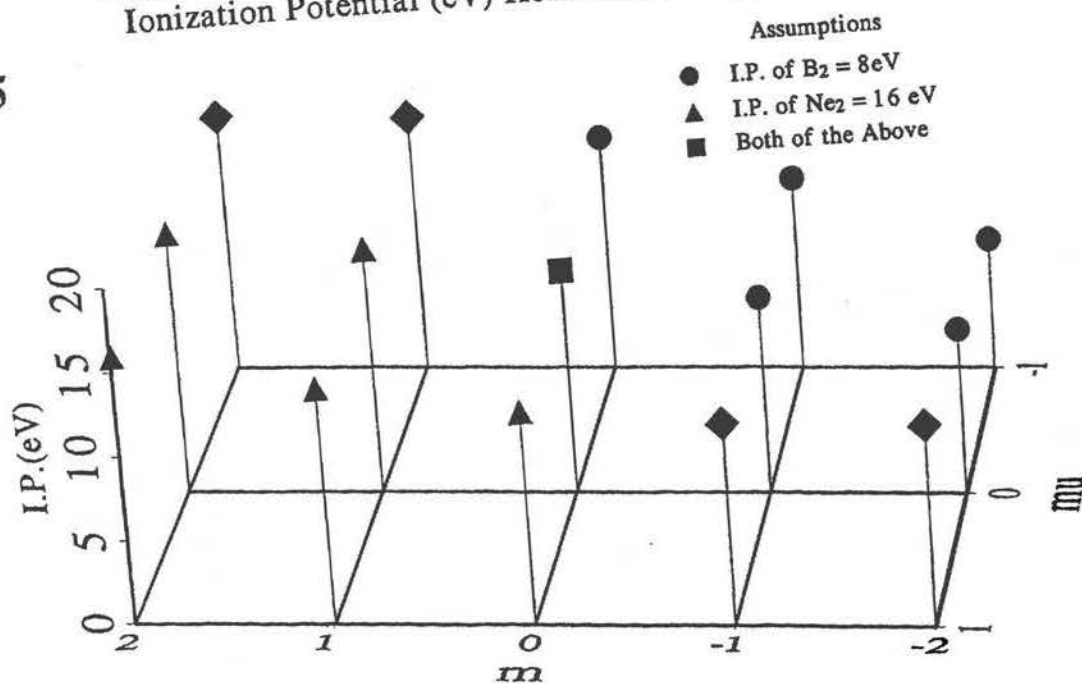
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Singlet P
Ionization Potential (eV) Homonuclear Approximation

A26
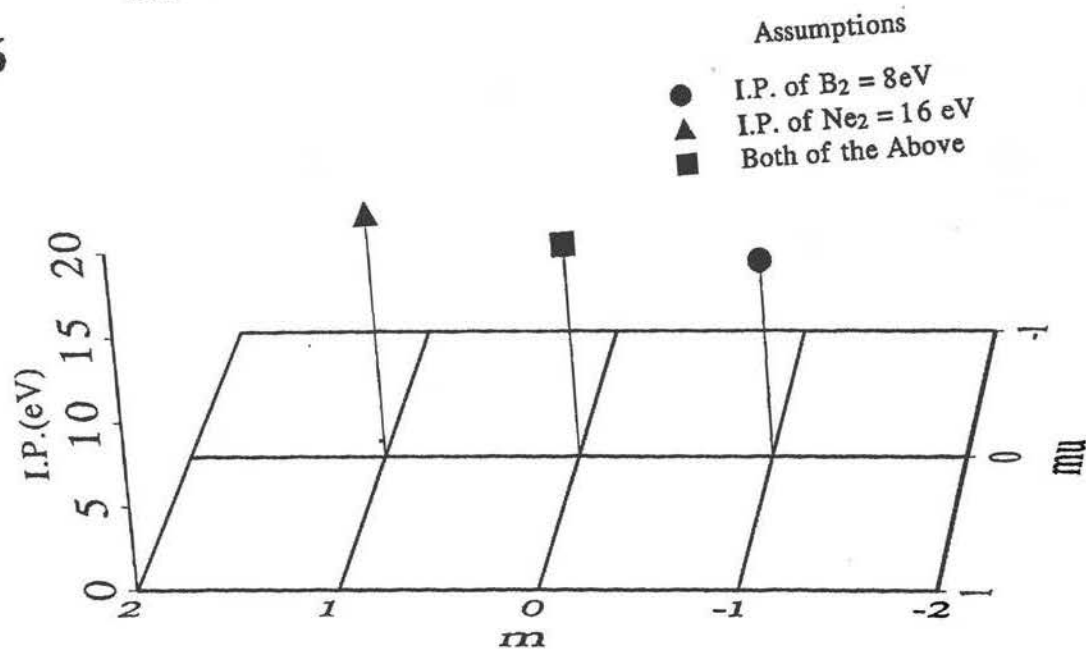
Assumptions

● I.P. of B₂ = 8eV
▲ I.P. of Ne₂ = 16 eV
■ Both of the Above

SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,2)$ Triplet S
Ionization Potential (eV) Homonuclear Approximation

A27

Assumptions

● I.P. of B_2 = 8eV
▲ I.P. of Ne_2 = 16 eV
■ Both of the Above
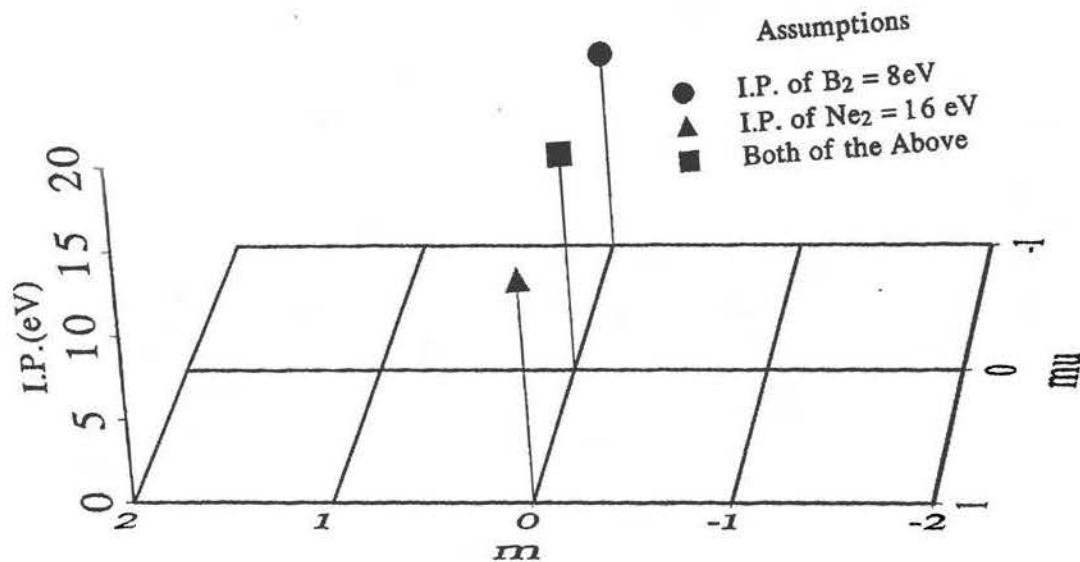
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,2)$ Triplet D
Ionization Potential (eV) Single-Particle Operator

A28
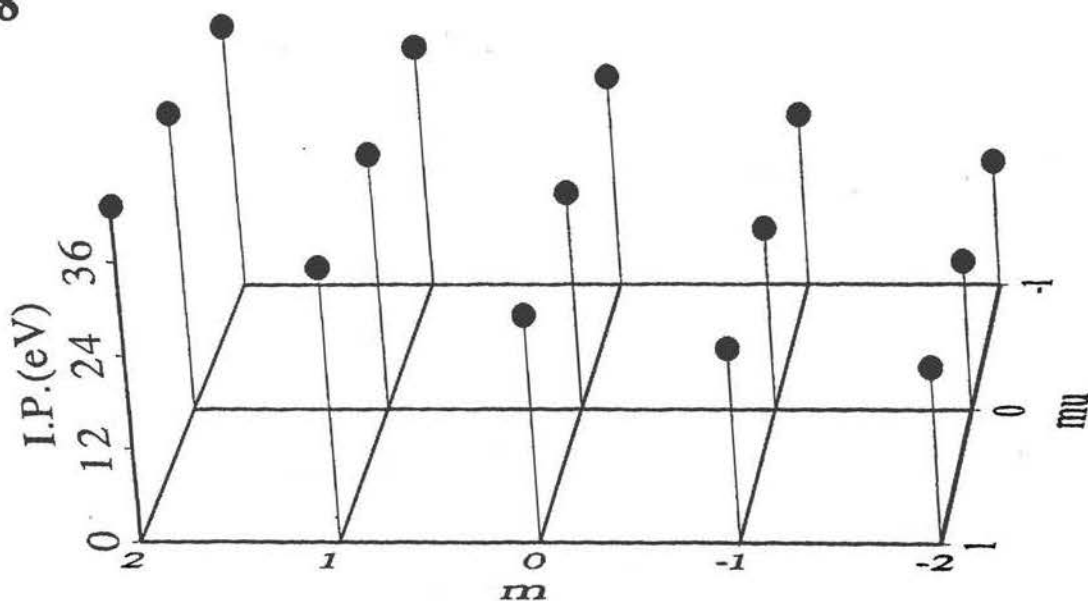
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Triplet S
Ionization Potential (eV) Single-Particle Operator

A29
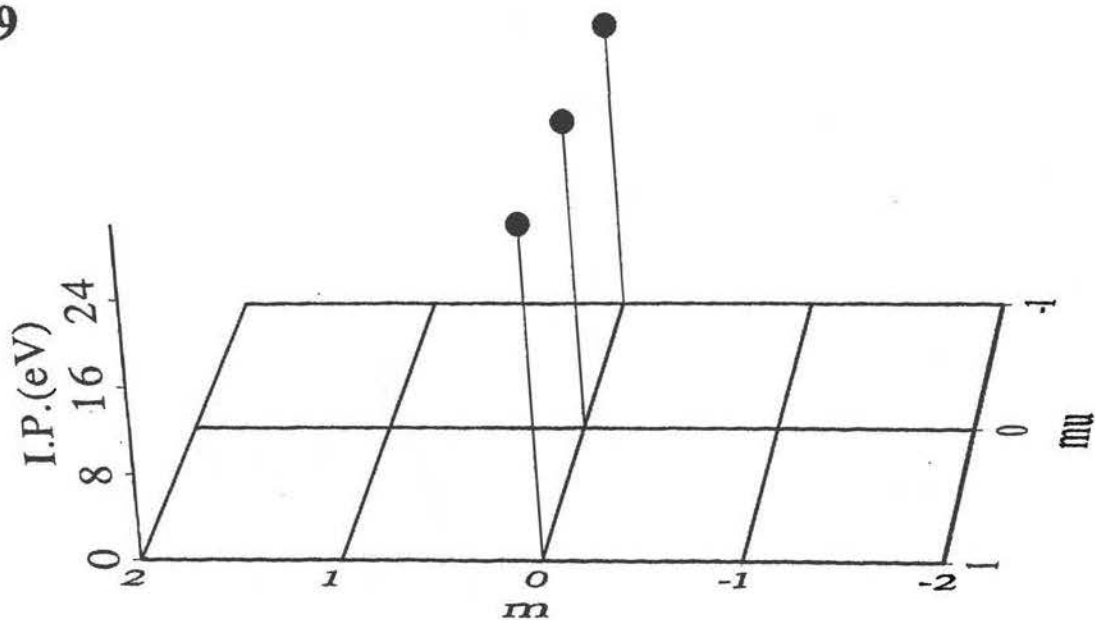
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(3,3) Triplet D
Ionization Potential (eV) Single-Particle Operator

A30
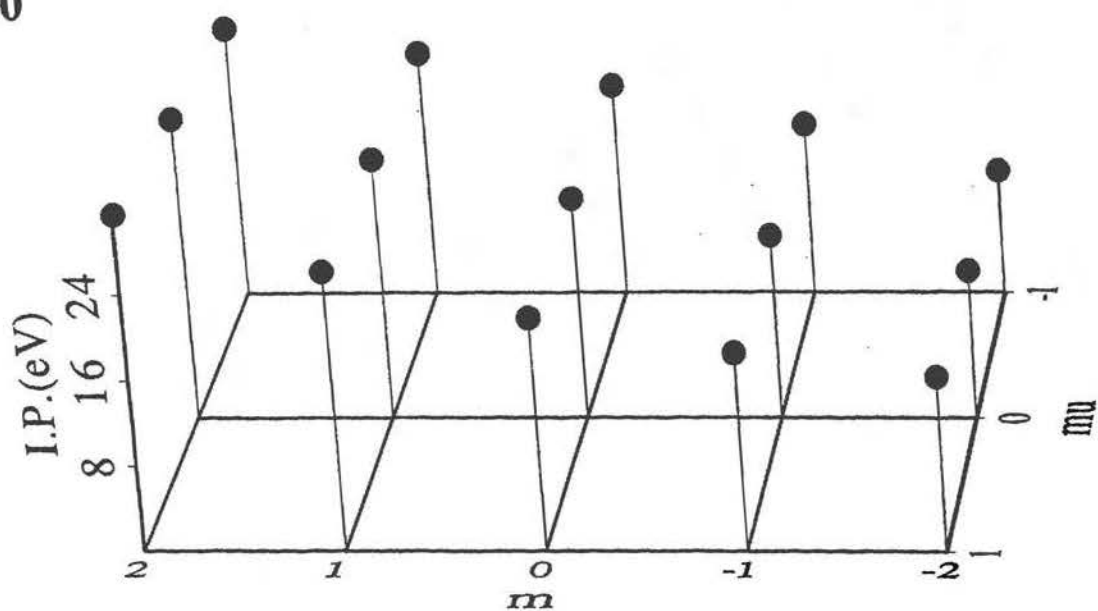
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(3,3) Triplet S
Ionization Potential (eV) Single-Particle Operator

A31
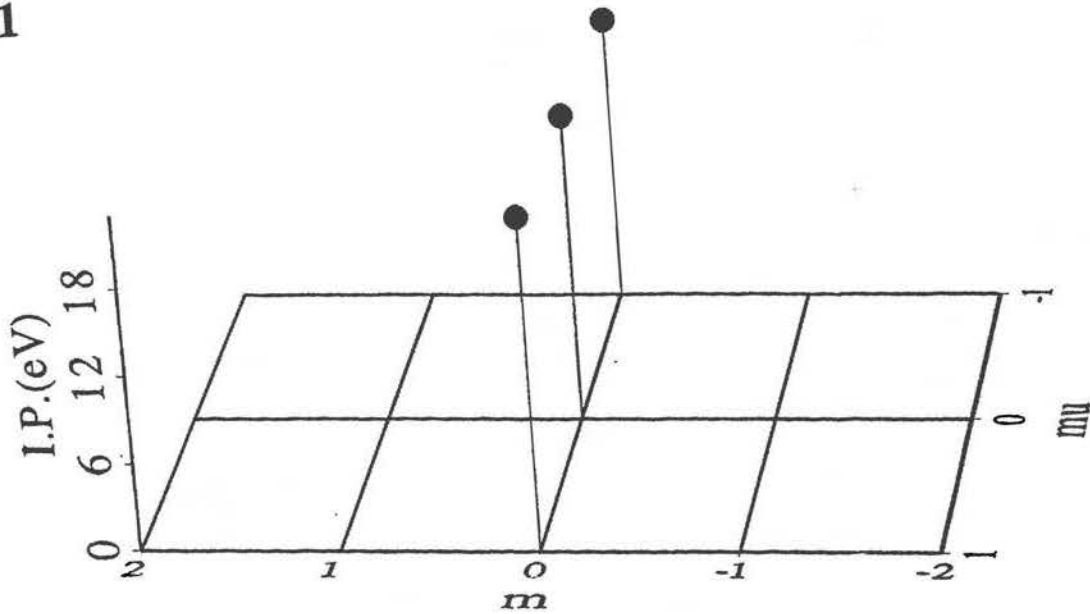
SO(3)xSU(2) Triatomic Molecules (R₁,R₂,R₃)=(2,2,2) Quartet F
Ionization Potential (eV) Single-Particle Operator

A32
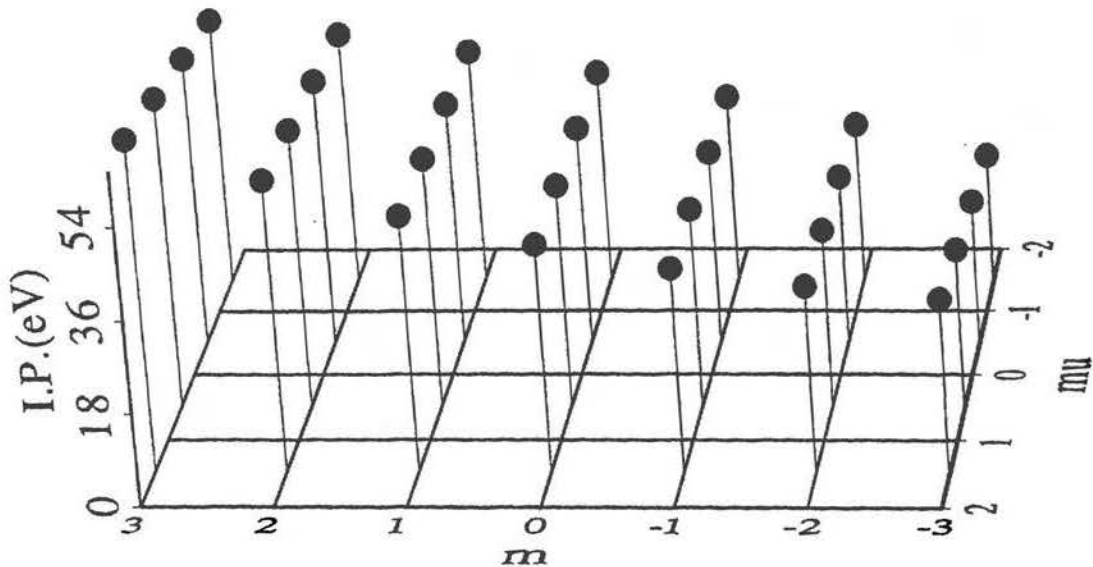
SO(3)xSU(2) Triatomic Molecules (R₁,R₂,R₃)=(2,2,2) Doublet D
Ionization Potential (eV) Single-Particle Operator

A33
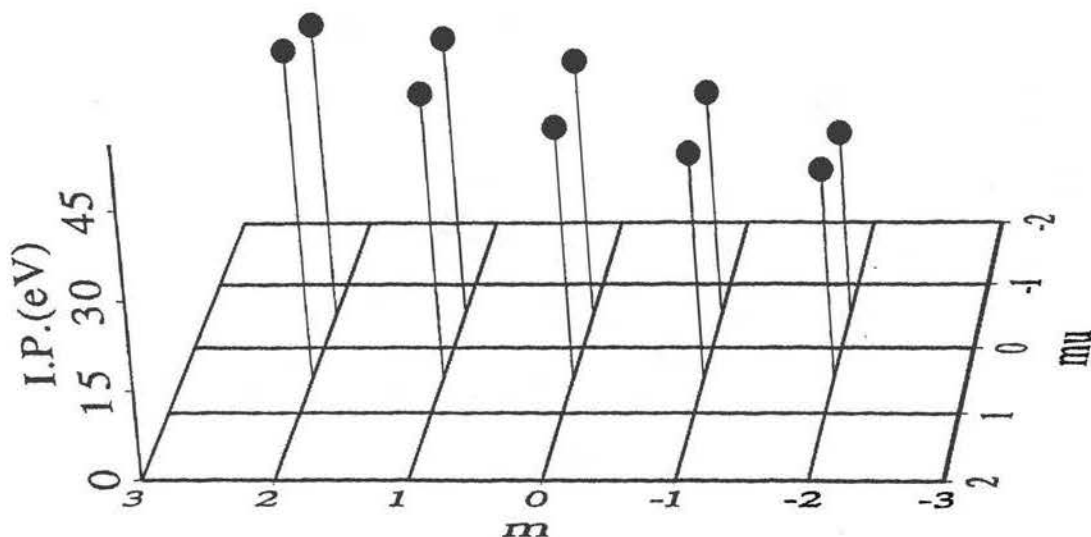
SO(3)xSU(2) Triatomic Molecules (R₁,R₂,R₃)=(2,2,2) Quartet F
Ionization Potential (eV) Two-Particle Operator

A34

Assumptions
■ I.P.(ARg) = 1/2 I.P.(A)
▲ I.P.(NeNe) = I.P.(FF)
◆ Both of the Above
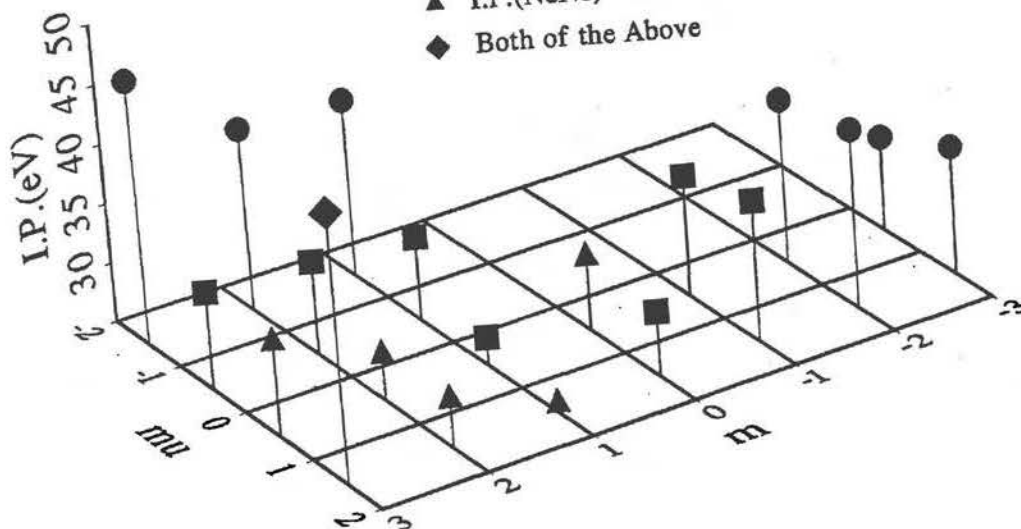
SO(3)xSU(2) Triatomic Molecules $(R_1,R_2,R_3)=(2,2,2)$ Doublet D
Ionization Potential (eV) Two-Particle Operator

A35

Assumptions

■ I.P.(ARg) = 1/2 I.P.(A)
▲ I.P.(NeNe) = I.P.(FF)
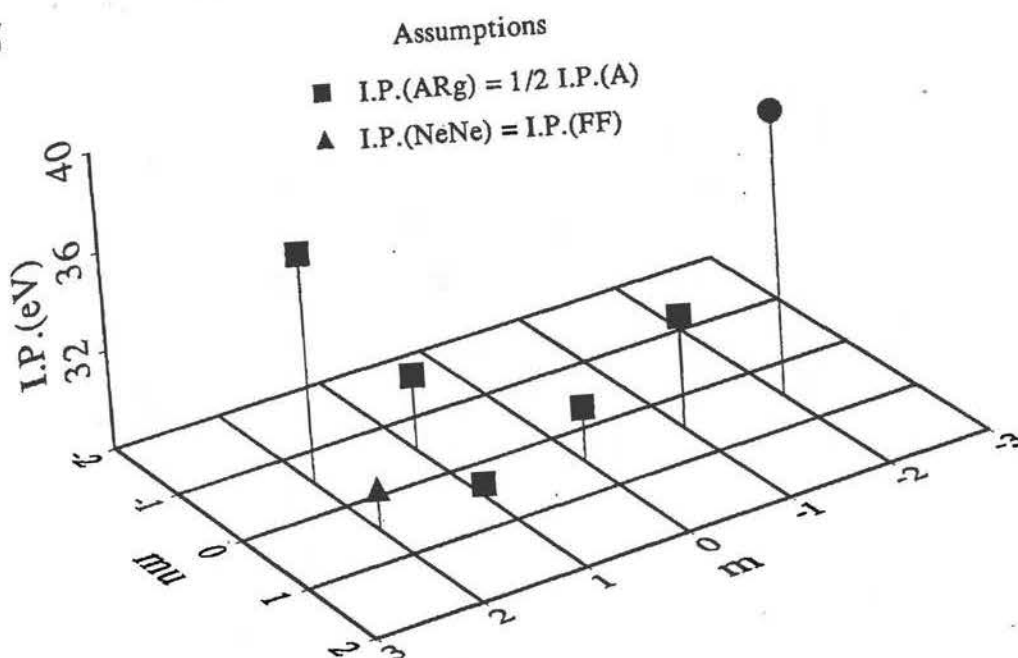
SO(3)xSU(2) Atoms (R)=(2) Doublet P
Entropy at 298K (cal/(mole degree))

A36
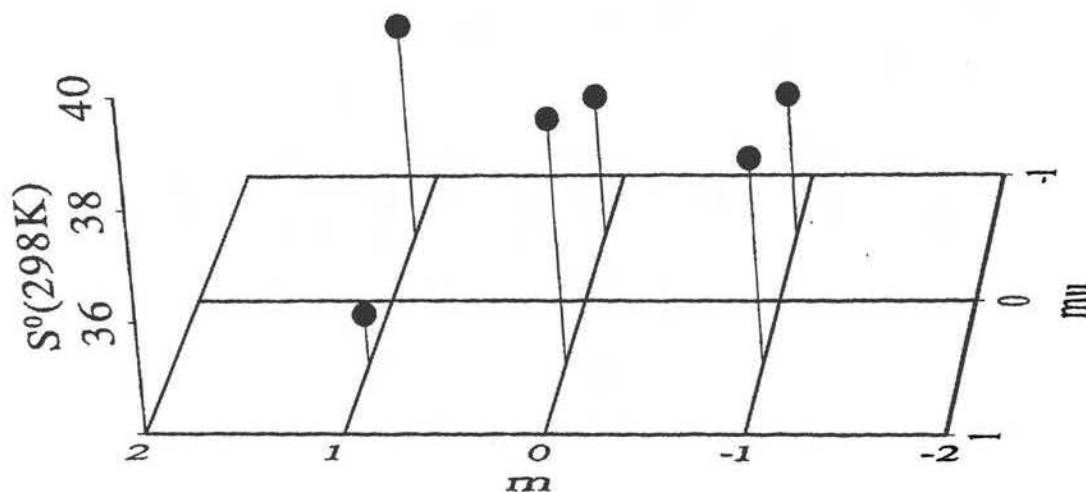
SO(3)xSU(2) Atoms (R)=(3) Doublet D
Entropy at 298K (cal/(mole degree))

A37
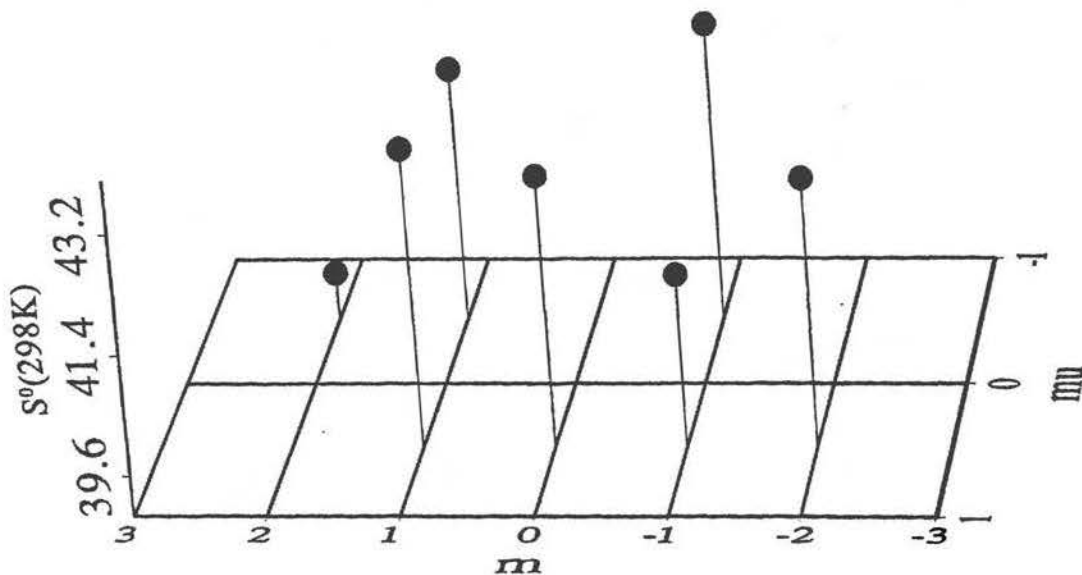
SO(3)xSU(2) Atoms (R)=(3) Doublet P
Entropy at 298K (cal/(mole degree))

A38

SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,2)$ Triplet D
Entropy at 298K (cal/(mole degree))

A39
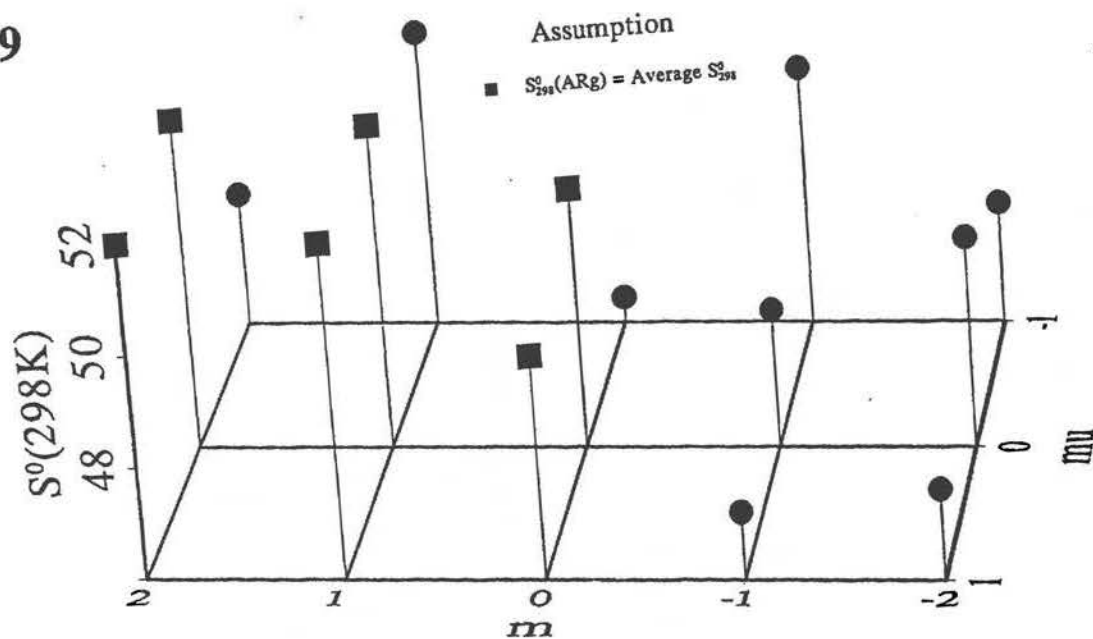
Assumption

■ $S^0_{298}(ARg) = $ Average S^0_{298}

SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,2)$ Singlet P
Entropy at 298K (cal/(mole degree))

A40

Assumption

■ $S^0_{298}(AAr) = $ Average S^0_{298}

SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Triplet S
Entropy at 298K (cal/(mole degree))

A41

Assumption

■ $S^0_{298}(AAr)$ = Average S^0_{298}

SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(3,3) Triplet D
Entropy at 298K (cal/(mole degree))

A42

Assumption

■ $S^0_{298}(AAr)$ = Average S^0_{298}

SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(3,3)$ Triplet S
Entropy at 298K (cal/(mole degree))

A43

Assumption

■ $S^0_{298}(AAr) = Average\ S^0_{298}$
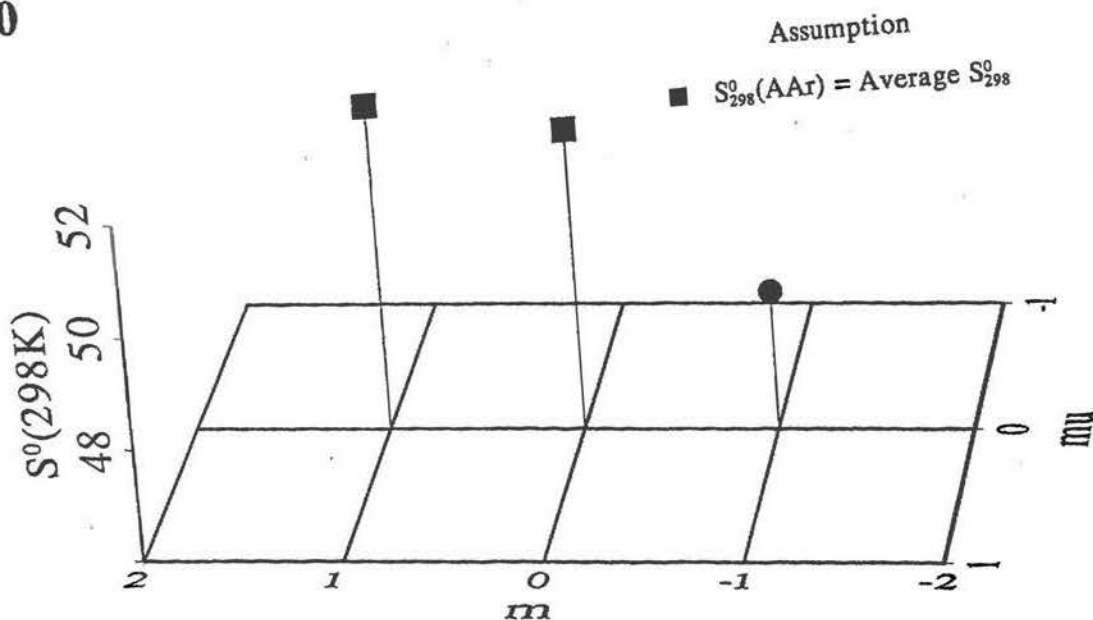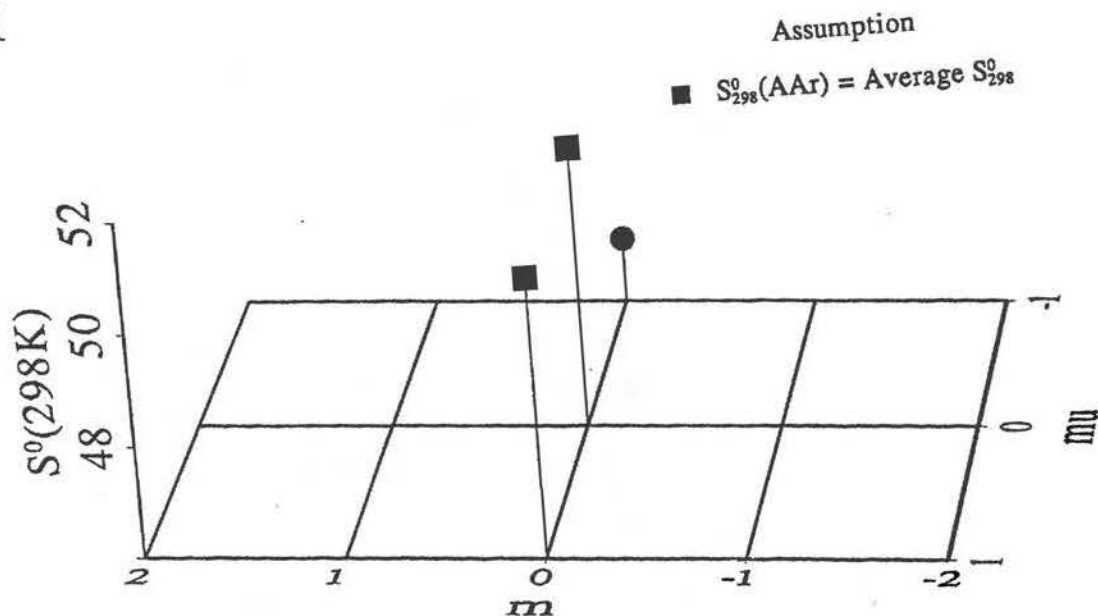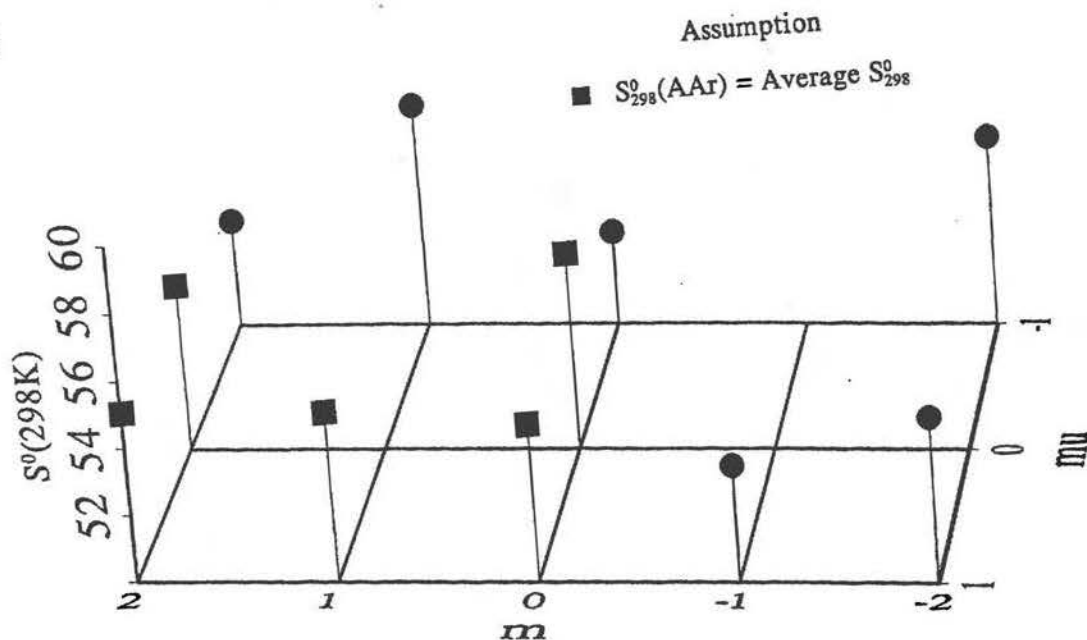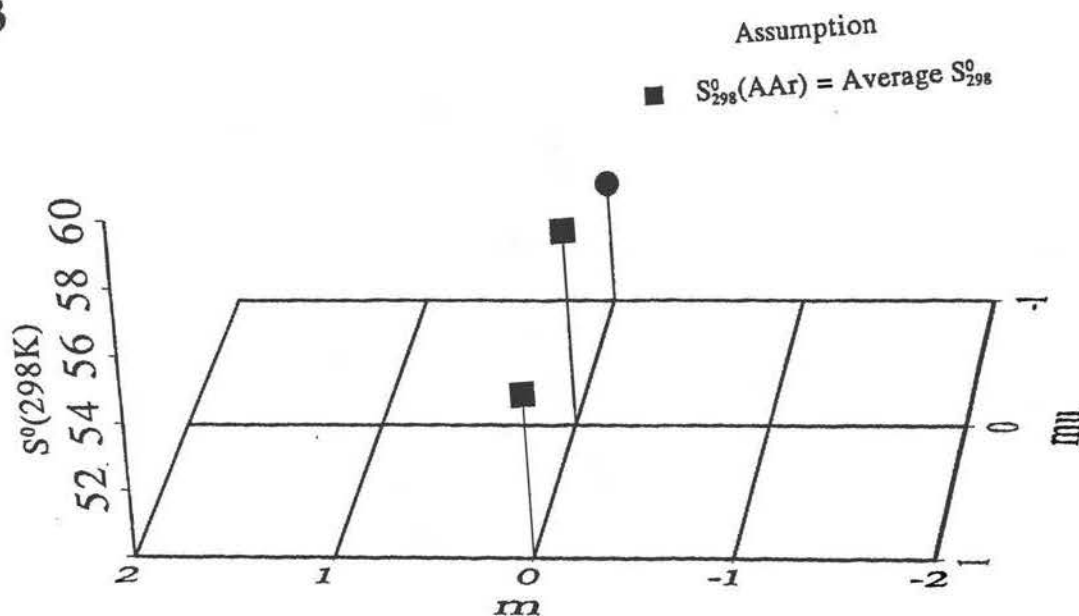
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,3)\ (l_1,l_2)=(1,1)$ ^3D
Entropy at 298K (cal/(mole degree))

A44

Assumption

■ $S^0_{298}(ARg) = Average\ S^0_{298}$
for any atom A
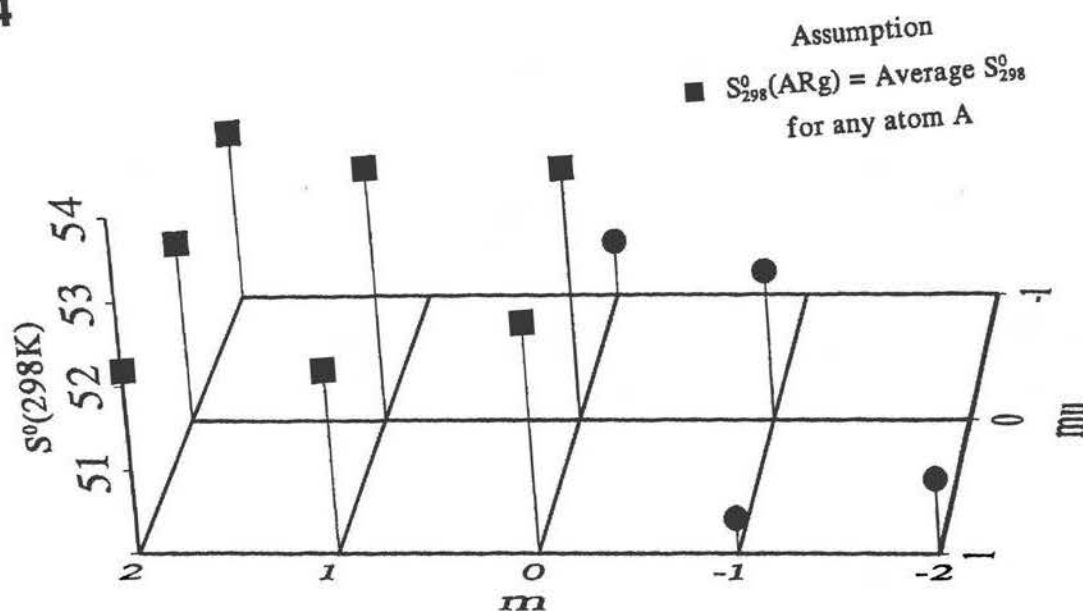
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,3) (l₁,l₂)=(1,1) ¹P
Entropy at 298K (cal/(mole degree))

A45

Assumption

■ $S^0_{298}(ARg)$ = Average S^0_{298}
for any atom A
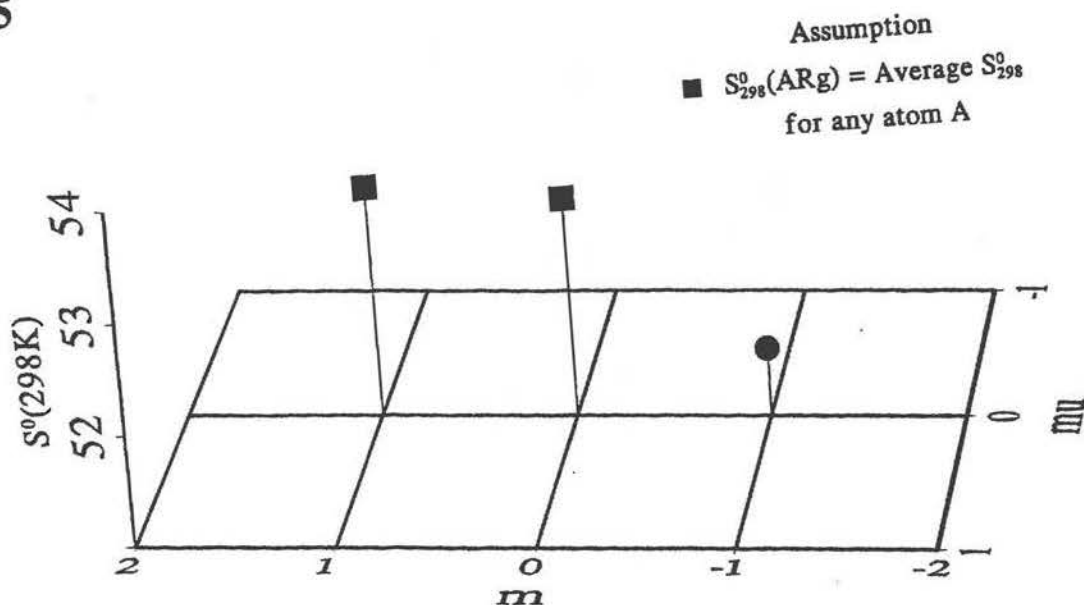
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,3) (l₁,l₂)=(1,1) ³P
Entropy at 298K (cal/(mole degree))

A46

Assumption

■ $S^0_{298}(ARg)$ = Average S^0_{298}
for any atom A
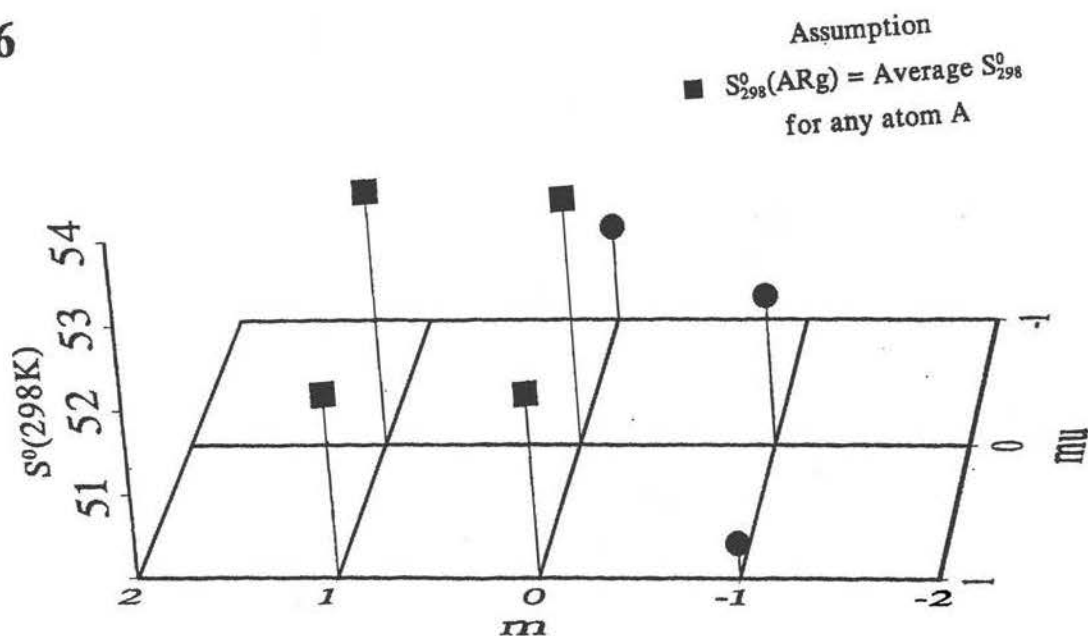
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,3)$ $(l_1,l_2)=(1,0)$ ^1P
Entropy at 298K (cal/(mole degree))

A47

Assumption

■ $S^0_{298}(ARg)$ = Average S^0_{298}
for any atom A
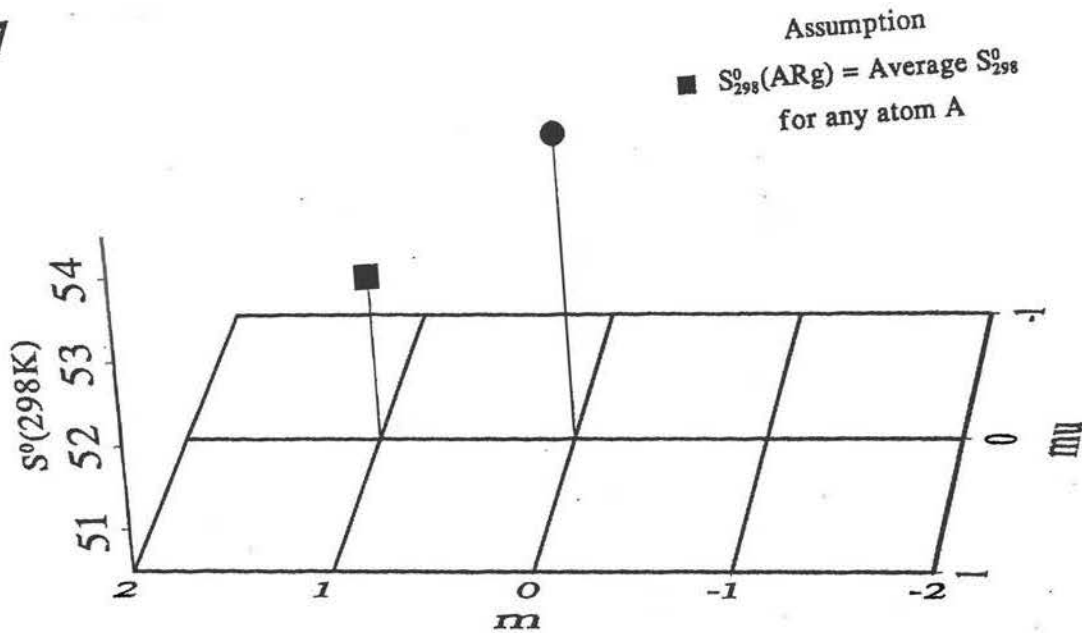
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,3)$ $(l_1,l_2)=(1,0)$ ^3P
Entropy at 298K (cal/(mole degree))

A48

Assumption

■ $S^0_{298}(ARg)$ = Average S^0_{298}
for any atom A
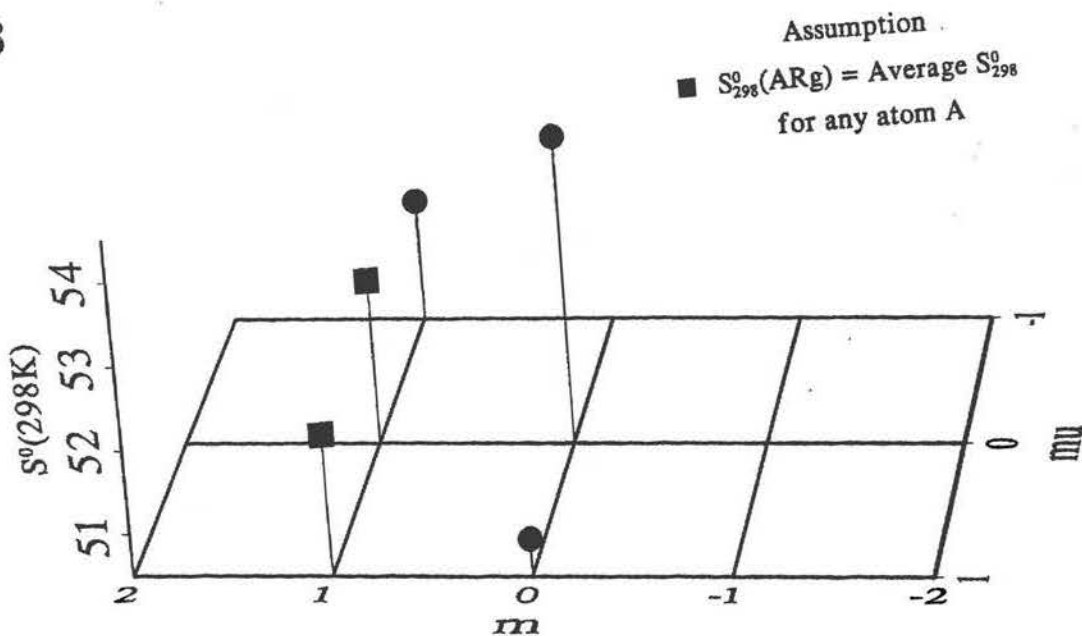
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,3)$ $(l_1,l_2)=(0,1)$ ^3P
Entropy at 298K (cal/(mole degree))

A49

Assumption

■ $S^0_{298}(ARg)$ = Average S^0_{298}
for any atom A
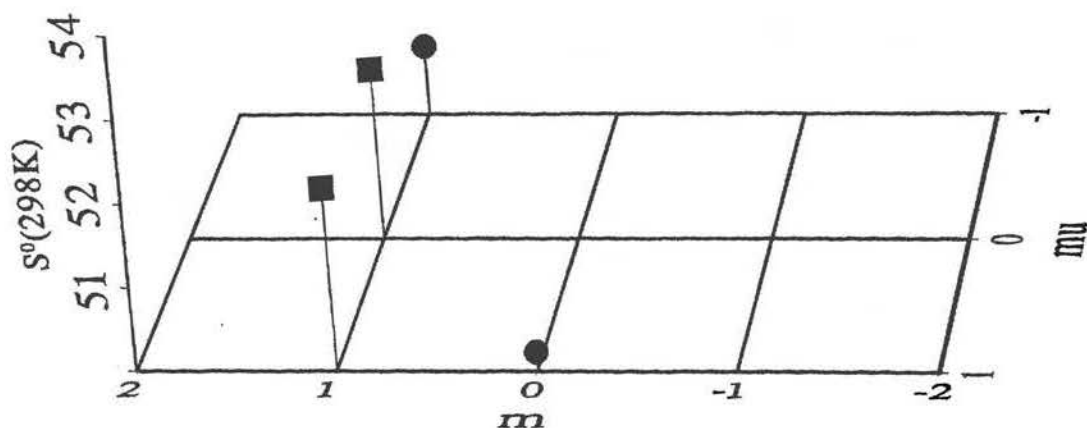
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,2)$ Triplet D
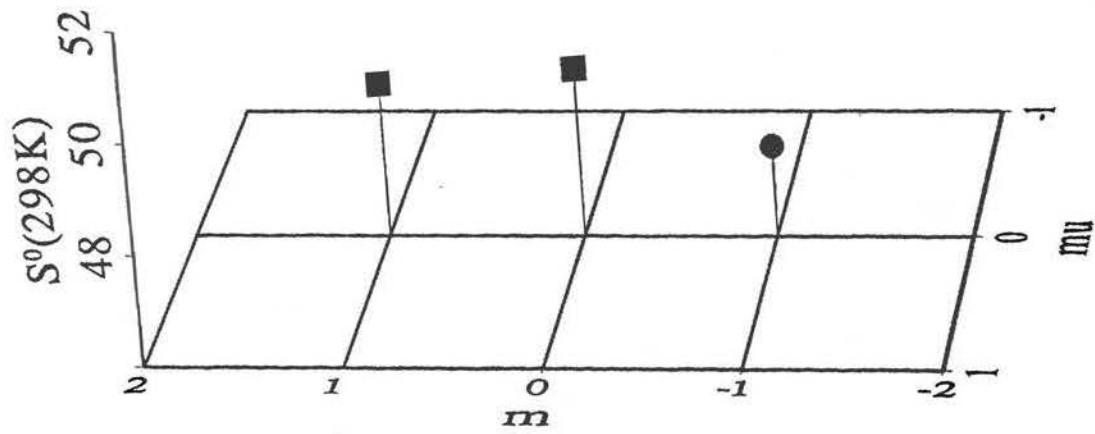Entropy at 298K (cal/(mole degree)) Homonuclear Approximation

A50

Assumption

■ $S^0_{298}(ARg)$ = Average S^0_{298}

SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Singlet P
Entropy at 298K (cal/(mole degree)) Homonuclear Approximation

A51

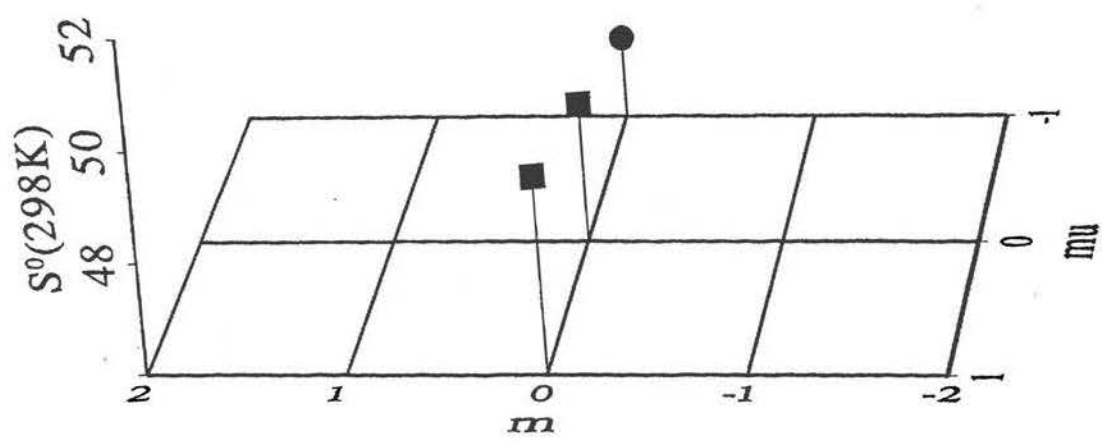Assumption

■ $S^0_{298}(ARg) = $ Average S^0_{298}

SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Triplet S
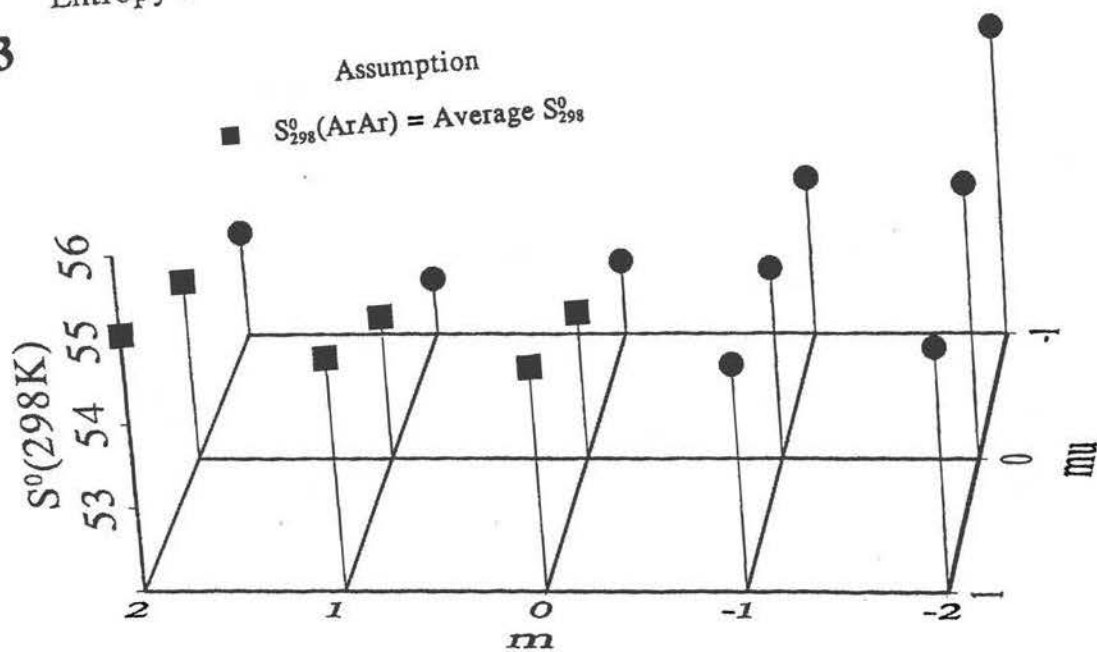Entropy at 298K (cal/(mole degree)) Homonuclear Approximation
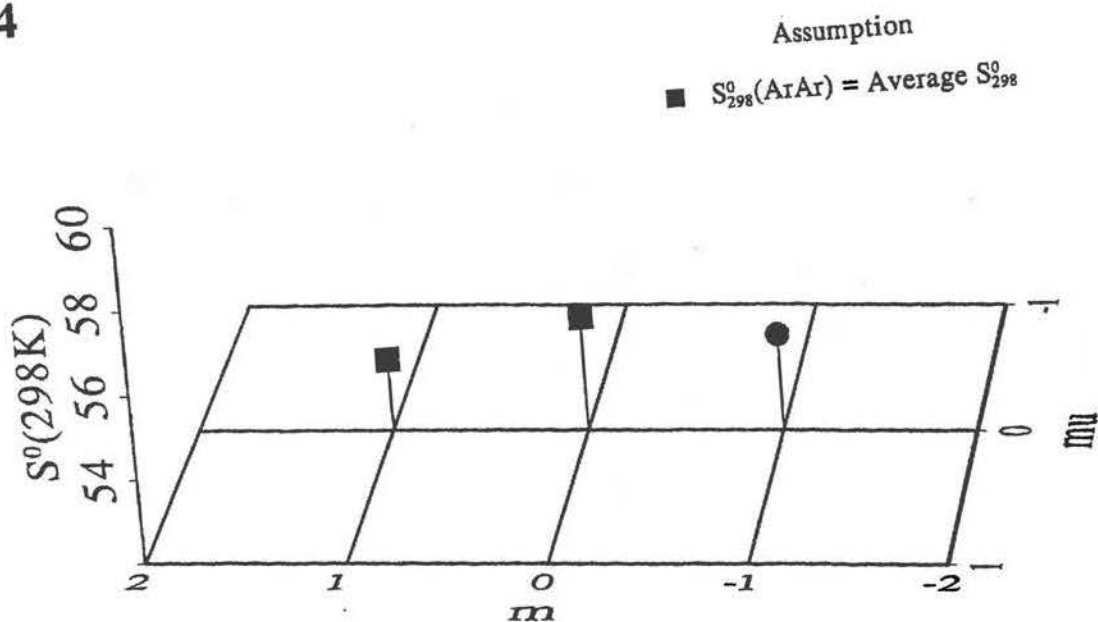
A52

Assumption

■ $S^0_{298}(ARg) = $ Average S^0_{298}

SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(3,3) Triplet D
Entropy at 298K (cal/(mole degree)) Homonuclear Approximation

A53

Assumption

■ $S^0_{298}(ArAr) = Average\ S^0_{298}$

SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(3,3) Singlet P
Entropy at 298K (cal/(mole degree)) Homonuclear Approximation
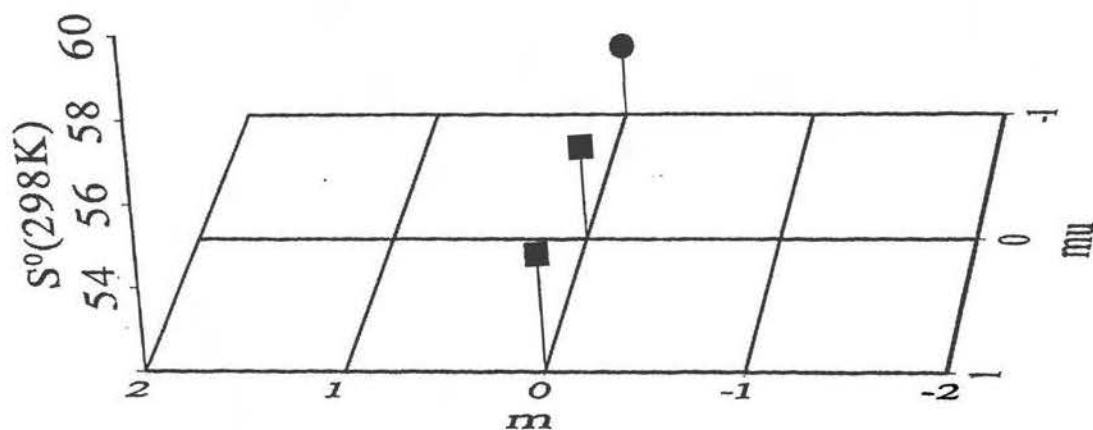
A54

Assumption

■ $S^0_{298}(ArAr) = Average\ S^0_{298}$

SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(3,3) Triplet S
Entropy at 298K (cal/(mole degree)) Homonuclear Approximation

A55

Assumption

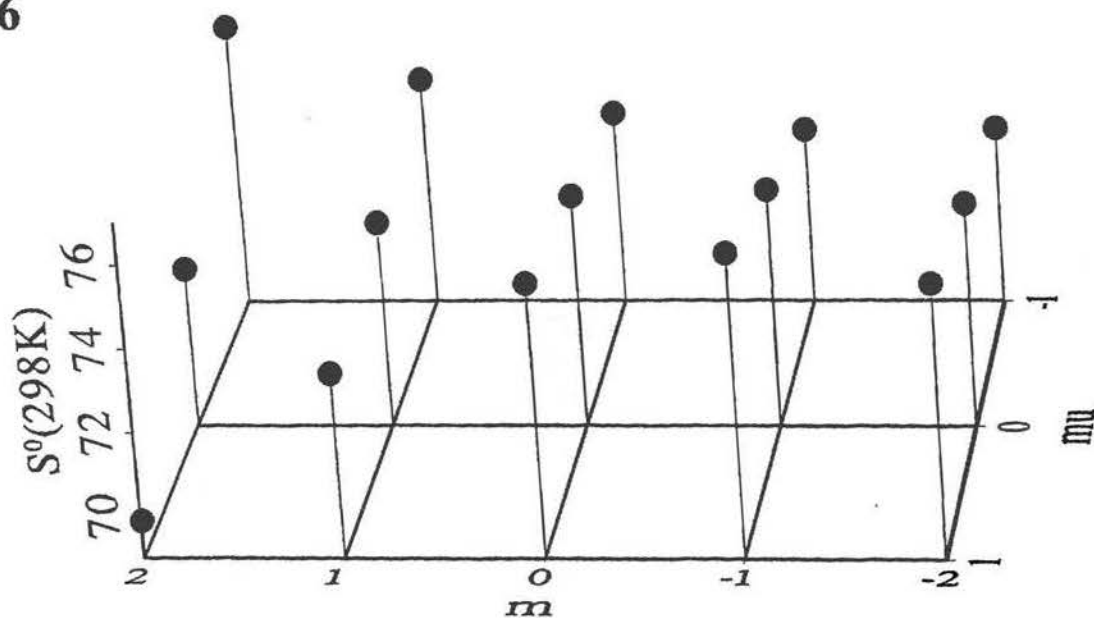■ $S^0_{298}(ArAr)$ = Average S^0_{298}

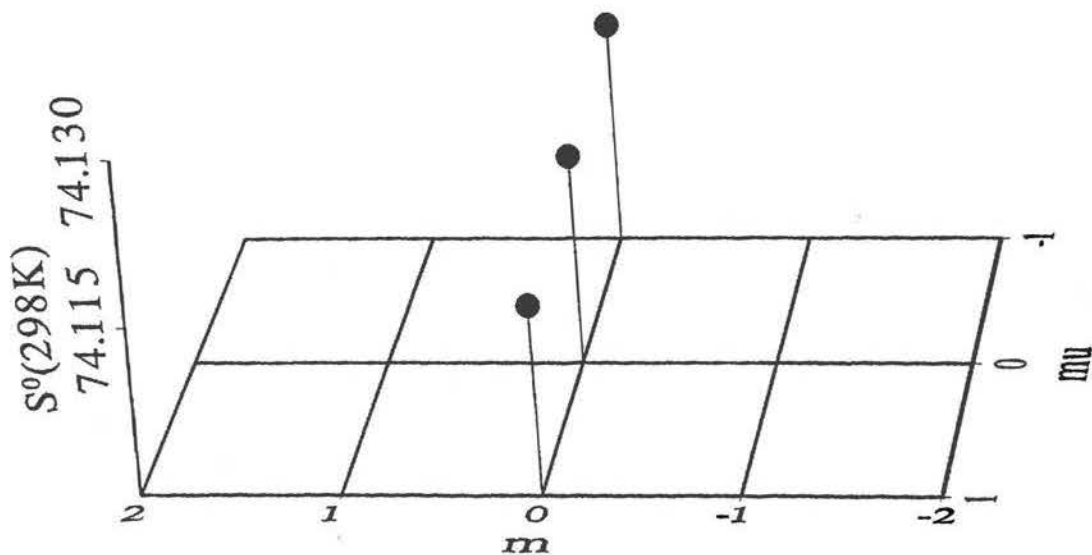SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Triplet D
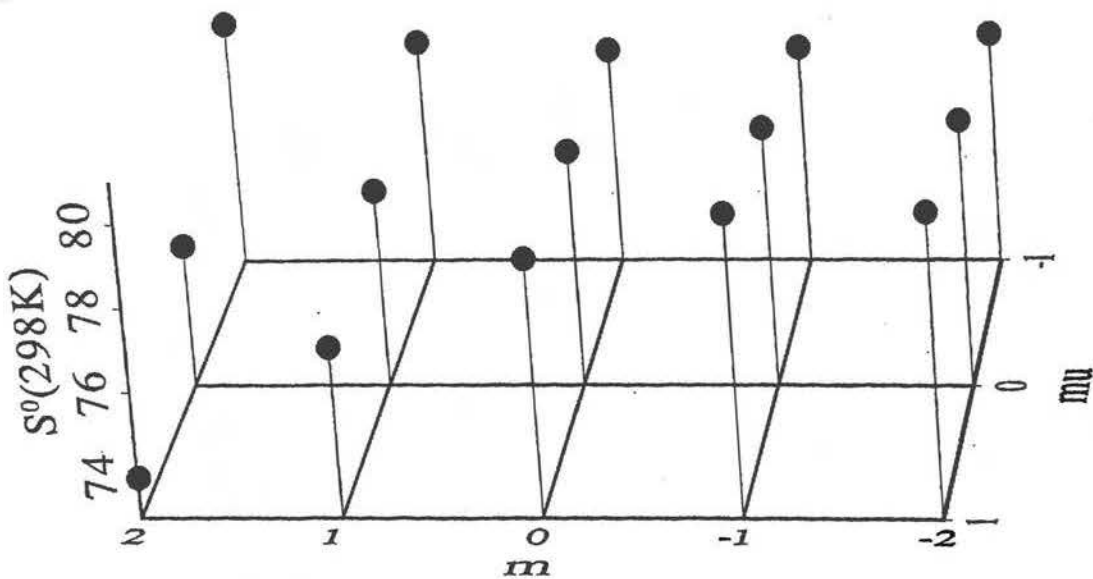Entropy at 298K (cal/(mole degree)) Single-Particle Operator

A56

76

SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,2)$ Triplet S
Entropy at 298K (cal/(mole degree)) Single-Particle Operator

A57

SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(3,3)$ Triplet D
Entropy at 298K (cal/(mole degree)) Single-Particle Operator

A58

SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(3,3)$ Triplet S
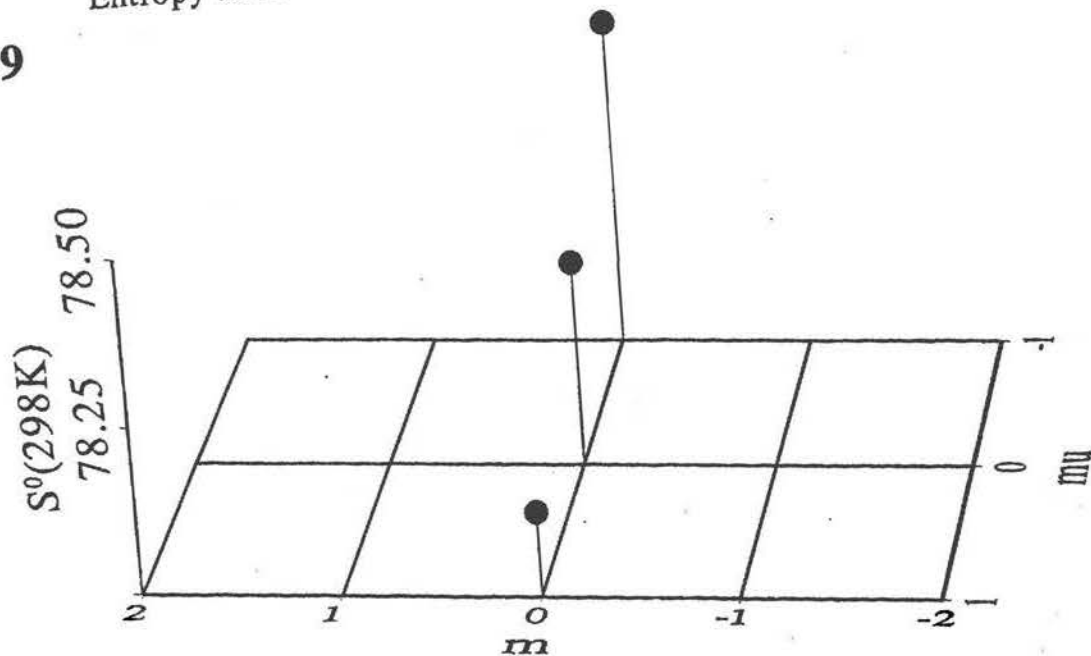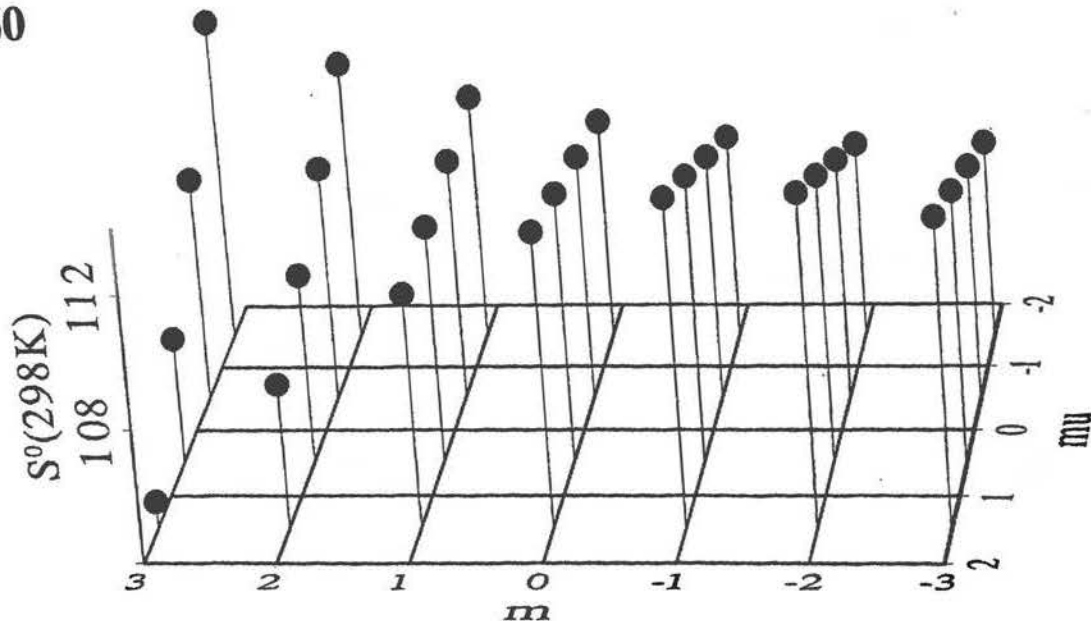Entropy at 298K (cal/(mole degree)) Single-Particle Operator

A59

SO(3)xSU(2) Triatomic Molecules $(R_1,R_2,R_3)=(2,2,2)$ Quartet F
Entropy at 298K (cal/(mole degree)) Single-Particle Operator

A60

SO(3)xSU(2) Triatomic Molecules $(R_1,R_2,R_3)=(2,2,2)$ Doublet D
Entropy at 298K (cal/(mole degree)) Single-Particle Operator

A61

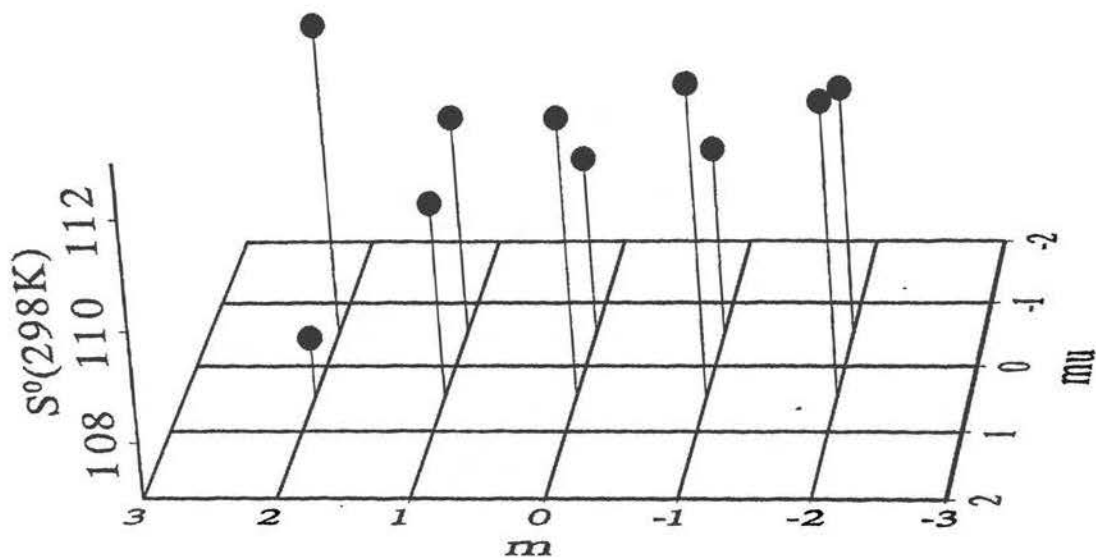
SO(3)xSU(2) Triatomic Molecules $(R_1,R_2,R_3)=(2,2,2)$ Quartet F
Entropy at 298K (cal/(mole degree)) Two-Particle Operator

A62

Assumption

■ $S^0_{298}(ARg)$ = Average S^0_{298}
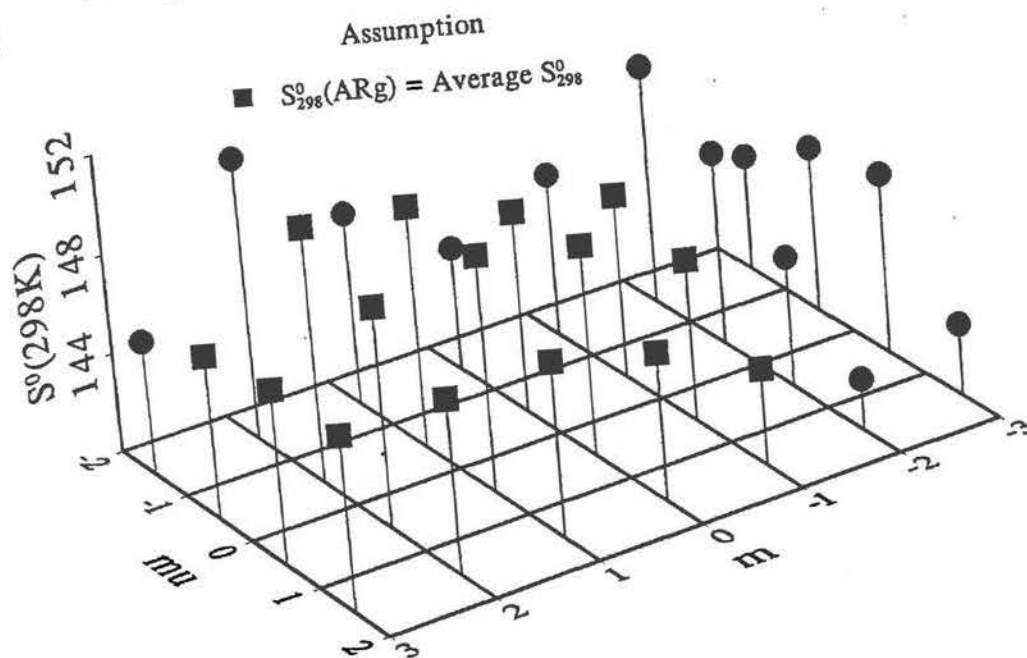
SO(3)xSU(2) Triatomic Molecules $(R_1,R_2,R_3)=(2,2,2)$ Doublet D
Entropy at 298K (cal/(mole degree)) Two-Particle Operator

Assumption

■ $S_{298}^0(ARg) = $ Average S_{298}^0

A63
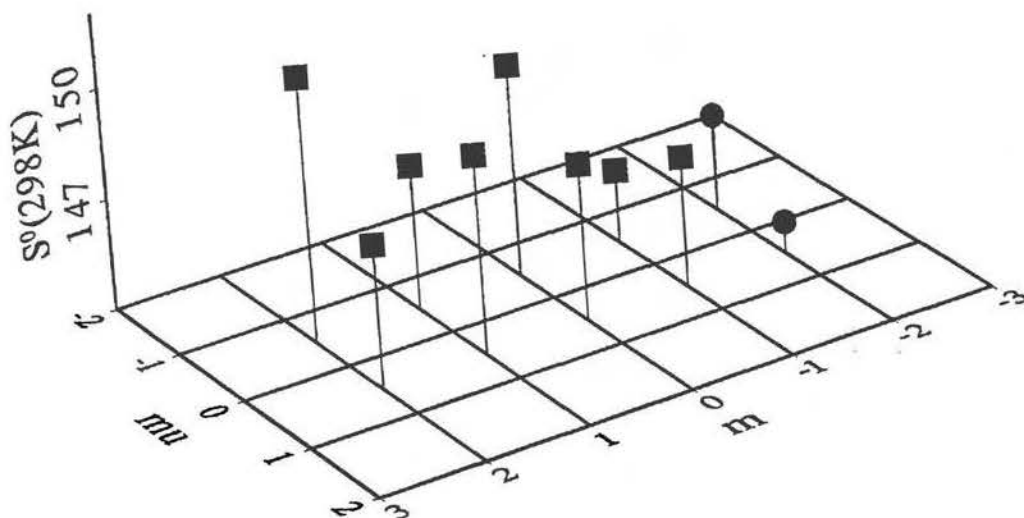
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,2)$ Triplet D
Vibration Frequency (cm^{-1})

A64

Assumption

■ $\omega_e(ARg) = 8\%$ of Average
for any atom A

▲ $\omega_e(FRg) = 42\%$ of Average

SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,2)$ Singlet P
Vibration Frequency (cm^{-1})

A65
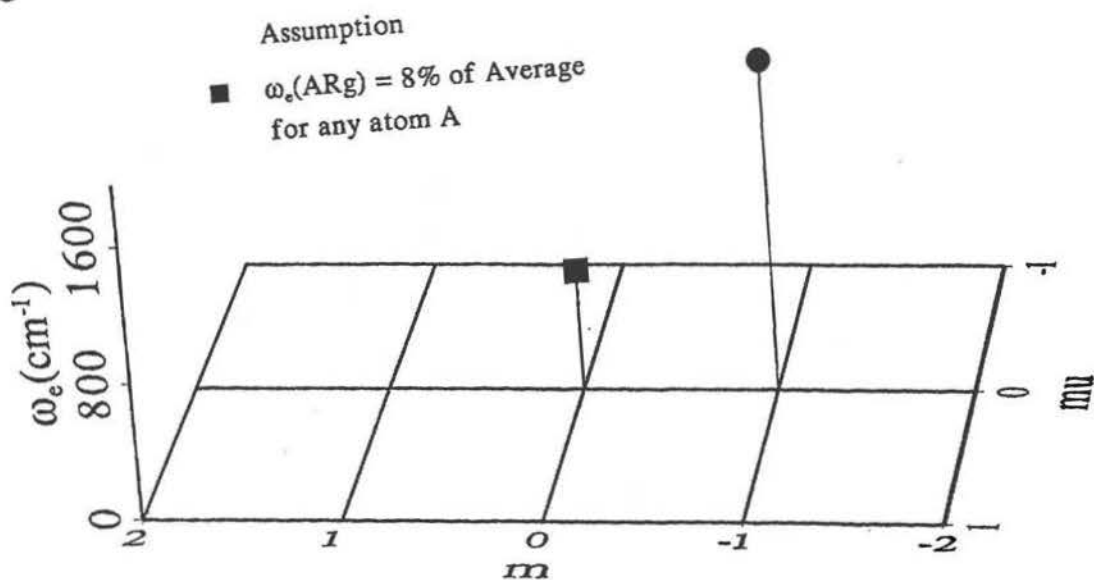
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,2)$ Triplet S
Vibration Frequency (cm^{-1})

A66
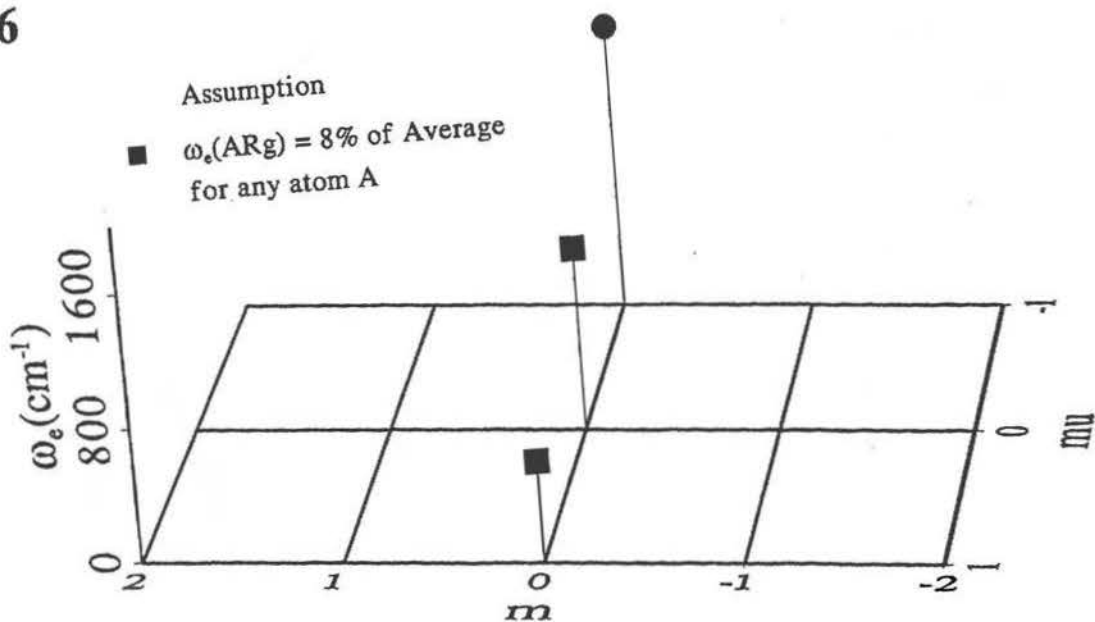
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(3,3)$ Triplet D
Vibration Frequency (cm^{-1})

A67
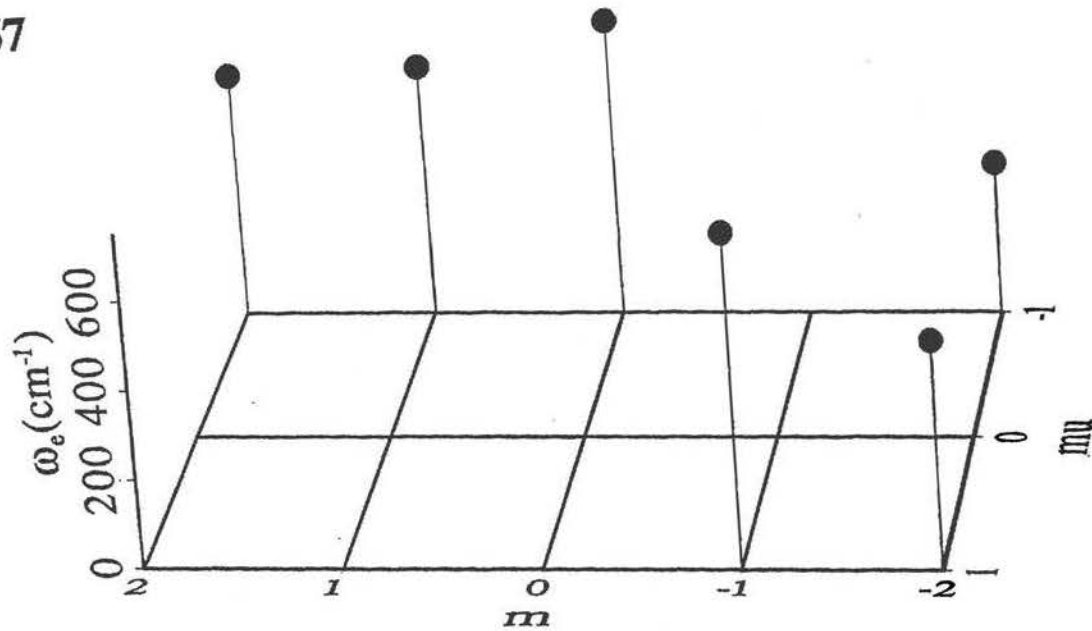
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(3,3)$ Triplet S
Vibration Frequency (cm^{-1})

A68
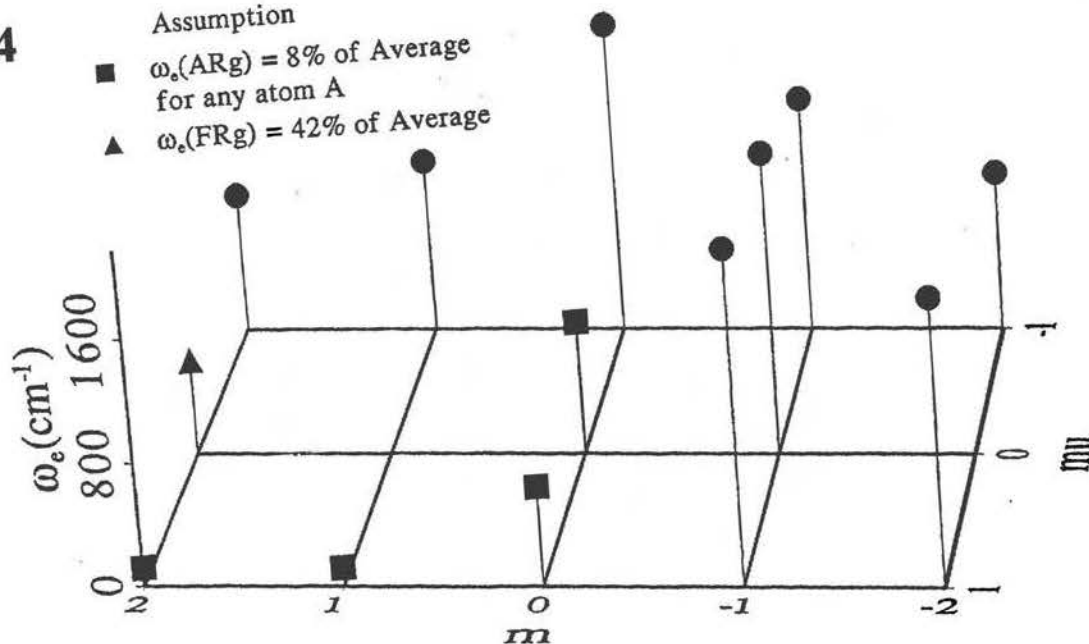
Assumption

■ $\omega_e(ARg) = 8\%$ of Average
for any atom A
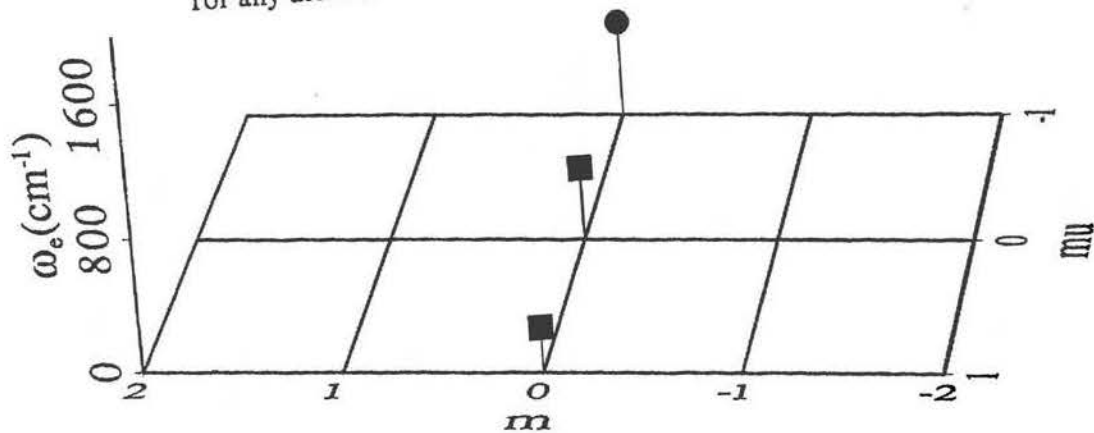
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,3) (l₁,l₂)=(1,1) ³D
Vibration Frequency (cm⁻¹)

A69

Assumption

■ ωₑ(ARg) = % of Average for any atom A
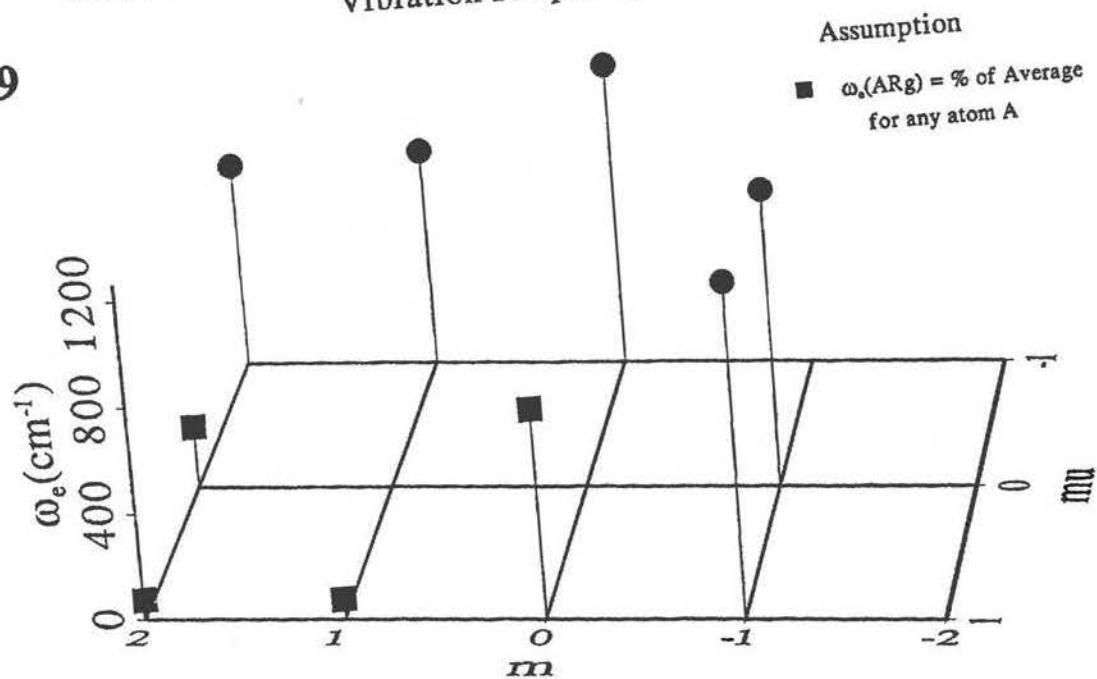
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,3) (l₁,l₂)=(1,1) ³S
Vibration Frequency (cm⁻¹)

A70

Assumption

■ ωₑ(ARg) = 8% of Average for any atom A

84
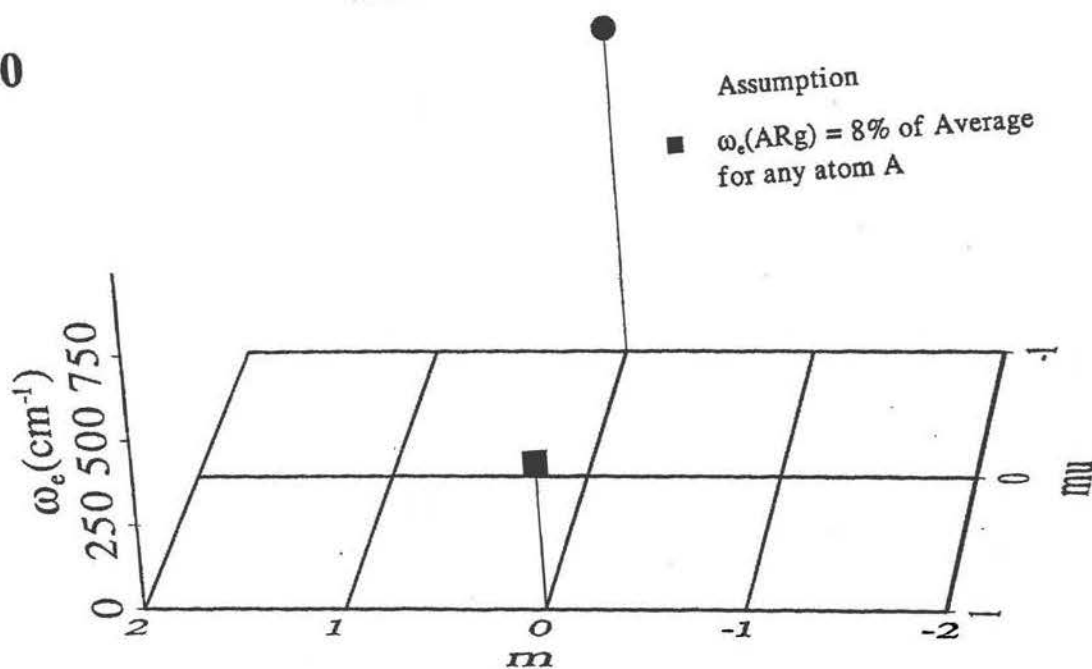
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,3)$ $(l_1,l_2)=(1,1)$ ^3P
Vibration Frequency (cm^{-1})

A71

Assumption

■ $\omega_e(ARg) = 8\%$ of Average for any atom A
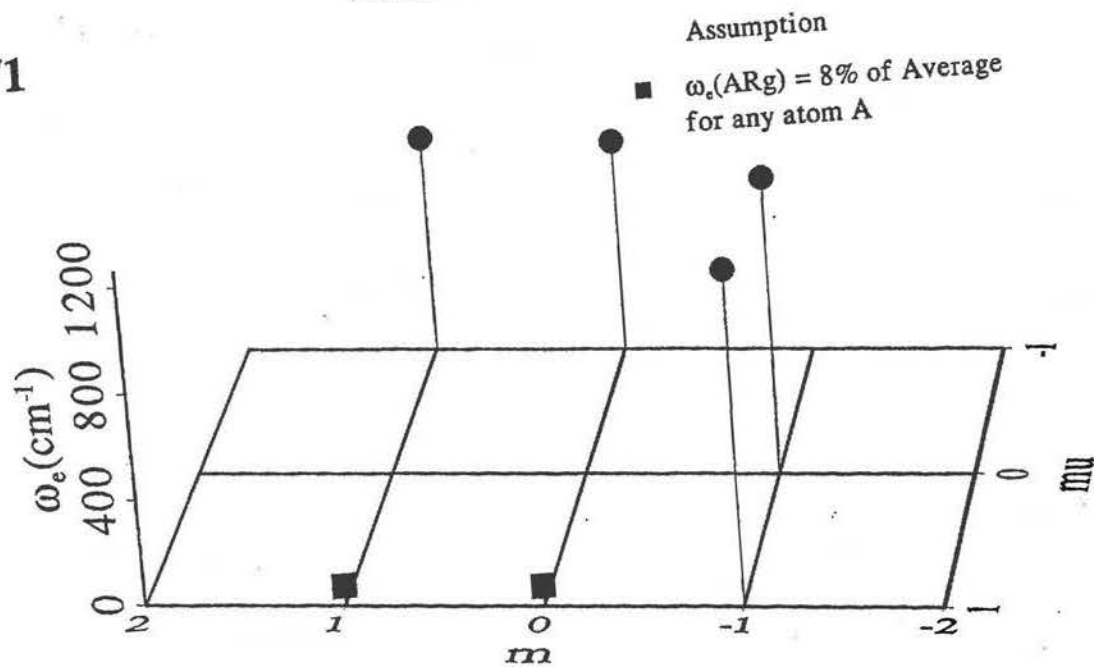
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,3)$ $(l_1,l_2)=(1,0)$ ^3P
Vibration Frequency (cm^{-1})

A72

Assumption

■ $\omega_e(ARg) = 8\%$ of Average for any atom A
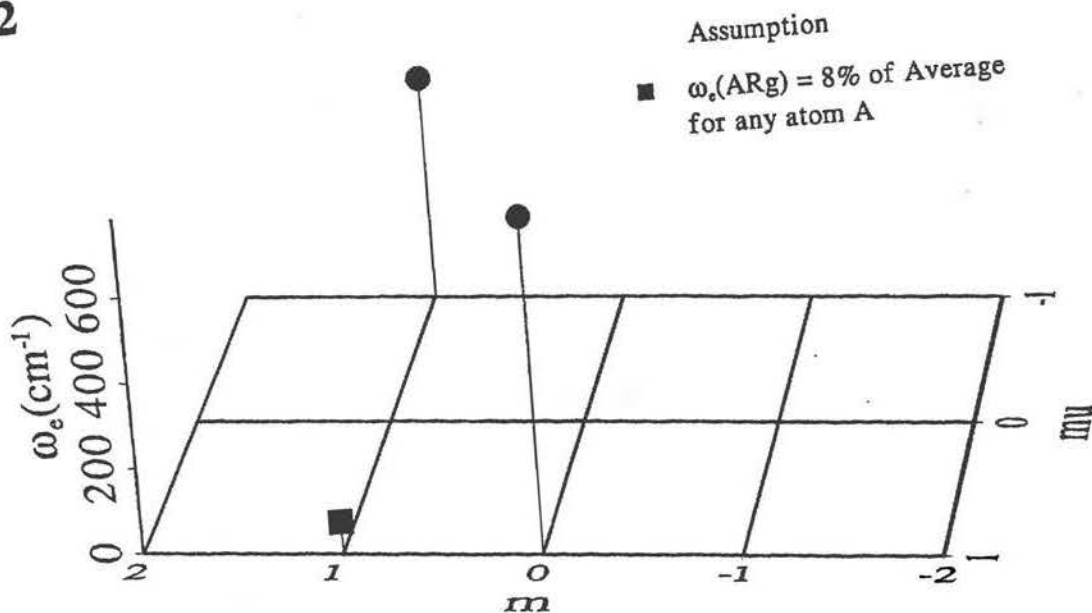
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,3)$ $(l_1,l_2)=(0,1)$ ^3P
Vibration Frequency (cm^{-1})

A73
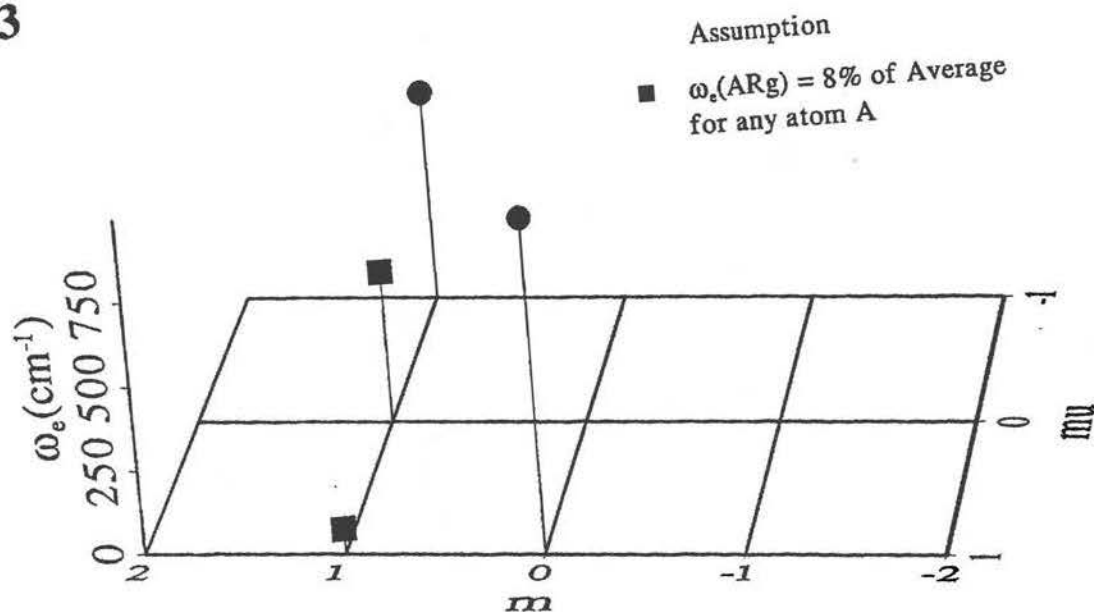
Assumption

■ $\omega_e(ARg) = 8\%$ of Average
for any atom A

SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(2,2)$ Triplet D
Vibration Frequency (cm^{-1}) Homonuclear Approximation

A74

Assumption

■ $\omega_e(RgRg) = 8\%$ of Avg.
for any rare gas Rg
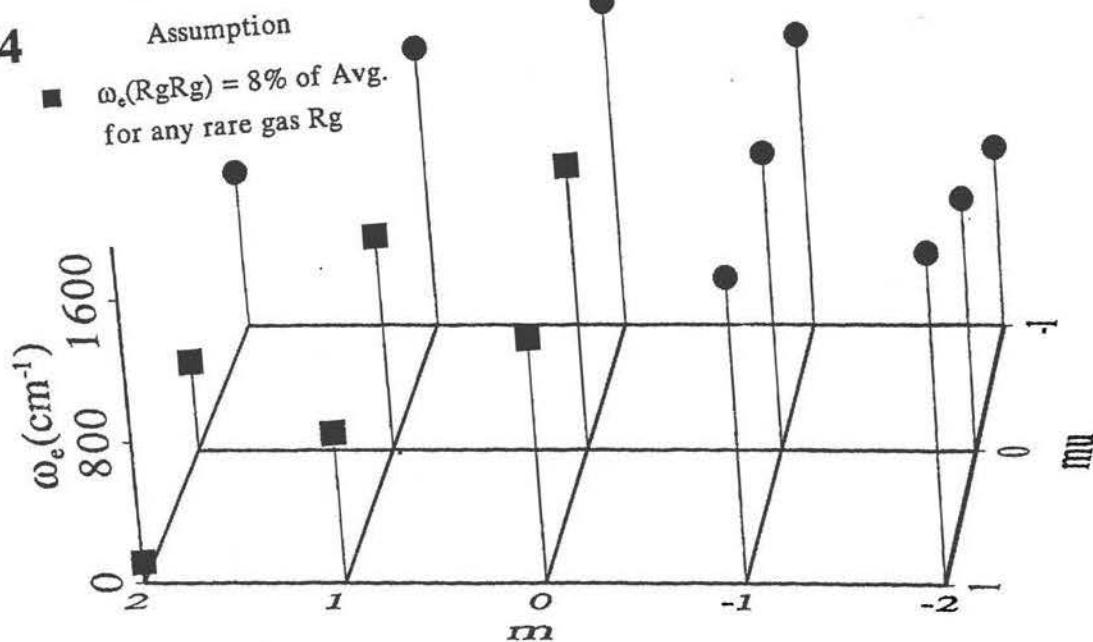
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Singlet P
Vibration Frequency (cm⁻¹) Homonuclear Approximation

A75
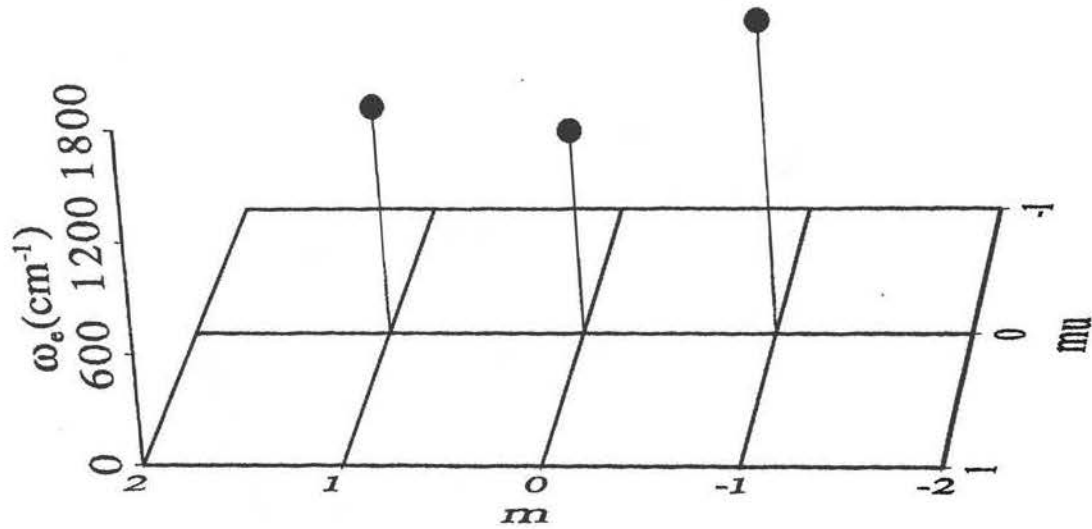
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(2,2) Triplet S
Vibration Frequency (cm⁻¹) Homonuclear Approximation

A76
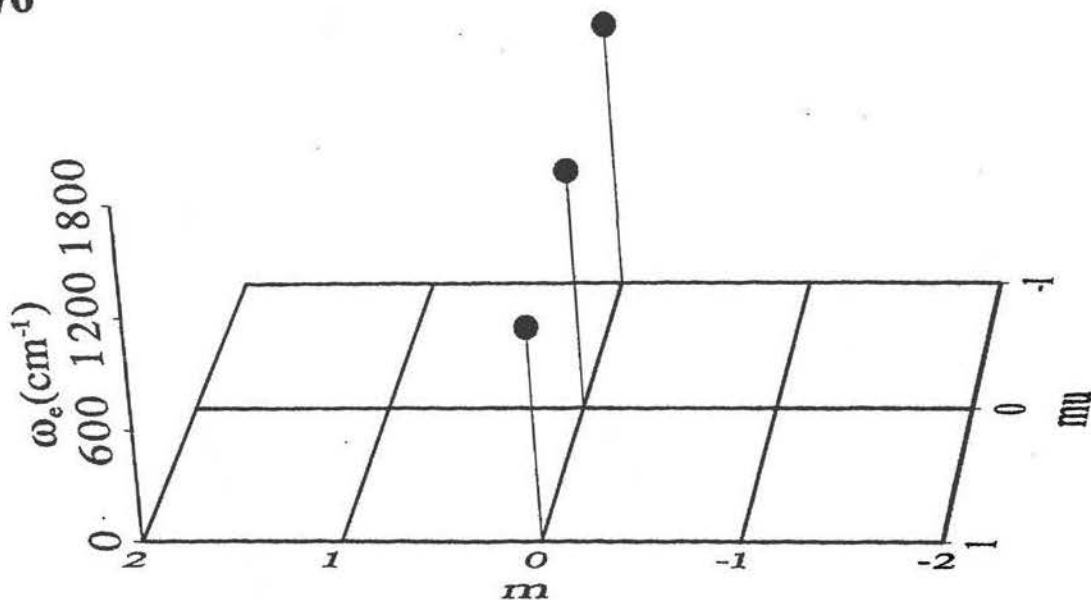
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(3,3) Triplet D
Vibration Frequency (cm⁻¹) Homonuclear Approximation

A77
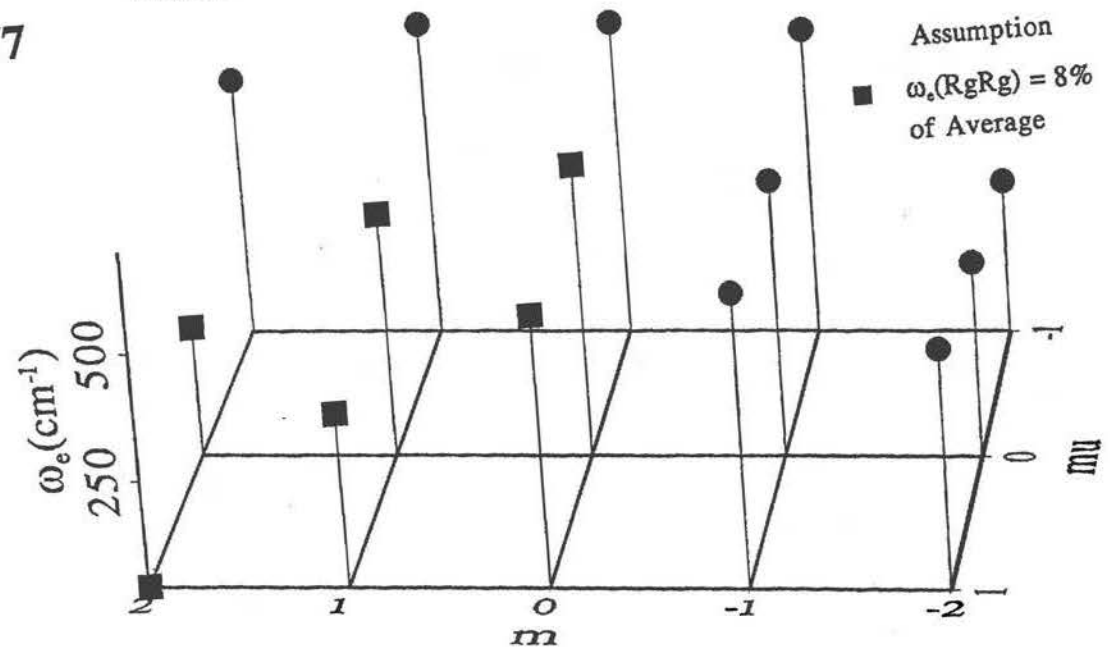
SO(3)xSU(2) Diatomic Molecules (R₁,R₂)=(3,3) Singlet P
Vibration Frequency (cm⁻¹) Homonuclear Approximation

A78
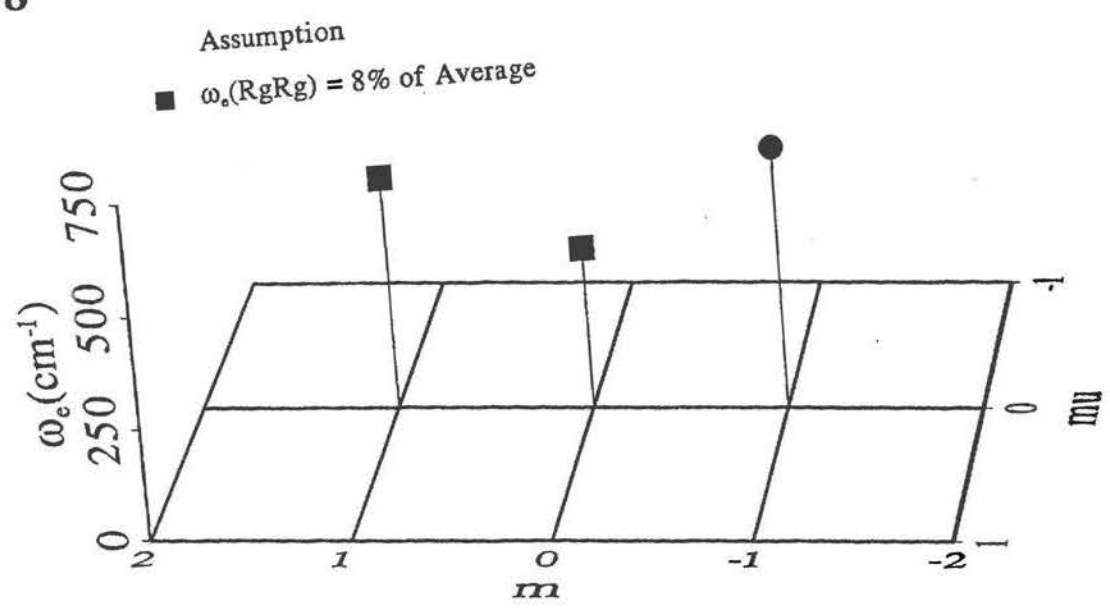
SO(3)xSU(2) Diatomic Molecules $(R_1,R_2)=(3,3)$ Triplet S
Vibration Frequency (cm^{-1}) Homonuclear Approximation

A79

Assumption

■ $\omega_e(RgRg)$ = 8% of Average
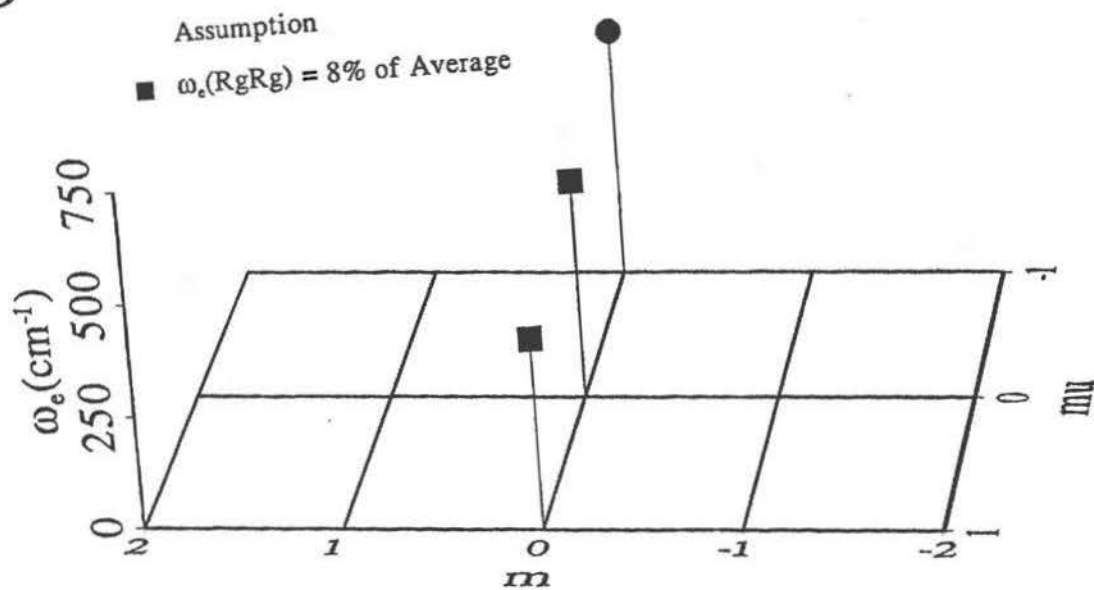
Appendix B:

Plots of ΔH_a, $I.P.$, S_{298}^0, and ω_e for $SO(2,1)$ symmetry group

SO(2,1) Diatomic Molecules $(l_1, l_2) = (0,1)$ Groups (1,7)
Heat of Atomization (eV)

B1
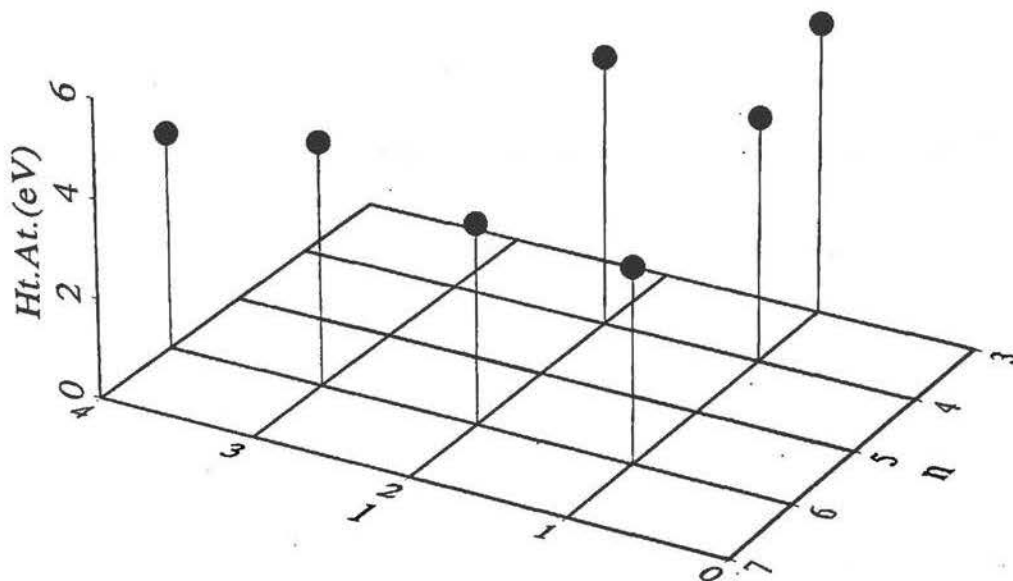
SO(2,1) Diatomic Molecules $(l_1, l_2) = (1,1)$ Groups (4,4)
Heat of Atomization (eV)

B2
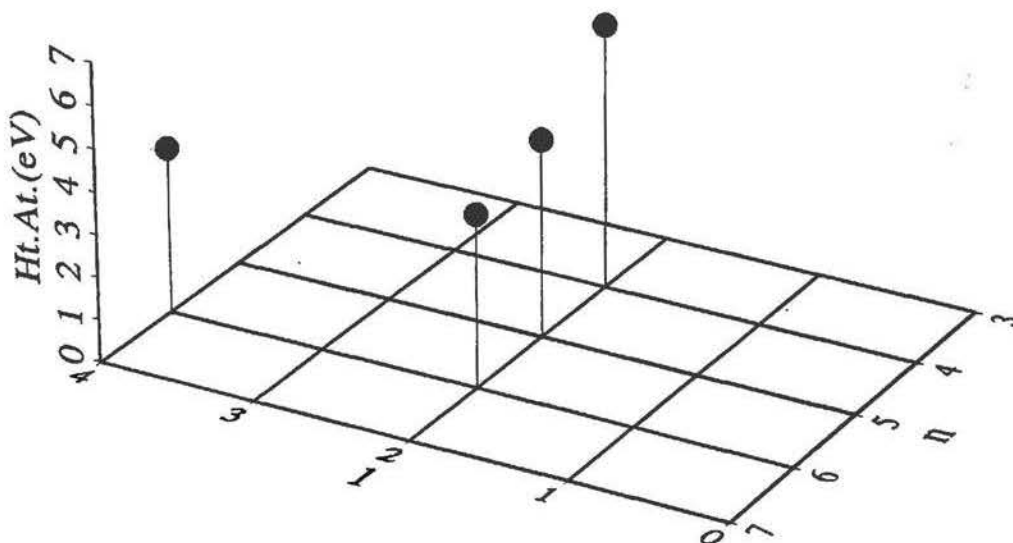
SO(2,1) Diatomic Molecules $(l_1,l_2)=(1,1)$ Groups (7,7)
Heat of Atomization (eV)

B3
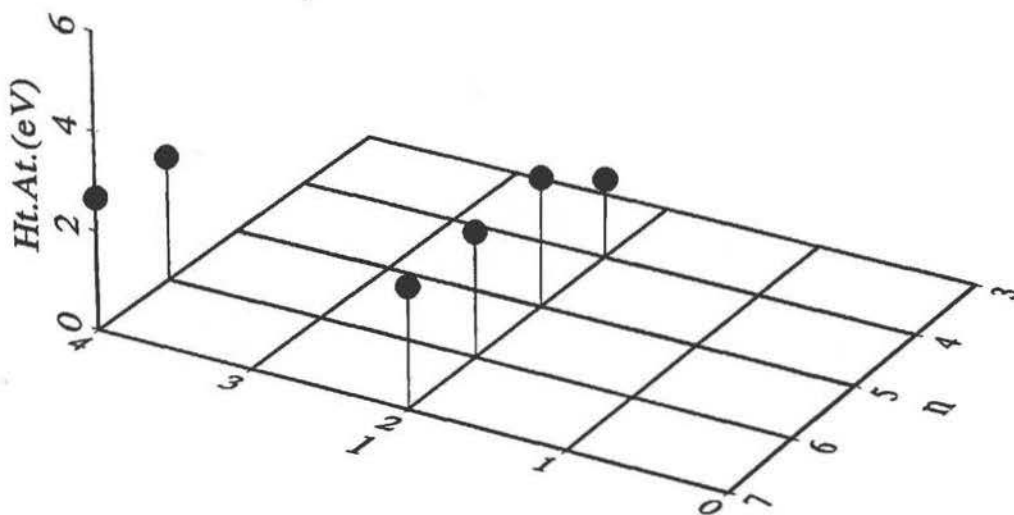
SO(2,1) Atoms $l = 0$ and 1 Groups 1 and 7
Ionization Potential (eV)

B4
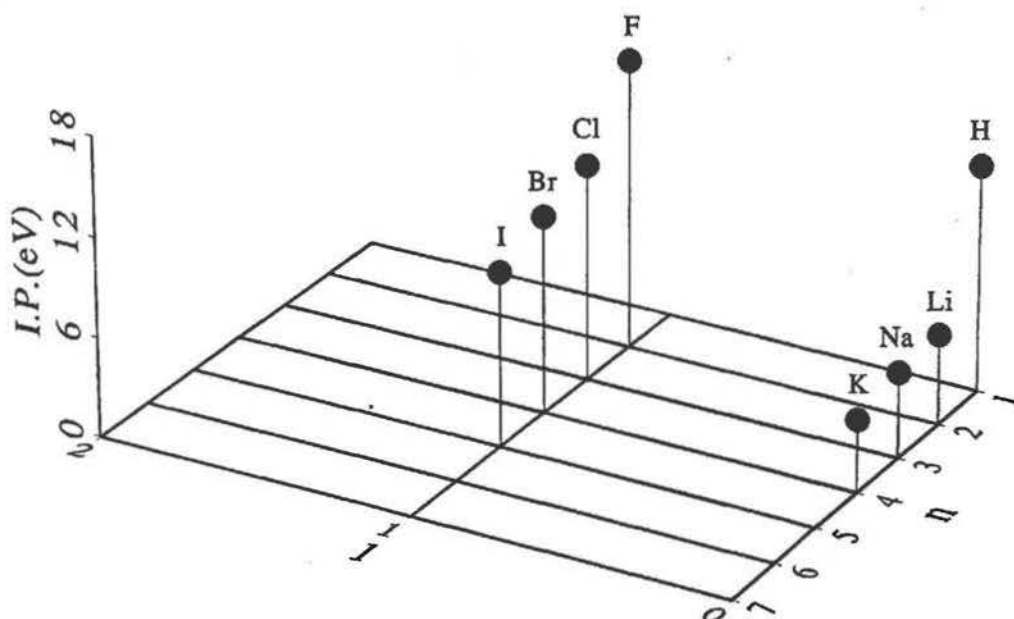
SO(2,1) Atoms l = 0 and 1 Groups 2 and 6
Ionization Potential (eV)

B5
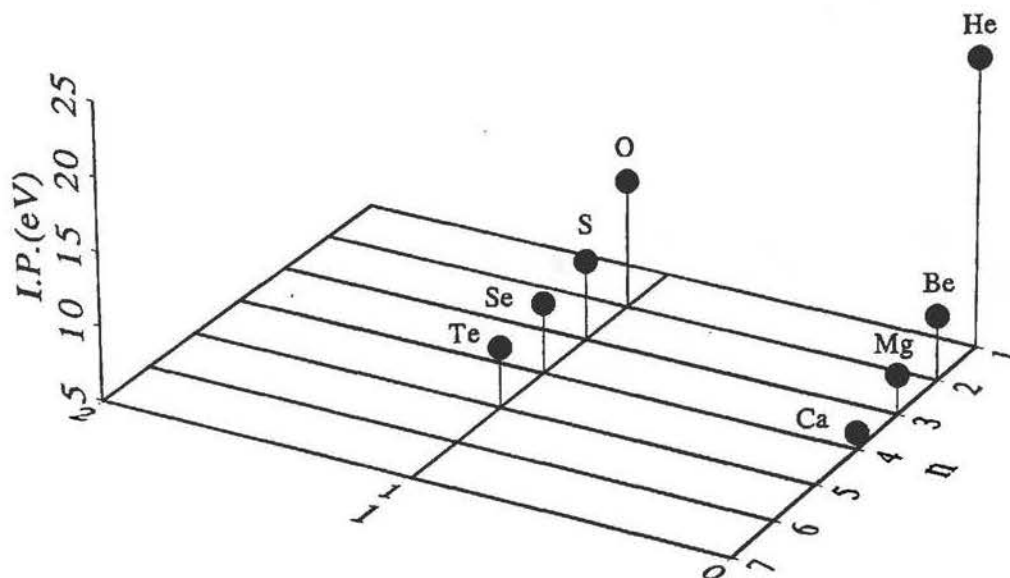
SO(2,1) Atoms l = 1 Group 4
Ionization Potential (eV)

B6
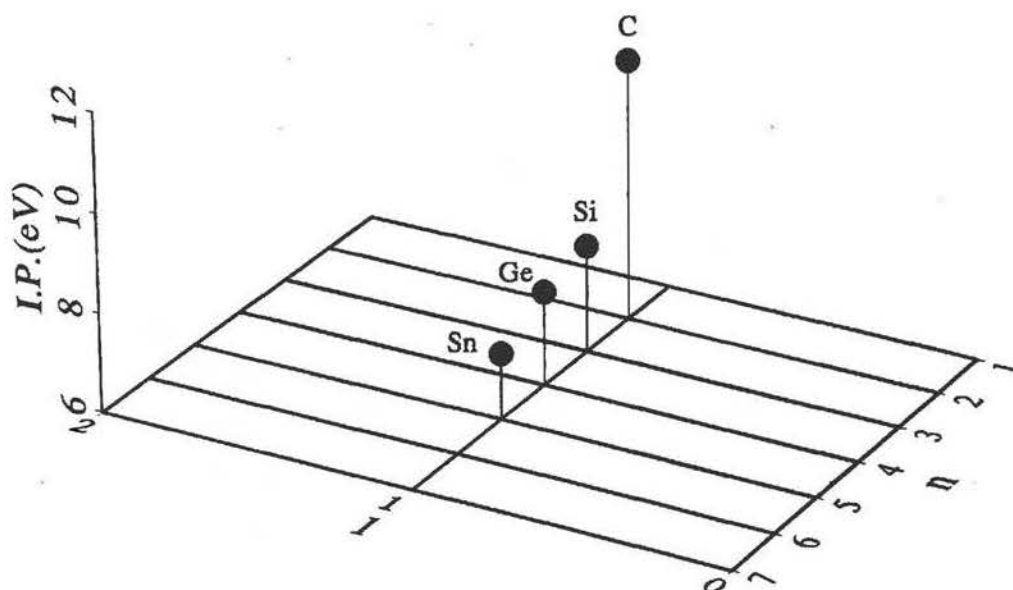
SO(2,1) Diatomic Molecules $(l_1,l_2)=(0,1)$ Groups (1,7)
Ionization Potential (eV)

B7
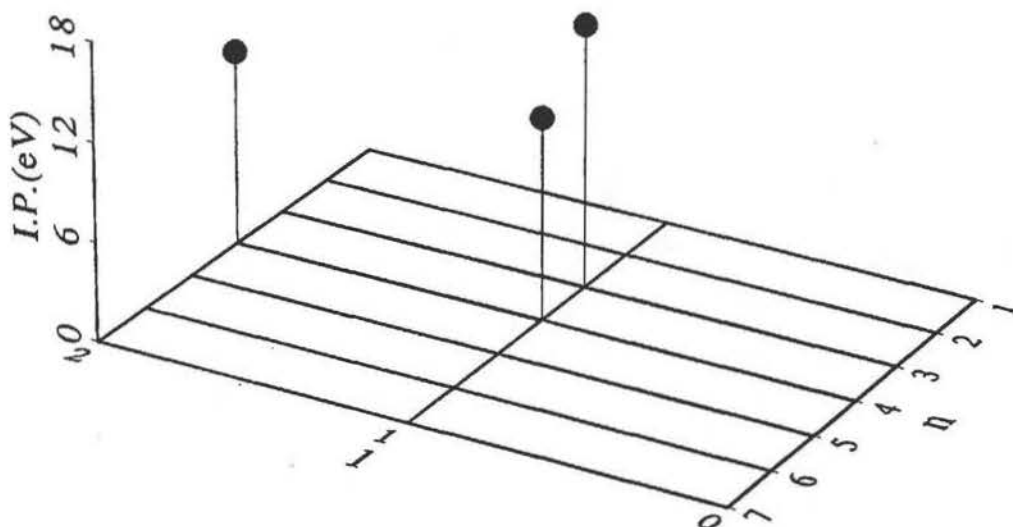
SO(2,1) Diatomic Molecules $(l_1,l_2)=(0,1)$ Groups (2,6)
Ionization Potential (eV)

B8

Assumption

■ IP(AHe) = 1/2 IP(A)
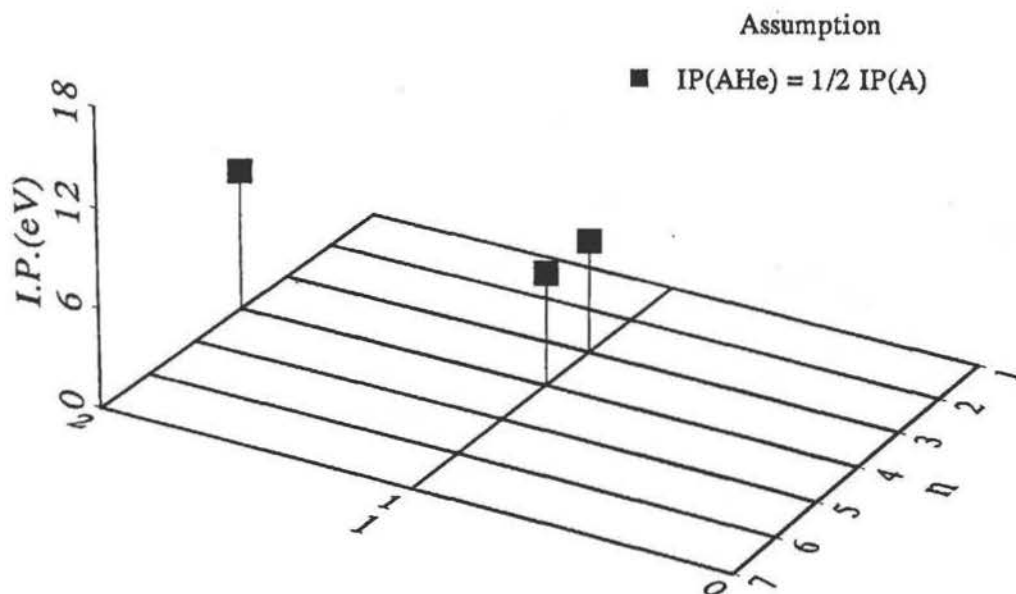
SO(2,1) Diatomic Molecules $(l_1, l_2) = (1,1)$ Groups (4,4)
Ionization Potential (eV)

B9
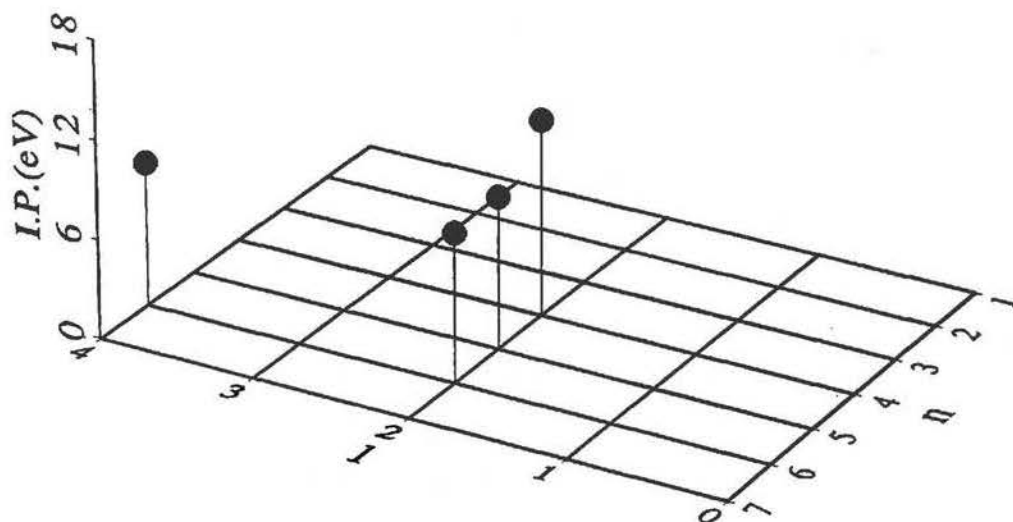
SO(2,1) Diatomic Molecules $(l_1, l_2) = (1,1)$ Groups (7,7)
Ionization Potential (eV)

B10
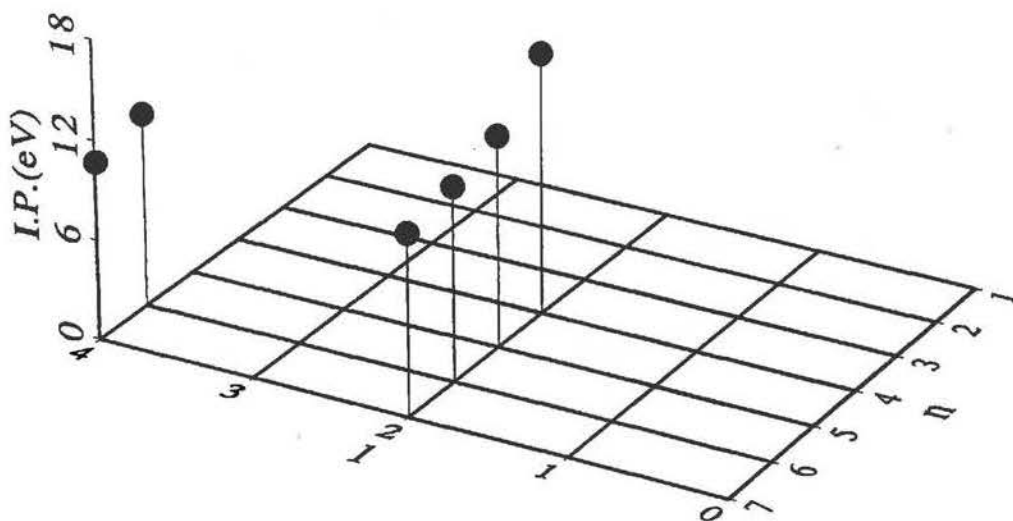
SO(2,1) Atoms l = 0 and 1 Groups 1 and 7
Entropy at 298K (cal/(mole degree))

B11
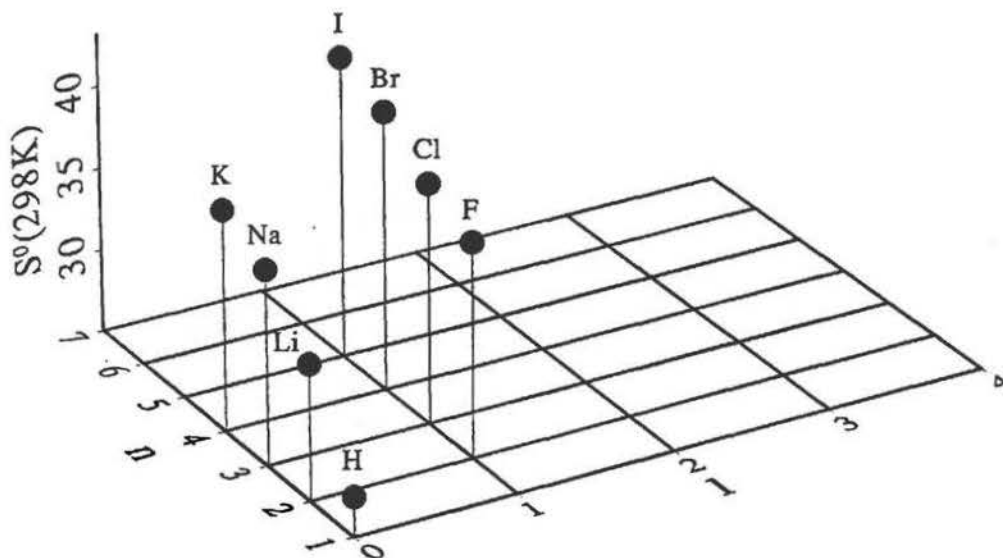
SO(2,1) Atoms l = 0 and 1 Groups 2 and 6
Entropy at 298K (cal/(mole degree))

B12
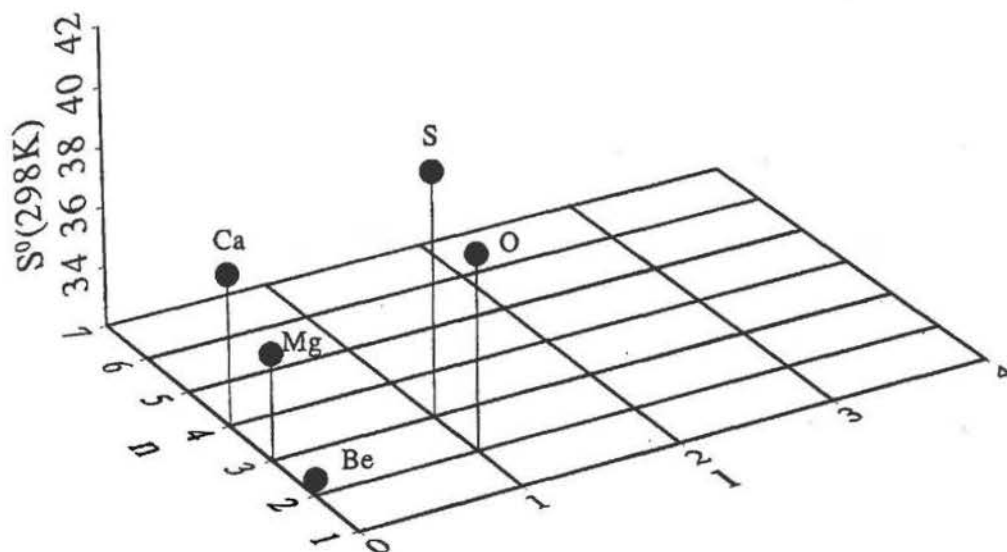
SO(2,1) Atoms l = 1 Group 4
Entropy at 298K (cal/(mole degree))

B13
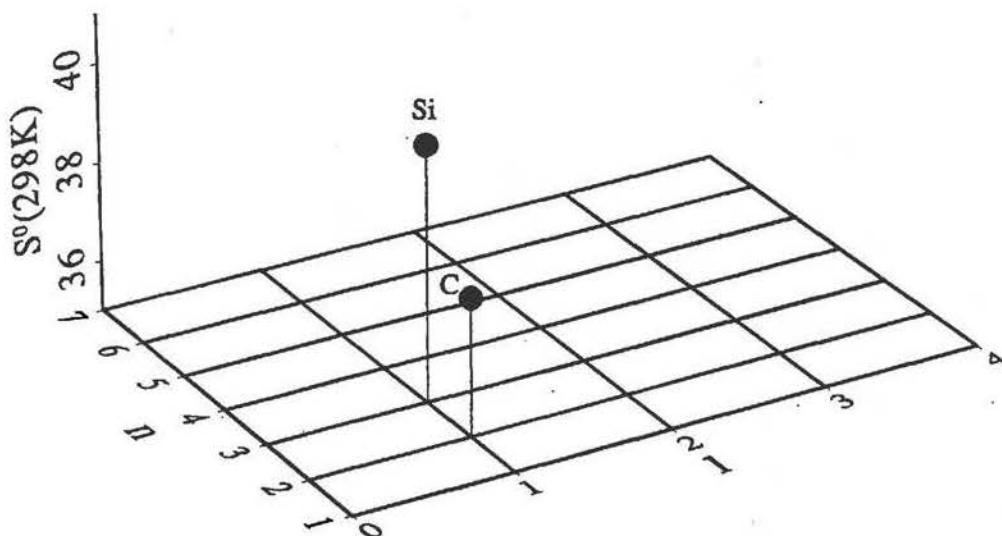
SO(2,1) Diatomic Molecules $(l_1, l_2) = (0,0)$ Groups (1,1)
Entropy at 298K (cal/(mole degree))

B14

SO(2,1) Diatomic Molecules $(l_1,l_2)=(0,1)$ Groups (1,7)
Entropy at 298K (cal/(mole degree))
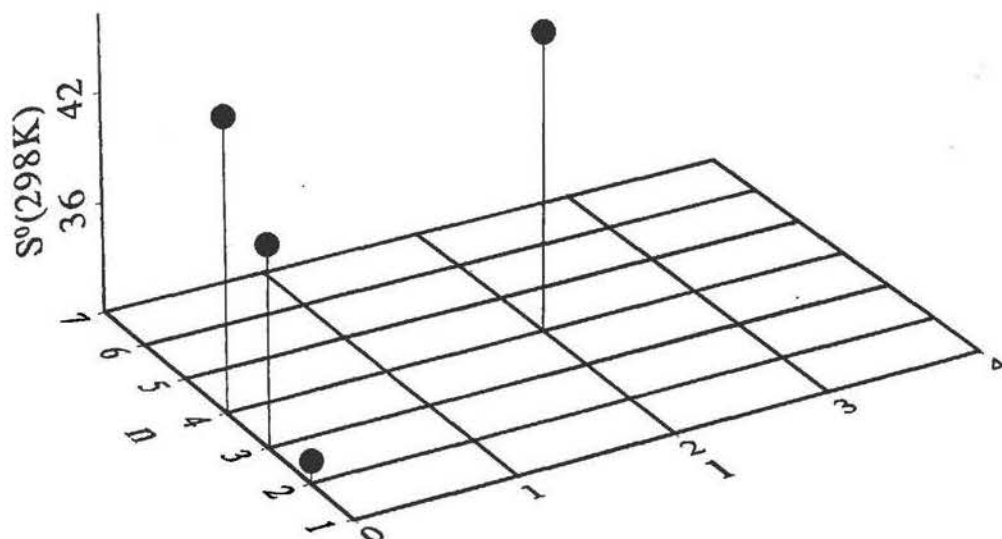
B15
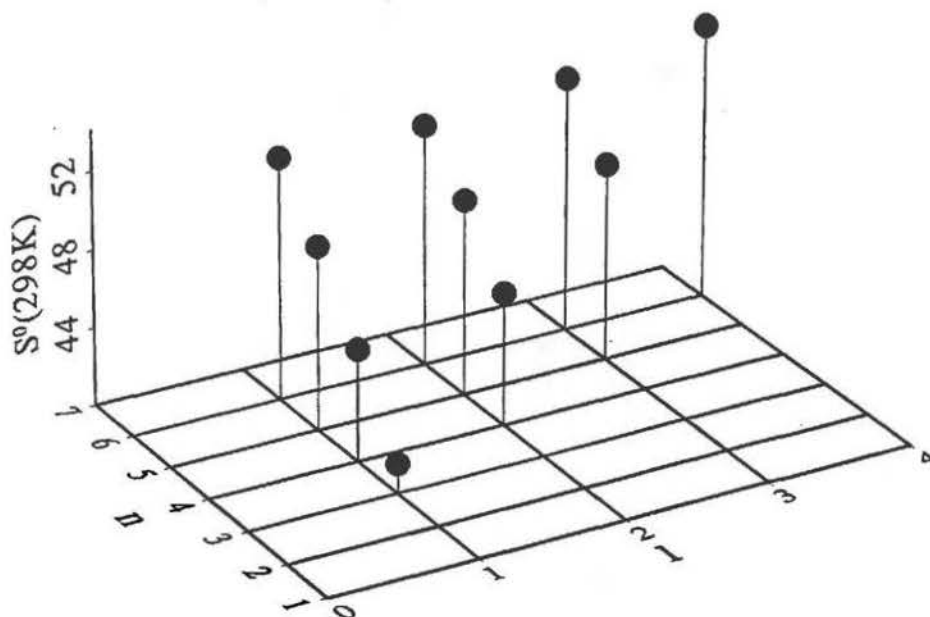
SO(2,1) Diatomic Molecules $(l_1,l_2)=(0,1)$ Groups (2,6)
Entropy at 298K (cal/(mole degree))

B16
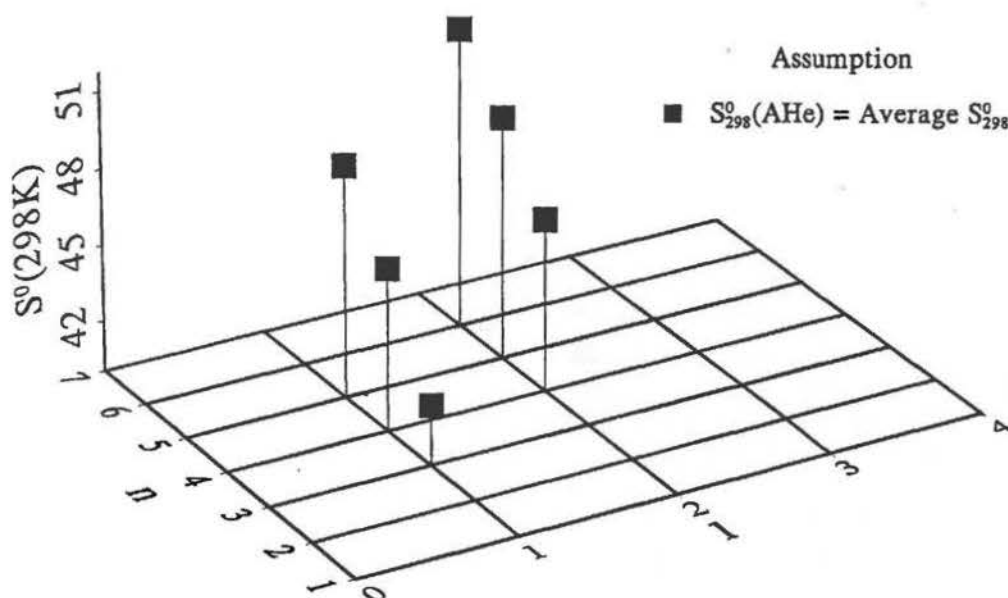
SO(2,1) Diatomic Molecules $(l_1,l_2)=(1,1)$ Groups (7,7)
Entropy at 298K (cal/(mole degree))

B17
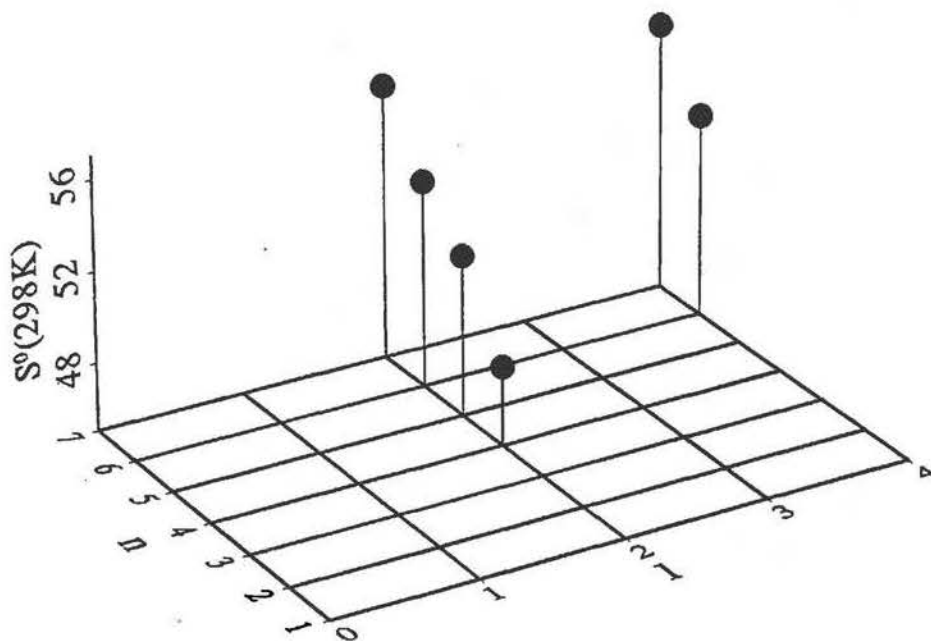
SO(2,1) Diatomic Molecules $(l_1,l_2)=(0,0)$ Groups (1,1)
Vibration Frequency (cm^{-1})

B18
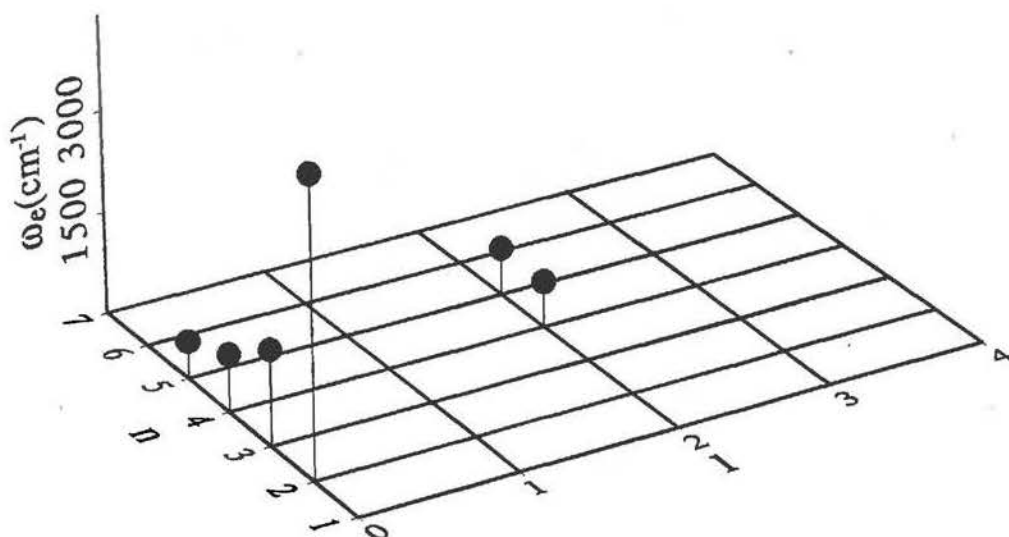
SO(2,1) Diatomic Molecules $(l_1,l_2)=(0,1)$ Groups (1,7)
Vibration Frequency (cm^{-1})

B19
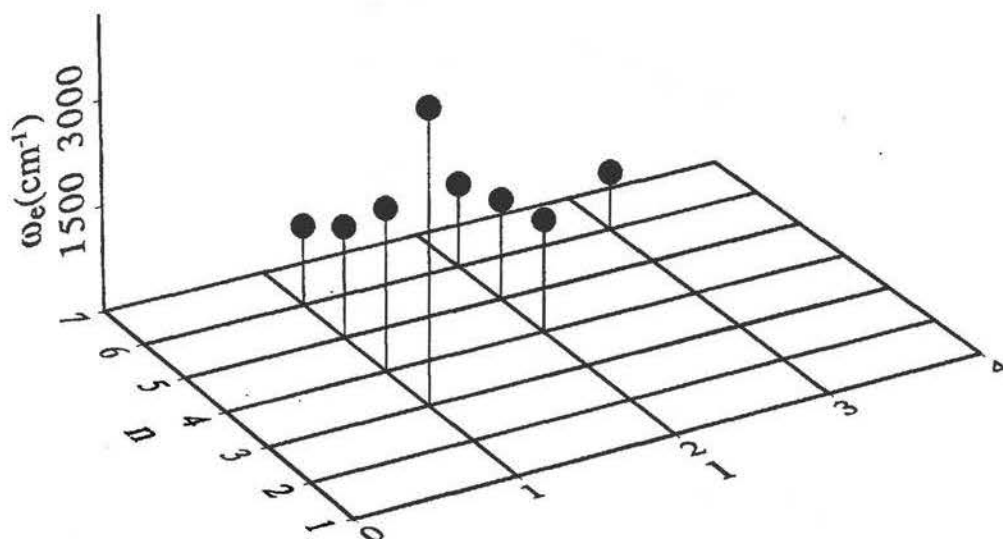
SO(2,1) Diatomic Molecules $(l_1,l_2)=(0,1)$ Groups (2,6)
Vibration Frequency (cm^{-1})

B20

Assumption

■ $\omega_e(ARg) = 8\%$ of Average
for any atom A
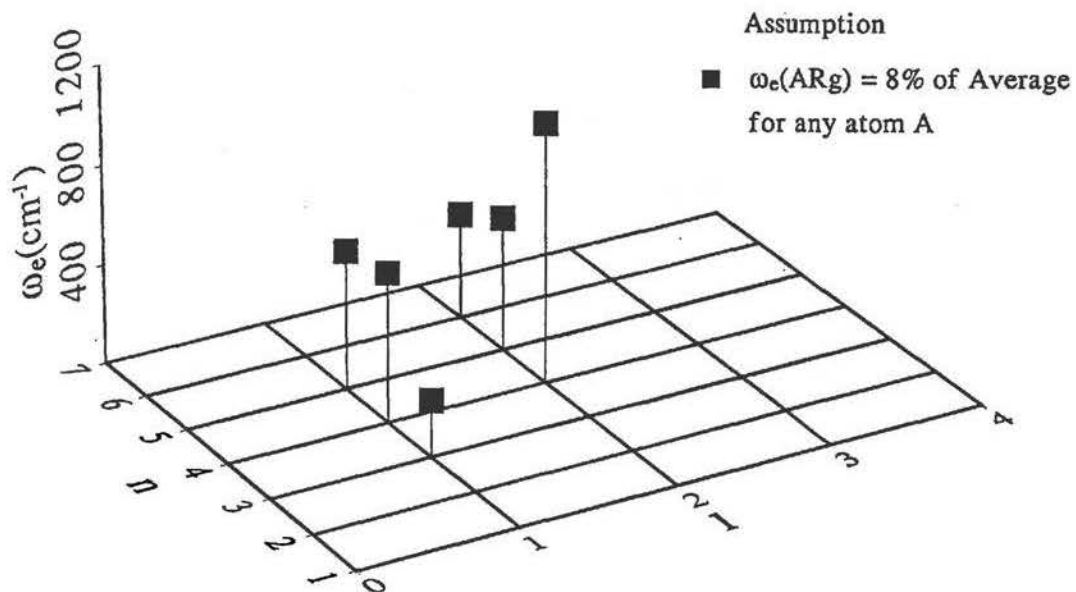
SO(2,1) Diatomic Molecules $(l_1,l_2)=(1,1)$ Groups (7,7)
Vibration Frequency (cm^{-1})

B21
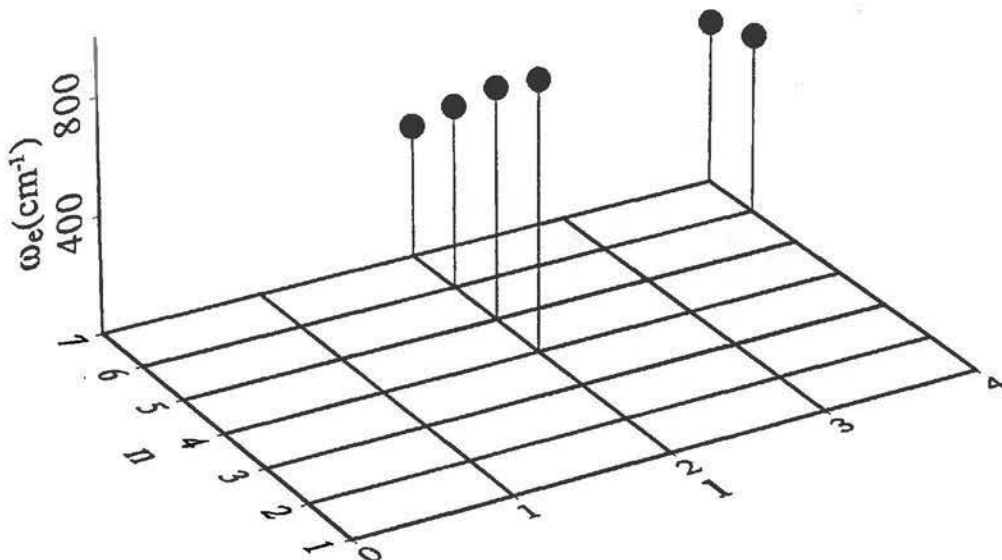
SO(2,1) Diatomic Molecules $(l_1,l_2)=(1,1)$ Groups (6,6)
Vibration Frequency (cm^{-1})

B22
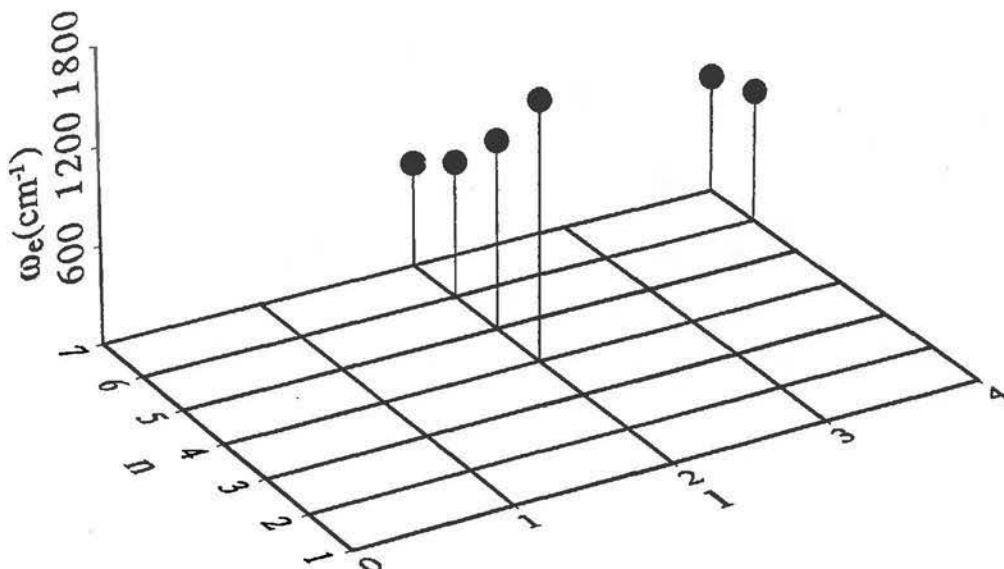
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TABLE I. Graphical interrelationships for heat of atomization.

Key: Wi;X,Y,Z;N;* where Wi = plot is "i"th graph in appendix W, X = no. of actual data,
Y = no. of points which include approx. data, Z = no. of predictable data (missing),
N = index of fittability of surface. Inclusively similar plots are connected with single (---) lines.
Completely similar plots are connected with double (==) lines. When lines would cross or detour,
inclusively similar plots are labeled with one of the symbols {*, !, @}, while completely similar
plots are labeled with one of the symbols {#, $, %}.

SO(3)xSU(2)	Oper.	Mult.	(R1, ...,Rn) (2, ...,2)	(R1, ...,Rn) (3, ...,3)	(R1, R2) (2,3)
N=2	P(2)	3D	A1;14,0,1;3;*# =	A4;10,0,5;3	
		1P	A2;3,0,0;5		
		3S	A3;3,0,0;5;* =	A5;2,0,1;5	
N=3	P(3)	4F	A6;6,0,22;2;#		
		2D			
		4P			
N=2 P(1) diatomic homonuclear	P(1)	3D	A7;15,0,0;5;#! =	A10;15,0,0;5	
		1P	A8;3,0,0;5 =	A11;3,0,0;5	
		3S	A9;3,0,0;5;*! =	A12;3,0,0;5	
N=3 P(1) triatomic homonuclear	P(1)	4F			
		2D			
		4P			
N=3	P(2)	4F			
		2D			
		4P			

SO(3)xSU(2) Oper.	Mult.	(R1, ...,Rn) (2, ...,2)	(R1, ...,Rn) (3, ...,3)	(R1, R2) (2,3)		
N=3 P(1) diatomic homonuclear	4F					
	2D					
	4P					

SO(2,1) Oper.	(l1,...,ln)	Groups (1, ...,1)	Groups (1, 7)	Groups (2, 6)	Groups (4, ...,4)	Groups (7, ...,7)
N=2 P(2)	(0,0)					
	(0,1)		B1;7,0,-;4;*			
	(1,1)				B2;4,0,-;4;*	B3;6,0,-;4
N=3 P(3)	(0,0,0)					
	(0,0,1)					
	(0,1,1)					
	(1,1,1)					
N=2 P(1) diatomic homonuclear	(0,0)					
	(0,1)					
	(1,1)					
N=3 P(1) triatomic homonuclear	(0,0,0)					
	(0,0,1)					
	(0,1,1)					
	(1,1,1)					

SO(2,1) Oper.	(l1,...,ln)	Groups (1, ...,1)	Groups (1, 7)	Groups (2, 6)	Groups (4, ...,4)	Groups (7, ...,7)
N=3 P(2)	(0,0,0)					
	(0,0,1)					
	(0,1,1)					
	(1,1,1)					
N=3 P(1) diatomic homonuclear	(0,0,0)					
	(0,0,1)					
	(0,1,1)					
	(1,1,1)					

TABLE II. Graphical interrelationships for ionization potential.

Key: Wi;X,Y,Z;N;* where Wi = plot is "i"th graph in appendix W, X = no. of actual data,
Y = no. of points which include approx. data, Z = no. of predictable data (missing),
N = index of fittability of surface. Inclusively similar plots are connected with single (---) lines.
Completely similar plots are connected with double (==) lines. When lines would cross or detour,
inclusively similar plots are labeled with one of the symbols {*, !, @}, while completely similar
plots are labeled with one of the symbols {#, $, %}.

SO(3)xSU(2) Oper	Mult.	(R1, ...,Rn) (2, ...,2)	(R1, ...,Rn) (3, ...,3)	(R1, ...,Rn) (4, ...,4)	(R1, ...,Rn) (5, ...,5)	(R1, ...,Rn) (6, ...,6)	(R1,R2) (2,3)
N=1 P(1)	2F			A16;12,0,2;2;*			
	2D		A14;10,0,0; =	A17;10,0,0; =	A18;9,0,1;4		
	2P	A13;6,0,0;5;* =	A15;6,0,0;5 ==================			A19;6,0,0;5	
N=2 P(2)	3D	A20;7,6,2;3;# =	A22;3,4,8;3 ========================				A23;3,4,8
	1P						
	3S	A21;1,2,0;4					
N=3 P(3)	4F	A24;4,0,24;3;#					
	2D						
	4P						
N=2 P(1) diatomic homonuclear	3D	A25;5,10,0;5;#*					
	1P	A26;1,2,0;5					
	3S	A27;1,2,0;5;*					
N=3 P(1) triatomic homonuclear	4F						
	2D						
	4P						

SO(3)xSU(2) Oper	Mult.	(R1, ...,Rn) (2, ...,2)	(R1, ...,Rn) (3, ...,3)	(R1, ...,Rn) (4, ...,4)	(R1, ...,Rn) (5, ...,5)	(R1, ...,Rn (6, ...,6)	(R1,R2 (2,3)
N=2 P(1)	3D	A28;15,0,0;5;# = A30;15,0,0;5					
	1P						
	3S	A29;3,0,0;5 = A31;3,0,0;5					
N=3 P(1)	4F	A32;28,0,0;5;#					
	2D	A33;8,0,0;5;#					
	4P						
N=3 P(2)	4F	A34;7,13,8;1					
	2D	A35;1,6,3;4					
	4P						
N=3 P(1) diatomic homonuclear	4F						
	2D						
	4P						

SO(2,1) Oper	(l1, ...,ln)	Groups (1, ...,1)	Groups (1, 7)	Groups (2, 6)	Groups (4, ...,4)	Groups (7, ...,7)	Groups (6, ...,6)
N=1 P(1)	0 & 1		B4;8,0,-;4; = B5;8,0,-;4				
	1				B6;4,0,-;4;#		
N=2 P(2)	(0,0)						
	(0,1)		B7;3,0,-;5 = B8;3,0,-;5				
	(1,1)				B9;4,0,-;4; = B10;6,0,-;4		

SO(2,1) Oper	$(l_1, ..., l_n)$	Groups (1, ...,1)	Groups (1, 7)	Groups (2, 6)	Groups (4, ...,4)	Groups (7, ...,7)	Groups (6, ...,6)
N=3　P(3)	(0,0,0)						
	(0,0,1)						
	(0,1,1)						
	(1,1,1)						
N=2　P(1) diatomic homonuclear	(0,0)						
	(0,1)						
	(1,1)						
N=3　P(1) triatomic homonuclear	(0,0,0)						
	(0,0,1)						
	(0,1,1)						
	(1,1,1)						
N=2　P(1)	(0,0)						
	(0,1)						
	(1,1)						
N=3　P(1)	(0,0,0)						
	(0,0,1)						
	(0,1,1)						
	(1,1,1)						

SO(2,1) Oper	(l1, ...,ln)	Groups (1, ...,1)	Groups (1, 7)	Groups (2, 6)	Groups (4, ...,4)	Groups (7, ...,7)	Groups (6, ...,6)
N=3 P(2)	(0,0,0)						
	(0,0,1)						
	(0,1,1)						
	(1,1,1)						
N=3 P(1) diatomic homonuclear	(0,0,0)						
	(0,0,1)						
	(0,1,1)						
	(1,1,1)						

TABLE III. Graphical interrelationships for entropy.

Key: Wi;X,Y,Z;N;* where Wi = plot is "i"th graph in appendix W, X = no. of actual data,
Y = no. of points which include approx. data, Z = no. of predictable data (missing),
N = index of fittability of surface. Inclusively similar plots are connected with single (---) lines.
Completely similar plots are connected with double (==) lines. When lines would cross or detour,
inclusively similar plots are labeled with one of the symbols {*, !, @}, while completely similar
plots are labeled with one of the symbols {#, $, %}.

SO(3)xSU(2) Oper.		Mult.	(R1, ...,Rn) (2, ...,2)	(R1, ...,Rn) (3, ...,3)	R L (2,3)(1,1)	R L (2,3)(1,0)	R L (2,3)(0,1)
N=1	P(1)	2D		A36;7,0,3;2			
		2P	A35;6,0,0;5;@# =	A37;6,0,0;5			
N=2	P(2)	3D	A38;9,6,0;2;* =	A41;6,5,4;2 =	A43;4,7,4;2		
		1P	A39;1,2,0;5	==========	A44;1,2,0;5	A46;1,1,1;5	
		3S	A40;1,2,0;5:* =	A42;1,2,0;5			
		3P			A45;3,4,2;3; =	A47;3,2,4;3 =	A48;2,2,5;3
N=3	P(3)	4F					
		2D					
		4P					
N=2 P(1) diatomic homonuclear		3D	A49;9,6,0;5;! =	A52;9,6,0;5			
		1P	A50;1,2,0;5 =	A53;1,2,0;5			
		3S	A51;1,2,0;5;! =	A54;1,2,0;5			
N=3 P(1) triatomic homonuclear		4F					
		2D					
		4P					

(Between A38 and A39 in the (2,...,2) column there is a single vertical | line.)

SO(3)xSU(2) Oper.		Mult.	(R1, ...,Rn) (2, ...,2)	(R1, ...,Rn) (3, ...,3)	R L (2,3)(1,1)	R L (2,3)(1,0)	R L (2,3)(0,1)
N=2	P(1)	3D	A55;15,0,0;5;@# =	A57;15,0,0;5			
		1P					
		3S	A56;3,0,0;5 =	A58;3,0,0;5			
N=3	P(1)	4F	A59;28,0,0;5;@#				
		2D	A60;10,0,0;5;@#				
		4P					
N=3	P(2)	4F	A61;13,15,0;2				
		2D	A62;2,8,0;1				
		4P					
N=3 P(1) diatomic homonuclear		4F					
		2D					
		4P					

SO(2,1) Oper.		(l1, ...,ln)	Groups (1, ...,1)	Groups (1, 7)	Groups (2, 6)	Groups (4, ...,4)	Groups (7, ...,7)
N=1	P(1)	0 & 1		B11;8,0,-;5;# =	B12;5,0,-;5		
		1				B13;2,0,-;5;#	
N=2	P(2)	(0,0)	B14;4,0,-;5;#				
		(0,1)		B15;10,0,-;5;# =	B16;0,6,-;5		
		(1,1)					B17;6,0,-;5;

SO(2,1)			Groups	Groups	Groups	Groups	Groups
	Oper.	(l1, ...,ln)	(1, ...,1)	(1, 7)	(2, 6)	(4, ...,4)	(7, ...,7)
N=3	P(3)	(0,0,0)					
		(0,0,1)					
		(0,1,1)					
		(1,1,1)					
N=2 diatomic homonuclear	P(1)	(0,0)					
		(0,1)					
		(1,1)					
N=3 triatomic homonuclear	P(1)	(0,0,0)					
		(0,0,1)					
		(0,1,1)					
		(1,1,1)					
N=2	P(1)	(0,0)					
		(0,1)					
		(1,1)					
N=3	P(1)	(0,0,0)					
		(0,0,1)					
		(0,1,1)					
		(1,1,1)					

SO(2,1) Oper.	$(l_1, ..., l_n)$	Groups (1, ...,1)	Groups (1, 7)	Groups (2, 6)	Groups (4, ...,4)	Groups (7, ...,7)
N=3 P(2)	(0,0,0)					
	(0,0,1)					
	(0,1,1)					
	(1,1,1)					
N=3 P(1) diatomic homonuclear	(0,0,0)					
	(0,0,1)					
	(0,1,1)					
	(1,1,1)					

TABLE IV. Graphical interrelationships for vibration frequency.

Key: Wi;X,Y,Z;N;* where Wi = plot is "i"th graph in appendix W, X = no. of actual data,
Y = no. of points which include approx. data, Z = no. of predictable data (missing),
N = index of fittability of surface. Inclusively similar plots are connected with single (---) lines.
Completely similar plots are connected with double (==) lines. When lines would cross or detour,
inclusively similar plots are labeled with one of the symbols {*, !, @}, while completely similar
plots are labeled with one of the symbols {#, $, %}.

SO(3)xSU(2)	Oper.	Mult.	(R1, R2) (2, 2)	(R1, R3) (3, 3)	R L (2,3)(1,1)	R L (2,3)(1,0)	R L (2,3)(0,1)
N=2	P(2)	3D	A63;8,5,2;3;#* =	A66;6,0,9;3 =	A68;5,4,6;3		
		1P	A64;1,1,1;5				
		3S	A65;1,2,0;5;*@ =	A67;1,2,0;5 =	A69;1,1,1;5		
		3P			A70;4,2,3;2;@	A71;2,1,6;5; =	A72;2,2,5;3
N=2 diatomic homonuclear	P(1)	3D	A73;9,6,0;5;#! =	A76;9,6,0;5			
		1P	A74;3,0,0;5;*@ =	A77;1,2,0;5			
		3S	A75;3,0,0;5;*! =	A78;1,2,0;5			
		3P					

SO(2,1)	Oper.	(l1, l2)	Groups (1, 1)	Groups (1, 7)	Groups (2, 6)	Groups (7, 7)	Groups (6, 6)
N=2	P(2)	(0,0)	B18;6,0,-;4;#				
		(0,1)		B19;8,0,-;4;# =	B20;0,5,-;4		
		(1,1)				B21;6,0,-;4	B22;6,0,-;4;#
N=2 diatomic homonuclear	P(1)	(0,0)					
		(0,1)					