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Publication Date
1981-12-01

LBL-13826
Preprint

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Submitted to the Journal of Molecular Spectroscopy

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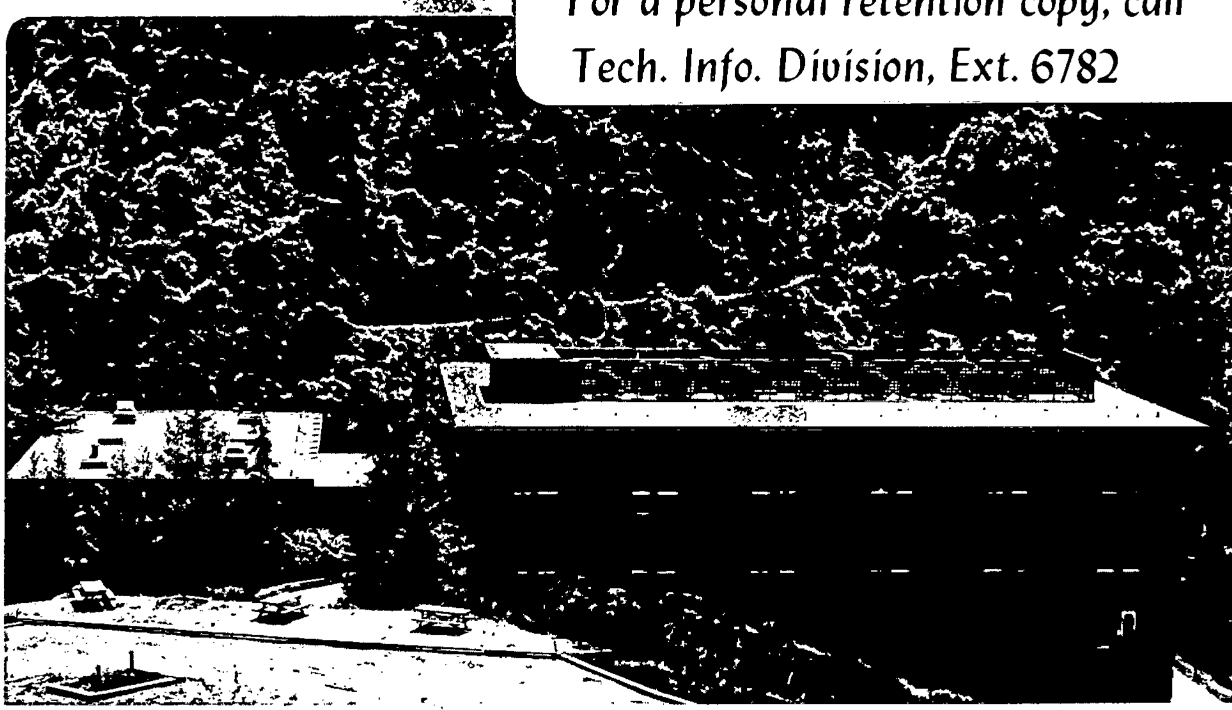
December 1981



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

Nuclear Spin Statistics of Cubane and Icosahedral Borohydride Ions

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While the nuclear spin statistics of spherically symmetric tetrahedral,[1,2] octahedral[3,4] and several other molecules of lower symmetry[5,6] are now quite well studied, this is not the case with molecules with very high symmetry such as cubane and the icosahedral borohydride ions ($B_{12}H_{12}^{-2}$). The recent revival of interest in nuclear spin statistics,[7-10] the fact that these two cases are still not solved in the literature and our recent experimental interest in the vibrational spectra of cubane[11] motivated us to investigate the nuclear spin statistics of these two structures.

For both these molecules the derivation of the symmetry of the spin function is difficult using just elementary methods[1] since the number of hydrogen spin functions for $C_8^{12}H_8$ is 256, and for $C_8^{12}D_8$ is 6,561 with correspondingly higher numbers for the icosahedral molecules. Once the symmetry species are given, the spin statistics of the individual rovibronic levels can be determined straightforwardly and complete tables constructed if necessary.[1,5] In this note we determine the species of the spin functions and briefly compare the results to the available experimental evidence. We use the general technique developed by Balasubramanian[7] for the nuclear spin statistics and the subsequent computational techniques[9-10] for this problem. The readers are referred to ref. 7 for the methodology. As Hougen[12] pointed out, in general it is necessary to classify the nuclear spin functions in the point group rather than just the rotational subgroups. However, when the symmetry group is just a direct product of a rotational subgroup and the inversion group, the statistical weights are unaffected by the inversion operation. The two molecules we consider belong to this case so that it is sufficient to find the nuclear spin statistical weights in O and I groups, respectively. The nuclear spin species thus obtained for C_8H_8 and C_8D_8 are shown in Tables I and II, respectively. We report here not only the total spin statistical weights but also the individual spin species which are useful in studying the hyperfine structure of the spectra. For the icosahedral borohydride $B_{12}H_{12}^{-2}$ proton and deuterium species, the results are shown in Tables III and IV, respectively. The overall spin species for the ^{11}B, H and D nuclei are shown below and in Tables 3 and 4.

$$\Gamma^{spin}_{B^{11}} = 280832\ A_g + 837888\ T_{1g} + 837888\ T_{2g} + 1118464\ G_g + 1399040\ H_g .$$

The total statistical weights for $^{11}B_{12}H_{12}^{-2}$ and $^{11}B_{12}D_{12}^{-2}$ can be easily obtained by multiplying the appropriate total spin species given above and in the tables.

For $B_{12}H_{12}^{-2}$ few vibrational spectra exist[14,15] and these are, of course, in condensed phase. However, the gas phase vibrational spectrum of cubane has recently been taken with a resolution sufficient to resolve the major rotational bands ("J-structure").[11] It is easy to find the statistical weights of a given rotational band using the symmetry species for the rotational wavefunctions given by Galbraith[4] and in many other places. A comparison between the statistical weights and the observed spectra was attempted for the P-branch bands of the 852 cm^{-1} vibration (skeletal stretch) of cubane as this branch seems to the least perturbed of those observed.[11] The spin weights[16] (without the M degeneracy) are 667 for J = 30, 665 for J = 31, 695 for J = 32, 715 for J = 33 and so on. These closely spaced numbers lead to predicted intensities that do not correspond to the observed spectra. This discrepancy is due to a combination of noise in the spectrum, rotational perturbations, and to insufficient resolution of the spectrum. Spectra taken with laser diode resolution[17] (such as those for SF_6) should demonstrate the effects of the spin statistics presented here.

Acknowledgments

This research was supported by the National Science Foundation and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy through Contract W-7405-ENG-48.

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Table 1. Proton Spin Species of Cubane[a]

Γ \ 2S + 1	9	7	5	3	1	Total Spin Weight
A_1	1	0	2	0	4	23
A_2	0	1	0	2	0	13
E	0	0	3	1	2	20
T_1	0	1	1	5	0	27
T_2	0	1	3	3	2	33

[a] Γ labels the irreducible representations. The entries in the Table give the number of times a multiplet occurs. The last column gives the spin weight for a given representation i.e., for A_1 the spin weight is $9\cdot1 + 5\cdot2 + 1\cdot4 = 23$. Note that $23\cdot1 + 13\cdot1 + 20\cdot2 + 27\cdot3 + 33\cdot3 = 256 = 2^8$ the total number of spin functions.

Table 2. Deuterium Spin Species of Cubane

Γ \ 2S + 1	17	15	13	11	9	7	5	3	1	Total
A_1	1	0	3	2	11	6	18	4	12	333
A_2	0	1	1	4	5	12	10	12	1	288
E	0	0	3	5	15	17	27	15	12	540
T_1	0	1	2	11	16	33	29	35	5	792
T_2	0	1	4	9	20	29	37	27	13	828

Table 3. Proton Spin Species of $B_{12}H_{12}^{-2}$

Γ \ 2S + 1	13	11	9	7	5	3	1	Total
A	1	0	2	2	7	2	10	96
T_1	0	1	1	9	10	19	2	192
T_2	0	1	1	9	10	19	2	192
G	0	0	4	12	17	19	10	272
H	0	1	6	10	28	21	14	352

Table 4. Deuterium Spin Species of $B_{12}D_{12}^{-2}$

Γ \ 2S + 1	25	23	21	19	17	15	13	11	9	7	5	3	1	Total
A_1	1	0	3	4	18	32	94	121	223	231	277	158	113	9009
T_1	0	1	2	15	38	116	220	421	581	769	720	597	176	26406
T_2	0	1	2	15	38	116	220	421	581	769	720	597	176	26406
G	0	0	4	20	57	147	312	540	806	1002	996	752	286	35424
H	0	1	7	20	79	179	396	671	1029	1217	1289	910	380	44442

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