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Simulation of NMR Hyperfine Structure Constant for AB_2, A_2B_2 and A_2B_3 Systems

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ABSTRACT: The energy matrices of molecules of AB_2, A_2B_2 and A_2B_3 type have been calculated for three different chemical shifts and several indirect spin-spin coupling coefficients (J_{ij}) to obtain the Nuclear Magnetic Resonance (NMR) hyperfine structure. A computer program implemented in JACOBI method, which is a numerical iterative method for solving linear equation systems or a matrix equation on a matrix that has no zeros among its main diagonal elements, was used to calculate the eigenvalues and eigenvectors of these systems. We have developed a code to obtain the transition probabilities and transition energies. The theoretically calculated spectra has been compared with the experimental spectra and it has been observed a quite acceptable compliance between them.

Keywords: Nuclear magnetic resonance, computer simulation, hyperfine structure, chemical shift, spin-spin coupling coefficients

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INTRODUCTION

NMR spectroscopy is a convenient method used in the study of molecular structures and has comprehensive applications in many areas such as physics, chemistry, biology, medicine and geophysics nowadays. In physical chemistry, NMR spectroscopy is an effective nondestructive analytical technique extensively used to determinate the structure and chemical properties of molecules (Behroozmand et al., 2015; Gerothanassis et al., 2002). NMR depends on the nuclear spin of a nucleus. All nuclei have the nuclear spins different from zero possess nuclear magnetic moments. The energy level of a nucleus which has a nuclear magnetic moment can be splited in the presence of an external magnetic field. This process is called the Zeeman Effect (Callaghan,1991). The nuclear magnetic moments of nuclei consisting of molecules can be interacted with each other, the surrounding electrons magnetic moments or external magnetic field. In case of a molecule, the molecular electrons, which are the weakly magnetized by each nucleus, produce a magnetic field at the location of the neighbouring nuclei. Therefore, nuclear spins are coupled together by means of the molecular electrons. Indirect spin-spin coupling (J-coupling) arises because of indirect magnetic interaction between the nuclear spins of nuclei and electrons (Helgaker et al., 2008). The other mechanism is called a hyperfine interaction. In this process, the magnetic moments of electrons, which are spinning around nuclei, can be interacted with the magnetic moment of nuclei (Tarucha et al., 2011). These processes lead to a greater number of the splitted lines in a NMR spectra. In this sense, a hyperfine interaction is also important as almost J coupling. Another crucial phenomenon in NMR spectroscopy is the chemical shift process. Under an external magnetic field, the electrons surrounding the nucleus start to precess in the direction of the applied magnetic field, and then induce a magnetic field in an opposite direction to the external magnetic field. The effective magnetic field experienced by the nucleus is therefore reduced. The differences in the effective magnetic field for non-equivalent nuclei lead to small shifts in the resonance frequencies and hence NMR spectra, which is call the chemical shift or sometimes fine structure (Holzgrabe et al., 1998; Al-Jalali and Mahzia2014). If this technique is used on the indirect spin-spin couplings between two non-identical nucleus groups with 1/2 spin, all molecules such as AB, AX, AB_2, A_2B_2, and A_2B_2, are considered. It is relatively easy to study molecules including nuclei with 1/2 spin such as ${}_1H^1$, ${}_6C^{13}$, and ${}_9F^{19}$ which are call for NMR-active nuclei (Gerald et al., 2001) and also NMR studies of these nuclei is common work (Katoh, 1994; Holzgrabe et al., 1998). Spin algebra and simulating 1D and 2D NMR experiments have also been realized (Grivet, 2015).

Abragam (Abragam, 1973) and Akitt (Akitt and Mann, 2002) have investigated the energy matrices of molecules of AB_2, A_2B_2 and A_2B_3 system. A computer program with JACOBI method (Golub and Van der Vorst, 2000) can be used to calculate the energy eigenvalues and eigenvectors of these systems. The same program is used to calculate the transition probabilities and energy; however, subroutines often need to be written for each system separately. Thus, the theoretical NMR spectra of one system are obtained and compared with experimental spectra. The purpose of this study is to obtain theoretical NMR spectra of molecules.

MATERIALS AND METHODS

The $\hbar\mathcal{H}$ Hamiltonian of a spin system in a homogeneous magnetic field, which is any combination of d.c. and r.f .fields, can be given by:

$$\hbar\mathcal{H} = -\gamma\hbar\vec{\mathcal{H}}\cdot\vec{I} + \hbar\sum_{p<q} J_{pq}\,\overrightarrow{I_p}\cdot\overrightarrow{I_q} + \vec{I}\sum_{p<q}\hbar J_{q'}I'_{q'} + \hbar\,\mathcal{H}_I(I') \tag{1}$$

where $\vec{I} = \vec{I_1} + \vec{I_2} + \ldots + \vec{I_n}$ and $\hbar\mathcal{H}_\mathrm{I}(\mathrm{I}')$ is an independent part of $\mathrm{I_p}$. Each of these has a $\mathrm{I}'_{\mathrm{q}'}$ spin and only one coupling constant $\mathrm{J}_{\mathrm{q}'}$ because the $\mathrm{I_p}$s are identical. The operator $\mathcal{H}_\mathrm{a} = \sum_{p<q} J_{pq}\, \vec{I_p} \cdot \vec{I_q}$ is commutative for all other terms of $\mathcal{H}$.

In the Schrödinger equation, $i\frac{\partial\Psi}{\partial t} = (\mathcal{H}_a + \mathcal{H}_b)\Psi$, if $\Psi = exp(-i\mathcal{H}_a t)\Phi$, Φ can be given by

$$I\frac{\partial\Phi}{\partial t} = H_b\Phi \tag{2}$$

where $\mathcal{H}_\mathrm{b} = \mathcal{H} - \mathcal{H}_\mathrm{a}$.

The observed signal is proportional to

$$S = \frac{d}{dt}\langle\Psi(t)|M_x|\Psi(t)\rangle = \frac{d}{dt}\langle\Phi(t)\left|e^{iH_a t}M_x e^{-iH_a t}\right|\Phi(t)\rangle.$$

Here, M is total nuclear magnetic moment operator of the sample and because $M_x = \gamma\hbar I_x + f(I')$ is commutative by $\mathcal{H}_\mathrm{a}$, the following equation can be written:

$$S = \frac{d}{dt}\langle\Phi(t)|M_x|\Phi(t)\rangle \tag{3}$$

The signal is determined by $\Phi(\mathrm{t})$ according to the equation $\Phi(t) \neq f(\mathcal{H}_a)$. $\mathrm{J_{pq}}$ couplings cannot be observed between identical spins. For example, while there is a J for HD, there is not a J for H_2.

Case J<<δ

Suppose that there are two groups: G and G′. The spins are such that $\mathrm{I_k}$ is p units and I'_k is p′ units. It is assumed that the mutual interaction constant J is much smaller than $\delta = (\gamma - \gamma')\mathcal{H}_0$. This condition is always true for different nucleus cases (except for weak fields). When irrelevant terms are excluded, the Hamiltonian is

$$\hbar\mathcal{H} = -(\gamma\hbar I_z + \gamma'\hbar I'_z)\mathcal{H}_0 + \hbar J \cdot \vec{I} \cdot \vec{I'} \tag{4}$$

where $\mathcal{H}_0|\gamma - \gamma'| \gg J$ and $\vec{I} = \sum_k I_k$, $\vec{I'} = \sum_{k'} \overrightarrow{I'_{k'}}$. The maskings of σ and σ′ are γ and γ′. In the method of the first perturbation, instead of $\hbar J \cdot \vec{I} \cdot \vec{I'}$, the small coupling term, which is a part of $\hbar J I_z I'_z$ and commutative by $= -(\gamma\hbar I_z + \gamma'\hbar I'_z)\mathcal{H}_0$, the main Hamiltonian is used.

In case of this, energy levels of system is given by

$$\hbar E_{MM'} = -(\gamma\hbar\mathcal{H}_0 M + \gamma'\hbar\mathcal{H}_0 M') + \hbar J M M' \tag{5}$$

where $I_z = M$, $I'_z = M'$. The transition frequencies are

$$\begin{cases} \Delta M = 1,\ \Delta M' = 0\ \ for\ \ \omega = -\gamma\mathcal{H}_0 + JM' \text{ and} \\ \Delta M = 0,\ \Delta M' = 1\ \ for\ \ \omega' = -\gamma\mathcal{H}_0 + JM \end{cases} \tag{6}$$

It is observed a multilayer structure for each group and they contain $(2p'i' + 1)(2pi + 1)$ components, where i is spin of p units of $\mathrm{I_k}$ spins in group G, and i′ is the spin of p′ units of I'_k for group G′.

The relative intensity of the component $\omega = -\gamma\mathcal{H}_0 + JM'$ depends on how many ways p′ units of I'_k spin gives $\mathrm{I}'_\mathrm{z} = \mathrm{M}'$, which is proportional to the coefficient of $x^{(p'i'+M')}$ in the expansion of $P(x) = \left(1 + x + \ldots + x^{2i'}\right)^{p'}$. If the experiment is performed in a scanning field at a fixed frequency, the intervals of ΔH and ΔH′, in other words, $|\mathrm{J}/\gamma|$and $|\mathrm{J}/\gamma'|$, occur between successive lines in multilayer structures of G and G′, which are independent of the applied field and the ratio of $|\gamma'/\gamma|$.

Case J δ

For group G with identical spin i, which is p units, and group G′ with identical spin i′, which is p′ units (AB_2, A_2B_2, A_2B_3.....), the Hamiltonian

$$\hbar\mathcal{H} = -(\gamma\hbar I_z + \gamma'\hbar I'_z)\mathcal{H}_0 + \hbar J \cdot \vec{I} \cdot \vec{I'} \tag{7}$$

should be performed diagonally, using $J \cdot \vec{I_z} \cdot \vec{I'_z}$ instead of $J \cdot \vec{I} \cdot \vec{I'}$. In the general case, when the following good quantum numbers are valid, the solution is simplified:

$$F_z = I_z + I'_z, \quad |\vec{I}|^2 = I(I+1), |\vec{I'}|^2 = I'(I'+1)$$

The eigenstates are written for the specific values of F_z, I and I′:

$$|\zeta \quad \rangle = \sum_M C_M \, |F_z, I,\ I',\ M\rangle \tag{8}$$

where M equals I_z and is not a good quantum number. All the states of the system are determined by solving a secular equation in order the smallest one than the most $2I + 1$ or $2I' + 1$ in the form of separate manifolds depending on the values of F_z, I and I′. If one of the sums of the spins I and I′ is 1/2, the equation is not higher than second order. Thus, the eigenstates and energy levels can be written explicitly.

The transition probabilities between two eigenstates are calculated using the following equation:

$$P_{\zeta\zeta'} \propto |\langle\zeta|I_x + I'_x|\zeta'\rangle|^2. \tag{9}$$

The small differences between γ and γ' are not considered in Equation (9). Because $I_x + I'_x$ and I and I′ are commutative, only the transitions of $\Delta I = 0,\ \Delta I' = 0, \Delta F_z = \pm 1$ were allowed. This state of system was not completely determined by F_z, I, I′ and I_z. For instance, if group G includes 3 units of 1/2 spins, I equals 1/2 in two ways, and there are two orthogonal states I = 1/2, I_z = 1/2. An additional quantum number λ is needed to completely determine the system: $|F_z, I,\ I',\ I_z,\ \lambda\rangle$. Different quantum states λ exhibit a variant symmetry character depending on the perturbation among i spins (or i′ spins). Because the Hamiltonian (including part of r.f.) is a symmetric function of i spins (and i′ spins), it is independent of λ. The transition frequencies and probabilities are calculated without considering λ.

The intensity for the transition of $\zeta(I,\ I',\ F_z) \rightarrow \zeta'(I,\ I',\ F_z - 1)$ has a weight of $N(I, I')$. This are many different ways of constructing I total spins from p units and i spins and I′ total spins from p′ units and i′ spins.

AB$_2$ System

According to the representations contained in the theory, in the AB$_2$ system, the following descriptions can be written:

$P_A = 1$ $i_A = 1/2$ $I^A = 1/2$ $I_z^A = \pm\frac{1}{2}$
$P_B = 2$ $i_B = 1/2$ $I^B = 1 : 0$ $I_z^B = 1, 0, -1; 0$

From Table 1, it can be seen wavelength functions of AB$_2$ system.

Table 1. Wavelength functions of AB$_2$ system.

F_z	$I^A = 1/2, I^B = 1$	$I^A = 1/2, I^B = 0$
-3/2	$\varphi_6 = \left\|-\frac{1}{2}, -1\right\rangle$	
-1/2	$\varphi_5 = \left\|-\frac{1}{2}, 0\right\rangle$ $\varphi_4 = \left\|+\frac{1}{2}, -1\right\rangle$	$\varphi_8 = \left\|-\frac{1}{2}, 0\right\rangle$
+1/2	$\varphi_3 = \left\|-\frac{1}{2}, +1\right\rangle$ $\varphi_2 = \left\|+\frac{1}{2}, 0\right\rangle$	$\varphi_7 = \left\|+\frac{1}{2}, 0\right\rangle$
+3/2	$\varphi_1 = \left\|+\frac{1}{2}, +1\right\rangle$	

Matrix Elements

The elements on the diagonal are calculated using the Hamiltonian

$$\mathcal{H}^0 = -\upsilon_A I_z^A - \upsilon_B I_z^B + J \cdot I_z^A \cdot I_z^B$$

according to $\langle\varphi_i|\mathcal{H}^0|\varphi_i\rangle$. For $\varphi_1 = \left|+\frac{1}{2}, +1\right\rangle$, it is obtained

$$1)\ \langle+\tfrac{1}{2},+1|\mathcal{H}^0|+\tfrac{1}{2},+1\rangle = -\frac{\upsilon_A}{2} - \upsilon_B + \frac{J}{2} = -\frac{3}{2}\frac{\upsilon_A+\upsilon_B}{2} + \frac{\delta}{4} + \frac{J}{2},$$

where $\upsilon_A - \upsilon_B = \delta$. The following equations are obtained in a similar manner:

$$2)\ \langle+\tfrac{1}{2},0|\mathcal{H}^0|+\tfrac{1}{2},0\rangle = -\frac{\upsilon_A}{2} = -\frac{1}{2}\frac{\upsilon_A+\upsilon_B}{2} - \frac{\delta}{4}$$

$$3)\ \langle-\tfrac{1}{2},+1|\mathcal{H}^0|-\tfrac{1}{2},+1\rangle = -\frac{\upsilon_A}{2} - \upsilon_B - \frac{J}{2} = -\frac{1}{2}\frac{\upsilon_A+\upsilon_B}{2} + \frac{3\delta}{4} - \frac{J}{2}$$

$$4)\ \langle+\tfrac{1}{2},-1|\mathcal{H}^0|+\tfrac{1}{2},-1\rangle = \frac{\upsilon_A}{2} + \upsilon_B - \frac{J}{2} = \frac{1}{2}\frac{\upsilon_A+\upsilon_B}{2} - \frac{3\delta}{4} - \frac{J}{2}$$

$$5)\ \langle-\tfrac{1}{2},0|\mathcal{H}^0|-\tfrac{1}{2},0\rangle = \frac{\upsilon_A}{2} = \frac{1}{2}\frac{\upsilon_A+\upsilon_B}{2} + \frac{\delta}{4}$$

$$6)\ \langle-\tfrac{1}{2},-1|\mathcal{H}^0|-\tfrac{1}{2},-1\rangle = \frac{\upsilon_A}{2} + \upsilon_B + \frac{J}{2} = \frac{3}{2}\frac{\upsilon_A+\upsilon_B}{2} - \frac{\delta}{4} + \frac{J}{2}$$

$$7)\ \langle+\tfrac{1}{2},0|\mathcal{H}^0|+\tfrac{1}{2},0\rangle = -\frac{\upsilon_A}{2} = -\frac{1}{2}\frac{\upsilon_A+\upsilon_B}{2} - \frac{\delta}{4}$$

$$8)\ \langle-\tfrac{1}{2},0|\mathcal{H}^0|-\tfrac{1}{2},0\rangle = \frac{\upsilon_A}{2} = \frac{1}{2}\frac{\upsilon_A+\upsilon_B}{2} + \frac{\delta}{4}.$$

All the elements except for the diagonal are obtained as follows according to $\langle\varphi_i|\mathcal{H}'|\varphi_j\rangle$using the Hamiltonian $\mathcal{H}' = \frac{J}{2}(I_+^A I_-^B + I_-^A I_+^B)$:

$$\langle\varphi_2|\mathcal{H}'|\varphi_3\rangle = \langle+\frac{1}{2},0|\mathcal{H}'|-\frac{1}{2},+1\rangle = +\frac{J}{2}$$

$$\langle\varphi_4|\mathcal{H}'|\varphi_5\rangle = \langle+\tfrac{1}{2},-1|\mathcal{H}'|-\tfrac{1}{2},0\rangle = +\frac{J}{2}.$$

Eigenvalues

φ_2 and φ_3 with the same F_z = + 1/2 value are mixed.

The secular determinant is

$$\begin{vmatrix} -\frac{1}{2}\frac{\upsilon_A+\upsilon_B}{2} - \frac{\delta}{4} - E & +\frac{J}{2} \\ +\frac{J}{2} & -\frac{1}{2}\frac{\upsilon_A+\upsilon_B}{2} + \frac{3\delta}{4} - \frac{J}{2} - E \end{vmatrix} = 0,$$

and the eigenvalues are obtained as follows:

$$E_{2,3} = -\frac{1}{2}\frac{\upsilon_A+\upsilon_B}{2} + \frac{\delta}{4} - \frac{J}{4} \pm \frac{J}{2}\sqrt{\frac{\delta^2}{J^2} - \frac{\delta}{J} + \frac{5}{4}}.$$

For φ_4 and φ_5 with the same F_z = -1/2 values, the secular determinant is

$$\begin{vmatrix} \frac{1}{2}\frac{\upsilon_A+\upsilon_B}{2} - \frac{3\delta}{4} - \frac{J}{2} - E & +\frac{J}{2} \\ +\frac{J}{2} & \frac{1}{2}\frac{\upsilon_A+\upsilon_B}{2} + \frac{\delta}{4} - E \end{vmatrix} = 0,$$

and the eigenvalues are determined as

$$E_{4,5} = \frac{1}{2}\frac{\upsilon_A+\upsilon_B}{2} - \frac{\delta}{4} - \frac{J}{4} \pm \frac{J}{2}\sqrt{\frac{\delta^2}{J^2} + \frac{\delta}{J} + \frac{5}{4}}$$

Energy levels of AB_2, A_2B_2 and A_2B_3 type molecules were determined by solving the energy matrices through the code of JACOBI method for chemical shifts and indirect spin-spin coupling coefficients (J_{ij}). Figure 1, Figure 2, Figure 3 show energy level diagrams of AB_2, A_2B_2 and A_2B_3 systems, respectively.

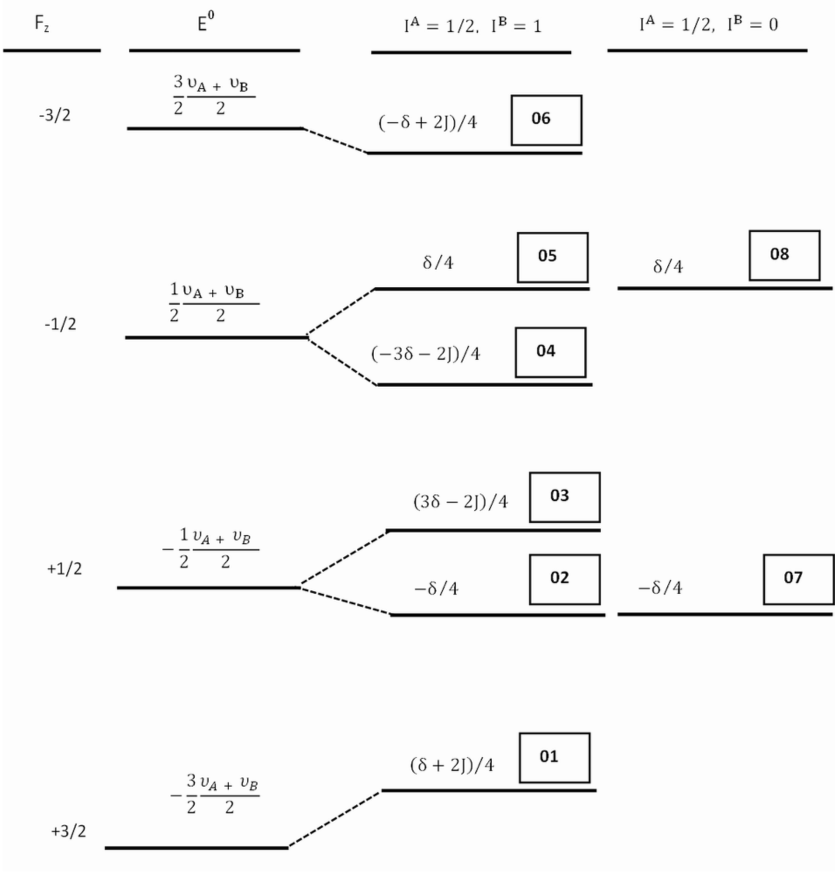


Figure 1. The energy level diagram for AB_2 system.

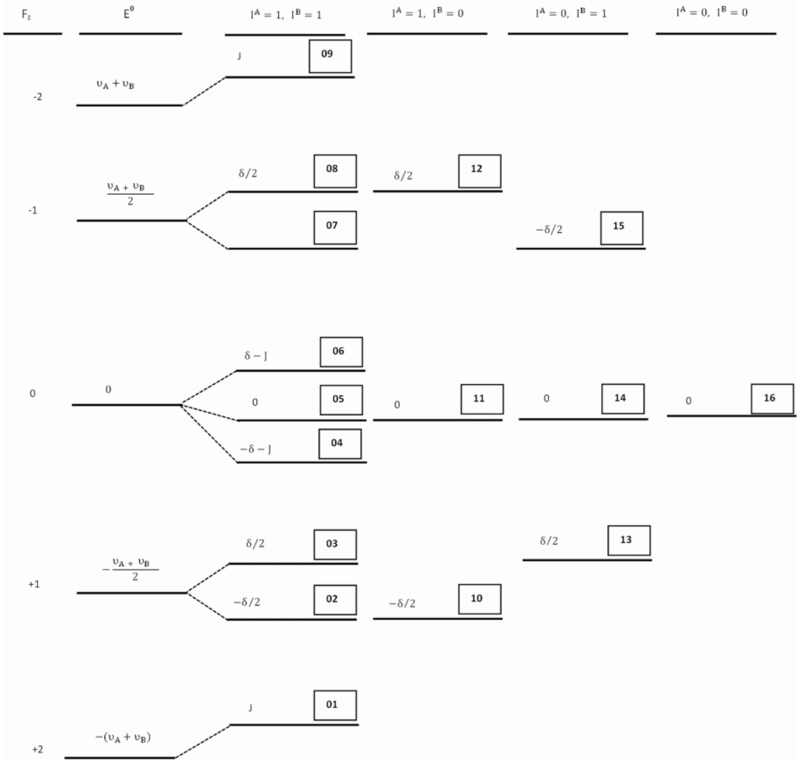


Figure 2. Energy level diagram for A_2B_2 system.

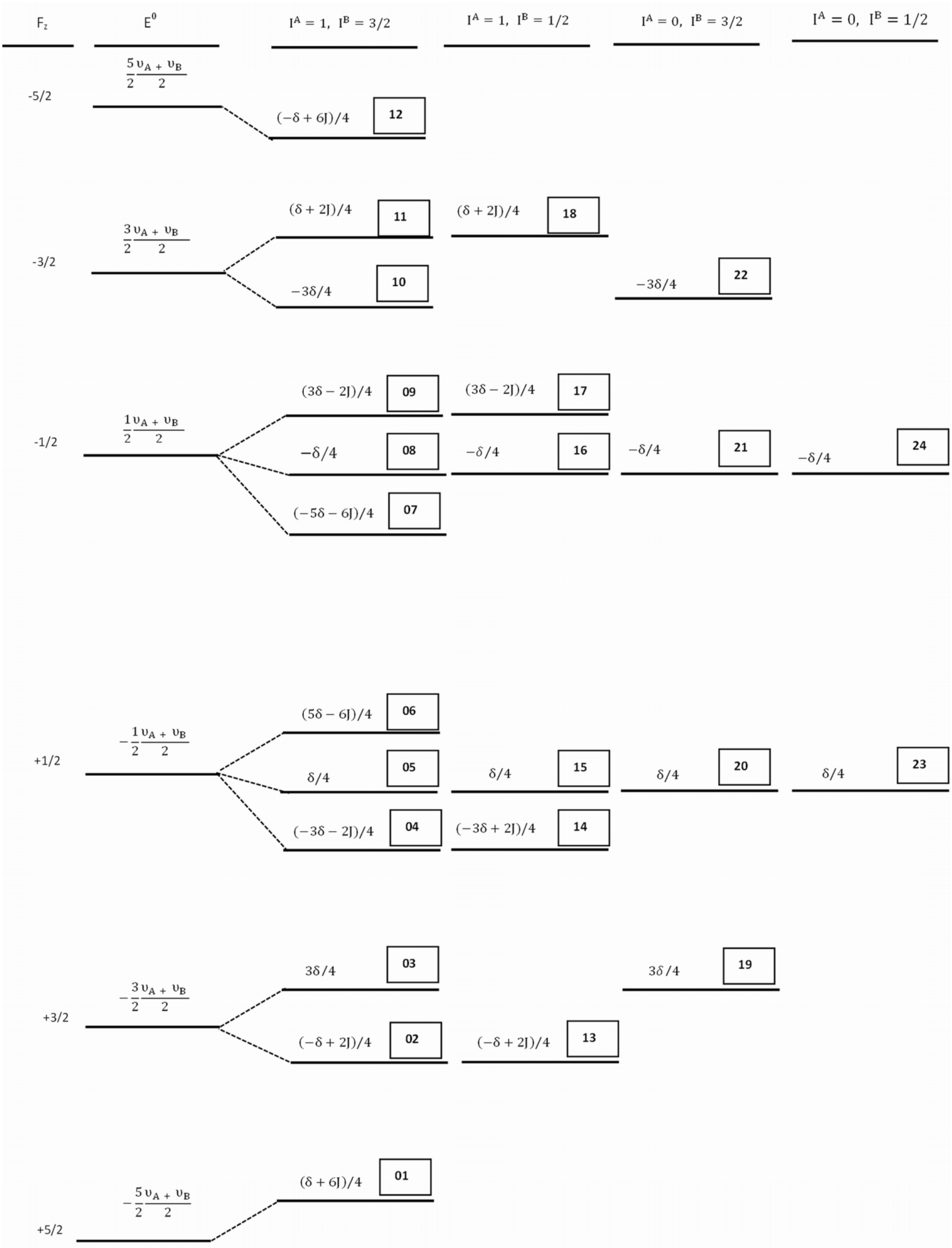


Figure 3. Energy level diagram for A_2B_3 system.

RESULTS AND DISCUSSION

AB_2 System

Mixing coefficient

The wave functions of φ_2 and φ_3 with the same *Fz* value are mixed to yield two wave functions, the antisymmetric wave function $\Psi_2 = a\varphi_2 + b\varphi_3$ and the symmetric wave function $\Psi_3 = a'\varphi_2 + b'\varphi_3$. In a similar manner, the wave functions of φ_4 and φ_5, which have the same *Fz* value, are mixed to give two wave functions, an antisymmetric wave function $\Psi_4 = c\varphi_4 + d\varphi_5$ and a symmetric wave function $\Psi_5 = c'\varphi_4 + d'\varphi_5$. The mixing coefficients were obtained using the JACOBI program and are listed in Table 2.

Table 2. Mixing coefficients for AB_2 system (δ=100 Hz; J=10 Hz)

a = 0.9986	b = -0.0524
a′= 0.0524	b′= 0.9986
c = 0.9989	d = -0.0475
c′= 0.0475	d′= 0.9989

Transition probabilities

$$P_{ij} = \left[\langle\varphi_j|\mathcal{H}''|\varphi_i\rangle\right]^2 \qquad \mathcal{H}'' = \frac{1}{2}\left(I_+^A + I_-^A + I_+^B + I_-^B\right)$$

$$P_{12} = \left[\langle a\left|\frac{1}{2},0\rangle + b\right|-\frac{1}{2},1\rangle|\mathcal{H}''|\frac{1}{2},1\rangle\right]^2 = \frac{1}{4}(a+b)^2, \qquad P_{13} = \frac{1}{4}(a'+b')^2$$

$$P_{24} = \left[\langle c\left|\frac{1}{2},-1\rangle + d\right|-\frac{1}{2},0\rangle|\mathcal{H}''|a\rangle + b\left|-\frac{1}{2},1\rangle\right.\right]^2 = \frac{1}{4}[a(c+d)+db]^2$$

$$P_{25} = \frac{1}{4}[a(c'+d')+c'b]^2 \quad P_{34} = \frac{1}{4}[a'(c+d)+db']^2 \quad P_{35} = \frac{1}{4}[a'(c'+d')+d'b']^2$$

$$P_{46} = \left[\langle-\frac{1}{2},-1\rangle\,|\mathcal{H}''|c\left|\frac{1}{2},-1\rangle + d\right|-\frac{1}{2},0\rangle\right]^2 = \frac{1}{4}(c+d)^2 \qquad P_{56} = \frac{1}{4}(c'+d')^2$$

$$P_{78} = \left[\langle-\frac{1}{2},0\rangle\,|\mathcal{H}''|\left|\frac{1}{2},0\rangle\right.\right]^2 = \frac{1}{4} = 0{,}25$$

The transition type, transition frequencies and intensities for the AB_2 system are listed in Table 3. The sample spectrum for δ=13.97 Hz, J=8.08 Hz is presented in Figure 4. The experimental spectra were acquired from (Corio, 1966).

Table 3. Transition frequencies and intensities of AB_2 system.

P_{ij}	**Transition Type**	**1. Sample**		**2. Sample**		**3. Sample**		**4. Sample**	
		δ=100Hz, J=10Hz		**δ= 40Hz, J=10Hz**		**δ=20 Hz, J=10Hz**		**δ=13,97 Hz, J=8,08 Hz**	
		Transition Frequency	**Intensity**	**Transition Frequency**	**Intensity**	**Transition Frequency**	**Intensity**	**Transition Frequency**	**Intensity**
$P_{1,2}$	**B**	-55.2624	0.448	-25.7003	0.362	-16.5139	0.222	-12.4610	0.184
$P_{1,3}$	**A**	40.2624	0.276	10.7003	0.319	1.5139	0.389	0.3410	0.408
$P_{2,4}$	**B**	-54.9752	0.454	-24.8486	0.398	-14.4490	0.332	-10.4537	0.316
$P_{2,5}$	**A**	50.5000	0.246	21.2492	0.228	12.4768	0.175	9.2857	0.156
$P_{3,5}$	**B**	-45.0248	0.554	-15.1514	0.646	-5.5510	0.818	-3.5163	0.870
$P_{4,6}$	**A**	60.2376	0.226	30.5489	0.196	20.9629	0.157	15.9297	0.148
$P_{5,6}$	**B**	-45.2376	0.548	-15.5489	0.608	-5.9629	0.686	-3.8097	0.704
$P_{7,8}$	**A**	50.0000	0.250	20.0000	0.250	10.0000	0.250	6.9850	0.250

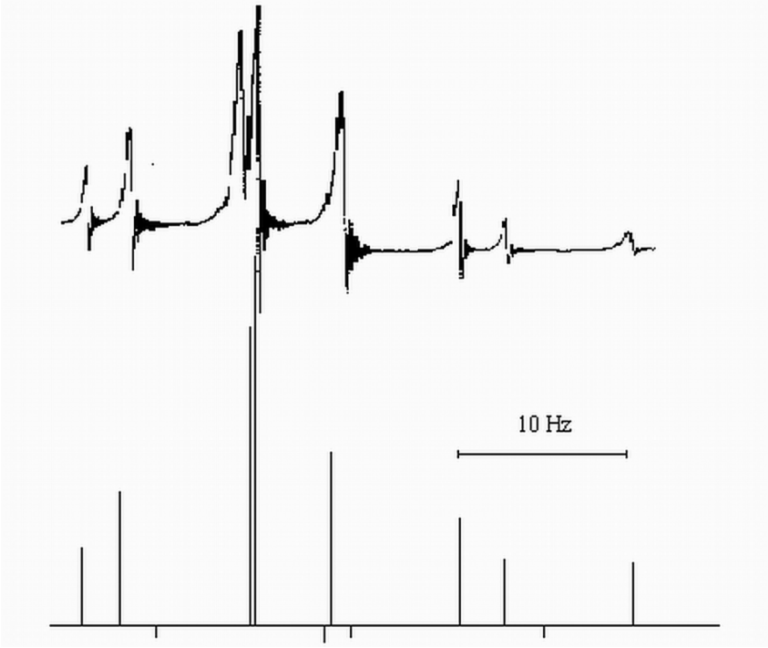


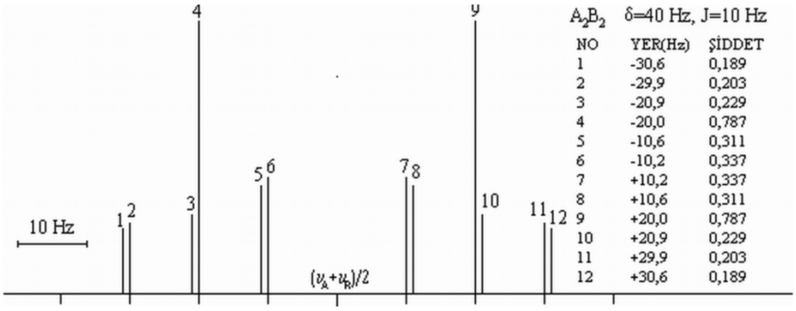
Figure 4. Experimental and theoretical proton spectra of 1,2,3-trichlorobenzene (δ = 13.97 Hz and J = 8.08 Hz).

A_2B_2 System

The mixing coefficients, transition probabilities and transition frequencies for the A_2B_2 system were calculated following the procedures performed for the AB_2 system and are listed in Table 4. The sample spectrum for δ=40 Hz, J=10 Hz is presented in Figure 5.

Table 4. Transition frequencies and intensities of the A_2B_2 system

P_{ij}	Transition Type	1. Sample		2. Sample		3. Sample	
		δ=20 Hz, J=10 Hz		δ=40 Hz, J=10 Hz		δ=100Hz, J=10 Hz	
		Transition Frequency	Intensity	Transition Frequency	Intensity	Transition Frequency	Intensity
$P_{1,2}$	B	-21.1803	0.138	-30.6155	0.189	-60.2494	0.225
$P_{1,3}$	A	1.1803	0.362	10.6155	0.311	40.2494	0.275
$P_{2,4}$	B	-19.6468	0.175	-29.8826	0.203	-59.9777	0.228
$P_{2,5}$	A	9.8463	0.209	20.2942	0.287	50.1992	0.247
$P_{3,5}$	B	-12.5143	0.135	-20.9368	0.229	-50.2996	0.246
$P_{2,6}$	Mixed	23.3414	0.004	-	-	-	-
$P_{3,6}$	A	0.9808	0.476	10.2039	0.337	40.0279	0.279
$P_{4,7}$	A	19.6468	0.175	29.8826	0.203	59.9777	0.228
$P_{5,7}$	B	-9.8463	0.209	-20.2943	0.287	-50.1992	0.247
$P_{6,7}$	Mixed	-23.3414	0.004	-	-	-	-
$P_{5,8}$	A	12.5143	0.135	20.9368	0.229	50.2996	0.246
$P_{6,8}$	B	-0.9808	0.476	-10.2039	0.337	-40.2494	0.279
$P_{7,9}$	A	21.1803	0.138	30.6155	0.189	60.2494	0.225
$P_{8,9}$	B	-1.1803	0.362	-10.6155	0.311	-40.2494	0.275
$P_{10,11}$	A	10.0000	0.250	20.0000	0.250	50.0000	0.250
$P_{11,12}$	A	10.0000	0.250	20.0000	0.250	50.0000	0.250
$P_{13,14}$	B	-10.0000	0.250	-20.0000	0.250	-50.0000	0.250
$P_{14,15}$	B	-10.0000	0.250	-20.0000	0.250	-50.0000	0.250



A_2B_2 δ=40 Hz, J=10 Hz

NO	YER(Hz)	ŞİDDET
1	-30,6	0,189
2	-29,9	0,203
3	-20,9	0,229
4	-20,0	0,787
5	-10,6	0,311
6	-10,2	0,337
7	+10,2	0,337
8	+10,6	0,311
9	+20,0	0,787
10	+20,9	0,229
11	+29,9	0,203
12	+30,6	0,189

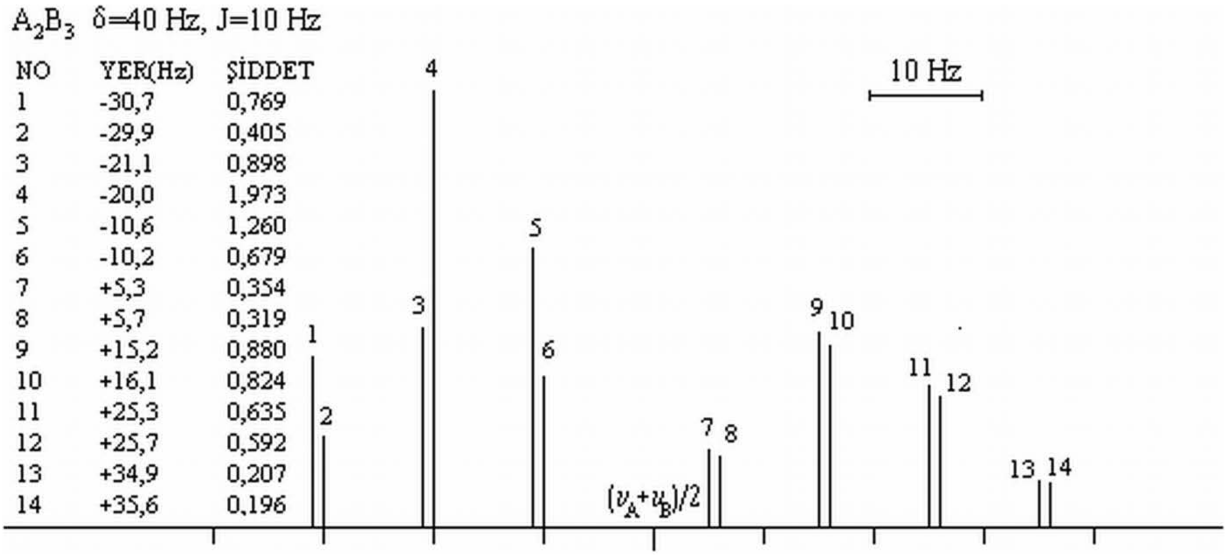
Figure 5. Sample spectrum for the A_2B_2 system and δ=40 Hz, J=10 Hz.

A_2B_3 System

The mixing coefficients, transition probabilities and transition frequencies for the A_2B_3 system were calculated following the procedures performed for the AB_2 system and are listed in Table 5. The sample spectrum for δ=40 Hz, J=10 Hz is presented in Figure 6.

Table 5. Transition frequencies and intensities of the A_2B_3 system

P_{ij}	Transition Type	1. Sample		2. Sample		3. Sample	
		δ=20 Hz, J=10 Hz		δ=40 Hz, J=10 Hz		δ=100 Hz, J=10 Hz	
		Transition Frequency	Intensity	Transition Frequency	Intensity	Transition Frequency	Intensity
$P_{1,2}$	B	-21.5139	0.111	-30.7003	0.181	-60.2624	0.224
$P_{1,3}$	A	-3.4861	0.389	5.7003	0.319	35.2624	0.276
$P_{2,4}$	B	-19.4779	0.162	-29.8528	0.198	-59.9754	0.227
$P_{2,5}$	A	4.1979	0.189	15.2777	0.233	45.2067	0.247
$P_{3,5}$	B	-13.8299	0.071	-21.1229	0.215	-50.3181	0.246
$P_{2,6}$	Mixed	14.8217	0.010	-	-	-	-
$P_{3,6}$	A	-3.2061	0.566	5.2754	0.354	35.0312	0.280
$P_{4,7}$	B	-19.7180	0.185	-29.9000	0.207	-59.9794	0.229
$P_{4,8}$	A	15.4429	0.216	25.3006	0.238	55.1922	0.248
$P_{5,8}$	B	-8.2329	0.193	-19.8299	0.235	-49.9899	0.247
$P_{6,8}$	Mixed	-18.8567	0.009	-	-	-	-
$P_{5,9}$	A	8.8716	0.074	16.1282	0.215	45.3185	0.246
$P_{6,9}$	B	-1.7522	0.569	-10.2701	0.354	-40.0308	0.280
$P_{7,10}$	A	24.7469	0.185	34.9042	0.207	64.9736	0.229
$P_{8,10}$	B	-10.4140	0.221	-20.2964	0.239	-50.1920	0.247
$P_{8,11}$	A	16.5118	0.176	25.8014	0.230	55.2832	0.247
$P_{9,11}$	B	-0.5927	0.416	-10.1567	0.324	-40.0252	0.277
$P_{10,12}$	A	25.9629	0.157	35.5489	0.196	65.2376	0.226
$P_{11,12}$	B	-0.9629	0.343	-10.5489	0.304	-40.2376	0.247
$P_{13,14}$	B	-20.9629	0.471	-30.5489	0.588	-60.2376	0.678
$P_{13,15}$	A	5.9629	0.686	15.5489	0.608	45.2376	0.548
$P_{14,16}$	A	14.4490	0.332	24.8486	0.398	54.9752	0.454
$P_{15,16}$	B	-12.4768	0.525	-21.2492	0.684	-50.5000	0.738
$P_{15,17}$	A	5.5510	0.818	15.1514	0.646	45.0248	0.554
$P_{16,18}$	A	16.5139	0.222	25.7003	0.362	55.2624	0.448
$P_{17,18}$	B	-1.5139	1.167	-10.7003	0.957	-40.2624	0.828
$P_{19,20}$	B	-10.0000	0.250	-20.0000	0.250	-50.0000	0.250
$P_{20,21}$	B	-10.0000	0.250	-20.0000	0.250	-50.0000	0.250
$P_{21,22}$	B	-10.0000	0.250	-20.0000	0.250	-50.0000	0.250
$P_{23,24}$	B	-10.0000	0.750	-20.0000	0.750	-50.0000	0.750



NO	YER(Hz)	ŞİDDET
1	-30,7	0,769
2	-29,9	0,405
3	-21,1	0,898
4	-20,0	1,973
5	-10,6	1,260
6	-10,2	0,679
7	+5,3	0,354
8	+5,7	0,319
9	+15,2	0,880
10	+16,1	0,824
11	+25,3	0,635
12	+25,7	0,592
13	+34,9	0,207
14	+35,6	0,196

Figure 6. Sample spectrum for the A_2B_3 system and δ=40 Hz, J=10 Hz.

CONCLUSION

The spectra obtained for AB_2, A_2B_2 and A_2B_3 type molecules studied in this work were compared with the experimental spectra of the molecules containing ${}_1H^1$, ${}_6C^{13}$ and ${}_9F^{19}$, and the results indicated that the theoretical and experimental spectra are compatible within the error limits.

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