Electron Spin Resonance of the Aromatic-Alkali Metal System. II

— *Temperature Dependence of the Na Hyperfine Splittings in the Naphthalene-Na Ion Pair* —

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The temperature effect on the Na hyperfine splittings in electron spin resonance of the naphthalene-Na system in solution is investigated theoretically. Assuming that the motion of Na positive ion under the electro-static field of the naphthalene negative ion is harmonic along the long axis of the naphthalene molecule, the temperature dependence of the Na hyperfine splittings is interpreted through the weight factor of the Boltzmann distribution. At room temperature the Na positive ion is found with largest probability to locate nearly above the center of one of the benzene rings in naphthalene, and at this position one obtains a reasonable order of magnitude for the Na hyperfine coupling constant.

§1. Introduction

In the previous paper which will be hereafter referred as I, we investigated theoretically the Na hyperfine splittings (hfs) in electron spin resonance (ESR) of the naphthalene-Na system in solution. The estimated value of about 1 gauss shows a reasonable agreement with the observation of Weissman et al. And further, in their paper the interesting behaviors of the Na hfs are also reported: The magnitude of the Na hfs increases with increasing temperature in various solvents (Fig. 1) and to some extent shows solvent effects, that is to say, in tetrahydrofuran it tends to vanish at low temperature (200°C), but in others not. Weissman et al. explained qualitatively this temperature dependence as follows. At low temperature Na⁺ is located at the center of the 9,10 bond of naphthalene where we expect the vanishing Na hfs since the spin density of the naphthalene negative ion is...
identically zero along these bonds due to the antisymmetrical property of the molecular orbital (MO) occupied by the unpaired electron in the first order approximation. On the other hand, at rather high temperature (e.g. room temperature) Na\(^+\) seems to have a large probability to be located at the center of one of the benzene rings of naphthalene where we obtain the largest value of the Na hfs coupling constant as shown in I.

In this paper, we aim chiefly to investigate this temperature effect on the Na hfs in such a way that the temperature dependence of the Na hfs will be interpreted through the temperature dependent motion of Na\(^+\) above the naphthalene molecular plane. First, we shall briefly summarize the charge-transfer mechanism of the Na hfs in the case of ESR of the naphthalene-Na system, then it is reasonably assumed that the electro-static potential of the ion pair under which Na\(^+\) is in oscillatory motion is approximated by a quadratic form of displacement. Thus we can employ the density matrix corresponding to this harmonic motion to evaluate the mean square amplitude of the Na\(^+\) motion and the magnitude of the Na hfs for various temperatures.

§2. The charge-transfer mechanism

In the aromatic (naphthalene)-Na system, Na is positively charged and the odd electron occupies the lowest vacant \(\pi\)-MO of the corresponding aromatic molecule in the first approximation. The wave function of this system will be written symbolically as

\[
\psi_0 = \psi(Ar^-, Na^+).
\]

In the next approximation, the non-bonding state which arises from the migration of the odd electron from the aromatic negative ion into Na\(^+\) as described by

\[
\psi_1 = \psi(Ar, Na)
\]

will mix with (1), and the wave function of this system in the ground state is approximated by

\[
\psi = \psi_0 + \lambda \psi_1.
\]

The mixing parameter \(\lambda\) is determined by the perturbation method as

\[
\lambda = -\frac{H_{10}}{\Delta E_{10}}
\]

with

\[
\Delta E_{10} = H_{11} - H_{00},
\]

\[
H_{00} = \langle \psi_0 | H | \psi_0 \rangle,
\]

where \(H\) is the electronic Hamiltonian of this system. In our treatment, (5) is approximated as
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\[ \Delta E_{10} = E(Ar) - I(Na) + V, \]  

(7)

where \( E(Ar) \) and \( I(Na) \) are the electron affinity of the aromatic molecule and the ionization potential of the Na atom, respectively. \( V \) is the electro-static stabilization energy of this ion pair, and it will be analyzed in detail later.

Here we shall introduce two coordinate systems, I and II. The first coordinate which will be designated with a prime has the origin at the \( \mu \)th carbon atom in the aromatic, and the second one without prime has the origin at the center of 9 and 10 bond of naphthalene (see Fig. 3). In both coordinate systems, indices under coordinates indicate the atoms under consideration except for Na of which coordinates will be written without suffix.

The stabilization energy of the ion pair in (7) is written as

\[ V = -e^2 \sum_{\mu} \rho_\mu / r', \]  

(8)

where \( r' \) is the interatomic distance between the \( \mu \)th carbon atom and Na\(^+\) and \( \rho_\mu \) is the unpaired electron density given by the square of the LCAO coefficient shown in Fig. 2,

\[ \rho_\mu = c_\mu^2. \]  

(9)

Expanding \( V \) in terms of the coordinate system II, we obtain for \( r > r_\mu \), which is valid in our case,

\[ 1/r' = (1/r) \sum_n P_n(\sigma_\mu) \Upsilon_\mu^n, \]  

(10)

where \( P_n(\sigma_\mu) \) is the Legendre polynomial of degree \( n \) with

\[ \sigma_\mu = \sin \theta \cos (\varphi - \varphi_\mu) \quad \text{and} \quad \Upsilon_\mu^n = r_\mu^n/r. \]  

(11)

In the above expansion, only the even terms with respect to \( n \) contribute to the result due to the symmetrical charge distribution on the carbon atoms. Neglecting higher terms than \( P_2(\sigma_\mu) \) in (10), we can find by straightforward calculation
that $V$ has the deepest valley along the long axis of naphthalene ($x$ axis), i.e. $\phi=0$ or $\pi$. Then we obtain

$$V = -\left(\frac{e^2}{2r}\right) \{1 - (1/2)\sum \rho_n \gamma_n^2 + (3/2) \sin^2 \theta \sum \rho_n \gamma_n^2 \cos^2 \phi_n\}. \tag{12}$$

If we assume that the separation distance is kept constant, as $z_0=7.0$ a.u. (3.7Å), the potential curve given by (12) is found to be shown by a solid line in Fig. 4. It has very shallow double minima near the origin, and may be approximated in the region of the molecular plane by a quadratic form as is shown by dotted lines in Fig. 4, namely

$$V = V_0 + (\alpha/2) x^2, \tag{13}$$

where $\alpha$ is an adjustable parameter chosen to reproduce (12) as far as possible, rather than estimated by mathematical expansion of (12).

Next, we shall estimate $H_{10}$ in (4) by a similar treatment as has been done for $V$, assuming that

$$H_{10} = \kappa \langle \psi_1 | \psi_0 \rangle, \tag{14}$$

where the proportionality factor $\kappa$ is determined as $\kappa = \beta \pi / S_\pi$ in terms of the resonance integral $\beta \pi$ and the overlap integral $S_\pi$ in benzene. $\langle \psi_1 | \psi_0 \rangle$ is written in terms of the atomic overlap integral between Na and the $\mu$th carbon as

$$\langle \psi_1 | \psi_0 \rangle = \sum_\mu c_{\mu} S_\mu \cos \theta' \sum_\mu c_{\mu} S_\mu e^{-\varepsilon \mu/\varepsilon'} (z/r') \equiv S_0 z (1 + \varepsilon r') \sum_\mu c_\mu (1/r'), \tag{15}$$

where $\Delta r' = r' - r$ and $S_0$ is the overlap integral between the hypothetical $2p\pi$ carbon atomic orbital at the origin of the coordinate system and the $3s$ atomic orbital of Na which is assumed to be situated exactly above the former. Here we assume the $r$ dependence of the overlap integral is exponential with a parameter $\varepsilon$. In expanding $1/r'$ in (15) by means of Legendre polynomials, it should be noted that, due to the antisymmetrical property of $c_\mu$'s, only the odd terms with respect to $n$ in (10) remain with nonvanishing contribution. The value of the antisymmetrical quantities sometimes depends critically upon the accuracy of the employed approximation. In case of (15), as the highest terms of the polynomial expansion of $1/r'$, we take $P_1(\sigma_n)$ for the $\alpha$ position and $P_3(\sigma_n)$ for the $\beta$ position.
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in naphthalene, since our expansion is less satisfactory for the latter than for the former. Then we have

$$\sum_n c_n (1/r') = (1/r) \left[ \sum_n^a c_n \tau_n P_1 (\sigma_n) + \sum_n^b c_n \{ \tau_n P_1 (\sigma_n) + \tau_n^b P_3 (\sigma_n) \} + \cdots \right]$$

$$= 2\sqrt{3} \left( \tau_0 / r \right) \sin \theta \cos \phi \left[ c_1 + 2c_2 - (39/4) \tau_0 ^3 c_2 \right], \quad (16)$$

where $\tau_0 = r_0 / r$, $r_0$ is the radius of the benzene ring and the superscript $\alpha$ or $\beta$ over summation designates to sum up only over the $\alpha$ or $\beta$ position in naphthalene, respectively. In deriving the last equality, we keep only linear terms of $\sigma_n$ in $P_n (\sigma_n)$. It is convenient for the following expression to express the $x$ dependence of $H_{10}$ explicitly:

$$H_{10} = \pm 2\sqrt{3} x (1 + x^2 + z^2) S_{00} e^{-z/(x^2 + z^2)}$$

$$\times (r_0 x z / (x^2 + z^2)^{3/2}) (c_1 + 2c_2 - (39/4) \tau_0 ^3 c_2), \quad (17)$$

where $S_{00}$ is $S_0$ of the standard separation distance $z_0$, and we take the positive sign in the right benzene ring ($\phi = 0$) and the negative sign in the left ($\phi = \pi$). Thus we have arrived at the position to calculate $\lambda$ by use of (4).

Once we obtain $\lambda$, we can estimate by the straightforward procedure of the $\text{Na}^+$ hfs as

$$a_N = x^2 (8\pi / 3) g \mu_B \lfloor \mu_N / I \rfloor |3s(0)|^2. \quad (18)$$

Here the standard notations are used; $g$ is the $g$ factor of electron, $\mu_B$ the Bohr magneton, $\mu_N$ the nuclear magnetic moment of Na and $I$ the total spin angular momentum of the Na nucleus, and $3s(0)$ is the value of the $3s$ SCF AO at the nucleus, which is approximated as

$$3s = 0.0223 (1s)_{10.7} - 0.0890 (2s)_{3.425} + 1.0037 (3s)_{0.733}, \quad (19)$$

where lower indices stand for orbital exponents given by the Slater rule.

§3. Temperature dependence

As discussed in the previous section, it may be plausible to assume the motion of $\text{Na}^+$ as a one-dimensional harmonic motion along the $x$ axis. Then the wave function of this motion is expressed by

$$F_n(x) = \{ a / (\pi^{1/2} 2^n n! ) \}^{1/2} \exp(-a^2 x^2 / 2) H_n(ax), \quad (20)$$

where

$$a^2 = (m \alpha)^{1/2} \hbar, \quad (21)$$

$m$ is the mass of Na, and $H_n$ is the Hermite polynomial:

$$H_n(x) = (-1)^n e^{\alpha^2} d^n e^{-\alpha^2} / dx^n, \quad (22)$$
with eigenvalue
\[ \varepsilon_n = \left( n + \frac{1}{2} \right) \hbar \omega, \quad \omega = \sqrt{\alpha/m}. \]  \hspace{1cm} (23)

Here we assume the Boltzmann distribution for each probability amplitude given by \( |F_n(x)|^2 \), and introduce the well known density matrix \( \rho(x, x') \) as
\[ \rho(x, x') = \sum_n F_n(x) F_n(x') e^{-\beta \varepsilon_n}. \]
\[ = (a/\sqrt{\pi}) \sum_n \exp \left\{ -\beta \left( n + \frac{1}{2} \right) \hbar \omega \right\} \cdot 1/(2^n n!) \times H_n(ax) H_n(ax') \exp \left\{ -a^2(x^2 + x'^2)/2 \right\}, \]  \hspace{1cm} (24)

where \( \beta = 1/kT \), \( k \) is the Boltzmann constant and \( T \) the absolute temperature. In our case, it is sufficient to take the diagonal term for \( \rho(x, x') \), putting \( x = x' \), to obtain the temperature dependence of the Na hfs. Thus the statistical average of the value of the Na hfs is given as
\[ \langle a_N \rangle = \int_{-\infty}^{\infty} a_N \rho(x) \, dx \int_{-\infty}^{\infty} \rho(x) \, dx. \]  \hspace{1cm} (25)

The above procedure is justified by the fact that the frequency of the oscillatory motion of Na\(^+\) is very much larger than that of the Na hfs. As \( H_{10} \) in (17) now depends only on \( x \), \( \lambda^2 \) is a function of \( x^2 \). Therefore, it may be a fairly good approximation to assume
\[ \langle \lambda^2 \rangle \equiv \lambda^2 \langle \langle x^2 \rangle \rangle. \]  \hspace{1cm} (26)

Here \( \langle x^2 \rangle \) is the mean square amplitude of Na\(^+\), given as
\[ \langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 \rho(x) \, dx \int_{-\infty}^{\infty} \rho(x) \, dx \]
\[ = (1/2a^2) \coth(\beta \hbar \omega/2). \]  \hspace{1cm} (27)

\section*{4. Results and discussions}

Numerical calculations are performed as follows. First we choose suitable values of \( a \) in (13) to reproduce the potential curve (12) in the region of the naphthalene molecular plane. Then we estimate \( \langle x^2 \rangle \) whose square roots as shown in Table I give the location of Na\(^+\) for various temperatures in the cases of two different \( a \)'s. Thus we obtain under the approximation (26) the values of \( \langle a_N \rangle \) shown in Table I. In this calculation we employed the following values for empirical parameters: The values of \( I(\text{Na}) \) and \( \beta \) are 5.138 eV and \(-1.9\) eV, respectively, as the same as predicted in paper I. However we choose the value of 3 eV for \( E(\text{Ar}) \) to obtain the better agreement with observation. The agreement between the estimated values in Table I and observed ones is satisfactory.
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especially for I and II in Fig. 1. A little different behavior of the curve III from I and II will be explained by introducing a potential function having a steeper slope near the origin. We attribute this phenomenon to a sort of solvent effect.

Table I. Temperature effect on the location of Na⁺ and on the Na hfs coupling constant.

<table>
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<th>T (°K)</th>
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<td>150</td>
<td>200</td>
<td>250</td>
<td>300</td>
<td></td>
</tr>
</tbody>
</table>

\[ \sqrt{\langle x^2 \rangle} \quad (\text{Å}) \]
- 0.618
- 0.704
- 0.861
- 0.995
- 1.11
- 1.23

\[ \langle ax \rangle \quad (\text{gauss}) \]
- 0.40
- 0.49
- 0.67
- 0.79
- 0.90
- 0.98

\[ \langle ax \rangle \quad (\text{gauss}) \]
- 0.22
- 0.27
- 0.39
- 0.50
- 0.59
- 0.67

We obtain an interesting result that at room temperature Na⁺ is found with largest probability nearly above the center of one of the two benzene rings.

Therefore it is adequate to adopt as in paper I the charge-transfer complex model that Na⁺ locates above the center of the benzene ring. Throughout the calculation, we assumed \( z_0 = 7.0 \) a.u. (3.7Å) as the standard separation distance. For this distance the double minima of the potential curve are so close to the origin that the approximation of the harmonic potential is fairly accurate. On the other hand we can see from a numerical estimation that the double minima are nearer to the center of the benzene rings, when the separation distance is shorter. Such behavior of the potential curve results in a finite value of the Na hfs coupling constant at extremely low temperature. That is to say, if in cases of I and II in Fig. 1, the above mentioned effect be likely and also if we consider that the values of Na hfs coupling constants in both cases are larger than that in III, such phenomenon may be interpreted as another kind of solvent effect, saying that the separation distances in the former two cases are a little shorter than that in the latter.

References

1) S. Aono and K. Oohashi, Prog. Theor. Phys. 30 (1963), 162.