Hyperfine Structure in Na_2^+ via Electron Spin Resonance at 4 K†

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The Na_2^+ ion was produced in neon plasma and isolated in solid neon at 4 K. Its X-band electron-spin-resonance (ESR) spectrum was analyzed to yield the isotropic hyperfine interaction of 441 MHz with the ^{23}Na ($I = {}^3/_2$) nucleus. An approximate interpretation of this value points to considerable pσ character in the predominantly sσ wave function of the single valence electron in the ground $^2\Sigma_g^+$ state.

Introduction

The one-valence-electron molecule Na_2^+ has been the continuing subject of much theoretical[1−15] and experimental[16−21] study. It has been modeled[1,15] quite successfully as one electron in the field of two polarizable Na^+ cores. Efforts have been made to establish potential energy curves over a large range of internuclear distances through ab initio and pseudopotential calculations because of the increasing accuracy of the experimental data. Presently, its vibrational and internuclear distance parameters in the ground $^2\Sigma_g^+$ state are known,[17] but hyperfine splittings (hfs) due to interaction with the Na ($I = {}^3/_2$) nuclei have not been observed or calculated.

Here Na_2^+ has been produced by laser vaporization of sodium metal into neon plasma, similar to that described by Jacox[22] and by Knight.[23] Its electron-spin-resonance (ESR) spectrum was subsequently measured by trapping it in solid neon at 4 K.

Experimental Section

A Bruker (ESP 300E) ESR spectrometer was used with the matrix prepared at 4 K on a copper rod, which was then lowered into the X-band cavity ($\nu \cong 9$ GHz). The usual ESR apparatus and accompanying cryogenics have been previously described.[24] Here sodium metal (Aldrich 99.9% pure) was vaporized using the 1064 nm fundamental of a pulsed Q-switched Nd:YAG laser. The sodium vapor was mixed with the neon plasma, generated by a 2450 MHz microwave discharge, just prior to condensation on the cold rod. Deposition took about 30 min with the rod at 4 K.

Results and Analysis

The ESR spectrum of Na_2^+ is shown in Figure 1. Also seen are signals resulting from sodium atoms, H atoms, and some unidentifiable signals at $g = 2$. The lines observed span from about 2500 to 3800 G. Assuming two equivalent nuclei with $I = {}^3/_2$, this allows J to take on values of 0, 1, 2, and 3. This will result in m_J ranging from $+J$ to $-J$ in each case. The large hyperfine interaction in Na_2^+ causes splitting of lines that would normally overlap. Thus, $J = 0$ gives one line at the g of the molecule. $J = 1$ will give three lines which fall at g plus a second-order term that varies with m_J;[25] correspondingly, $J = 3$ will result in 7 lines. There are a total of 32 predicted lines including both perpendicular and parallel contributions. However, only 23 assignments can be made due to interference at $g = 2$ and overlap of Na atom lines at high field. Figure 2 shows an expanded view of two regions of the Na_2^+ spectrum.

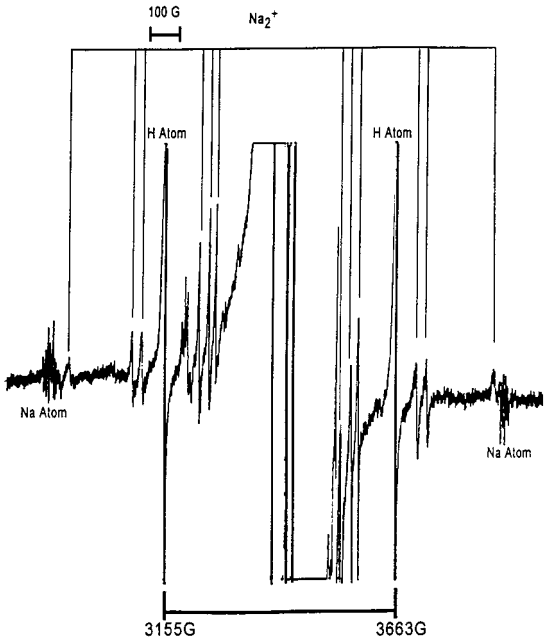

Figure 1. ESR spectrum of Na_2^+ in solid neon at 4 K.

The perpendicular lines as indicated in Table 1 were fit by obtaining the eigenvalues generated by the appropriate spin Hamiltonian for this system, which is given in eq 1.[25] To

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{\parallel} J_z S_z + A_{\perp}\beta(J_x S_x + J_y S_y) \quad (1)$$

evaluate $H_{\perp}$ or $H_{\parallel}$, a matrix of the order $(2S + 1)(2J + 1) = 2(2J + 1)$ was solved, where $J = |I_1 + I_2|, ..., |I_1 - I_2|$, and $M_j = J, J - 1, ..., -J$, since $S = {}^1/_2$, $M_s \pm {}^1/_2$. The spin matrix was set up individually for each I value. A suitable fit was generated by carefully varying the magnetic parameters $A_{\perp}$ and $A_{\parallel}$ and then comparing the calculated to the observed perpendicular line positions. The parallel parameters influenced this fit but to a lesser degree, so that they could not be reliably determined in this way. The weak parallel lines were difficult to identify and assign; however, one obtains $g_{\parallel} = 2.0006(20)$ and $A_{\parallel} =$

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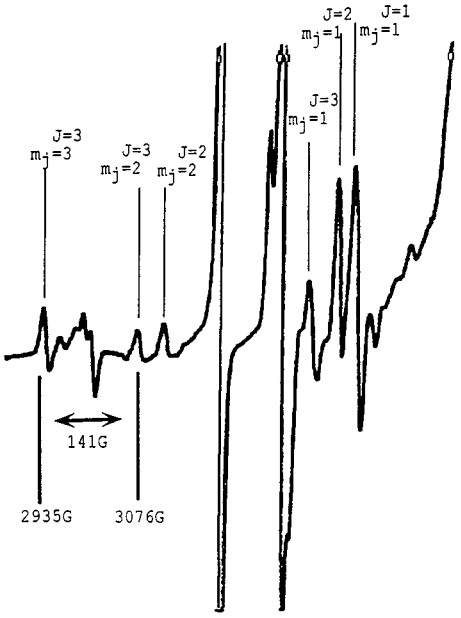

Figure 2. Expanded view of the ESR spectrum of Na_2^+ in solid neon, showing the low-field perpendicular lines.

TABLE 1: Observed Perpendicular Line Positions of the ESR Spectrum of Na_2^+ in Solid Neon Compared to the Calculated Values (ν = 9.5855 GHz)

J, M_j	$H_\perp$ obs (±1 G)	$H_\perp$ calc (G)[a]	J, M_j	$H_\perp$ obs (±1 G)	$H_\perp$ calc (G)[a]
3, 3	2935.0	2935.1	1, 0	3414.3	3414.5
3, 2	3075.5	3075.7	0, 0		3421.2
2, 2	3099.9	3101.6	3, −1	3539.4	3538.8
3, 1	3222.5	3222.0	2, −1	3561.6	3561.4
2, 1	3245.0	3245.3	1, −1	3576.5	3576.8
1, 1	3259.8	3260.5	3, −2	3709.3	3709.2
3, 0	3378.0	3378.1	2, −2	3731.9	3732.6
2, 0		3400.2	3, −3		3884.0

[a] Calculated using the parameters given in Table 2.

TABLE 2: Derived Magnetic Parameters for Na_2^+ in Solid Neon at 4 K

derived parameter	
$g_\parallel$	2.0006(20)
$g_\perp$	2.0017(9)
$A_\parallel$	155(20) G
	434(60) MHz
$A_\perp$	158.4(9) G
	444(3) MHz
A_{iso}	441(20) MHz

155(20) G, with estimated uncertainties. (Because of the large hfs, second-order perturbation[26] is not expected to yield accurate parameters. If applied, it gives $A_\perp$ = 158.4G, $A_\parallel$ = 164.8 G.)

Discussion

Values for the isotropic $A_{iso} = (A_\parallel + 2A_\perp)/3$ and dipolar $A_{dip} = (A_\parallel - A_\perp)/3$ hyperfine parameters are included in Table 2. A_{iso} = 441 MHz, representing the sσ contribution to the valence electron wave function. When multiplied by 2 to account for the two equivalent nuclei, it is of the same magnitude as the corresponding neutral atomic value tabulated by Morton and Preston,[27] 927.1 MHz. In the usual approximate procedure,[25] one then finds 882/927 = 95% sσ character. (These are a set of self-consistent parameters. The experimental value[28] for the Na atom is 885.8 MHz, which makes this calculated sσ character even higher.) However, here our model involves interaction with the nuclei in two Na^+ cores, where the hfs will be larger because of the positive charge. According to Goudsmit's formula,[29] this interaction would increase by approximately a factor of 4 from the neutral to the cationic alkali metal atom. Since the electron is shared by two nuclei here, comparison could be made with a value of 2 × 927.1 MHz, yielding, probably a minimum, sσ character of 48%. A_{dip} is even more difficult to interpret. One can only suggest that the evidence indicates that there is appreciable pσ character in the unpaired-electron wave function. Because of the large uncertainty in $A_\parallel$, A_{dip} can vary from −24 to +18 MHz, and therefore does not provide the usual information about the pσ contribution.

These considerations concerning the character of the one valence electron are similar to those considered in some detail in our earlier work on the Cu_2^+, Ag_2^+, Au_2^+ ESR spectra.[30] There, $2A_{iso}$ for Cu_2^+ and Ag_2^+ were 112 and 114%, respectively, of that of the neutral atom. It was estimated that the σ electron contained 100 and 70(20)% s character.

An interesting comparison can also be made with the Na_3 molecule. The sodium trimer was observed via ESR by Lindsay et al.[31] and was found to have two equivalent sodium atoms in an isosceles triangle geometry. The unpaired spin density was concentrated on the equivalent atoms and was found to have predominately s character, A_{iso} = 420 MHz.

Our measured $g_\perp$ value (Table 2) could not be determined accurately enough to provide a reliable calculation of the mixing of excited Π electronic states into the ground state. The observed $\Delta g_\perp = g_\perp - g_e$ is negative, which indicates the coupling occurs to a $^2\Pi_r$ excited state, presumably the lowest observed $^2\Pi_u$ state[17] at about 23 000 cm^{-1}. Substituting a spin−orbit coupling constant for the observed state, ξ = 10.9 cm^{-1} (or the sodium atom value = 11.46 cm^{-1}) into

$$\Delta g_\perp = (2\xi|\Delta E)\langle\Pi|L_x|\Sigma\rangle\langle\Sigma|L_x|\Pi\rangle$$

yields ΔE = 11 000 cm^{-1}.

Although there are theoretical treatments of Li_2^+,[4,9−11,13] there are again no hyperfine structure data on it or the heavier alkali metal molecules.

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