Characterization of the outer well of NaH C1Σ+ state by fluorescence depletion spectroscopy

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1. Introduction

Sodium hydride is one of the simplest heteronuclear molecules. Since the early 1930s, several experimental [1–9] and theoretical computational [10–12] studies of the spectra and interactions of sodium hydride have been published. However, spectroscopic observations of sodium hydride have only been made of the ground state X1Σ+ and the first excited state A1Σ+. Orth et al. [2] observed the vibrational levels ν′ = 0–8 of the ground state X1Σ+ and ν′ = 0–20 of the first excited state A1Σ+ state by laser-induced fluorescence and presented RKR potential curves, in which the R0, R values were 1.8872 Å and 3.1934 Å, respectively. Their results were consistent, to within experimental error, with the data obtained by Pesl et al. [13] using laser excitation. Most studies of the states with higher electronic configurations have involved theoretical computations. Olson and Liu [14] sketched the potentials of seven low-lying states (X, A, B, C, C1Σ+, C2Σ+) of NaH based on extensive ab initio calculations of configuration interaction (CI), in which the R0, RDF values of the X, A, C1Σ+ states were 3.558 a0, 1.922 eV; 5.992 a0, 1.239 eV; and 11.87 a0, 0.787 eV, respectively. In calculating the excitation potentials of NaH using an effective core potential method, Lee et al. [15] extended the calculations of the dissociation of the Σ+ and Σ− states of NaH into the 3s–5s states of Na. Both calculations revealed that the excited potential curves differed from the regular Morse potentials due to the mutual effects of avoided crossing among the electronic configurations with the same symmetry, and formed the potential structures with double well. With respect to the C1Σ+ state (dissociated to Na (4s) + H (1s)), the effects of valence and Rydberg atomic configurations formed a small inner potential well at its internuclear distance at around 2.5 Å, whereas the ionic and neutral configurations formed an outer potential well in its internuclear separation at around 6.5 Å. Chen et al. [16] reached the same conclusions by observing the irregular rovibrational progressions of the LiH molecule. In this study, fluorescence depletion in optical–optical double resonance (ODDR) spectroscopy [17] was applied to observe the vibrational levels ν = 5–33 of the C1Σ+ state of NaH. This electronic state has not been experimentally observed. The absolute vibrational quantum number is confirmed by comparing the observed intensities with the calculated Franck–Condon factors (FCFs). To elucidate the rovibrational levels in the outer well, a set of molecular constants and RKR potential curve are determined.

2. Experiments

Fig. 1 presents a block diagram of experimental setup [18]. Sodium metal was loaded into the five-arm stainless steel heat pipe, which was then filled with 1 torr of argon as a buffer gas, and heated to 410 °C. Sodium hydride was formed by the direct reaction of hydrogen with sodium vapor. The Nd-YAG laser (Continuum Powerlite 8000) that was used to pump two dye lasers had a repetition rate of 10 Hz, a pulse width of 5–7 ns, and pulse energy of 50 mJ. Two dye lasers (all Lambda Physik Scanmate II) were used to generate laser energy required with a linewidth of around 0.15 cm−1 and a pulse energy of 0.3–4.5 mJ. The third harmonic (355 nm) and second harmonic (532 nm) of the Nd-YAG laser were used to pump the dye lasers to generate violet light and red to near-infrared light, respectively. The dye used to generate the violet light was LC3990. This light was used to excite the A1Σ+(ν′,
$J' = X^1\Sigma^+ (v', J')$ transitions [2]. Atomic neon lines produced from a Fe filled hollow cathode tube (Hamamatsu L233) were used to calibrate the frequency of the violet light [19]. The dyes used to generate red to near-infrared light were DCM, LDS698, LDS759, and a Fe filled hollow cathode tube (Hamamatsu L233) were used to populate the intermediate level with $J' = J'' - 1$ (P-pump) of the $A^1\Sigma^+$ state. Then, a probe laser energy ($L_2$) is used to populate the excited level with $J' = J''$ of the $C^1\Sigma^+$ state (R-probe). On the other side, laser energy $L_1$ and $L_2$ are provided via a R-pump and a P-probe, to detect the same excited energy level of the $C^1\Sigma^+$ state with $J' = J''$. This process confirms the identity of the OODR signal. However, signals generated by stimulated-emission pumping (SEP) are occasionally produced during the scan, when the intermediate level the $A^1\Sigma^+$ state release energy and return to the levels of ground $X^1\Sigma^+$ state upon stimulation by the probe laser. Fortunately, the separation of the PR pair ($A_F$) can be used to distinguish among the signals of SEP and stepwise OODR.

4. Absolute vibrational quantum number

The outer well has 29 vibrational levels observed in this experiment. However, the large internuclear separation, $R_e$ between the equilibrium position of $A^1\Sigma^+$ and that of the outer well of the $C^1\Sigma^+$ state prevents observation of several of the lowest vibrational levels of $C^1\Sigma^+$ state given the lasing capacity of the probe dye laser. This finding agrees with the results obtained by calculating the

$$A_F = 108.90 \text{ cm}^{-1}$$
calculated FCFs [22]. However, the resolved fluorescence from is comparing the intensities of the resolved fluorescence with the The other way to assign the absolute vibrational quantum number separations is between the depletion intensities, . Then, the energy from those intermediate levels to the lower vibrational levels for the probe laser is only approximately 5000 cm$^{-1}$ (wavelength, $\lambda = 2000$ nm), which is far from the lasing range of the probe laser system used herein. Hence, investigating the bottom of the C$^1\Sigma^+$ state potential is difficult.

Two methods were adapted to determine the absolute vibrational quantum number of the observed vibrational progressions. One involves comparing the theoretical computations of the vibrational separations $\Delta G_{v+1/2}$, while the other involves the experimentally comparing the FCFs. First, the CI potential curve that was provided by Olson and Liu [14] is analyzed; the Schrodinger equation is solved numerically to acquire eigenfunctions and eigenvalues; the $\Delta G_{v+1/2}$, of each vibrational level is calculated, and compared with the corresponding experimental value. The average absolute difference $\delta_1 \left( \delta_1 = \frac{\sum|\Delta G_{v+1/2}(\text{theo})-\Delta G_{v+1/2}(\text{expt})|}{n} \right)$ between theoretical $\Delta G_{v+1/2}(\text{theo})$ and experimental $\Delta G_{v+1/2}(\text{expt})$ is determined for giving a tentatively assigned lowest vibrational quantum number observed, $v'$. The total number of 26 vibrational separations is $v' = v' + 26$. This results reveal that the vibrational quantum $v'=6$ is associated with the smallest difference of $\delta_1$. The other way to assign the absolute vibrational quantum number is comparing the intensities of the resolved fluorescence with the calculated FCFs [22]. However, the resolved fluorescence from the C–A states is within the range 640–800 nm, and is affected by the Na$_2$ A–X band as one can see in the background of Fig. 3. The correct $v$ value cannot be derived by the resolved fluorescence. Alternatively, the intensities of fluorescence depletion are compared with the FCF values associated with the A$^3\Sigma^+$ to C$^1\Sigma^+$ states to determine $v'$ [23,24]. As the lowest vibrational quantum number observed $v'$ is changed, a set of corresponding FCFs is produced, and each set of FCFs is compared with the intensities of the depletion signals. The difference $\delta_2 \left( \delta_2 = \frac{\sum|I_{\text{spectrum}}-I_{\text{calc}}|^2}{n} \right)$ between the depletion intensities, $I_{\text{spectrum}}$, and calculated FCFs, $I_{\text{calc}}$ based on the assumed $v'$ is plotted in Fig. 4, in which the FCFs and the depletion intensities are normalized by sum rules to enable them to be compared. Two intermediate levels of the A$^3\Sigma^+$ state, $v' = 7$ and 9, are used in Fig. 4 and both results reveal that the best matches with the calculated FCFs are obtained when the lowest observed vibrational quantum number $v'$ is 5. We posit that the accuracy of the experiment must exceed that of the ab initio calculations. Consequently, the conclusion of Fig. 4, based on the assumption that the lowest observed vibrational quantum number $v'$ is 5, is considered. The absolute vibrational number given by Franck-Condon argument could be sensitive to saturation effects.

### Table 1

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<tr>
<th>This Letter</th>
<th>Olson and Liu (Ref.14)</th>
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<tr>
<td>$V_{00}$</td>
<td>35163.5 ± 0.2</td>
</tr>
<tr>
<td>$V_{01}$</td>
<td>218.25 ± 0.13</td>
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<tr>
<td>$V_{02}$</td>
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<tr>
<td>$Y_{01} \times 10^3$</td>
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<td>$Y_{10} \times 10^2$</td>
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<td>$Y_{30} \times 10^6$</td>
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<td>$Y_{31} \times 10^5$</td>
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### Fig. 4

Absolute vibrational quantum number assigned through the comparison of relative intensities of ODDR lines and FCF of A–C transitions. The minimum difference occurs at $v' = 5$.

### Fig. 5

Comparison of vibrational and rotational energy of NaH C$^1\Sigma^+$ state. Square: vibrational energy $G_v$ (solid: this Letter, open: Olson and Liu) and circle: rotational energy $B_J$ (solid: this Letter, open: Olson and Liu).

### Fig. 6

The potential curve of NaH C$^1\Sigma^+$ state constructed form the Dunham coefficients (open square) and ab initio configuration interaction calculation potential (solid line).
and varied with the transition dipole moment with bond length
and could be off by one or two quanta.

5. Molecular constants

To extrapolate the unobserved lower part of the vibrational levels, the CI potential provided by Olson and Liu [14] is adopted to derive the eigenvalues of the lower vibrational levels. Fig. 5 presents the $G_v$ and $B_v$ values derived from the CI potential of Olson and Liu, along with the results obtained, which show that the lowest observed vibrational quantum number is five. This plot reveals that Olson's computation of the potential curve around equilibrium is quite accurate. Hence, 15 rovibrational levels ($v = 0–4, J = 0, 5, and 10$), derived from Olson's theory, are used to extrapolate the unobserved portion of the eigenvalues. The values ($v = 5–6, J = 1–11$) derived from Olson's theory are used to joint the observed term values by shifting a constant energy to minimize the standard deviations in the Dunham fitting. Together, the results obtained using Olson's theory plus 456 rovibrational levels ($v = 5–33, J = 1–11$) identified in the experiment are used to generate the molecular constants and RKR potential curve. A set of Dunham coefficients of NaH $C_1^*\Sigma^+$ state is obtained using Eq. (1).

$$T_{ij} = \sum_{ij} Y_{ij}\left(\nu + \frac{1}{2}\right)\left[j(j + 1) - \Lambda^2\right], \quad (\Lambda = 1 \text{ for } \Omega \text{ state}),$$ (1)

as presented in Table 1. The standard deviation of the fitting is 0.29 cm$^{-1}$, which is within the experimental error. The observed term values, $T_{ij}$ ($v = 5–33, J = 1–11$), calculated from the Dunham coefficients given in Table 1 are the experimental observations. Then, from the molecular constants, the rotationless RKR potential curve is plotted, as displayed in Fig. 6. It is compared with the CI potential of Olson's work. The experimentally obtained $C_1^*\Sigma^+$ potential curve yields $T_e = 35163.5$ cm$^{-1}$ and $R_e = 6.2565$ Å. The following relation is used to derive the $D_v$ value of the $C_1^*\Sigma^+$ state [25], $D_v(C_1^*\Sigma^+) = D_v(X^1\Sigma^+) + \Delta\varepsilon$ (Na 4s–3s – $T_e(C_1^*\Sigma^+)$). The dissociation energy of the ground state $X^1\Sigma^+$ is 15815(5) cm$^{-1}$, which is derived from the observation of the highest vibrational quantum number $v = 21$ [26], $\Delta\varepsilon$ (Na 4s–3s), the atomic energy difference of sodium 4s–3s, is 25739.86 cm$^{-1}$ [27]. Accordingly, the $D_v$ value of the $C_1^*\Sigma^+$ state is 6391(5) cm$^{-1}$. Table 2 compares the theoretical and experimental $R_e$ and $D_v$ values of the $C_1^*\Sigma^+$ state of NaH. The $T_e$ value of Olson's is approximately 300 cm$^{-1}$ lower than the observed value. The error is less than 1%.

### Table 2
Comparison of the potential parameters for NaH $C_1^*\Sigma^+$ state.

<table>
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<th>Lee et al. (theo, Ref. [15])</th>
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</thead>
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<tr>
<td>$T_e$ (cm$^{-1}$)</td>
<td>35163.5</td>
<td>34860 (4.322 eV)</td>
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</tr>
<tr>
<td>$D_v$ (cm$^{-1}$)</td>
<td>6391</td>
<td>6350 (0.787 eV)</td>
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<tr>
<td>$R_e$ (Å)</td>
<td>6.2565</td>
<td>6.28 (11.87 a$_0$)</td>
<td>6.26 (11.83 a$_0$)</td>
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<tr>
<td>$\alpha_v$ (cm$^{-1}$)</td>
<td>218.25</td>
<td>213.9</td>
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</tr>
<tr>
<td>$B_v$ (cm$^{-1}$)</td>
<td>0.4532</td>
<td>0.442</td>
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### 6. Conclusions

In this investigation, the OODR method is used to observe 456 rovibrational levels, including $v = 5–33$ and $J = 1–11$, of the $C_1^*\Sigma^+$ state of the NaH molecule, which dissociates to Na (4s) + H (1s). A set of Dunham constants and the RKR potential curve are obtained. However, the theoretical computation [14,15,28] reveals that the $C_1^*\Sigma^+$ state has a small inner well with a internuclear separation of around 2.5 Å and $T_e$ approximately 40900 cm$^{-1}$. Accordingly, the eigenvalues of the higher rovibrational levels of $C_1^*\Sigma^+$ state vary irregularly, and hence the vibration constants and rotation constant. The spectra recorded in this experiment include eight observed irregular rovibrational progressions (for $v > 33$), which are very close to the dissociation limit. Further processing and analysis are required to verify the assignment, and obtain the complete $C_1^*\Sigma^+$ potential curve. This will be presented elsewhere.

### Acknowledgement

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### References