Dissociation energy of the ground state of NaH

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(Received 11 March 2010; accepted 10 June 2010; published online 22 July 2010)

The dissociation energy of the ground state of NaH was determined by analyzing the observed near dissociation rovibrational levels. These levels were reached by stimulated emission pumping and fluorescence depletion spectroscopy. A total of 114 rovibrational levels in the ranges 9 ≤ ν" ≤ 21 and 1 ≤ J" ≤ 14 were assigned to the X 1Σ+ state of NaH. The highest vibrational level observed was only about 40 cm−1 from the dissociation limit in the ground state. One quasibound state, above the dissociation limit and confined by the centrifugal barrier, was observed. Determining the vibrational quantum number at dissociation vD from the highest four vibrational levels yielded the dissociation energy Dv=15 815 ± 5 cm−1. Based on new observations and available data, a set of Dunham coefficients and the rotationless Rydberg–Klein–Rees curve were constructed. The effective potential curve and the quasibound states were discussed. © 2010 American Institute of Physics. [doi:10.1063/1.3458914]

I. INTRODUCTION

Since the invention of laser in 1960, laser applications have promoted the efficiency and scope of spectroscopic analysis. Spectral interpretation yields information on atoms and molecules. For example, the application of external electromagnetic waves to atoms or molecules generates absorption or emission spectra, from which the states of, the structure of, and even the interactive forces between, atoms can be derived.1 In the past few decades, scientists have shown much interest in alkali hydrides because they have a relatively simple outer electronic configuration. The reaction channels and the properties of the electron cloud are easily predicted and analyzed. Generally, according to experimental results and theoretical computations, the ground states of the molecule are the building blocks of the molecules. Additionally, the dissociation energy of the molecules is useful in various research areas, including thermodynamics, molecular spectroscopy, the physics of collisions between atoms, and others.2–4 Hence, research on the ground state potential curve of NaH is important to understand the interactions between atoms. Increasing the accuracy of the dissociation energy of the ground state energy can increase the accuracy of follow-up research on highly excited states.

Several experimental studies have addressed the ground state potential curve of NaH. Traditional methods of experimental spectroscopy use absorption5,6 or emission7,8 electronic spectra, and microwaves and infrared9,10,11 spectra to analyze A-X emission signals, while more recent research employs lasers as light sources. In 1980, Giroud and Nedelec12 observed the ground state of NaH using laser-induced fluorescence, observing 15 vibrational levels. They later extended their experiments13 by using a pulsed dye laser to excite the first excited A 1Σ+ state of NaH up to ν′ = 21, allowing it to fluoresce back to the ground state. The observed vibrational levels in the ground state were ν" = 19. Accordingly, they provided the dissociation energy of ground state as Dv=15 758 ± 20 cm−1. The highest observed vibrational level was only 200 cm−1 from the dissociation limit in the ground state. However, the vibrational quantum numbers ν" = 16–19 could be missassigned. In early the 1990s, Stwalley et al.14 published an excellent review of literature on alkali hydrides including NaH, KH, RbH, CsH, and others. This review mentioned that the dissociation energy of the ground state of NaH was 15 900 ± 100 cm−1. In 2000, Pesl et al.15 investigated the excitation spectrum of NaH in the energy range of 630–670 nm, which was produced by colliding crossed molecular beams of H and Na. This range included the transition wavenumbers between the vibrational levels for the first excited and the ground states, 2–8 and 6–9, respectively. Pesl et al. combined their own data with those in earlier studies to determine accurately the molecular constants and the Rydberg–Klein–Rees (RKR) potential curve of the ground state of NaH.

In this experiment, the second and third harmonics of Nd-YAG (yttrium aluminum garnet) lasers were used to pump dye lasers to generate near-IR and near-violet laser beams, which were applied to the NaH molecules. The laser excitation fluorescence was recorded, and the vibrational and rotational quantum numbers of the excitation spectrum were confirmed via laser-induced fluorescence. The signal range included the transitions A(v′ = 7–12) − X(v" = 0). The experiment also adopted the stimulated emission pumping (SEP) optical-optical double resonance (OODR) method to extend research on the ground state potential of NaH to ν" = 21, covering 114 rovibrational levels and the ranges 9 ≤ ν" ≤ 21 and 1 ≤ J" ≤ 14, respectively. Finally, integrating the experimental results and the work done by Pesl et al. yields a set of molecular constants and a RKR potential curve. Extrapolat-
ing from the energy of vibrational levels to the dissociation limit, the dissociation energy of NaH \( X^1\Sigma^+ \) was also obtained in this work.

II. EXPERIMENTAL SETUP

The experimental setup\(^{16}\) displayed in Fig. 1, used the second harmonic (532 nm) and third harmonic (355 nm) generated from a Nd:YAG (Continuum Powerlite 8000, Santa Clara, CA), laser were applied to pump two dye lasers (both Lambda Physik Scanmate II, Ft. Lauderdale, FL). The repetition rate of the Nd:YAG laser was 10 Hz, with a 5–7 ns pulse width and 50 mJ/pulse. The first dye laser (pumped by a 355 nm Nd:YAG) produced near-violet laser light and was the pumping laser. The main function of the pumping laser was to provide the energy required to excite the ground state \( X^1\Sigma^+ \) to the first excited \( A^1\Sigma^+ \) state. The second dye laser (pumped by a 532 nm Nd:YAG) generated red and infrared light sources, and was the probing laser whose main function is to induce the transition of molecules from the excited state to the ground state. Several dyes were used in the experiment to enable the dye laser to produce required frequency range. Two dyes, LC3990 and 392E, were used in the pumping laser to generate light that could cause a transition from the ground state \( X^1\Sigma^+(v=0, J) \) to the first excited state \( A^1\Sigma^+(v=7–12, J) \). Several dyes, DCM, LDS698, LDS759, LDS821, LDS867, and LDS925, were used in the probing laser and provided energies in the range of 10 500–16 200 cm\(^{-1} \) to induce the excited state molecules to return to the ground state.

The spectrum from a Cr hollow cathode tube (PHOTRON-P812, Australia) filled with Ne was utilized to calibrate the wavelength of the pumping laser. The energy uncertainty is around 2 cm\(^{-1} \) since there were only a few Ne lines in one recorded spectrum. For the calibration of the probing laser, the excitation spectrum from the \( I_2 \) cell was used in the range of 13 880–16 185 cm\(^{-1} \) or a hollow cathode tube (Hamamatsu-L233, Japan) was used for energies of less than 13 880 cm\(^{-1} \). The accuracy of the absolute frequency calibrated from \( I_2 \) cell was approximately 0.2 cm\(^{-1} \). The pumping and probing lasers were counterpropagated in the heat pipe to reduce the Doppler broadening. \(^{17}\) The heat pipe was a five-armed stainless steel tube that was filled with sufficient sodium with 1 Torr of argon as a buffer gas, and heated to 410 °C. Two irises at the ends of the long arm of the heat pipe promoted the overlap of the laser beams and reduced the scattering of light. Both laser beams were focused at the center of the heat pipe to increase the intensity of the induced fluorescence.

The two main approaches that were used in this experiment were laser-induced fluorescence (LIF) and fluorescence depletion OODR spectroscopy. Scanning the pumping laser caused the NaH molecules to be excited to the \( A^1\Sigma^+ \) state, before decaying to the ground state \( X^1\Sigma^+ \) and emitting a photon. This fluorescence was then analyzed using the monochromator to identify the \( A-X \) transitions. The technique of fluorescence depletion in OODR depended on two laser beams.\(^{18}\) The energy of the pumping laser was set to excite the molecules to the \( A^1\Sigma^+ \) state and release a constant fluorescence to the monochromator at a selected transition; at the same time, the probing laser was scanned. When the energy of the probing laser equaled that of any of the \( A-X \) transitions, the molecules in the excited state would be stimulated by the probing laser and the spontaneous emission was quenched. Hence, the intensity of the selected transition in the monochromator was weakened because the probing laser stimulated most of the molecules in the excited state. The fluorescence was collected through a system of lenses and directed into a monochromator; it was then detected by a photomultiplier tube (Hamamatsu-R928, Japan) and processed using a boxcar integrator (Stanford Research Systems: SR245, SR250, and SR280, Sunnyvale, CA). The time sequence of two dye lasers and data acquisition were synchronized with the Nd:YAG laser and finally, through an oscilloscope, the data were retrieved, collected, and recorded on a computer.

III. RESULTS AND DISCUSSION

A. Spectral signals

When the temperature in the heat pipe is maintained around 410 °C, 90% of gaseous NaH molecules are in the lowest vibrational quantum state \( v=0 \). Therefore, the observed excitations are primarily generated from \( v''=0 \) of the ground state. To induce the pumping laser to induce the most likely transitions, laser dyes, LC3990 and 392E, were used in the pumping laser to provide light with the right energy range to cause a transition of the molecules to \( A^1\Sigma^+(v'=7–12, J'=1–12) \). These rovibrational levels are used as the intermediate states in the follow-up experiments. Four Ne lines (386.367, 387.710, 389.412, and 391.632 nm) from the hollow cathode tube are adopted to calibrate the frequency of the pumping laser.\(^{19}\) However, transitions in the same energy range from the experimental data in Ref 20 are used as an additional confirmation. Six dyes, DCM, LDS698, LDS759, LDS821, LDS867, and LDS925, are used in the probing laser. In the lasing range of these dyes, thirteen, three, four, two, three, and two lines of Ne transitions, respectively, can be used for calibration. As the laser dyes move gradually toward the red regime, the decline in the output laser power weakens the calibration lines.

Measuring the decrease in the intensity of the selected \( A-X \) transitions yields the fluorescence depletion of the OODR spectrum. Since two lasers are involved in the transitions, the OODR signals of the SEP type, with transitions
downward to the \( X^{1\Sigma^+} \) ground state and those of the step-up type, with transitions upward to the \( C^{1\Sigma^+} \) state can occasionally be observed at the same time in the spectrum.\(^{21,22}\) As displayed in Fig. 2, from the same intermediate level \( A^{1\Sigma^+}(11,11) \) the probing laser can induce the step-up transitions to the \( C^{1\Sigma^+}(16^+,10) \) and \( (16^+,12) \) levels \( (16^+ \) is a tentative assignment) and can also stimulate emissions to the \( X^{1\Sigma^+}(20,10) \) and \( (20,12) \) levels. The energy separation between the two signals, \( C(16^+,10) \) and \( C(16^+,12) \), is \( 34.01 \text{ cm}^{-1} \), while that between the two signals \( X(20,10) \) and \( X(20,12) \) is \( 104.44 \text{ cm}^{-1} \). The full width at half maximum of the lines in Fig. 2 is around \( 0.60 \text{ cm}^{-1} \) for the \( C^{1\Sigma^+} \) state and \( 0.30 \text{ cm}^{-1} \) for the \( X^{1\Sigma^+} \) state. An easy way to distinguish between these two vibrational progressions, apart from adapting the molecular constants from Ref. 23 to predict the various experimental term values in this work \( (\nu''=9–21) \), from the work of Pesl et al. \((\nu''=0–9)\), and from solving for the eigenvalues from the reported potential curve by Yang et al. \((\nu''=0–21)\).

Extrapolation from the energy spacing of the highest vibrational quantum at dissociation limit, which is not an integer, may not be an integer due to interactions with constant anharmonicity, while the higher vibrational quantum numbers are substituted into the formula, an easy way to distinguish between these two vibrational progressions to minimize the standard deviation of the Dunham coefficients.\(^{23}\) In the fitting procedure, the levels in \( \nu''=16 \) have larger errors than the other observed levels. However, the error is small when fitting is performed with only \( \nu'' = 16 \), suggesting that this vibrational level may exhibit a constant shift. The recorded spectrum for \( \nu''=16 \) includes only one Ne line for calibration, and its linewidth is large, producing an error in the energy shift. To solve the problem, a constant is deducted from the values of this vibrational progression to minimize the standard deviation of the Dunham fitting. Figure 3 plots the observed data \((\nu''=16)\), experimental data \((\nu''=9)\), and from solving for the eigenvalues from the reported potential curve by Yang et al. \((\nu''=0–21)\). The lower vibrational term values for the ground state \( 0 \leq \nu'' \leq 9 \) are taken from the data in Ref. 15 and there are seven vibrational levels of \( X^{1\Sigma^+}(\nu''=9, J' = 4–10) \), which overlap with our experimental observations. The difference of these overlaps is in the range of \( 0.06–0.9 \text{ cm}^{-1} \), which is within the experimental error.

Then, the rotational levels associated with each vibrational quantum number are substituted into the formula, \( G(v)=G_v+B_v(J+1) \), to yield the corresponding \( G_v \) and \( B_v \) values.\(^{25}\) Figures 4 and 5 plot the corresponding \( \Delta G_{v+1/2} \) and \( B_v \) values of each vibrational quantum number as solid squares.\(^{25}\) Figure 4 reveals two regions of \( \Delta G_{v+1/2} \) values: the lower vibrational quantum numbers, \( \nu''=0–14 \), with a smaller slope of \( \Delta G_{v+1/2} \) versus \( \nu'' \), reveals regular harmonic interactions with constant anharmonicity, while the higher vibrational quantum numbers, starting at \( \nu''=15 \), which are affected by the ion potential curve and begin to exhibit atomic characteristics are associated with a greater slope.

**FIG. 2.** Recorded spectrum of the OODR signals. The spectrum portrays two-step OODR fluorescence depletion spectra of NaH from the intermediate state \( A^{1\Sigma^+}(11,11) \): the SEP-type transition to \( X(20,10) \) and \( X(20,12) \) with \( \Delta F = 106.44 \text{ cm}^{-1} \), and the stepwise-type transition to \( C(16^+,10) \) and \( C(16^+,12) \) with \( \Delta F = 34.01 \text{ cm}^{-1} \).

**FIG. 3.** Plot of the term values \( T(\nu,J) \) with respect to \( J(J+1) \). Plot of various experimental term values in this work \((\nu''=9–21)\), from the work of Pesl et al. \((\nu''=0–9)\), and from solving for the eigenvalues from the reported potential curve by Yang et al. \((\nu''=0–21)\).
The molecules LiH (Ref. 26) and CsH (Refs. 27 and 28) exhibit similar behaviors. The last three points on the plot are close to the dissociation energy and are governed by the long range coefficients, $C_6$, $C_8$, and $C_{10}$. Figure 4 also plots results taken from the literature for comparison; consistency is strong except with the data for $v''=16–19$ from Refs. 13 and 23 perhaps because one vibrational level, $v''=16$, was misassigned. Figure 5 that plots $B_v$ versus $v$ reveals similar behavior as in Fig. 4.

### C. Dissociation energy of $X^1Σ^+$ state

The dissociation energy of a diatomic molecule AB is the energy required to dissociate the molecule in the lowest level ($v=0$, $J=1$) of the electronic ground state into normal atoms, A+B, plus the zero point energy. Various methods exist for determining the dissociation energy, $D_e$, in this investigation, extrapolation is applied to find the converging limit of $D_e$. First, $ΔG_{v+1/2}$ versus $v$ is plotted and a second order polynomial is obtained to find $v_D$. From this formula, $ΔG_{v+1/2}$ equals 0 when $v_D=21.97$. Hence, the highest vibrational quantum number in the ground state of NaH is probably 21, which is the same as that determined from the spectrum. Next, $G_v$ is plotted against $v$ and a second order polynomial is obtained; the value of $G_v$ with vibrational quantum number at dissociation limit $23$ is $15815±5$ cm$^{-1}$. The uncertainty, 5 cm$^{-1}$, is contributed from the experimental error (4 cm$^{-1}$ from the pumping and probing lasers) and the extrapolation of $G_v$ (about 1 cm$^{-1}$ in the range of $v_D=21.9±0.1$). The frequency uncertainties of the pump and probe lasers are due to the lack of calibration lines in some portions of the spectra. Table I compares this result with other experimental and computational results. In another investigation, this value was determined to be $15785±20$ cm$^{-1}$. This value was used to predict that dissociation occurred between $v''=20$ and $v''=21$.

**TABLE I.** Experimental and computational estimates of NaH dissociation energies. All values are reported in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Dissociation energy</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>15 815 ± 5</td>
<td>Binding energy of $v''=21$</td>
</tr>
<tr>
<td>Stwalley et al.$^a$</td>
<td>15 900 ± 100</td>
<td>Binding energy of $v''=19$</td>
</tr>
<tr>
<td>Nedelec and Giroud$^b$</td>
<td>15 785 ± 20</td>
<td>Polynomial Birge–Sponer extrapolation</td>
</tr>
<tr>
<td>Giroud and Nedelec$^c$</td>
<td>16 300 ± 500</td>
<td>Polynomial Birge–Sponer extrapolation</td>
</tr>
<tr>
<td>Aymar et al.$^d$</td>
<td>15 671.3</td>
<td>CIPSI</td>
</tr>
<tr>
<td>Yang et al.$^e$</td>
<td>15 814</td>
<td>MRCI</td>
</tr>
<tr>
<td>Taylor and Newman$^f$</td>
<td>15 814</td>
<td>CCSD(T)</td>
</tr>
<tr>
<td>Geum et al.$^g$</td>
<td>15 638</td>
<td>MRCI</td>
</tr>
<tr>
<td>Olson and Liu$^h$</td>
<td>15 502</td>
<td>CVCI</td>
</tr>
<tr>
<td>Karo et al.$^i$</td>
<td>14 334</td>
<td>MCSCF</td>
</tr>
<tr>
<td>Meyer and Rosmus$^j$</td>
<td>15 486</td>
<td>CEPA</td>
</tr>
<tr>
<td>Sachs et al.$^k$</td>
<td>15 144</td>
<td>MCSCF (frozen core)</td>
</tr>
</tbody>
</table>

$^a$Reference 14.
$^b$Reference 13.
$^c$Reference 12.
$^d$Reference 32.
$^e$Reference 24.
$^f$Reference 45.
$^g$Reference 46.
$^h$Reference 12.
$^i$Reference 32.
$^j$Reference 48.
$^k$Reference 49.
TABLE II. Dunham coefficients (Y_ij, all in cm^{-1}) for the NaH X ^1Σ^+ state.

<table>
<thead>
<tr>
<th>Y_10</th>
<th>Y_20</th>
<th>Y_30</th>
<th>Y_40</th>
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<th>Y_60 x 10^3</th>
<th>Y_70 x 10^4</th>
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<tr>
<td>1174.5267 ± 0.35</td>
<td>-21.970779 ± 0.22</td>
<td>0.874 176 ± 0.054</td>
<td>-0.106 484 ± 0.0068</td>
<td>0.710 245 ± 0.044</td>
<td>-0.236 03 ± 0.015</td>
<td>0.256 81 ± 0.019</td>
</tr>
<tr>
<td>1171.968 ± 0.012</td>
<td>-19.703 ± 0.010</td>
<td>0.175 ± 0.002</td>
<td>-0.006 58 ± 0.0015</td>
<td>0.172 ± 0.004</td>
<td>-0.015 ± 0.002</td>
<td>0.191 ± 0.003</td>
</tr>
</tbody>
</table>

Reference 15.

D. Molecular constants and RKR potential curve

Equation (1) is the Dunham double series expansion,

\[ T_{ij} = \sum_{i,j} Y_{ij} \left( v + \frac{1}{2} \right) \left( J(J+1) - \Lambda^2 \right)^{ij} \]

(\[ \Lambda = 0 \text{ for } \sum \text{ state}. \])

To provide a set of constants that can generate the ground state potential energy up to \( v''=21 \), the experimental data, 286 data points from this work (9 \( v'' \leq 21 \) and 1 \( \leq J'' \leq 14 \) combined with 160 data points obtained from Ref. 15 (0 \( \leq v'' \leq 9 \) and 0 \( \leq J'' \leq 15 \)), are plugged into the Dunham equation to acquire a set of molecular constants. The spacing of adjacent vibrational levels is inversely proportional to the square root of the reduced mass; therefore, NaH has larger energy separations than those of molecule Na2. In Fig. 4, \( \Delta G_{v+1/2} \) varies from the minimal value 122 cm^{-1} to the maximal value 1133 cm^{-1} by a factor of approximately ten. Hence, the Dunham fitting requires more terms to describe correctly all rovibrational values. In this work, a total of 21 terms are used in the Dunham fitting to account for the corrections such as the higher-order centrifugal distortions. The average error between the fitting results and the observed values is 0.49 cm^{-1}, and the standard deviation of the fitting is 0.67 cm^{-1}. Table II lists the molecular constants and those of Pesl et al. for comparison. Some coefficients, such as \( Y_{02}, Y_{03}, \) and \( Y_{13} \), have uncertainties larger than their values. Such coefficients are significant in evaluating the Dunham formula, but are not physically significant. The Dunham coefficients were used to construct a rotationless RKR potential energy curve for vibration quantum numbers \( v''=0-21 \) (method 1). However, because the traditional way of solving the potential curve cannot effectively yield the internuclear separations close to the dissociation limit, the RKR potential curve generated from Dunham coefficients cannot reproduce the eigenvalues accurately. Therefore, the method proposed by Stwalley is adopted to construct the RKR potential curve by spline interpolations for vibrational and rotational values as a function of vibrational quantum number (method 2); the eigenvalues versus turning points are shown in Table III. In Fig. 6, the solid squares plot the results obtained from method 2, while solid line plot the CIPSI (configuration interaction by perturbation of a multiconfiguration wave function selected iteratively) potential curve from Ref. 32.

Figure 7 plots the long range portion of the NaH X ^1Σ^+ state. The highest outer turning point obtained from Dunham coefficients (method 1) is too large. The RKR potential constructed from fitting of individual \( R_r \) and \( G_r \) (method 2) is better for reproducing the observed eigenvalues. The Murrell–Sorbie potential curve from Refs. 23 and 24 agrees well with the RKR potential obtained from method 2. The long range portion obtained from \( C_n \) coefficients \(^{33} \) is valid with internuclear separation larger than \( \sim 14a_0 (\sim 7.4 \text{ Å}) \).\(^{34,35} \) This radius, called the Le Roy radius, \(^{36} \) is the criterion for the onset of breakdown of the \( -C_n/R^2 \) expansion and is defined as \( R_{LR}=2\left(\langle r_A^2 \rangle^{1/2}+\langle r_B^2 \rangle^{1/2}\right) \), where \( \langle r_A^2 \rangle^{1/2} \) and \( \langle r_B^2 \rangle^{1/2} \) are the expected radii of atoms A and B, respectively. The most outer turning point of the RKR potential is \( R_{max}(v''=21)=6.15 \text{ Å}, \) which is within the \( R_{LR}. \) In Ref. 23, the near dissociation theory \(^{37-41} \) (NDT) was applied to \( \Delta G_{v+1/2} \) versus \( v \) and \( \Delta G_{v+1/2} \) versus \( G(v+1/2)=\langle G(v+1) \rangle /2 \) (for \( n=6 \) as the leading term of \( C_n \) coefficients). The last four points \( (v=18 \text{ to } 21) \) are not linearly dependent as we expected from the NDT since they are within Le Roy’s long range criterion. Therefore, no near dissociation expansion type analysis pioneered by Le Roy \(^{42} \) was performed for this data set. The outer turning points from Taylor and Newman \(^{43} \) seems high. However, for internuclear separation larger than the \( R_{LR} \) the potential from different \( C_n \) coefficients and long range analysis are merged together.

The experimental data show that the energy of a rovibrational level exceeds the rotationless dissociation limit; this level is quasibound and confined by the effective potential energy from the centrifugal barrier. The effective potential energy \( U_{eff} \) can be determined by adding the rotational energy to rotationless potential as described in Eq. (2).

\[ U_{eff}(R,J) = U_0(R) + \frac{\hbar}{8\pi^2\varepsilon \mu R^2} J(J+1), \]

in which \( U_0 \) stands for the RKR potential curve without rotational energy. Figure 8(a) displays the long range potential barrier for different rotational energies. \( U_0 \) is the potential curve taken from Yang’s work \(^{24} \) and the energy at the dissociation limit is set to be zero. Figure 8(b) plots the observed rovibrational levels (by subtracting the dissociation energy) and the maximum of the \( U_{eff} \) as a function of \( J(J+1) \). The dotted line represents the dissociation limit. The figure reveals that \( v''=21 \) is the highest vibrational quantum number and one quasibound state \( (v''=20, \ J''=12) \) is observed.
IV. CONCLUSIONS

The OODR fluorescence depletion approach is utilized to observe vibrational quantum numbers of up to \( v/H_11033 = 21\) in the ground state of NaH. Extrapolation from the energy of vibrational separations and the recorded spectra demonstrate that \( v/H_11033 = 21\) is the highest bound vibrational level. In this experiment, a total of 114 rovibrational levels were identified, corresponding to vibrational and rotational quantum numbers in the ranges \( 9 \leq v/H_11033 \leq 21\) and \( 1 \leq J/H_11349 \leq 14\). A set of Dunham coefficients was also derived to represent the vibrational levels of the \( X_1\Sigma^+\) state from the potential minimum to close to the dissociation limit. The rotationless RKR potential curve was constructed using various methods. Finding the vibrational quantum number at dissociation \( v/D\) yields an estimate of the dissociation energy of the ground state to be \( 15\,815\pm 5\) cm\(^{-1}\).

In this experiment, the molecule dissociation energy is determined by extrapolating the spectroscopic data and this method is indirect. In work on the \( \text{Na}_2 X_1\Sigma^+\) state, instead of fitting and extrapolating the potential curve to the dissociation limit, Jones et al. \( ^{44}\) directly measured the energy difference between two free ground state atoms and the lowest bound level of the molecule ground state by combining three separate spectroscopic measurements—OODR, LIF, and photoassociation spectroscopy—that share common levels. The method can be adapted in the future work to measure the dissociation energy of the ground state of NaH to a higher accuracy.

<table>
<thead>
<tr>
<th>( v )</th>
<th>( B_v ) (cm(^{-1}))</th>
<th>( G_v ) (cm(^{-1}))</th>
<th>( \Delta G_{v+1/2} ) (cm(^{-1}))</th>
<th>( R_{\text{min}} ) (Å)</th>
<th>( R_{\text{max}} ) (Å)</th>
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This work (Method 2)
FIG. 8. (a) Effective energy curves with even rotational quantum number (taken with the dissociation limit as the base line). (b) The barrier maximum and observed term values vs J(J+1) (squares and circles on solid lines: the observed vibrational levels in this work; triangle: the barrier maximum for each J). The dashed line represents the dissociation limit at 15 815 cm⁻¹.

ACKNOWLEDGMENTS

We gratefully acknowledge the support of this work by the National Science Council, Taiwan (NSC 88-2113-M006-003). Ted Knoy is appreciated for his editorial assistance.

23. See supplementary material at http://dx.doi.org/10.1063/1.3458914 for (1) Dunham constants of NaH X 1Σ⁺ state; (2) Dunham fit output of the NaH X 1Σ⁺ state; (3) comparison of term values for NaH X 1Σ⁺ state; (4) vibrational and rotational constants of the NaH X 1Σ⁺ state; (5) extrapolation of dissociation limit; (6) eigenvalues calculated “backward” from the RRK potential curve constructed from the Dunham coefficients; (7) long range portion of the NaH X 1Σ⁺ state; (8) Murrell–Sorbie potential energy function of Yang et al.; (9) effective potential curves of the NaH X 1Σ⁺ state.

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