Molecular constants and Rydberg−Klein−Rees (RKR) potential curve for the Na$_2$ 1 $^3\Sigma_g^-$ state

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Transitions into the doubly excited Na$_2$ 1 $^3\Sigma_g^-$ state have been analyzed using near-dissociation expansions (NDE) to represent the vibrational energies and inertial rotational constants, while the centrifugal distortion constants were held fixed at ''mechanically consistent'' values calculated from the Rydberg–Klein–Rees (RKR) potential implied by those $G(v)$ and B_v functions. The input data cover the range $v=0$ to 57 and N up to 47, and the fit yields $v_D=61.41(\pm 0.10)$ and $D_0 = 3385.70(\pm 0.2)$ cm^{-1}. © *1999 American Institute of Physics.* [S0021-9606(99)01031-4]

In a previous publication, some of us reported an experimental and theoretical study of the 1 $^3\Sigma_g^-$ state of Na$_2$.[1] More than 400 transitions from the b $^3\Pi_u$ state into the $v=0–57$, $N=2–24$ levels of the 1 $^3\Sigma_g^-$ state were observed by perturbation facilitated optical–optical double resonance (PFOODR) fluorescence excitation spectroscopy, and molecular constants were reported. Unfortunately, only a simple Dunham fit was performed and mechanically consistent centrifugal distortion constants were not incorporated into that analysis. In earlier work, using two-step polarization labeling spectroscopy, Jones *et al.*[2,3] observed 180 transitions from the b $^3\Pi_u$ state into a Na$_2$ triplet gerade state, which was tentatively assigned as the $3s+4d$ $^3\Pi_g$ state, but later recognized to be the 1 $^3\Sigma_g^-$ state.[1] The vibrational levels observed by Jones *et al.* range from $v=3–28$ and the rotational levels include the high-N values of 43, 45, and 47. In both sets of measurements, the line position uncertainty was typically 0.2 cm^{-1} except for the very highest levels ($v>53$), where the calibration lines were not close and the uncertainties are considerably larger.

The present work reanalyzed the combined PFOODR fluorescence excitation and two-step polarization labeling data sets using near-dissociation expansion (NDE) expressions for the vibrational energies and inertial rotational constants. Since the molecular constants for the ground and intermediate states are well-known,[4,5] the experimental data were converted into a set of final-state level energies, expressed relative to the ground electronic state potential minimum. The fitting procedure was then applied to this set of final-state term values.[6]

For vibrational levels lying close to dissociation, the characteristic behavior of the energies, rotational constants, and other properties of a diatomic molecule are defined by the nature of the asymptotically dominant attractive inverse-power term in the long-range internuclear potential

$$E(R) \approx D - \frac{C_n}{R^n}, \tag{1}$$

where D is the dissociation energy and C_n the leading long-range potential coefficient.[7–11] Use of NDE expressions for vibrational energies and rotational constants, which incorporate the theoretically predicted limiting near-dissociation behavior implied by Eq. (1),[7–9,11] yields both compact representations of the data to which it was fitted, and reliable extrapolations for those and other properties.[12–15] They also yield particularly compact and reliable expressions for representing very large data sets spanning a large fraction of a potential energy well.[16–18] This approach is therefore used here to describe the 1 $^3\Sigma_g^-$ state of Na$_2$.

The NDE expression for the vibrational energies used in the present work has the form

$$G_v = D - X_0(n)(v_D - v)^{2n/(n-2)}[L/M], \tag{2}$$

where v_D is the effective vibrational index at dissociation (which usually is noninteger), $X_k(n) = \bar{X}_k(n)/[\mu^n (C_n)^2]^{1/(n-2)}$, μ is the diatom reduced mass (in amu), and $\bar{X}_k(n)$ is a known numerical factor depending only on the physical constants and the value of the integer n,[7,8,19] and $[L/M]$ is a rational polynomial with orders L and M

$$[L/M] = \frac{1 + \Sigma_{i=1}^{L} p_i^0 (\nu_D - \nu)^i}{1 + \Sigma_{i=1}^{M} q_i (\nu_D - \nu)^i}. \quad (3)$$

The NDE expression used for the inertial rotational constants is

$$B_\nu = X_1(n)(\nu_D - \nu)^{2n/(n-2)} \exp\left[\sum_{i=1}^{L} p_i^1 (\nu_D - \nu)^i\right], \quad (4)$$

where $X_1(n)$ is defined above [with[19] $\bar{X}_0(6) = 7932.0$ and $\bar{X}_1(6) = 546.64$]. Computer programs GvNDE and ExpNDE for performing (nonlinear) least-squares fits to Eqs. (2) and (4), respectively, may be obtained from one of us (RJL) on request.[20] While a number of other types of expansions have sometimes been used for the vibrational energies, including an exponential expansion analogous to Eq. (4),[15,16] in our experience mixed numerator/denominator rational polynomials of the type shown in Eq. (3) usually yield the best fits for a given number of parameters. For a given total number of vibrational expansion parameters, GvNDE automatically performs fits to a variety of different expansions, which facilitates the choice of the most compact and accurate NDE form for a given case. While other choices would do nearly as well, a [3,2] ''outer expansion'' based on Eqs. (2) and (3) was chosen here.

According to theory, the 0_g^+ and the 1_g components of the 1 $^3\Sigma_g^-$ state dissociate to the $P_{1/2} + P_{1/2}$ and $P_{1/2} + P_{3/2}$ atomic limits, respectively,[21,22] and $n = 6$ is the power of the dominant term in the long-range interaction potential for $R > 20$ bohr.[21] The theoretical value of the coefficient C_6 is 2.0578×10^7 cm^{-1} Å^6,[21–24] in our NDE fits, C_6 is fixed at this value. The dissociation limit of this state, defined as the sum of the dissociation energy for the ground X $^1\Sigma_g^+$ state of Na$_2$ determined by Jones *et al.*,[25] $D_e = 6022.0186$ (± 0.0053) cm^{-1}, plus the known[26] $^2P_{1/2}$ and $^2P_{3/2}$ atomic excitation energies, is a more accurate value than can be determined from the present data. The present analysis therefore fixed this limit at that value, D(limit) $= 39\,951.591$ cm^{-1}, expressed relative to the ground-state potential minimum.

The present analysis procedure consists of the following steps:

(1) Determine initial estimates of G_ν and B_ν for the observed levels from band-by-band fits to the raw experimental data;
(2) Use the GvNDE and ExpNDE codes[20] to fit the sets of individual G_ν and B_ν values to Eqs. (2) and (4), respectively, to obtain preliminary estimates of ν_D and of the form and parameters $\{p_i^j\}$ and $\{q_i\}$ of the empirical expansions in Eqs. (2)–(4);
(3) Calculate an RKR potential energy curve from those NDE expansions using the program RKR1;[20,27]
(4) Use the program LEVEL[20,28] to calculate the centrifugal distortion constants (up to O_ν) for the observed vibrational levels, from the RKR potential obtained in step (3);
(5) Subtracting the contributions of the centrifugal distortion constants determined in step (4), use the program DSPARFIT[20,29] to refit the raw experimental data to deter-

TABLE I. Parameters defining the NDE functions determined for the vibrational energies and B_ν constants of the 1 $^3\Sigma_g^-$ state of Na$_2$, obtained with $C_6 = 2.057\,74 \times 10^7$ cm^{-1} Å^6, $\nu_D = 61.41(\pm 0.10)$ and D(limit) $= 39\,951.591$ cm^{-1} (relative to the ground-state potential minimum). This recommended vibrational expansion implies $D_0(1\ ^3\Sigma_g^-) = 3385.70$ (± 0.2) cm^{-1}, $D_e(1\ ^3\Sigma_g^-) = 3432.46(\pm 0.2)$ cm^{-1}, and $T_e = 36\,519.13$ (± 0.2) cm^{-1}.

	$G(\nu) = [j=0]$	$B_\nu[j=1]$
$X_j(6)$/cm^{-1}	4.4867×10^{-2}	3.0921×10^{-3}
p_1^j	0.436 636	0.1341
p_2^j	-3.529×10^{-3}	-1.6863×10^{-2}
p_3^j	1.54×10^{-5}	9.2×10^{-4}
p_4^j	...	$-2.810\,837 \times 10^{-5}$
p_5^j	...	4.924×10^{-7}
p_6^j	...	$-4.619\,52 \times 10^{-9}$
p_7^j	...	-1.8×10^{-11}
q_1	4.8×10^{-2}	...
q_2	1.366×10^{-2}	...

mine refined values of ν_D and of the $\{p_i^j\}$ and $\{q_i\}$ parameters defining the NDE functions for $G(\nu)$ and B_ν;
(6) Repeat steps (3)–(5) until convergence is achieved. When this occurs, the ν_D value was rounded at the second digit of its uncertainty and the fit repeated while applying the sequential rounding and refitting procedure of Ref. 30. This had no effect on the quality of the fit to the experimental data.

The final NDE expansion parameters determined in this way are given in Table I, while the associated calculated values for the first three centrifugal distortion constants are listed in Table II; while higher-order distortion constants were also computed, their effect is much smaller than the uncertainties in the data. The reduced precision for the B_ν values for levels above $\nu = 28$ listed in Table II reflects the fact that data for the lower levels involve rotational sublevels up to $N = 47$, while those for the higher vibrational levels are restricted to $N < 25$. The final fit had a dimensionless standard error[30] of $\bar{\sigma}_f = 1.04$, which means that on average the differences between the calculated and observed term values are within (only 4% larger than) the estimated experimental uncertainties of ca. 0.2 cm^{-1}. In contrast, predictions yielded by the Dunham constants reported in Ref. 1 yielded $\bar{\sigma}_f = 1.99$ for this data set.

The values and derivatives of our NDE expressions for $G(\nu)$ and B_ν at $\nu = -1/2$ also yield improved estimates of the conventional spectroscopic parameters: $\omega_e = 93.74$ (± 0.05), $\omega_e x_e = 0.452(\pm 0.016)$, $B_e = 0.1183(\pm 0.0010)$, and $\alpha_e = 1.9(\pm 0.5) \times 10^{-3}$ cm^{-1}, whose uncertainties are fully correlated values generated from the results of the fit using Eq. (7) of Ref. 30. These constants in turn yield $R_e = 3.520(\pm 0.015)$ Å and $Y_{00} = 0.171$ cm^{-1}. The size of this Y_{00} value indicates that higher-order terms in the semiclassical quantization condition are relatively large for this rather anharmonic potential. This was approximately taken into account by our use of the Kaiser correction (integration from $\nu = -1/2 - Y_{00}/\omega_e$) (Ref. 31) in the RKR calculation to determine the potential function from which the centrifugal dis-

TABLE II. Band constants (in cm^{-1}) and turning points (in Å) of the $1\,^3\Sigma_g^-$ state of Na$_2$ yielded by the present analysis.

v	G_v	B_v	D_v	H_v	L_v	$R_1(v)$	$R_2(v)$
0	0.00	0.117 477	7.42×10^{-7}	1.21×10^{-12}	2.55×10^{-17}	3.356	3.711
1	92.75	0.115 957	7.22×10^{-7}	3.70×10^{-12}	-6.90×10^{-17}	3.250	3.867
2	184.65	0.114 701	7.14×10^{-7}	5.31×10^{-12}	-1.14×10^{-16}	3.182	3.981
3	275.68	0.113 633	7.14×10^{-7}	6.20×10^{-12}	-1.22×10^{-16}	3.128	4.077
4	365.83	0.112 692	7.18×10^{-7}	6.53×10^{-12}	-1.07×10^{-16}	3.082	4.163
5	455.09	0.111 830	7.23×10^{-7}	6.45×10^{-12}	-7.88×10^{-17}	3.042	4.242
6	543.46	0.111 011	7.28×10^{-7}	6.10×10^{-12}	-4.73×10^{-17}	3.006	4.316
7	630.93	0.110 209	7.32×10^{-7}	5.60×10^{-12}	-1.89×10^{-17}	2.973	4.386
8	717.48	0.109 406	7.36×10^{-7}	5.04×10^{-12}	2.13×10^{-18}	2.943	4.454
9	803.13	0.108 591	7.38×10^{-7}	4.51×10^{-12}	1.32×10^{-17}	2.915	4.519
10	887.85	0.107 757	7.39×10^{-7}	4.05×10^{-12}	1.34×10^{-17}	2.889	4.583
11	971.64	0.106 901	7.39×10^{-7}	3.69×10^{-12}	3.09×10^{-18}	2.865	4.646
12	1054.49	0.106 021	7.39×10^{-7}	3.46×10^{-12}	-1.58×10^{-17}	2.842	4.708
13	1136.39	0.105 118	7.39×10^{-7}	3.35×10^{-12}	-4.06×10^{-17}	2.821	4.769
14	1217.32	0.104 195	7.39×10^{-7}	3.35×10^{-12}	-6.79×10^{-17}	2.801	4.830
15	1297.29	0.103 252	7.40×10^{-7}	3.44×10^{-12}	-9.44×10^{-17}	2.782	4.890
16	1376.26	0.102 291	7.42×10^{-7}	3.58×10^{-12}	-1.16×10^{-16}	2.764	4.950
17	1454.24	0.101 314	7.44×10^{-7}	3.74×10^{-12}	-1.31×10^{-16}	2.747	5.010
18	1531.19	0.100 322	7.48×10^{-7}	3.88×10^{-12}	-1.35×10^{-16}	2.731	5.069
19	1607.11	0.099 314	7.52×10^{-7}	3.96×10^{-12}	-1.27×10^{-16}	2.716	5.129
20	1681.96	0.098 289	7.58×10^{-7}	3.94×10^{-12}	-1.06×10^{-16}	2.701	5.190
21	1755.75	0.097 248	7.64×10^{-7}	3.81×10^{-12}	-7.29×10^{-17}	2.687	5.250
22	1828.43	0.096 187	7.71×10^{-7}	3.53×10^{-12}	-2.85×10^{-17}	2.674	5.311
23	1899.98	0.095 104	7.78×10^{-7}	3.10×10^{-12}	2.33×10^{-17}	2.661	5.373
24	1970.39	0.093 997	7.86×10^{-7}	2.52×10^{-12}	7.80×10^{-17}	2.648	5.435
25	2039.63	0.092 863	7.93×10^{-7}	1.81×10^{-12}	1.30×10^{-16}	2.636	5.497
26	2107.65	0.091 699	8.01×10^{-7}	9.96×10^{-13}	1.73×10^{-16}	2.625	5.561
27	2174.45	0.090 502	8.09×10^{-7}	1.06×10^{-13}	2.02×10^{-16}	2.614	5.626
28	2239.97	0.089 269	8.17×10^{-7}	-8.15×10^{-13}	2.12×10^{-16}	2.604	5.692
29	2304.20	0.088 00	8.26×10^{-7}	-1.73×10^{-12}	2.01×10^{-16}	2.594	5.759
30	2367.09	0.086 69	8.35×10^{-7}	-2.61×10^{-12}	1.68×10^{-16}	2.584	5.828
31	2428.61	0.085 34	8.45×10^{-7}	-3.42×10^{-12}	1.15×10^{-16}	2.575	5.899
32	2488.72	0.083 94	8.56×10^{-7}	-4.15×10^{-12}	4.42×10^{-17}	2.566	5.971
33	2547.38	0.082 50	8.69×10^{-7}	-4.83×10^{-12}	-4.01×10^{-17}	2.558	6.045
34	2604.56	0.081 01	8.83×10^{-7}	-5.48×10^{-12}	-1.34×10^{-16}	2.550	6.122
35	2660.21	0.079 47	8.99×10^{-7}	-6.14×10^{-12}	-2.31×10^{-16}	2.542	6.201
36	2714.28	0.077 88	9.18×10^{-7}	-6.84×10^{-12}	-3.16×10^{-16}	2.535	6.283
37	2766.74	0.076 23	9.40×10^{-7}	-7.56×10^{-12}	-3.95×10^{-16}	2.528	6.368
38	2817.52	0.074 53	9.65×10^{-7}	-8.42×10^{-12}	-4.84×10^{-16}	2.521	6.457
39	2866.58	0.072 76	9.93×10^{-7}	-9.49×10^{-16}	-5.61×10^{-16}	2.515	6.549
40	2913.87	0.070 93	1.03×10^{-6}	-1.08×10^{-11}	-6.38×10^{-16}	2.509	6.646
41	2959.32	0.069 02	1.06×10^{-6}	-1.24×10^{-11}	-7.42×10^{-16}	2.503	6.748
42	3002.88	0.067 04	1.10×10^{-6}	-1.44×10^{-11}	-8.44×10^{-16}	2.498	6.855
43	3044.48	0.064 97	1.15×10^{-6}	-1.69×10^{-11}	-1.01×10^{-15}	2.493	6.969
44	3084.05	0.062 81	1.21×10^{-6}	-2.01×10^{-11}	-1.20×10^{-15}	2.488	7.090
45	3121.53	0.060 55	1.27×10^{-6}	-2.41×10^{-11}	-1.50×10^{-15}	2.484	7.220
46	3156.82	0.058 18	1.34×10^{-6}	-2.92×10^{-11}	-1.91×10^{-15}	2.480	7.359
47	3189.87	0.055 68	1.43×10^{-6}	-3.57×10^{-11}	-2.50×10^{-15}	2.476	7.511
48	3220.57	0.053 04	1.52×10^{-6}	-4.41×10^{-11}	-3.38×10^{-15}	2.473	7.678
49	3248.84	0.050 24	1.64×10^{-6}	-5.51×10^{-11}	-4.66×10^{-15}	2.469	7.862
50	3274.60	0.047 28	1.78×10^{-6}	-6.98×10^{-11}	-6.65×10^{-15}	2.466	8.068
51	3297.73	0.044 11	1.95×10^{-6}	-8.98×10^{-11}	-9.84×10^{-15}	2.464	8.302
52	3318.17	0.040 74	2.15×10^{-6}	-1.18×10^{-10}	-1.52×10^{-15}	2.462	8.572
53	3335.83	0.037 13	2.39×10^{-6}	-1.59×10^{-10}	-2.47×10^{-15}	2.460	8.891
54	3350.65	0.033 27	2.70×10^{-6}	-2.21×10^{-10}	-4.34×10^{-15}	2.458	9.276
55	3362.62	0.029 16	3.08×10^{-6}	-3.26×10^{-10}	-8.52×10^{-15}	2.457	9.756
56	3371.79	0.024 81	3.58×10^{-6}	-5.16×10^{-10}	-1.87×10^{-13}	2.456	10.381
57	3378.32	0.020 28	4.23×10^{-6}	-8.97×10^{-10}	-5.61×10^{-13}	2.455	11.239

tortion constants were calculated. However, this correction is only a first approximation to the treatment of higher-order semiclassical terms, so one may expect to find (see below) small discrepancies between quantal eigenvalues and B_v's

calculated on this semiclassical potential and the values defined by the NDE functions used as input to the RKR calculation.

Values of band constants calculated[28] from the RKR po-

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tential generated[27] from these NDE expansions, together with rounded values of the RKR turning points themselves, are listed in Table II. More precise RKR points may be readily generated from our $G(v)$ and B_v expansions using standard programs,[20,27] and a listing appropriate for computational applications is available on request.[6] The $G(v)$ and B_v values listed in Table II differ slightly from those implied by our NDE expansions because of two minor sources of inconsistency in the iterative procedure described above. The first is the fact that while the tabulated band constants were obtained by performing a quantal calculation on the RKR potential, the RKR inversion procedure is based on the first-order semiclassical or Jeffreys–Wentzel–Kramers–Brillouin (JWKB) approximation. The second is the fact that because of uncertainties in the experimental B_v determination, the inner-wall RKR turning points must be smoothed (here, for $v > 34$) in order to prevent anomalous ''wiggling'' of the inner potential wall, and this smoothing implicitly changes the B_v values for levels above its onset. The program RKR1 performs such inner-wall smoothing (and the associated outer turning point adjustment[28]) by extrapolating above a given (user-selected) point with an exponential fitted to the preceding three inner turning points; the maximum resulting turning point shift was only ca. 0.01 Å. Moreover, below the onset of the inner-wall smoothing, the discrepancies in the B_v values were typically less than 0.01%, while those associated with the vibrational spacings are typically less than 0.02 cm^{-1}, so quantal/semiclassical discrepancies are significantly less than our experimental uncertainties. In any case, predictions of the data generated from the (quantal) calculated band constants of Table II are essentially identical (within the uncertainties) to those implied by the $G(v)$ and B_v expansions of Table I (and the centrifugal distortion constants of Table II), so these potential sources of inconsistency have no significant effect on the present analysis.

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ERRATA

Erratum: "Molecular constants and Rydberg–Klein–Rees (RKR) potential curve for the Na₂ 1 $^3\Sigma_g^-$ state" [J. Chem. Phys. 111, 3494 (1999)]

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The power in Eq. (4) is incorrect. The near-dissociation expansion expression for the inertial rotational constant should read

$$B_v = X_1(n)(v_{\mathfrak{D}} - v)^{4/(n-2)} \exp\left[\sum_{i=1}^{L} p_i^1 (v_{\mathfrak{D}} - v)^i\right]. \tag{4}$$

Erratum: "Molecular constants and Rydberg–Klein–Rees (RKR) potential curve for the Na$_2$ 1 $^3\Sigma_g^-$ state" [J. Chem. Phys. 111, 3494 (1999)]

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The final parameter in the exponential NDE expansion for B_v in Table I was shown with the wrong sign; it should be $p_7^1 = +1.8 \times 10^{-11}$. As noted previously,[1] the NDE expression for B_v in Eq. (4) should have read $B_v = X_1(n) \times (v_\mathfrak{D} - v)^{4/(n-2)} \exp(\Sigma_{i=1}^L p_i^1 (v_\mathfrak{D} - v)^i)$.

[1] Y. Liu, J. Li, D. Chen, L. Li, K. M. Jones, B. Ji, and R. J. Le Roy, J. Chem. Phys. **117**, 6380 (2002).