The NaLi 1 $^1\Sigma^+$(X) electronic ground-state dissociation limit

C. E. Fellows

Articles you may be interested in

The Na ^{7}Li 3 $^1\Sigma^+$(C) and 1 $^1\Pi$(B) electronic states through collision energy transfer
The Journal of Chemical Physics 93, 6281 (1990); 10.1063/1.458997

Ultracold photoassociative spectroscopy of heteronuclear alkali-metal diatomic molecules
The Journal of Chemical Physics 108, 5767 (1998); 10.1063/1.475987

The X $1\Sigma^+$ state of LiRb studied by Fourier-transform spectroscopy
The Journal of Chemical Physics 134, 024321 (2011); 10.1063/1.3524312
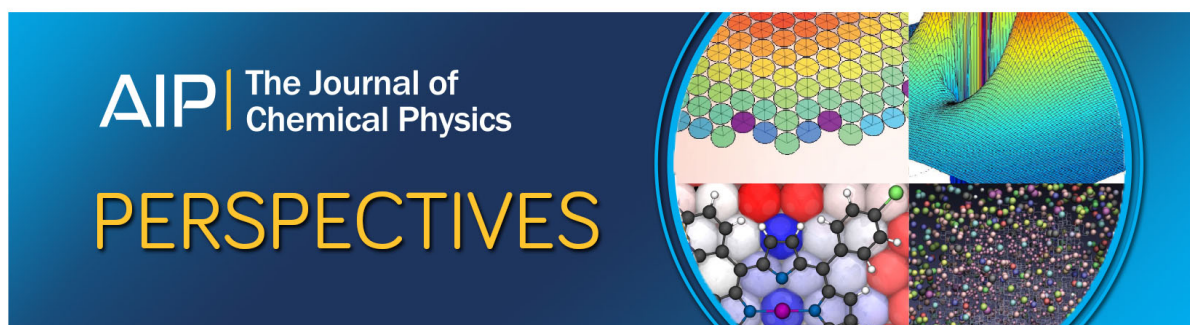
Inelastic collisions of cold polar molecules in nonparallel electric and magnetic fields
The Journal of Chemical Physics 127, 044302 (2007); 10.1063/1.2748770

Dissociation Energy and Long-Range Potential of Diatomic Molecules from Vibrational Spacings of Higher Levels
The Journal of Chemical Physics 52, 3869 (1970); 10.1063/1.1673585

The NaLi 1 $^1\Sigma^+$(X) electronic ground-state dissociation limit

C. E. Fellows

Laboratoire Aimé Cotton,[a] *Centre National de la Recherche Scientifique II, Bâtiment 505, Campus d'Orsay, 91405 Orsay, Cedex, France*

The NaLi 1 $^1\Sigma^+$ (X) electronic ground state has been studied by Fourier transform spectroscopy and laser-induced fluorescence up to near the dissociation limit. The fluorescence has been induced by Ar^+, Kr^+ and dye (DCM and rhodamine 6G) laser lines. Fluorescence spectra have been observed up to $v'' = 43$ and accurate molecular constants have been calculated for the electronic ground state after reducing the wave numbers of 6417 assigned lines in a least-squares fit. With the molecular constants an inverted-perturbation-approach potential curve has been calculated. A value for the dissociation energy of $D_e = 7105.5 \pm 1.0$ cm^{-1} has been obtained by fitting the energy levels with high vibrational quantum numbers to a multipolar expansion in the inverse power of the internuclear distance. The multipolar expansion coefficients C_6, C_8, and C_{10} have been obtained, showing a good agreement with theoretical values calculated earlier. In the fluorescence spectrum induced by the 476.5 nm Ar^+ laser line, extra fluorescence series have been observed. The possible collisional energy transfer in the 1 $^1\Pi$(B) electronic state at the origin of these lines is discussed.

I. INTRODUCTION

The knowledge of the potential-energy curves of diatomic molecules, principally the long-range part close to the dissociation limit, is of considerable interest for the quantitative understanding of scattering problems, recombination processes, and line-broadening phenomena. The diatomic alkali molecules are proving to be a fertile testing ground both of current experimental techniques, such as laser spectroscopy, and of *ab initio* and semiempirical calculations. Homonuclear molecules of the group are better known than heteronuclear ones, though NaLi has been the subject of detailed *ab initio* calculations performed by Schmidt-Mink, Müller, and Meyer.[1] In their work 16 low-lying electronic states of NaLi were investigated by self-consistent-field (SCF) valence configuration-interaction (CI) calculations including core-polarization effects, by means of an effective potential. Regarding the long-range part of the electronic ground state, the theoretical results presented by Schmidt-Mink, Müller, and Meyer[1] were in disagreement with the experimental results obtained by Engelke, Ennen, and Meiwes.[2] These authors have reported a dissociation energy value $D_e = 7068 \pm 4$ cm^{-1} for the 1 $^1\Sigma^+$ (X) state, after assignment of the observed fluorescence series in the 1 $^1\Pi$(B) → 1 $^1\Sigma^+$ (X) transition, to 43 bound vibrational levels. Taking into account that the experimental value differed by only 11 cm^{-1} from their calculated value, which was considerably less than the defect of 50 cm^{-1} observed in the calculation of the Li$_2$ dissociation energy, Schmidt-Mink, Müller, and Meyer[1] doubted the extrapolated empirical value. Comparing their calculated potential curve with the one obtained by Engelke, Ennen, and Meiwes,[2] they concluded that their dissociation energy value was in error by 25 ± 5 cm^{-1}, and they suggested a value of 7093 ± 5 cm^{-1} for the electronic ground state.

In a previous paper[3] we reported the results of a study of Ar^+ and Kr^+ laser-induced fluorescence spectra. In that

paper the studied range of v'' values was limited to $0 \leqslant v'' \leqslant 20$, in spite of the fact that a $Q(37)$ series, excited by the 476.5 nm Ar^+ laser line, had been observed up to $v'' = 40$. In this work the obtained molecular constants as well as the inverted-perturbation-approach potential curve calculated with these constants were in good agreement with the theoretical values obtained by Schmidt-Mink, Müller, and Meyer.[1] Two other subsequent papers dealing with excited electronic states of the NaLi molecule[4,5] have been published confirming the reliability of theoretical calculations.[1]

In the present paper the 1 $^1\Sigma^+$ (X) electronic ground state of the NaLi molecule is studied nearly up to the dissociation limit by laser-induced fluorescence combined with Fourier transform spectroscopy. Several excitation wavelengths issued from both Ar^+, Kr^+ fixed frequency lasers and tunable dye laser (DCM and rhodamine 6G) have been used to induce fluorescence in the NaLi molecules. High-accuracy determinations of rovibronic (v'',J'') term energy values for vibrational levels of the 1 $^1\Sigma^+$ (X) ground state with v'' ranging from $v'' = 0$ up to $v'' = 43$, which represents 99.5% of the potential curve depth, have been obtained.

In the Sec. II we present the experimental apparatus with typical observed spectra. In Sec. III the data treatment is discussed as well as the determination of the parameters and dissociation energy. In Sec. IV a comparison between our results and others, both experimental and theoretical, is done. Extra fluorescence series observed in the spectrum of the 1 $^1\Pi$(B) → 1 $^1\Sigma^+$ (X) transition, induced by the 476.5 nm Ar^+ laser line, are shown and their possible origin discussed in Sec. V. Finally, the conclusions are presented in Sec. VI.

II. EXPERIMENT

The production of NaLi molecules was ensured by a heat-pipe oven based on a slightly modified version of the model developed by Vidal and Cooper.[6] These modifications have been done following the heat-pipe oven constructed by Hessel and Jankowsky[7] for NaLi molecules produc-

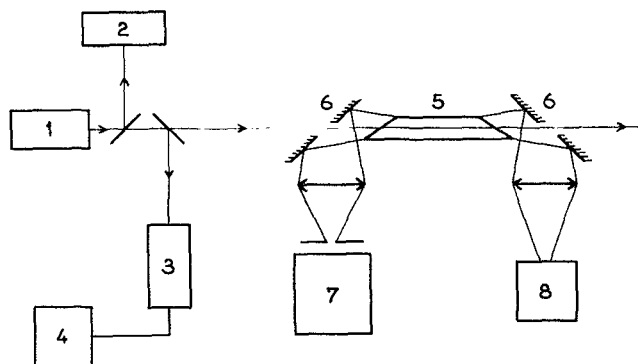[a] The Laboratoire Aimé Cotton is associated with Université Paris-Sud.

FIG. 1. Scheme of the experimental setup. (1) Laser source (Ar$^+$, Kr$^+$, or CW dye laser). (2) Lambdameter. (3) Fabry–Pérot spectrum analyzer. (4) Oscilloscope recording the transmission fringes of the spectrum analyzer. (5) Heat-pipe oven. (6) Pierced mirrors collecting the fluorescence light in the forward and backward directions with respect to the laser beam. (7) Fourier transform spectrometer. (8) Photomultiplier tube to check the stability of the fluorescence intensity. Devices 2, 3, 4, and 8 are only used with the tunable laser excitations of the NaLi.

tion. The heat pipe used in this work was a double-heated one, and a more detailed explanation of the construction and working principle can be found elsewhere.[3–5]

The optical pumping of the NaLi molecules has been accomplished with the fixed frequency lines of an Ar$^+$ laser (Spectra Physics 171-19) oscillating in multimode or monomode conditions, by a Kr$^+$ laser (Coherent Radiation Innova K-3000) oscillating only in multimode conditions and by a monomode dye laser (Coherent Radiation 599-21) pumped by an Ar$^+$ laser operating with DCM or rhodamine 6G dyes. The fluorescence was focused into the entrance iris of a 2 m optical path-length Fourier transform spectrometer constructed at the Laboratoire Aimé Cotton (Orsay, France). A diagram of the experimental setup is shown in Fig. 1.

The recorded fluorescence covers a region of 10 000 cm^{-1} in the direction of the lower wave numbers, and 3000 cm^{-1} in the direction of higher wave numbers around the laser line with a resolution limit ranging from 0.020 to 0.080 cm^{-1}. The absolute wave-number measurement uncertainties vary from 0.005 cm^{-1} for the strongest transitions to 0.030 cm^{-1} for the weaker ones.

The fluorescence induced by these laser lines covers the transitions in the $1\,^1\Pi(B) \rightarrow 1\,^1\Sigma^+(X)$ and $2\,^1\Sigma^+(A) \rightarrow 1\,^1\Sigma^+(X)$ systems. It has been observed in the homonuclear cases, Na_2 and Li_2, that the best way to obtain fluorescence up to the highest vibrational quantum levels of the ground state is to pump the first excited $^1\Sigma^+$ electronic state,[8,9] that is, the $2\,^1\Sigma_u^+$. The same holds in our case: due to the relative positions of the internuclear equilibrium distances between the $2\,^1\Sigma^+(A)$ and the $1\,^1\Sigma^+(X)$, the best way to obtain spectra up to near the dissociation limit of the electronic ground state was to excite the first $^1\Sigma^+$ state, i.e., the $2\,^1\Sigma^+(A)$ state. Typical spectra of the $2\,^1\Sigma^+(A) \rightarrow 1\,^1\Sigma^+(X)$ and $1\,^1\Pi(B) \rightarrow 1\,^1\Sigma^+(X)$ transitions are shown in Figs. 2 and 3, respectively. In the first figure, the series issued from the upper level with $J' = 22$ [$P(23), R(21)$] is clearly observed up to $v'' = 43$. The second figure shows the well-known $Q(37)$ series observable up to $v'' = 40$. A second series [$P(47), R(45)$] is also present in the spectrum.

III. ANALYSIS

A. Data reduction and potential-energy curve

With a good set of spectroscopic constants, the assignment of the strongest transitions is quite straightforward. To each spectral line a set of rovibronic quantum numbers (v'',J'') is associated which corresponds to a term value T'' of the ground electronic state. Then, using the Ritz–Rydberg combination principle, each line with a wave number σ is
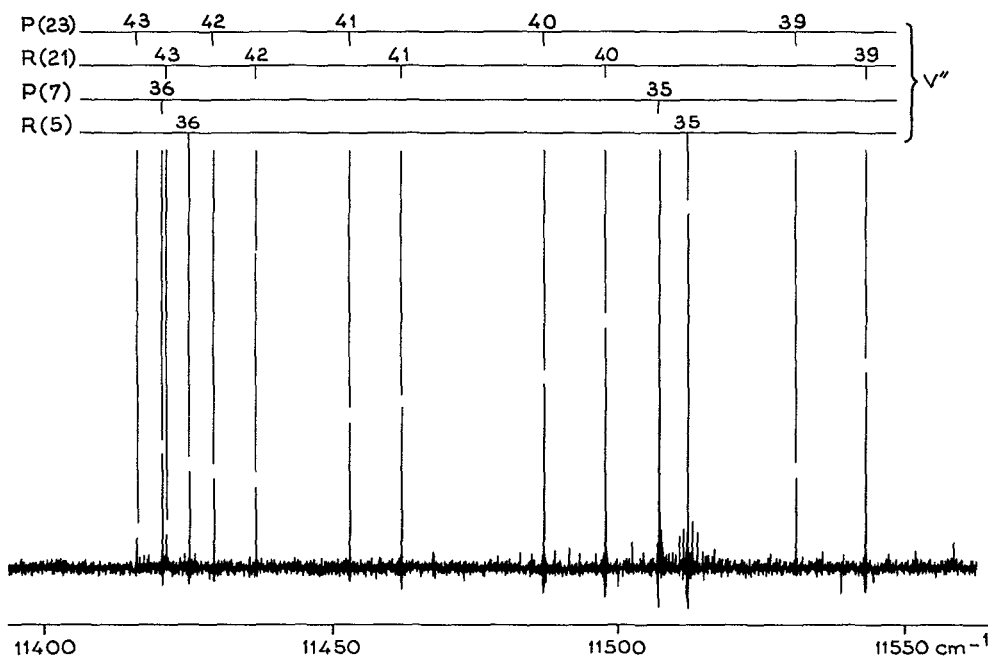

FIG. 2. Fluorescence spectrum induced by the 580.1 nm rhodamine 6G laser line. Two series of doublets are observed, a $P(7)/R(5)$ and a $P(23)/R(21)$. In this last one transitions up to $v'' = 43$ of the $1\,^1\Sigma^+(X)$ ground state can be observed.
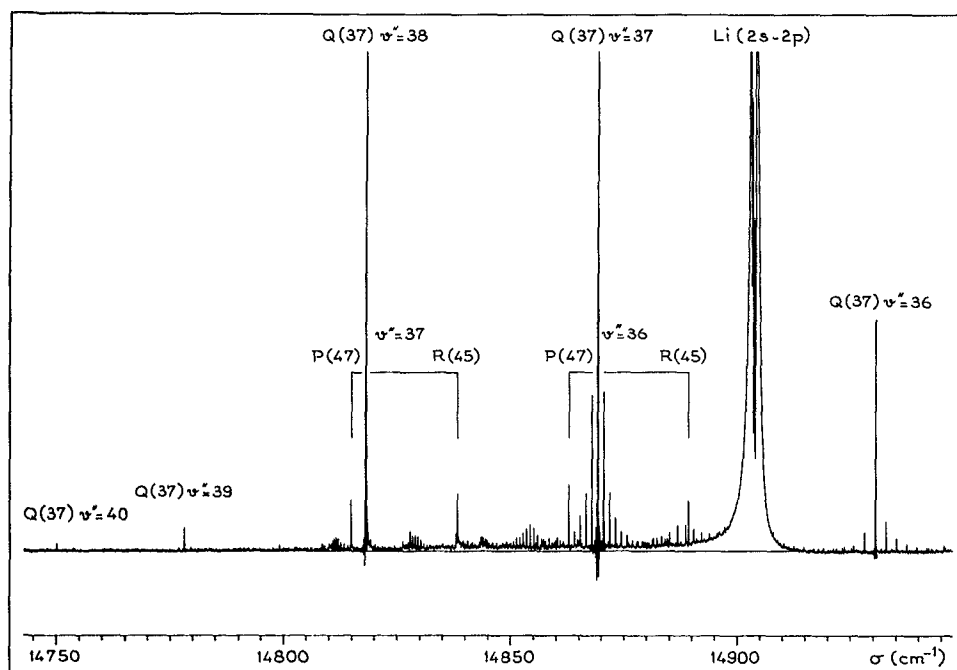
FIG. 3. Fluorescence spectrum induced by the 476.5 nm Ar $^+$ laser line, oscillating in multimode conditions.

associated with the difference between the term value, $T'(v',J')$, of the excited electronic state and the corresponding term value, $T''(v'',J'')$, of the ground state by the equation

$$\sigma = T'(v',J') - T''(v'',J'').$$

The term values T'' for the electronic ground state are then developed in a Dunham-type expression,

$$T''(v'',J'') = \sum_{i,j} Y_{ij} [\rho(v'' + \tfrac{1}{2})]^i [\rho^2 J''(J''+1)]^j, \quad (1)$$

with $\rho = 1.0$ for the Na ^{7}Li, $\rho = 1.061\ 832\ 15$ for Na ^{6}Li, and Y_{ij} are the Dunham coefficients for the electronic ground state. The term values T' for the excited states are kept as free parameters and are calculated in the fitting.

Using this procedure, a total of 6417 wave numbers have been reduced to molecular constants in a linear least-squares fit with an root-mean-square (rms) error of 5.0×10^{-3} cm^{-1}. The obtained constants are listed in Table I. The rotationless potential, within the energy range of vibrational quantum numbers from $v'' = 0$ to $v'' = 43$, has been obtained by the "inverted perturbation approach" (IPA). This method, proposed originally by Kosman and Hinze,[10] has been developed by Vidal and Scheingraber,[11] who applied this technique to the accurate calculation of potential curves for several diatomic molecules.[12,13] The same method has been applied by several authors in the studies of dissociation limits of alkaline diatomic molecules.[14,15]

The IPA method is based on an optimization procedure of the rotationless potential $V_0(r)$, which is the Rydberg–Klein–Rees (RKR) potential[16] calculated using the Dunham-type constants listed in Table I. This RKR potential curve serves as a starting point of the variational method, and to the calculations of the eigenfunctions Ψ^0_{vJ} and eigenvalues E^0_{vJ} of the Schrödinger equation. Changing the poten-

tial to $V_0(r) + \Delta V_0(r)$ changes the energies according to first-order perturbation theory by

$$\Delta E_{vJ} = \langle \Psi^0_{vJ} | \Delta V_0(r) | \Psi^0_{vJ} \rangle. \quad (2)$$

The modifications of the potential curve are described by a linear combination of function $g_i(r)$ which is represented by products of Legendre polynomials and Gaussian functions.[11] In this way,

$$\Delta V_0(r) = \sum_i c_i \cdot g_i(r), \quad (3)$$

and since the "true" potential can yield the measured eigenvalues E^{meas}_{vJ}, the coefficients c_i can be calculated by a least-squares fit to the linear system of equations,

$$\Delta E_{vJ} = E^{\text{meas}}_{vJ} - E^0_{vJ} = \sum_i c_i \langle \Psi^0_{vJ} | g_i(r) | \Psi^0_{vJ} \rangle. \quad (4)$$

The corrected potential $V_0(r) + \Delta V_0(r)$ is used for the next iteration step and generally convergence is obtained after two or three iterations. The output of this IPA program yields, for a given vibrational quantum number v'', the vibrational term values $G(v'')$, the rotational constants $B_{v''}$, and the corresponding turning points $r_{\min}$ and $r_{\max}$ of the IPA potential. These results are listed in Table II. Using the following data field, J'' $(v_{\min}, v_{\max})$:

6(3,36), 15(0,34), 22(0,43), 27(0,39), 29(0,36),

31(0,36), 37(2,40), 46(3,32), 51(3,29), 61(3,10),

the arithmetic means of the deviations ΔE_{vJ} was 0.005 cm^{-1} after three iterations.

B. Long-range potential and dissociation energy

At long enough internuclear distances of the potential-energy curve, the potential can be developed in the form

TABLE I. Dunham type coefficients[a] of the $1\,^1\Sigma^+$ (X) state of NaLi (in cm^{-1}).

i	j	Y_{ij}	$\sigma(Y_{ij})$
1	0	0.256 457 712 5 (03)	0.144 8 (−02)
2	0	− 0.158 084 555 9 (01)	0.608 1 (−03)
3	0	− 0.141 276 642 4 (−01)	0.122 9 (−03)
4	0	0.117 147 328 0 (−02)	0.119 3 (−04)
5	0	− 0.891 788 674 8 (−04)	0.230 5 (−06)
6	0	0.327 024 887 5 (−05)	0.451 6 (−07)
7	0	− 0.450 075 242 4 (−07)	0.140 0 (−08)
8	0	− 0.964 338 767 2 (−09)	0.453 6 (−10)
9	0	0.306 921 126 6 (−10)	0.184 7 (−11)
10	0	0.725 221 176 0 (−12)	0.286 5 (−13)
11	0	− 0.485 460 818 5 (−13)	0.100 0 (−14)
12	0	0.102 525 563 2 (−14)	0.159 3 (−16)
13	0	− 0.109 041 051 2 (−16)	0.243 4 (−18)
14	0	0.514 202 268 5 (−19)	0.203 6 (−20)
0	1	0.375 785 152 3 (00)	0.586 8 (−05)
1	1	− 0.302 207 863 9 (−2)	0.236 4 (−05)
2	1	− 0.630 075 860 5 (−04)	0.883 9 (−06)
3	1	0.773 051 891 0 (−05)	0.250 4 (−06)
4	1	− 0.722 941 650 4 (−06)	0.288 9 (−07)
5	1	0.265 312 601 2 (−07)	0.171 2 (−08)
6	1	0.284 866 675 7 (−09)	0.570 7 (−10)
7	1	− 0.597 253 027 7 (−10)	0.128 1 (−11)
8	1	0.157 853 700 0 (−11)	0.444 2 (−13)
9	1	0.928 662 374 1 (−14)	0.314 4 (−15)
10	1	− 0.532 645 277 5 (−15)	0.374 4 (−16)
11	1	− 0.329 835 631 7 (−16)	0.951 3 (−18)
12	1	0.164 689 943 3 (−17)	0.300 0 (−19)
13	1	− 0.265 948 823 4 (−19)	0.550 0 (−21)
14	1	0.152 733 112 4 (−21)	0.393 7 (−23)
0	2	− 0.318 489 723 9 (−05)	0.541 1 (−08)
1	2	− 0.587 622 664 0 (−07)	0.310 1 (−08)
2	2	0.734 231 583 4 (−08)	0.669 4 (−09)
3	2	0.287 881 639 7 (−09)	0.607 9 (−10)
4	2	− 0.260 214 185 7 (−09)	0.551 9 (−11)
5	2	0.339 196 255 9 (−10)	0.515 3 (−12)
6	2	− 0.221 464 206 0 (−11)	0.191 2 (−13)
7	2	0.841 100 504 0 (−13)	0.845 2 (−15)
8	2	− 0.190 341 540 1 (−14)	0.315 9 (−16)
9	2	0.240 526 590 7 (−16)	0.489 8 (−18)
10	2	− 0.131 924 214 1 (−18)	0.290 2 (−20)
0	3	0.155 315 674 8 (−10)	0.151 0 (−11)
1	3	0.108 019 920 6 (−10)	0.932 3 (−12)
2	3	− 0.318 470 078 3 (−11)	0.216 1 (−12)
3	3	0.397 176 017 9 (−12)	0.229 5 (−13)
4	3	− 0.236 054 581 5 (−13)	0.120 8 (−14)
5	3	0.662 802 331 7 (−15)	0.304 9 (−16)
6	3	− 0.720 543 532 6 (−17)	0.293 7 (−18)

[a] The number in parentheses that follows the quantity is the exponent of 10 that multiplies the quantity.

$$V(r) = D_e - \sum_n C_n/r^n, \qquad (5)$$

where the C_n coefficients can be obtained theoretically by second-order perturbation theory. For the ground electronic state of NaLi dissociating into Na($3s^2S$) + Li($2s^2S$) atomic levels, the values of $n = 6, 8,$ and 10, which always contribute to the potential, are positive (attractive).[17] Leroy and Bernstein[18] have developed a WKB-based method which yields better results than the formerly used graphical Birge–Sponer extrapolation. In cases where one of the C_n/r^n terms in the potential expansion (5) represents the dominant contribution, estimates of the C_n coefficients, as well as the dis-

sociation energy D_e, can be derived from the slope of a Leroy–Bernstein plot,

$$\frac{dG(v)}{dv} = K_n [D_e - G(v)]^{(n+2)/2n}, \quad K_n \propto C_n^{-1/n}, \qquad (6)$$

of the measured vibrational term values $G(v)$. In our case Eq. (5) has been used in order to fit the higher-energy values of the ground-state potential curve.

At small internuclear distances r the increasing overlap of the electron clouds of the two atoms leads both to the addition of exchange terms to the potential, and to the increasing inappropriateness of Eq. (5) for describing the Coulombic interaction. Equation (5) then becomes

$$V(r) = D_e - \sum_n \frac{C_n}{r^n} - V_{\text{exch}}, \qquad (7)$$

TABLE II. Vibrational term values $G(v'')$, turning points $r_{\min}$ and $r_{\max}$ and rotational constants $B_{v'}$ for the rotationless IPA potential obtained using the constants of Table II. (All values in cm^{-1}, except $r_{\min}$ and $r_{\max}$ in Å.)

v''	$G(v'')$	$r_{\min}$	$r_{\max}$	$B_{v'} \times 10^2$
0	127.832	2.740 1	3.053 5	37.430 02
1	381.122	2.640 6	3.186 6	37.111 05
2	631.115	2.576 2	3.285 0	36.790 80
3	877.788	2.526 3	3.369 6	36.466 41
4	1 121.117	2.484 7	3.446 3	36.137 06
5	1 361.068	2.448 8	3.518 1	35.802 65
6	1 597.603	2.417 0	3.586 4	35.463 08
7	1 830.678	2.388 4	3.652 2	35.118 01
8	2 060.250	2.362 3	3.716 2	34.766 81
9	2 286.274	2.338 5	3.779 0	34.408 83
10	2 508.699	2.316 4	3.840 7	34.043 41
11	2 727.472	2.295 8	3.901 9	33.670 00
12	2 942.532	2.276 6	3.962 7	33.288 11
13	3 153.812	2.258 6	4.023 4	32.897 21
14	3 361.239	2.241 6	4.084 2	32.496 61
15	3 564.735	2.225 5	4.145 2	32.085 49
16	3 764.218	2.210 4	4.206 7	31.662 88
17	3 959.599	2.196 1	4.268 9	31.227 69
18	4 150.783	2.182 6	4.331 9	30.778 80
19	4 337.668	2.169 7	4.395 9	30.315 09
20	4 520.143	2.157 5	4.461 2	29.835 42
21	4 698.088	2.145 8	4.527 9	29.338 58
22	4 871.372	2.134 5	4.596 3	28.823 22
23	5 039.856	2.123 8	4.666 7	28.287 76
24	5 203.386	2.113 6	4.739 3	27.730 39
25	5 361.800	2.104 1	4.814 5	27.149 04
26	5 514.924	2.095 3	4.892 7	26.541 40
27	5 662.570	2.087 4	4.974 3	25.904 96
28	5 804.537	2.080 1	5.059 9	25.236 99
29	5 940.608	2.073 3	5.150 1	24.534 50
30	6 070.551	2.066 8	5.245 5	23.794 20
31	6 194.117	2.060 5	5.347 3	23.012 37
32	6 311.039	2.054 0	5.456 3	22.184 76
33	6 421.035	2.047 1	5.574 1	21.306 46
34	6 523.801	2.039 3	5.702 5	20.371 83
35	6 619.022	2.030 4	5.843 8	19.374 42
36	6 706.364	2.022 1	6.000 9	18.306 89
37	6 785.485	2.015 6	6.178 2	17.161 00
38	6 856.042	2.011 9	6.381 5	15.927 73
39	6 917.706	2.009 5	6.619 3	14.597 72
40	6 970.192	2.007 6	6.904 3	13.162 77
41	7 013.318	2.006 1	7.256 5	11.618 33
42	7 047.079	2.005 0	7.709 0	9.961 93
43	7 071.644	2.004 2	8.332 3	8.148 34

TABLE III. D_e, van der Waals C_n coefficients and exchange energy constants obtained in this work, compared with previous values.[a,b]

	D_e (cm^{-1})	C_6 (cm^{-1}Å^6)	C_8 (cm^{-1}Å^8)	C_{10} (cm^{-1}Å^{10})	C_{ex} (cm^{-1})	a (Å^{-1})
This work	7105.6[a]	6.890×10^6 [a]	1.329×10^8 [a]	1.072×10^{10} [a]	1.485×10^3 [a]	0.934[a]
	7105.3[b]	6.840×10^6 [b]	1.334×10^8 [b]	0.339×10^{10} [b]	1.387×10^5 [b]	1.224[b]
Ref. 1	7093					
Ref. 2	7068	9.280×10^6				
Ref. 20		6.988×10^6	1.311×10^8	0.334×10^{10}		
Ref. 21		7.282×10^6	1.334×10^8			
Ref. 22		7.359×10^6	1.188×10^8			
Ref. 23		6.978×10^6				
Ref. 24		7.084×10^6				
Ref. 25		7.108×10^6				

[a] Values calculated for r greater than 6.1 Å, as explained in the text.
[b] Values calculated for r greater than 7.15 Å, as explained in the text.

where V_{exch} is the exchange energy term which increases exponentially with decreasing r value.[17] Since the breakdown of Eq. (5) can be correlated with the decreasing distance between the two atoms, it seems reasonable to link a lower limit for the validity of this equation with some measure of the atomic radii. It has been suggested by Leroy[17] that Eq. (5) should not be used at distances smaller than

$$r > 2[\langle r_A^2 \rangle^{1/2} + \langle r_B^2 \rangle^{1/2}], \qquad (8)$$

where $\langle r_A^2 \rangle$ and $\langle r_B^2 \rangle$ are the expectation values of the squares of the outer electron radii of atoms A and B, respectively.

In the NaLi 1 $^1\Sigma^+$ (X) electronic ground-state case, which dissociates to Na($3s^2S$) and Li($2s^2S$) atomic states, the lower limit for r can be calculated by taking empirical values[19] for $\langle r^2 \rangle$, and is found to be about 9.1 Å.

From the IPA potential-energy curve listed in Table II it can be observed that the highest r_{max} value is lower than this lower limit calculated above. This means that the contribution of the exchange term V_{exch} is still important in the observed region of the potential curve, and that Eq. (7) is more appropriate in this case than Eq. (5). Another problem can be discussed here too. As seen above, an estimate of the leading coefficient C_n ($n = 6$),[17] and of the dissociation energy D_e, can be obtained by fitting the quantity $dG(v)/dv \approx (1/2)[G(v+1) - G(v-1)]$ as a function of v using the expression of $dG(v)/dv$ in Eq. (6). But, as has been shown above, the r range is still quite far from the lower acceptable limit of validity of Eq. (5), and even farther from the case where only *one* of the C_n terms represents the dominant contribution. This means that by directly using Eq. (6) in a trial to obtain the C_6 and the D_e values, results can be biased by other contributions of higher-order terms in the multipolar expansion. For all these reasons Eq. (7) has been used in the fitting of the long-range part of the potential curve.

The choice of the external turning points and the corresponding energy values to be used in the fit has been done following Leroy's[17] suggestion that the term $n + 2$ of the multipolar expansion in (7) is no longer valid for $r \lesssim (2C_{n+2}/C_n)^{1/2}$. Using the theoretical values for the C_6

and C_8 coefficients,[20-22] we can obtain a range of r values varying from 5.7 to 6.1 Å. Taking into account these values, the vibrational quantum numbers above $v'' \geqslant 37$, which correspond to a r_{max} value greater than 6.1 Å, have been considered. As will be discussed below, the C_{10}/r^{10} term, although certainly without physical meaning, has been introduced in the calculations in order to obtain reliable parameters C_6 and C_8. The fitting has been performed using the following truncated expression:

$$V(r) = D_e - \frac{C_6}{r^6} - \frac{C_8}{r^8} - \frac{C_{10}}{r^{10}} - C_{ex}e^{-ar}, \qquad (9)$$

where the expression for $V_{exch} = C_{ex}e^{-ar}$ has already been used by other authors.[26-28]

The fit of the $V(r)$ potential-energy values by Eq. (9) has been performed using the following procedure:

In a first step all the coefficients were left free and the calculations performed.

Secondly, D_e, C_6, C_8, and C_{10} parameters have been held fixed with the values obtained in the first step and C_{ex} and a calculated as free parameters.

After that C_{ex} and a have been fixed with the values obtained in the second step, and D_e and C_6 fixed with values calculated in the first step. C_8 and C_{10} are then left free to calculations.

In a final step, D_e and C_6 are left free and all other coefficients fixed in their last obtained values.

The last three steps have been repeated until convergence was reached for all determinations. The values of D_e, the van der Waals coefficients $C_{6,8,10}$ and constants C_{ex}, and a of the exchange term obtained in this procedure are shown in Table III, footnote a. The uncertainty in C_6 is estimated to be 2%, while the higher coefficients C_n and exchange energy constants may have larger errors.

Some comments can be made about the C_{10} value listed on Table III. Comparing this value with the theoretical one, it can be noted that the first is greater than the latter. If the condition $r \lesssim (2C_{n+2}/C_n)^{1/2}$ is now applied for the couple of coefficients C_8 and C_{10} reported by Tang, Norbeck, and Certain,[20] it can be noted that the lower limit of r becomes 7.15 Å. As mentioned by Leroy,[29] in the case where this

condition is not fulfilled the C_{10} value can be unrealistically large. This means in practice "that in a region where the third ($n = 10$) second-order perturbation term makes a reasonably large contribution to the potential, it cannot be adequately represented by the asymptotic C_{10}/r^{10} form."[29]

In order to correct the C_{10} value a simple action has been employed. Following the observations that in the molecular states that arise from pairs of S atomic states, an empirical relation has been suggested by Leroy,[29]

$$C_{10} \approx \tfrac{4}{3}(C_8)^2/C_6.$$

Using the C_6 and C_8 values determined above, $C_{10} = 0.341$ cm^{-1} Å^{10} has been calculated. With this value new calculations have been performed using only the r_{max} values in the potential curve greater than 7.15 Å. For these calculations, in a first step the D_e, C_6, C_8, and C_{10} were held fixed with new values for C_{ex} and a calculated. Then, these latter were held fixed with D_e and C_6, C_8, and C_{10} left as free parameters in the calculations. Finally, D_e and C_6 were left free and the other parameters constrained to their last obtained values. This procedure was repeated, as above, until a convergence was reached. The values of D_e, the C_n's coefficients, and the exchange energy constants C_{ex} and a obtained in this way are listed in Table III, footnote b.

From Table III it can be observed that the difference in the dissociation energy values obtained in each procedure differs only by 0.3 cm^{-1}. The calculated standard deviation for the D_e values in the final iteration was about 0.4 cm^{-1} in both procedures, showing that the observed discrepancy between these two values is in the range of the calculated standard deviation.

In addition, considering that the highest experimental vibrational quantum level observed in the spectra is still 34 cm^{-1} away from the calculated D_e, it is preferable to overestimate the error. The value of $D_e = 7105.5 \pm 1$ cm^{-1} is obtained for the dissociation energy value of the $1\,^1\Sigma^+$ (X) electronic ground state.

IV. COMPARISONS WITH PREVIOUS RESULTS

A. Potential-energy curves

It is interesting to compare our potential-energy values with those calculated theoretically by Schmidt-Mink, Müller, and Meyer.[1] The agreement is impressive, as can be verified in Fig. 4, where the differences $\Delta G(v)$ between experimental and theoretical $G(v)$ values vs the experimental $G(v)$ values up to $v'' = 24$ are plotted. The maximum difference is less than 3 cm^{-1}. Unfortunately, the theoretical data are only available up to this vibrational quantum level, and no further comparison can be made for higher vibrational levels.

B. Dissociation energy

With the obtained value for the dissociation energy of the $1\,^1\Sigma^+$ (X) electronic state, a comparison with previous experimental and theoretical results can be done. Engelke, Ennen, and Meiwes[2] reported an experimental dissociation energy value of 7068 ± 4 cm^{-1}. The difference with our determination reaches 37 cm^{-1}. Two possibilities can ex-
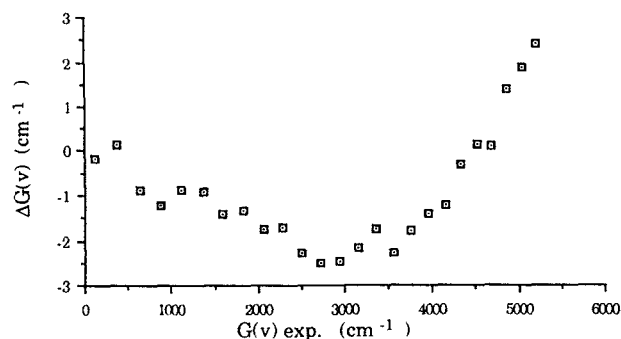

FIG. 4. Difference $\Delta G(v)$ between the experimental and theoretical (Ref. 1) $G(v)$ values up to $v'' = 24$ plotted as a function of experimental $G(v)$ values.

plain this discrepancy. The first one, suggested by Fellows, Vergès, and Amiot,[3] is that in the molecular constant reduction of their wave numbers both the ground state and the excited state $1\,^1\Pi(B)$ state data have been simultaneously fitted. The $1\,^1\Pi(B)$ state being strongly perturbed,[5] the Dunham-type constants obtained for the ground state can be affected by this kind of fitting.

The second possibility concerns the assignment of the higher vibrational bound levels observed in their experiment. As seen in Fig. 3, the stronger $Q(37)$ series appears with groups of bell-shaped lines (that will be discussed in the next section), and with a series of $P(47)$, $R(45)$ doublets. These doublets have been observed only in the very end of the long-wavelength side of the spectrum excited by the 476.5 nm Ar$^+$ laser line oscillating in multimode conditions. No lines belonging to this series have been observed for low values of the vibrational quantum levels, surely due to the unfavorable Franck–Condon factors for this transition. Engelke, Ennen, and Meiwes,[2] using the same Ar$^+$ laser line, assigned only transitions to the $Q(37)$ series. It is not impossible that these $P(47)$, $R(45)$ transition wave numbers have been inserted in the fit as being $Q(37)$ lines. It should be pointed out that we performed the same error in a first analysis of the spectrum.

The dissociation energy value 7093 ± 5 cm^{-1}, reported by Schmidt-Mink, Müller, and Meyer,[1] differs from the one reported here by 12 cm^{-1}. This discrepancy has been introduced in their evaluation simply because they corrected their calculated potential-energy curve using Engelke's potential-energy curve as a reference. Their original value of 7057 cm^{-1} differs from our value of 7105 cm^{-1} by 48 cm^{-1}. In a similar calculation performed on Li_2, the differences between the predicted value of Schmidt-Mink, Müller, and Meyer[30] and the best experimental determination of Vergès et al.[31] reaches 50 cm^{-1}. The discrepancy is of the same order of magnitude as the 48 cm^{-1} found in the NaLi case.

C. Multipolar expansion and C_n parameters

The results obtained in the present work are compared with previous theoretical results in Table III. A graphical representation of the energy contributions of each of the parameters C_n and V_{exch} is shown in Fig. 5. The contribution of
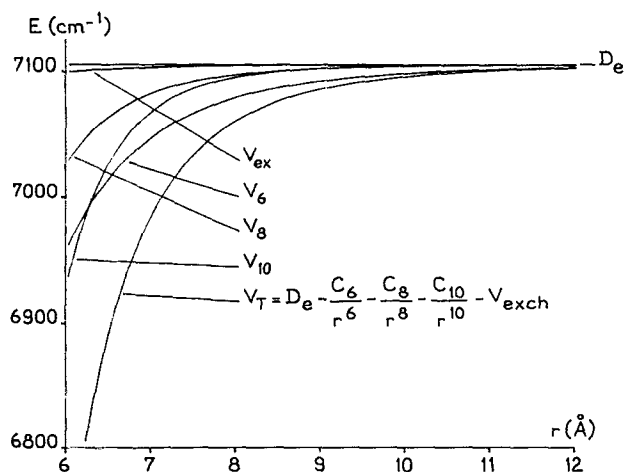
FIG. 5. Contribution of C_n van der Waals coefficients and exchange energy, calculated for $r > 6.1$ Å, to the potential-energy curve. $V_n = D_e - C_n/r^n$ ($n = 6$, 8, and 10) and $V_{ex} = D_e - (C_{ex} e^{-ar})$. The V_T represents $D_e - (\Sigma_{n=6}^{10} C_n/r^n + V_{exch})$.

the C_{10}/r^{10} term is anomalously strong, even greater than the C_8 contribution, differing completely from the "normal" shape of the other C_n/r^n terms. On the other hand, the contribution of the exchange energy is very weak. These facts support the discussion in the preceding section about the validity of the $n = 10$ term in the multipolar expansion when r is lower than $(2C_{10}/C_8)$. It can be clearly noted from this figure that the behavior of the C_{10} term is completely different from that expected for a $1/r^{10}$ dependence. This anomalous contribution therefore clearly affects the exchange energy term.

Secondly, the same analysis can be made for the C_n coefficients and exchange energy constants, C_{ex} and a, listed in Table III, calculated for r values greater than $(2C_{10}/C_8)$ as discussed at the end of Sec. III. Plotting their contributions in Fig. 6, it can be noted that the behaviors change drastical-
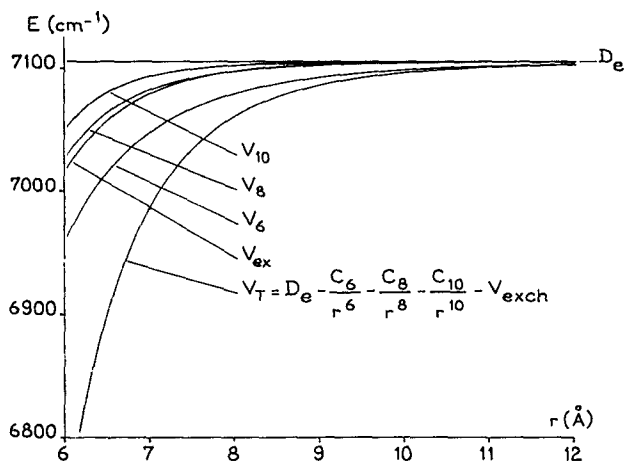
ly. The three coefficients C_6, C_8, and C_{10} present now an expected shape, typical of the $1/r^n$ asymptotic form. The exchange energy contribution is now greater than in the previous case. Evidently, the possibility of the exchange energy term being still mixed with higher-order van der Waals terms ($1/r^n$ with $n = 12$, 14,...) can not be discarded, and, possibly, this last term should be considered as a global contribution of all those neglected in the multipolar expansion near the dissociation limit.

D Vibrational quantum number at dissociation

With the obtained dissociation energy value, the last bound vibrational quantum level of the 1 $^1\Sigma^+$ ground state can be estimated in the following procedure. Integrating Eq. (6) gives[17]

$$G(v) = D_e - [(v_D - v)H_n]^{2n/(n-2)},$$

$$H_n = \frac{\overline{H}_n}{\mu^{1/2}[C_n]^{1/n}}, \tag{10}$$

where $n = 6$, μ is the reduced mass of the molecule, v_D is an integration constant, and $\overline{H}_n$ is a tabulated constant[6] ($\overline{H}_6 = 19.943\,36$ assuming units of energy, length, and mass to be cm^{-1}, Å, and amu, respectively). For $n > 2$, v_D takes the physical significance of the effective vibrational quantum number at the dissociation limit. Using the value $D_e = 7105.5$ cm^{-1}, and plotting $[D_e - G(v)]^{1/3} = H_6(v_D - v)$ as a function of v (Fig. 7), the value $v_D \approx 48.5$ cm^{-1} is derived. From the same figure an estimated value for C_6 equal to 8.594×10^6 cm^{-1} Å^6 can be obtained, being in reasonable agreement with the C_6 values in Table III. With the v_D value obtained by Eq. (10), being generally a noninteger one, the value of the last bound vibrational quantum number for the 1 $^1\Sigma^+$ (X) electronic ground state can be predicted to be equal to 48.

V. EXTRAFLUORESCENCE SERIES

As discussed above, in the 1 $^1\Sigma^+$ (X) → 1 $^1\Pi(B)$ transition fluorescence spectrum induced by the 476.5 nm Ar$^+$ laser line, apart from the $Q(37)$ and the $P(47)/R(45)$ series, some extra fluorescence series forming well-resolved packets of lines have been observed. From the beginning, the
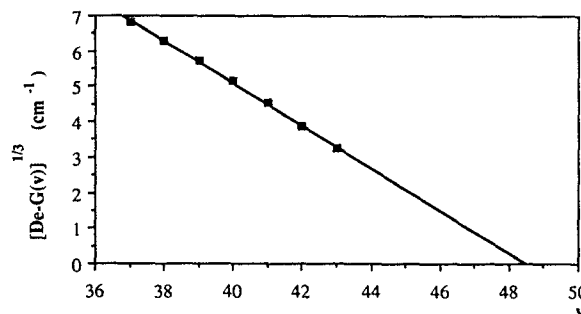

FIG. 6. Contributions of C_n van der Waals coefficients and exchange energy calculated for $r > 7.15$ Å. V_n, V_{ex}, and V_T have the same signification as in Fig. 5.

FIG. 7. LeRoy–Bernstein $[D_e - G(v)]^{1/3}$ plot as function of v for the last observed vibrational quantum numbers of the electronic ground state of the NaLi molecule.
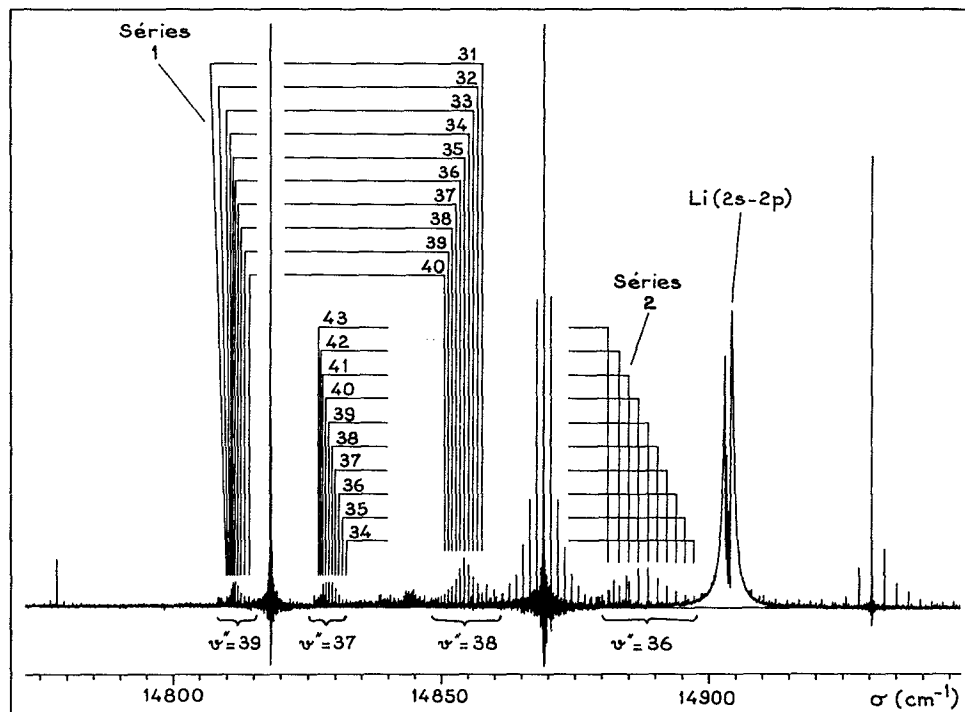
FIG. 8. Fluorescence spectrum induced by the 476.5 nm Ar $^+$ laser line, oscillating in monomode conditions.

supposition that this series was produced by direct excitation of the laser line seemed reasonable. In order to verify this hypothesis, an intracavity étalon (Spectra Physics Model 589C air spaced étalon) has been introduced in the Ar$^+$ laser, reducing the linewidth of the laser line from 6 GHz to about 30 MHz. Tuning the étalon in the range of the gain profile where a monomode oscillation could be ensured, it has been observed that

the $Q(37)$ series was always excited,

the $P(47)$, $R(45)$ series was no more excited when the mode was tuned out of one of the edges of the monomode range.

In Fig. 8 we show the extreme part of the fluorescence spectrum induced by a monomode oscillation tuned near the center of the gain profile of the transition. Extra fluorescence series are observed with intensity distributions differing drastically from those of the main $Q(37)$ series. These lines have been assigned as being Q lines with J values around 37 (series 1 and 2). Their wave numbers have been introduced in the global fitting, using Eq. (3), and the corresponding T' values from the $1\,^1\Pi(B)$ calculated as explained in Sec. III A.

A vibrational assignment of these excited term values has not been possible using the constants reported previously[5] due to the fact that they involve excited vibrational levels of the $1\,^1\Pi(B)$ electronic state higher than the previously observed ones.[5] Using the theoretical data from Schmidt-Mink, Müller, and Meyer,[1] a tentative assignment gave $v' = 14$ for series 1, $v' = 16$ for series 2, and $v' = 15$ for the main series, corresponding to the vibrational assignment of Engelke, Ennen, and Meiwes.[2] The term values T' for the three series are represented as a function of $J(J+1)$ in Fig. 9.

If the intensities in these extra fluorescence series are taken into account, some interesting features can be observed. In Fig. 10 the normalized intensities are plotted as a function of the vibrational quantum number for each series. It can be seen that the most intense lines have rotational quantum numbers:

displaced to J values higher than 37 in the series 1;
displaced to J values lower than 37 in series 2.

Also, an asymmetry in the intensity distribution for both series is observed, the second more intense line corresponding to a T' energy value closer to the upper state energy of the $Q(37)$ transition directly excited by the laser line (cf. Fig. 9).

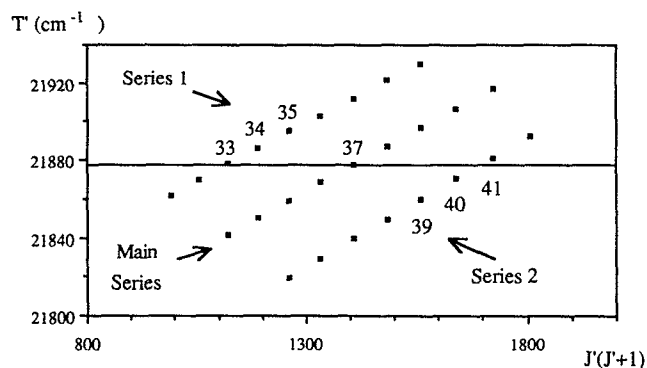The extra fluorescence series are not directly populated by the laser for two reasons:

FIG. 9. T' term energy values from the principal $Q(37)$ series and rotational relaxation and series 1 and 2 from Fig. 8 plotted as a function of $J'(J'+1)$. The right line represents the energy of the $Q(37)$ energy term value directly excited by the laser line. Some of the corresponding J' values are assigned.
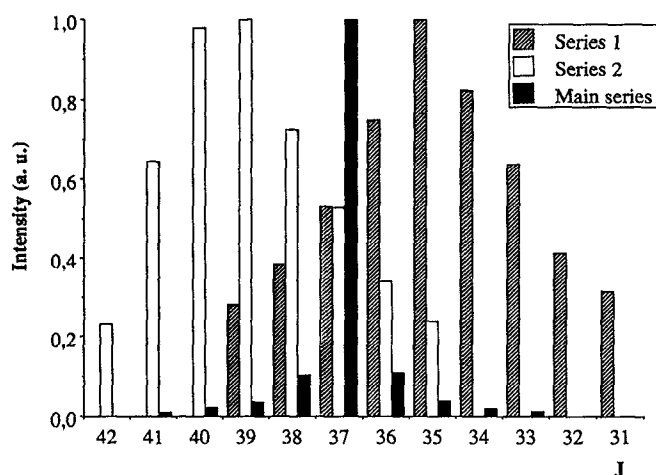
FIG. 10. Normalized intensities of the main series, series 1 and 2 from Fig. 8 plotted as a function of J'.

the difference between the energies of the excited levels and the corresponding ones of the $1\ ^1\Sigma^+$ (X) ground state is not equal to the energy provided by the laser line;
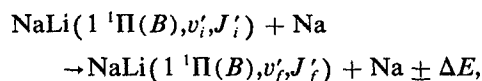
the intensity distribution for the series 1 and 2 are not similar to that of the main series.

Disregarding a direct optical pumping by the laser line, the possibility that seemed the most plausible is a collisional energy transfer from the directly excited $J' = 37$ rotational level. This hypothesis is strengthened after consideration of the collisional energy-transfer studies performed in the Na_2,[32] Li_2,[33] and N_2^+ (Refs. 34 and 35) molecules. This hypothesis can explain the intensity variation to the smaller J values in series 2 for which the transfer is done to higher vibrational quantum levels, as well as the intensity shift to higher J values in series 1, for which the transfer is done to lower vibrational quantum levels.
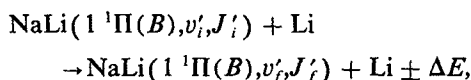
Concerning the $\Delta J \sim 0$ and the $\Delta E \sim 0$ "propensity rules" observed in the previous studies,[32-35] there seems to be a compromise between the final rovibrational energy and the initial one. If the $\Delta E \sim 0$ rule were more efficient, the transfer should be more important to $J = 33$ in series 1, and to $J = 40$ in series 2, which is not observed in the spectra of Fig. 8. The same remark can be made for the $\Delta J \sim 0$ rule. If this last "propensity rule" were more important, the most intense lines in series 1 and 2 would be those with $J' = 37$, and not $J' = 35$ and 39, respectively. It can be observed that a compromise between these two rules is satisfied, leaving room to believe that a collisional energy transfer is responsible for this phenomenon. However, the asymmetric shift in the intensity profile for series 1 and 2 seems to be proof that, contrary to the suggestion of Katayama,[34,35] that the $\Delta E \sim 0$ rule is not negligible in the transfer process.

It must be noted that possibly a similar phenomena was observed by Engelke, Ennen, and Meiwes-Broer[36] in the NaLi molecule after excitation of the $1\ ^1\Pi(B)$ electronic state with the 496.5 nm Ar^+ laser. Unfortunately, in this article no assignment of the transitions involved in the process, nor the intensity profile of the lines, has been shown, and therefore no comparison can be made.

Considering the work of Hussein et al.[32] in the Na_2 and that of Carrot et al.[33] in the Li_2 case, possible reactions between the NaLi molecules and the Na and Li atoms can be supposed,

$$NaLi(1\ ^1\Pi(B),v_i',J_i') + Na$$
$$\rightarrow NaLi(1\ ^1\Pi(B),v_f',J_f') + Na \pm \Delta E,$$

or

$$NaLi(1\ ^1\Pi(B),v_i',J_i') + Li$$
$$\rightarrow NaLi(1\ ^1\Pi(B),v_f',J_f') + Li \pm \Delta E,$$

where the the Na and Li atoms can be either in their electronic ground state ($3s^2S$ and $2s^2S$, respectively) or in their first excited states ($3p^2P$ and $2p^2P$, respectively). Another possibility is that the reaction partners can be the Ar buffer gas atoms, but they are less numerous in quantity in the reaction region, i.e., in the central part of the heat pipe, and their action in the process may be neglected. Unfortunately, the experimental data concerning this collisional phenomenum is still not sufficient to permit a quantitative study of the problem.

VI. CONCLUSION

In this paper improved molecular constants have been obtained for the $1\ ^1\Sigma^+$ (X) electronic ground state of the NaLi molecule. With these constants an IPA potential curve has been calculated. The van der Waals coefficients and the exchange energy constants have been derived through a study of the long-range tail of the potential curve. A new value for the dissociation energy $D_e = 7105.5 \pm 1\ cm^{-1}$ has been obtained, correcting those reported previously. With this dissociation energy value for the $1\ ^1\Sigma^+$ (X) ground state, the dissociation energy for the excited states of the NaLi molecule observed experimentally[4,5] can be estimated. For the $2\ ^1\Sigma^+$ (A) and the $1\ ^1\Pi(B)$ electronic states that dissociate into the atomic products $Na(3s^2S_{1/2}) + Li^*(2p^2P_{1/2})$, the dissociation limit energy can be derived from the relation,

$$D_e = \sigma[Na(3s) + Li(2p) \rightarrow Na(3s) + Li(2s)]$$
$$+ D_e(1\ ^1\Sigma^+(X)) - T_e.$$

The quantity σ can be obtained from atomic data:[37]

$$\sigma = 14\ 904.00\ cm^{-1},$$

and T_e is the minimum of the potential curve. With $T_e = 14\ 205.28 \pm 0.03\ cm^{-1}$ for the $2\ ^1\Sigma^+$ (A) state[4] and $T_e = 20\ 088 \pm 6\ cm^{-1}$ for the $1\ ^1\Pi(B)$ state,[5] we obtain

$$D_e(2\ ^1\Sigma^+(A)) = 7804.3 \pm 1\ cm^{-1}$$

and

$$D_e(1\ ^1\Pi(B)) = 1921 \pm 6\ cm^{-1}.$$

For the $3\ ^1\Sigma^+$ (C) electronic state[5] the T_e value is equal to $196\ 10.93 \pm 0.03\ cm^{-1}$, and considering that this electronic state dissociates to the atomic products $Na(3p^2P_{1/2}) + Li^*(2s^2S_{1/2})$, the dissociation energy can be calculated by

$$D_e = \sigma[Na(3p) + Li(2s) \to Na(3s) + Li(2s)]$$
$$+ D_e(1\ {}^1\Sigma^+(X)) - T_e.$$

Using $\sigma = 16\,968.00\ cm^{-1}$,[37]

$$D_e(3\ {}^1\Sigma^+(C)) = 4462.67 \pm 1\ cm^{-1}.$$

Some anomalies in the fluorescence spectrum induced by the 476.5 nm of the Ar$^+$ laser line have been observed, and the possibility of these anomalies being generated by a collisional energy transfer is discussed. It is interesting to note that in spite of the observation of the two *propensity rules* $\Delta J \sim 0$ and the $\Delta E \sim 0$, an asymmetry can be observed in the intensity profile of both series. This behavior implies that the $\Delta E \sim 0$ rule is more important than the $\Delta J \sim 0$, at least in the $\Delta v = \pm 1$ collisional energy-transfer conditions, but the lack of experimental data rules out extrapolation.

ACKNOWLEDGMENTS

[1] I. Schmidt-Mink, W. Müller, and W. Meyer, Chem. Phys. Lett. **112**, 120 (1984).

[2] F. Engelke, G. Ennen, and K. H. Meiwes, Chem. Phys. **66**, 391 (1982).

[3] C. E. Fellows, J. Vergès, and C. Amiot, Mol. Phys. **63**, 1115 (1988).

[4] C. E. Fellows, J. Mol. Spectrosc. **136**, 369 (1988).

[5] C. E. Fellows, J. Vergès, and C. Amiot, J. Chem. Phys. **93**, 6281 (1990).

[6] C. R. Vidal and J. Cooper, J. Appl. Phys. **40**, 3370 (1969).

[7] M. M. Hessel and P. Jankowsky, J. Appl. Phys. **43**, 209 (1972).

[8] R. F. Barrow, J. Vergès, C. Effantin, K. Hussein, and J. D'Incan, Chem. Phys. Lett. **104**, 179 (1984).

[9] J. Vergès, R. Bacis, B. Barakat, P. Carrot, S. Churrasy, and P. Crozet, Chem. Phys. Lett. **98**, 203 (1983).

[10] W. M. Kosman and J. Hinze, J. Mol. Spectrosc. **56**, 93 (1975).

[11] C. R. Vidal and H. Scheingraber, J. Mol. Spectrosc. **65**, 46 (1977).

[12] M. Raab, G. Höning, W. Demtröder, and C. R. Vidal, J. Chem. Phys. **76**, 4370 (1982).

[13] C. R. Vidal, *Proceedings of the International Conference on Laser 81* (Society of Optical Quantum Electronics, Mc Lean, VA, 1981), p. 199.

[14] H. Weickenmeier, U. Diemer, M. Wahl, M. Raab, W. Demtröder, and W. Müller, J. Chem. Phys. **82**, 5354 (1988).

[15] C. Amiot, W. Demtröder, and C. R. Vidal, J. Chem. Phys. **88**, 5265 (1988).

[16] R. N. Zare, A. L. Schmeltekopf, W. J. Hartrop, and D. L. Albritton, J. Mol. Spectrosc. **46**, 37 (1973).

[17] R. J. Leroy, *Molecular Spectroscopy, Specialist Periodical Reports* (Chemical Society Burlington House, London, 1973), Vol. 1, p. 113.

[18] R. J. Leroy and R. B. Bernstein, J. Chem. Phys. **52**, 3869 (1970).

[19] T. R. Proctor and W. C. Stwalley, J. Chem. Phys. **66**, 2063 (1977).

[20] K. T. Tang, J. M. Norbeck, and P. R. Certain, J. Chem. Phys. **64**, 3063 (1976).

[21] M. E. Rosenkrantz, R. M. Regan, and D. D. Konowalow, J. Phys. Chem. **89**, 2804 (1985).

[22] B. Bussery, Y. Achkar, and M. Aubert-Frécon, Chem. Phys. **116**, 319 (1987).

[23] W. Müller, J. Flesch, and W. Meyer, J. Chem. Phys. **80**, 3297 (1984).

[24] A. Dalgarno and W. D. Davison, Mol. Phys. **13**, 479 (1967).

[25] M. Movre and R. Beuc, Phys. Rev. A **31**, 2957 (1985).

[26] E. A. Mason and L. Monlick, *Advances in Chemical Physics*, edited by J. O. Hirschfelder (Wiley, New York, 1967), Vol. XII, p. 329.

[27] H. O. Knox and M. R. H. Rudge, Mol. Phys. **17**, 377 (1969).

[28] D. D. Konowalow and M. E. Rosenkrantz, J. Phys. Chem. **86**, 1099 (1982).

[29] R. J. Leroy, Can. J. Phys. **52**, 246 (1974).

[30] I. Schmidt-Mink, W. Müller, and W. Meyer, Chem. Phys. **92**, 263 (1985).

[31] J. Vergès, R. Bacis, B. Barakat, P. Carrot, S. Churassy, and P. Crozet, Chem. Phys. Lett. **98**, 203 (1983).

[32] K. Hussein, M. Aubert-Frécon, O. Babaky, J. D'Incan, and J. Vergès, J. Mol. Spectrosc. **114**, 105 (1985).

[33] F. Carrot, M. Aubert-Frécon, R. Bacis, S. Churrassy, and J. Vergès, Phys. Rev. Lett. **57**, 420 (1986).

[34] D. H. Katayama, J. Chem. Phys. **81**, 3495 (1984).

[35] D. H. Katayama, Phys. Rev. Lett. **54**, 657 (1985).

[36] F. Engelke, G. Ennen, and K. H. Meiwes-Broer, Chem. Phys. **83**, 187 (1984).

[37] C. E. Moore, *Atomic Energy Levels* (U.S. GPO, Washington, DC, 1949), Vol. 1.