Experimental Observation of the NaLi Molecule*

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The existence of a stable NaLi molecule has been demonstrated for the first time. Spectra of the Na^7Li molecule were produced by laser excitation. With the aid of the technique of collision-induced energy transfer the molecular constants have been determined and the excited level assigned to a $^1\Pi$ electronic state. The measured molecular constants are within 10 % of the Na^7Li constants predicted by *ab initio* calculations.

Recently, ab initio calculations[1] for the NaLi molecule predicted this species to be stable and also predicted its molecular constants. This fourteen-electron system is one of the larger systems for which ab initio calculations have provided such information. In addition, NaLi is the first polar molecule studied by the optimized valence configuration method[1] (a restricted form of the multiconfiguration self-consistent field technique). Previous investigators[2,3] have failed to observe the spectrum of NaLi probably because of overlap with those of Na_2 and Li_2. The observations reported in this paper are the first to provide information about the NaLi molecule and allow the determination of the NaLi molecular constants.

A laser-induced fluorescence technique[4-6] has been used to produce a NaLi spectrum. Sodium and ^7Li (99.8%) were placed in a stainless-steel heat-pipe oven[7] in which argon was used as a buffer gas. The oven was made in the form of a right-angle cross. The beam from an Ar^+ laser entered the oven and induced fluorescence of Na_2 at 450°C and Li_2 and NaLi at 650°C with an argon pressure of 3-5 Torr. The fluorescence was photographed on a 3.4-m Ebert grating spectrograph whose axis was perpendicular to the laser beam. The 4965-Å Ar^+ line induced an intense Na^7Li R-P doublet series as well as a strong $^7Li_2$ and a weak Na_2 fluorescent series.

The laser line excites the molecule from a ground state vibrational, v'', and rotational, J'', level to an upper excited electronic state (v', J'). The molecule decays to the ground state giving a fluorescence series of single lines (Q branch) if $\Delta J = 0$ or doublets for $\Delta J = \pm 1$ (P and R branches).[8] The transition frequency to the ground state, ν, can be expressed in terms of the molecular constants and quantum numbers of the ground and excited states:

$$\nu = T_e + G'(v' + \tfrac{1}{2}) + B_{v'}'(J')(J'+1) - D_{v'}'[(J')(J'+1)]^2 - \omega_e''(v''+\tfrac{1}{2}) - \omega_e'' x_e''(v''+\tfrac{1}{2})^2 - \omega_e'' y_e''(v''+\tfrac{1}{2})^3 + \cdots$$

$$- [B_e'' - \alpha_e''(v''+\tfrac{1}{2})]J''(J''+1) + D_{v'}'[J''(J''+1)]^2 + \cdots, \qquad (1)$$

where T_e is the separation between the minima of the ground-state and excited electronic-state potential curves, and $G'(v'+\tfrac{1}{2})$ is the upper-state vibrational term value. The ground-state vibrational term value is explicitly written out as well as the dependence of the rotational constant on vibrational level. The effects of higher order vibrational and rotational terms are small and can be neglected with respect to the precision of these experiments.

The frequencies of the NaLi R-P series induced

Table I. Frequencies, in cm^{-1}, of the intense Na^7Li fluorescence induced by the 4965-Å Ar^+ line $(v', J'=28) \to (v'', J''=27, 29)$.

v''	$\nu_R(27)$	$\nu_{obs}-\nu_{calc}$ [a]	$\nu_P(29)$	$\nu_{obs}-\nu_{calc}$ [a]
0	20 178.62	0.01	20 135.08 [b]	0.00
1	19 927.93	−0.02	19 884.81	0.00
2	...	...	...	...
3	19 436.55	0.00	19 394.19	−0.03
4	19 195.91	0.02	19 154.00	0.03
5	18 958.68	0.01	18 917.17	0.02
6	18 724.89	−0.03	18 683.78	−0.02
7	18 494.70	0.00	18 453.96	−0.01
8	18 268.04	0.00	18 227.69	0.01

[a] The least-square constants from fit of data, $\omega_e'' - \alpha_e''(J'')(J''+1)$, $\omega_e'' X_e''$, $\omega_e'' y_e''$, are 253.90, 1.608, 0.0078 cm^{-1}, respectively, for the R branch and 253.52, 1.616, 0.0072 cm^{-1} for the P branch.

[b] Laser line.

by the 4965-Å Ar^+ line are shown in Table I. The laser doublet frequencies are assigned $v''=0$ since no anti-Stokes doublets have been observed. It is possible that the actual v'' may be larger than this but in general, for Na_2 and Li_2, with a laser-excited level of $v''>0$ the anti-Stokes lines have been observed. The rotational quantum numbers are determined from further data to be discussed later. From Eq. (1) we see that the frequencies of each series may be fitted by a cubic polynomial in $(v''+\frac{1}{2})$. The fit is excellent; the differences between the observed and calculated line positions are less than 0.03 cm^{-1} and are given in Table I. The constants obtained by fitting the data are $\omega_e'' - \alpha_e''(J'')(J''+1)$, $\omega_e'' x_e''$, and $\omega_e'' y_e''$ and are given in Table I for each series.

To obtain ω_e'' and α_e'' the rotational numbering, J'', and the rotational constants, $B_{v''}''$, must be determined for at least two vibrational levels. This is done with the experimental technique of collision-induced energy transfer.[5,6,9] An increase in the temperature and pressure of the heat pipe above that at which fluorescence lines were first observed produced weak satellite lines centered about the R-P doublets. The lines occur because the molecules in excited (v', J') states are transferred by collisions to other rotational levels of the same v' state, from which they then produce a fluorescent series. The frequencies of satellite lines were assigned either to R, P, or Q transitions. The presence of Q-branch lines indicates that the upper excited state is a $^1\Pi$ electronic level. The relative rotational numbering between the R and P branches is easily established since the intense laser-ex-

cited doublets belong to the same J' level. From Eq. (1) we find that $\Delta_2 F'' = \nu_R(J') - \nu_P(J') \approx 4B_{v''}''(J'+\frac{1}{2})$. A plot of $(J'+\frac{1}{2})$ or any arbitrary integer numbering of the R-P doublets against the observed $\Delta_2 F''$ values should yield $B_{v''}''$ and the absolute rotational numbering. From the raw data in Table II for which both R and P branch frequencies have been measured the $\Delta_2 F''$ values can be determined and the rotational numbering established, within a J' of 1.

If we substitute $\Delta J = 0, \pm 1$ into Eq. (1) we find

$$\nu = \nu_{v', v''} + (B_{v'}' + B_{v''}'')mq + (B_{v'}' - B_{v''}'')m^2 + \delta(J)(J+1)s + (D_{v'}' + D_{v''}'')m^3 q + \cdots, \quad (2)$$

where $\nu_{v', v''} = T_e + G'(v'+\frac{1}{2}) - G''(v''+\frac{1}{2})$ and $m=J$ for the R branch and $-(J+1)$ for the P branch, with $q=1$ and $s=0$ for the R and P branches. For the Q branch $m^2 = J(J+1)$, $q=0$, and $s=1$. The constant δ is the lambda doubling constant,[8] and it is assumed that the rotational constants are related by $B_{v'}'(R$-P branch$) = B_{v'}'(Q$ branch$) + \delta'$. To obtain the absolute rotational numbering more precisely, all the observed data in Table II were independently fitted for $v''=0$ and for $v''=1$ by a polynomial of the form of Eq. (2). The smoothed data were then used to compute the $\Delta_2 F''$ values and the rotational numbering. The values of J' for both the $v''=0$ and $v''=1$ vibrational levels agree within 0.1 of the assigned quantum number. The 4965-Å laser line excites the $^1\Sigma(v''=0, J'' =29)$ ground state to the $^1\Pi(v', J'=28)$ excited state. The values of the rotational constants can now be obtained by a least-squares fit of the data in Table II by Eq. (2) for each vibrational level. In this table the differences, $\Delta\nu$, between the ob-

Table II. Observed frequencies, in cm^{-1}, of satellite lines induced by collisions.

J'	ν_R	I	$\Delta\nu$	ν_Q	I	$\Delta\nu$	ν_P	I	$\Delta\nu$
$v''=0$									
19	20208.52	2	$-.12$						
20	20205.98	3	$-.04$						
21	20203.08	2	$-.14$						
22	20200.26	1	.02						
23	20197.22	4	.12				20160.79[b]	2	$-.05$
24	20193.92	5	.14	20175.17	4	$-.06$	20156.11[b]	2	.07
25	20190.43	7	.15	20170.93	7	$-.03$	20151.11	4	.03
26	20186.68	10	.06	20166.50	7	$-.02$	20146.02	5	.06
27	20182.85	9	.07	20161.95	8	$-.04$	20140.72	10	.04
28	20178.62	a	$-.14$	20157.27	7	.00	20135.08	a	$-.15$
29	20174.56	8	.02	20152.30	8	.02	20129.65	10	.04
30	20170.21	8	.00	20147.22	5	.00	20123.87	7	.04
31	20165.68	3	.01	20142.01	5	.06	20117.93	4	.04
32	20160.79[b]	2	$-.17$	20136.60	2	.08	20111.76	3	$-.03$
33	20.156.11[b]	2	.04	20130.98	2	$-.03$	20105.51	2	$-.01$
34				20125.21	2	.04	20099.04	1	$-.05$
35				20119.23	1	$-.03$			
36				20113.17	1	$-.03$			
37				20106.98	1	.04			
38				20100.42	1	$-.02$			
$v''=1$									
25	19938.88	2	$-.04$				19900.24	1	.05
26	19935.57	3	.13	19915.60[b]	8	.02	19895.26	3	.01
27	19931.85	9	.05	19911.17[b]	8	$-.02$	19890.18	10	.03
28	19927.93	a	$-.07$	19906.61	6	$-.04$	19884.81	a	$-.08$
29	19924.00	9	$-.03$	19901.92	8	$-.01$	19879.45	8	$-.02$
30	19919.83	8	$-.07$	19897.05	5	$-.02$	19873.88	4	$-.01$
31	19915.60[b]	8	.00	19892.02	3	$-.02$	19868.19	6	.04
32	19911.17[b]	8	.04	19886.80	1	$-.04$	19862.23	3	$-.02$
33				19881.55	1	.07			
34				19876.00		.04			

[a]These lines are from the main fluorescence series and are very intense.

[b]These lines are assigned twice.

served values and those calculated by a least-squares fit and the intensities, I, of the satellite lines are shown. The constants determined by this least-squares fit are given in Table III. Only constants through the term $(D_{v'}{}' + D_{v''}{}'')$ were found to be significant. The value of $\alpha_e{}''$ may be obtained most accurately from the differences between the $B_{v'}{}' - B_{v''}{}''$ values of the $v'' = 0$ and

$v''=1$ levels since these are small numbers. With the knowledge of J' and $\alpha_e{}''$ we can obtain $\omega_e{}''$ as described previously. As an independent check we may also compute $\omega_e{}''$ from $\nu_{v',0} - \nu_{v',1} = G''(0 + \frac{1}{2}) - G''(1 + \frac{1}{2}) = \omega_e{}'' - 2\omega_e{}'' x_e{}''$. The two methods yield $\omega_e{}'' = 256.6$ and 256.7 cm^{-1}, respectively. The same excited-state rotational constant, $B_{v'}{}'$, is obtained from the least-squares fit to the v''

Table III. Determination of molecular constants, in cm^{-1}, from least-squares fit of satellite frequencies by Eq. (2).

	$v'' = 0$	$v'' = 1$
$\nu_{v',v''}$	$20\,226.01 \pm 0.05$	$19\,972.56 \pm 0.06$
$B_{v'}{}'$	0.309 ± 0.003	0.305 ± 0.003
$B_{v''}{}''$	0.394 ± 0.003	0.385 ± 0.003
$B_{v'}{}' - B_{v''}{}''$	$-0.084\,56 \pm 0.000\,11$	$-0.080\,98 \pm 0.000\,08$
$B_{v'}{}' + B_{v''}{}''$	0.7035 ± 0.0022	0.6900 ± 0.0029
δ'	$-(1.9 \pm 0.2) \times 10^{-4}$	$-(2.0 \pm 0.2) \times 10^{-4}$
$D_{v'}{}' + D_{v''}{}''$	$-(3.0 \pm 0.3) \times 10^{-5}$	$-(1.8 \pm 0.3) \times 10^{-5}$

Table IV. Molecular constants for the Na^{7}Li molecule, in cm^{-1}.

	Na^{7}Li[a] (expt)	Na^{7}Li[a] (theory)	Na$_2$[c]	Li$_2$[c]
	$^1\Sigma$ ground state			
ω_e	256.8	248–250	159.13	351.43
$\omega_e x_e$	1.612		0.726	2.610
$\omega_e y_e$	-7.5×10^{-3}		-9.2×10^{-4}	-2.95×10^{-3}
B_e	0.396	0.361	0.1548	0.6726
α_e	3.6×10^{-3}		8.56×10^{-4}	6.87×10^{-3}
	$^1\Pi$ excited state			
B_e	0.307[f]		0.1107[e]	0.4975[e]
δ	2.0×10^{-4}			1.8×10^{-4} [e]

[a] This work. The uncertainty is in the last place.
[b] See Ref. 1.
[c] See Ref. 5.
[d] See Ref. 4.
[e] See Ref. 8.
[f] This is $B_v{}'$, where v' is unknown.

=0 and to $v''=1$ data, within experimental error.

As a further check of the data the $\Delta_2 F' = \nu_R(J'+1) - \nu_P(J'-1) \approx 4B_{v'}{}'(J'+\frac{1}{2})$ depends only on the upper state and must be the same for $v''=0$ and for $v''=1$. The $\Delta_2 F'$ values computed from the $v''=1$ observed frequencies and compared with those of $v''=0$ for the same J' agree within an experimental error of about 0.15 cm^{-1}.

The final molecular constants for Na^{7}Li along with theoretical values and those of Na$_2$ and Li$_2$ are presented in Table IV. The values of all the NaLi constants fall between those of Na$_2$ and Li$_2$, as might be expected. For the diatomic sodium and lithium molecules the theoretical values of ω_e'' agree within 10% and B_e'' within 3% of the measured values.[10] The ω_e'' obtained in this work is in excellent agreement with theory but the B_e'' differs by about 10%, somewhat higher than expected.[10] If the vibrational quantum numbers v'' were incorrectly assigned they would have to be increased thereby increasing the discrepancy between the experimental and theoretical values of both constants.

The existence of a stable NaLi molecule has been demonstrated. The values of the molecular constants obtained agree with those predicted by ab initio calculations to within 10%. The technique of collision-induced energy transfer allowed the assignment of the rotational numbering and the determination of the molecular constants and configuration of the upper electronic state.

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[1] P. J. Bertoncini, G. Das, and A. C. Wahl, J. Chem. Phys. 52, 5112 (1970).
[2] J. M. Walter and S. Barratt, Proc. Roy. Soc., Ser. A 119, 257 (1958).
[3] B. B. Phillips, H. M. Froslie, and R. H. McFarland, Phys. Rev. 81, 898 (1951).
[4] W. Demtroder, M. McClintock, and R. N. Zare, J. Chem. Phys. 51, 5495 (1969), and references contained therein.
[5] R. Velasco, Ch. Ottinger, and R. N. Zare, J. Chem. Phys. 51, 5522 (1969).
[6] K. Sakurai, S. E. Johnson, and H. P. Broida, J. Chem. Phys. 52, 1625 (1970).
[7] Details of this heat pipe are in preparation for publication. Also see C. R. Vidal and J. W. Cooper, J. Appl. Phys. 40, 3370 (1969).
[8] G. Herzberg, Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules (Van Nostrand, Princeton, N. J., 1950).
[9] Ch. Ottinger, R. Velasco, and R. N. Zare, J. Chem. Phys. 52, 1636 (1970).
[10] A. C. Wahl, private communication.