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Laser-induced Fluorescence of the NaCs Molecule

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Laser-induced fluorescence of NaCs is observed when a mixture of sodium and cesium is irradiated by the 5682 Å laser line. The spectroscopic constants of the ground state $X\,^1\Sigma^+$ have been determined and the potential energy curve was calculated by the RKR method. The excited state was identified as $D\,^1\Pi$, and the potential curve was estimated from the analysis of the fluorescence intensities.

The alkali heteronuclear diatomic molecule NaCs coexists with sodium and cesium atoms and Na_2 and Cs_2 molecules in the vapor of a mixture of sodium and cesium metals. Liveing and Dewar[1] referred an absorption in the yellow-green either to Cs_2 or to NaCs. Walter and Barratt[2] concluded that this absorption is due to the NaCs molecule, and they found another band of NaCs molecule in the violet region between 4315 and 3930 Å. Weizel and Kulp[3] assigned the lines observed by Walter and Barratt. According to their study, the vibrational constants ω_e are 98±1, 65±2, and 60±3 $\mathrm{cm^{-1}}$ for the ground state, the yellow-green band, and the violet band, respectively.

The absorption of NaCs in the yellow-green region is overlapped with that of Cs_2, and spectroscopic analysis of the absorption spectrum is very difficult. However, a suitably chosen laser line may excite the NaCs molecule to only one specific rotational-vibrational level of the excited state. The resulting fluorescence will be simple, and it will be superior for studying such mixed alkali metal molecules. Nevertheless, no study of the laser-induced fluorescence of NaCs has been reported. We have succeeded in observing the fluorescence spectrum of the NaCs molecule; the results will be reported in this article.

As in the case for NaK,[4] we denote the ground and low-lying molecular states resulting from ground and excited atoms of Na and Cs as follows: $X\,^1\Sigma^+$ and $a\,^3\Sigma^+$ (from Na 3 ^{2}S+Cs 6 ^{2}S); $A\,^1\Sigma^+$, $b\,^3\Pi$, $B\,^1\Pi$, and $c\,^3\Sigma^+$ (from Na 3 ^{2}S+Cs 6 ^{2}P); $C\,^1\Sigma^+$, $d\,^3\Pi$, $D\,^1\Pi$, and $e\,^3\Sigma^+$ (from Na 3 ^{2}P+Cs 6 ^{2}S);···. In addition to these, there are molecular states resulting from Na 3 ^{2}S and Cs 5 ^{2}D. The states will have a shallow potential minimum at long internuclear distance, but the excited state of the yellow-green band is known to have a potential curve of $\omega_e=65\pm2\ \mathrm{cm^{-1}}$ and the anharmonicity is not so large.[3] Therefore we will not take account of these states in the present analysis.

Experimental

Cesium metal, which was 99.9% pure and contained sodium as 0.1% impurity, was enclosed in an optical cell and heated to a temperature of about 570 K. The vapor pressure of Na, Na_2, Cs, and Cs_2 at 570 K are 1.3×10^{-2}, 1.2×10^{-4}, 2.2, and 1.3×10^{-2} Torr (1 Torr=133.322 Pa), respectively,[5] and that of NaCs is estimated to be 2.6×10^{-3} Torr by means of the Gibson-Heitler equation.[6] The experimental arrangement to observe the fluorescence spectrum is the same as our previous report.[7] A polarization scrambler was placed in front of the entrance slit of the spectrometer. Polarization of the fluorescence line was observed by placing a polarization analyser between the sample and the polarization scrambler. The intensity of the fluorescence line polarized parallel to the polarization of the laser line, $I_{/\!/}$, and the one polarized perpendicular to the direction of polarization of laser line, $I_\perp$, were observed.

Results and Discussion

When the cell which contained a mixture of sodium and cesium was irradiated by the 5682 Å $\mathrm{Kr^+}$ laser line, several series of fluorescence lines with a vibrational spacing of about 99 $\mathrm{cm^{-1}}$ at the high energy end were observed in the region between 17000 and 18400 $\mathrm{cm^{-1}}$. The vibrational spacing is close to that of NaCs, which was assigned by Weizel and Kulp.[3] The vibrational constants ω_e of the coexisting molecules Cs_2 and Na_2 are known to be about 42 and 159 $\mathrm{cm^{-1}}$, respectively.[8] Therefore the observed lines can be identified as those of the NaCs molecule. One of the fluorescence spectra is shown in Fig. 1. The predominant lines are a series of *P* and *R* doublets of a large rotational quantum number *J*. When the frequency of the laser line was changed slightly by changing the angle of the etalon installed within the laser cavity, another series of fluorescence lines, as shown in Fig. 2, was observed. Whether an observed series of line is formed by a *Q*-branch or closely spaced *P*- and *R*-branches of small *J* has been distinguished by measuring the degree of polarization. The degree of polarization[9]

$$P_l=\frac{I_{/\!/}-I_\perp}{I_{/\!/}+I_\perp}, \tag{1}$$

of the lines of singlet bands in resonance fluorescence excited by linearly polarized light are given by[10]

$$P_l[P\text{ branch excited by }P(J)\text{ line}]=\frac{2J^2-5J+3}{14J^2+5J+1}, \tag{2}$$

$$P_l[R\text{ branch excited by }P(J)\text{ line}]=\frac{1}{7}, \tag{3}$$

$$P_l[P\text{ branch excited by }R(J)\text{ line}]=\frac{1}{7}, \tag{4}$$

$$P_l[R\text{ branch excited by }R(J)\text{ line}]=\frac{2J^2+9J+10}{14J^2+23J+10}, \tag{5}$$

$$P_l[Q\text{ branch excited by }Q(J)\text{ line}]=\frac{4J^2+4J-3}{8J^2+8J-1}. \tag{6}$$

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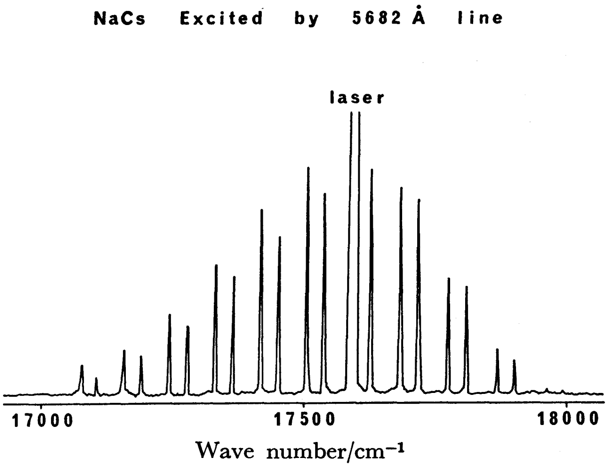

Fig. 1. Fluorescence spectrum of NaCs excited by a single mode 5682 Å line of Kr$^+$ laser. This P and R doublet series is assigned as the $D\,^1\Pi(v'=0,\ J'=109)\rightarrow X\,^1\Sigma^+(v'',J''=108$ and $110)$ transitions.

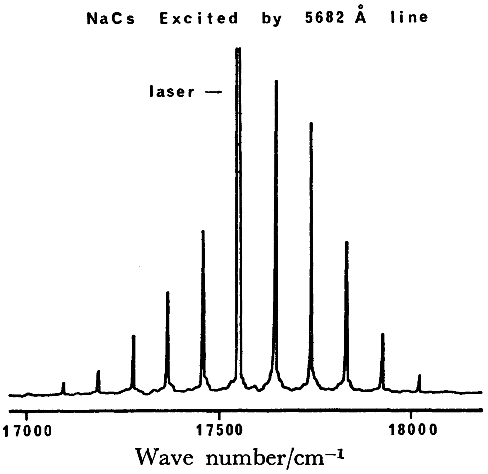

Fig. 2. Fluorescence spectrum of NaCs excited by another single mode 5682 Å line of Kr$^+$ laser. This fluorescence is assigned as a Q-line series of $D\,^1\Pi(0,\ J)\rightarrow X\,^1\Sigma^+(v'',\ J)$ transition. The value of J could not be assigned.

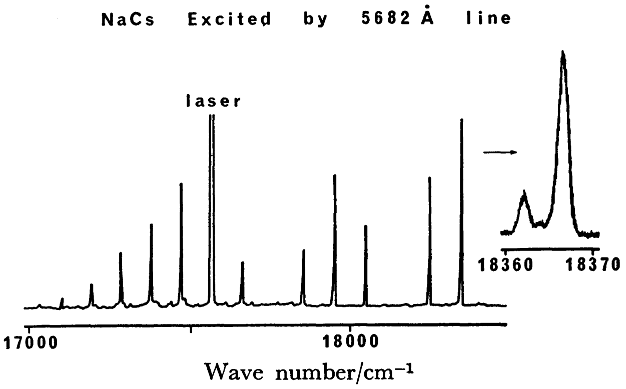

Fig. 3. Fluorescence spectrum of NaCs excited by another single mode 5682 Å line of Kr$^+$ laser. Each line at low resolution is composed of doublet lines of different intensities at high resolution as shown on the right. These lines are assigned as a series of $D\,^1\Pi(2,\ 18)\rightarrow X\,^1\Sigma^+(v'',J''=17$ and $19)$ transitions and a series of $D\,^1\Pi(2,\ 12)\rightarrow X\,^1\Sigma^+(v'',\ 12)$ transitions. The transitions $D\,^1\Pi(2,\ 18)\rightarrow X\,^1\Sigma^+(v'',\ 17)$ and $D\,^1\Pi(2,\ 12)\rightarrow X\,^1\Sigma^+(v'',\ 12)$ could not be resolved in the present resolution limit.

The fluorescence lines. in Fig. 2 are identified as a Q line from the polarization measurement, since the degree of polarization was observed to be 0.5 The intensity decreases monotonically on either side of a single intensity maximum, and this is the same for fluorescence in Fig. 1. This result suggests that the fluorescence in Figs. 1 and 2 originates from the $v'=0$ level.

After the same procedure of changing the laser line, another series of fluorescence lines, shown in Fig. 3, was observed. This spectrum exhibits three intensity maxima. Therefore, it is reasonable to suppose that the fluorescence originates from the $v'=2$ level. Each fluorescence line in a low resolution spectrum was found to be composed of doublet lines of different intensities in a high resolution spectrum (See Fig. 3). If the doublet lines are P and R doublets from the same upper state$(v',\ J')$ level, the rotational quantum number J' is estimated to be about 18 from the spacing between the P line and the R line. The line strengths of P and R doublets of such J' are expected to have almost the same magnitude.$^{9)}$ The degree of polarization was 0.1 for the line on the low-energy side and 0.3 for the line on the high-energy side. Thus we identified a fluorescence series of P and R lines and another fluorescence series of a Q line for the spectrum in Fig. 3, where an R line of a P and R doublets fluorescence series is overlapped with a Q line of another fluorescence series.

For a $^1\Pi$–$^1\Sigma$ transition, only Q lines appear in fluorescence for excitation by a Q line and both P and R lines appear for excitation by a P or R line. On the other hand, only $\Delta J=\pm 1$ transitions are allowed for $^1\Sigma$–$^1\Sigma$ transition and $\Delta J=0$ is forbidden.$^{9)}$ We observed both Q-line series and P- and R-lines series for the yellow-green band of NaCs, but not P, Q, and R triplets from the same upper state$(v',\ J')$ level. This band system is thus identified as a $^1\Pi$–$^1\Sigma$ transition.

Since the vibrational quantum numbers v' of the excited levels are small in the present case, it is easy to assign the v'' and v' quantum numbers to each line. The rotational numbering is more difficult, especially for Q-line series. It is necessary to know the rotational constant B_e in order to assign J, but the value is not known yet. We assumed therefore a tentative constant B_e which was estimated by additivity of atomic radii,$^{11)}$ and we estimated the rotational numbering for a P and R doublet series. The rotational constants are determined by making a least-squares fit of the spacing between the two doublet members $(v'',\ J'+1)$ and $(v'',\ J'-1)$ of fluorescence series against v''. Then the members of another series are identified and assigned. This procedure is repeated until all the observed series can be assigned consistently. The spectroscopic constants of the ground state are improved by making a least-squares fit to all the lines in different series. The resulting spectroscopic constants of the $X\,^1\Sigma^+$ ground state are listed in Table

Table 1. Spectroscopic constants for the $X\,^1\Sigma^+$ and $D\,^1\Pi$ states of the NaCs molecule (cm^{-1})

	$X\,^1\Sigma^+$	$D\,^1\Pi$
ω_e	99.389	65.0
$\omega_e x_e$	0.380	0.293
$\omega_e y_e$	1.804×10^{-3}	
B_e	5.732×10^{-2}	4.69×10^{-2}
α_e	5.824×10^{-4}	3.05×10^{-4}
D_e	-8.598×10^{-7}	
β_e	-6.646×10^{-9}	
T_{00}	0	18250
D^e	4800[a)]	3600[a)]
R_e/Å	3.874	4.28

a) Estimated value. See text.

1, and the assignment of each fluorescence series is described in the caption of each spectrum.

Since the excited state is found to be $^1\Pi$, the state is either the $B\,^1\Pi$ state, which decomposes into Na(3 ^{2}S) and Cs(6 ^{2}P), or the $D\,^1\Pi$ state, which decomposes into Na(3 ^{2}P) and Cs(6 ^{2}S). The dissociation energy of the $X\,^1\Sigma^+$ ground state is roughly estimated as 4800 cm^{-1}, which is the average value of dissociation energies of Na_2 and Cs_2. The dissociation limit of the $B\,^1\Pi$ state will be then 16532 cm^{-1} from the bottom of the potential curve of the $X\,^1\Sigma^+$ state, where 16532 cm^{-1} is the sum of the dissociation energy of the $X\,^1\Sigma^+$ state and the energy of the atomic line Cs(6 $^2P_{3/2}\rightarrow$6 $^2S_{1/2}$). The excitation energy of the 5682 Å (17595 cm^{-1}) laser line exceeds the dissociation limit. The excited state is therefore identified as the $D\,^1\Pi$ state. Although there will be some error in the estimation of the dissociation energy of the $X\,^1\Sigma^+$ state, we are convinced this identification to be correct because the 5682 Å laser line excited to the levels of small vibrational quantum numbers v'; hence the excited level should be close to the potential minimum.

Since the number of excitations is small in the present study, we could not determine the spectroscopic constant of the excited state from the analysis of energies of the excited levels alone. Since the vibrational quantum number of the excited level is small, we would be able to estimate the equilibrium internuclear distance with a reasonable accuracy from the analysis of the intensity distribution of the fluorescence lines.

The intensity for the emission of a light quantum $h\nu$ in an electric dipole transition can be written as

$$I(e'v'J' \rightarrow e''v''J'') \propto \mu_e^2\nu^4|\langle v'|v''\rangle|^2, \qquad (7)$$

where μ_e is the electronic transition moment and $|v'\rangle$ and $|v''\rangle$ are the vibrational wave functions of the initial and final state. Here the electronic transition moment is assumed to be independent of the internuclear distance in the range of vibration, since the vibrational quantum number of the excited level is small. The vibrational wave functions appropriate to any one-dimensional potential are obtained by solving the radial Schrödinger equation,[12)] and the Franck-Condon factor $|\langle v'|v''\rangle|^2$ can be calculated.

The potential curve of the $X\,^1\Sigma^+$ state is calculated by the RKR method[13)] from the molecular constants listed in Table 1. The potential curve of the $D\,^1\Pi$ state is approximated by a Morse function. The vibrational constant ω_e is assumed to be 65 cm^{-1}. The dissociation limit will be at 16956 cm^{-1} above the dissociation limit of the $X\,^1\Sigma^+$ state, where 16956 cm^{-1} is the energy of the atomic line Na(3 $^2P_{1/2}\rightarrow$ 3 $^2S_{1/2}$). The energy of the excited vibrational level is known from the assignment. The Morse function is therefore fixed if the equilibrium internuclear distance R_e is determined.

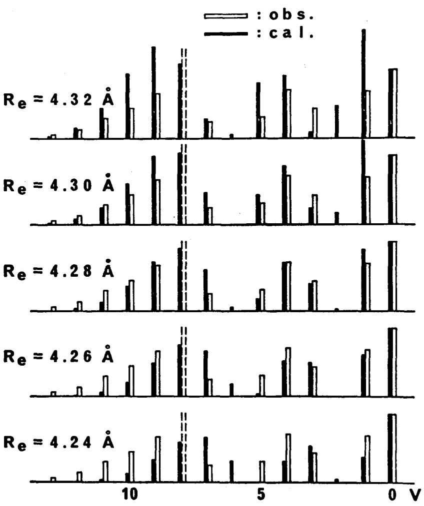

Fig. 4. Comparison of the observed (open bars) and calculated (full bars) intensity distribution $\nu^4|\langle v'|v''\rangle|^2$ of the $D\,^1\Pi(v'=2)\rightarrow X\,^1\Sigma^+(v'')$ transitions for five different values of equilibrium internuclear distance of the $D\,^1\Pi$ state.

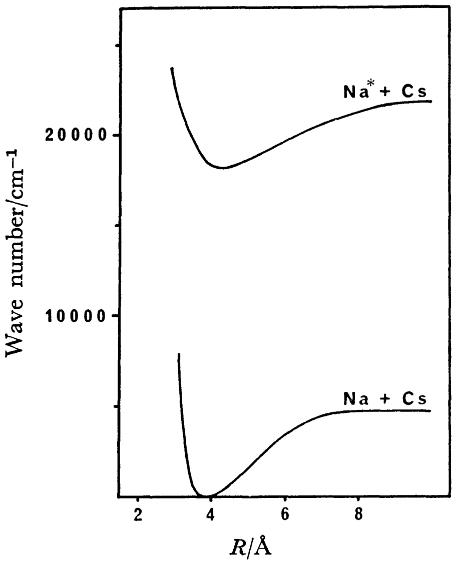

Fig. 5. Potential energy curves for NaCs. The potential curve of the $X\,^1\Sigma^+$ state is calculated by the RKR method. The potential curve of the $D\,^1\Pi$ state is approximated by a Morse function. The spectroscopic constants of these are listed in Table 1.

We have calculated the intensity distribution of the fluorescence lines as a function of R_e. The results are schematically shown in Fig. 4. The equilibrium internuclear distance of the $D\,^1\Pi$ state is determined to be 4.28±0.01 Å. The resulting molecular constants are listed in Table 1, and the potential curves of the $X\,^1\Sigma^+$ and $D\,^1\Pi$ states are schematically shown in Fig. 5.

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References

1) G. D. Liveing and J. Dewar, *Proc. R. Soc. London*, **27**, 350 (1878).

2) J. M. Walter and S. Barratt, *Proc. R. Soc. London, Ser. A*, **119**, 257 (1928).

3) W. Weizel and M. Kulp, *Ann. Phys. (Leipzig)*, **4**, 971 (1930).

4) H. Katô and C. Noda, *J. Chem. Phys.*, **73**, 4940 (1980).

5) A. N. Nesmeyanov, "Vapor Pressure of the Chemical Elements," Elsevier, New York (1963).

6) G. E. Gibson and W. Heitler, *Z. Phys.*, **49**, 465 (1928).

7) H. Katô, T. Matsui, and C. Noda, *J. Chem. Phys.*, **76**, 5678 (1982).

8) K. P. Huber and G. Herzberg, "Constants of Diatomic Molecules," Van Nostrand Reinhold, New York (1979), pp. 188 and 432.

9) G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand Reinhold, New York (1950), pp. 305 and 208.

10) P. P. Feofilov, "The Physical Basis of Polarised Emission," Consultants Bureau, New York (1961), p. 101.

11) P. J. Dagdigian and L. Wharton, *J. Chem. Phys.*, **57**, 1487 (1972).

12) R. N. Zare, *J. Chem. Phys.*, **40**, 1934 (1964).

13) R. Rydberg, *Z. Phys.*, **73**, 376 (1931); O. Klein, *ibid.*, **76**, 226 (1932); A. L. G. Rees, *Proc. Phys, Soc., Ser. A*, **59**, 998 (1947).