

Relative photodissociation cross-section of NaCs molecule, using argon ion laser lines

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Abstract. Laser-induced photodissociation of NaCs molecule has been observed when a mixture of Na and Cs metal vapour in a glass cell was irradiated by most of the lines of an argon ion laser. The photodissociation results in the 3P state of Na atoms which is correlated with the $F^1\Sigma^+$ and $G^1\pi$ molecular states of NaCs. Distribution of photofragments over fine structure components $3^2P_{3/2}$ and $3^2P_{1/2}$ of Na has been studied. The ratio of intensity of D_2 line (5890 Å) to D_1 line (5896 Å) of Na varies from around 2 at 5145 Å to about 3.5 at 4579 Å. The relative photodissociation cross-section increases monotonically as the wavelength of laser light decreases from 5145 Å to 4579 Å. It is seen that the 4579 Å photon is about 200 times more effective than the 5145 Å photon in causing the photoreaction $\text{NaCs} + (\text{Ar}^+ \text{ photon}) \rightarrow \text{Na}^*(3P) + \text{Cs}(6S)$.

Keywords. NaCs; photodissociation; argon ion laser.

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1. Introduction

Photodissociation of alkali dimers is a widely studied phenomenon. Absolute photodissociation cross sections have been measured for Na_2 and K_2 (Janson and Papernov 1982) and for Rb_2 (Papernov *et al* 1984). Rothe *et al* (1980) studied the distribution of photofragments over fine structure levels in an experiment using argon ion laser to photodissociate Na_2 and Rb_2 using supersonic molecular beams. From the distribution they could conclude that Na_2 photodissociates in $B^1\pi_u$ and that Rb_2 is first excited to the $C^1\pi_u$ state followed by predissociation into $B^1\pi_u$ state. Similar experiment was done by Feldman and Zare (1976) with Rb_2 . Their work was also the first example of the production of a single fine structure component in photodissociation. As far as we know there exists no experimental study of photodissociation of NaCs. In their laser-induced fluorescence work on NaRb molecule, Takahashi and Kato (1981) observed atomic NaD lines which they ascribe to the photodissociation of NaRb molecule. However, no quantitative study was done.

2. Experimental procedure

The experimental arrangement is shown in figure 1. A small amount of alkali metal is introduced in a pyrex cell, which is placed inside a double-walled pyrex furnace for

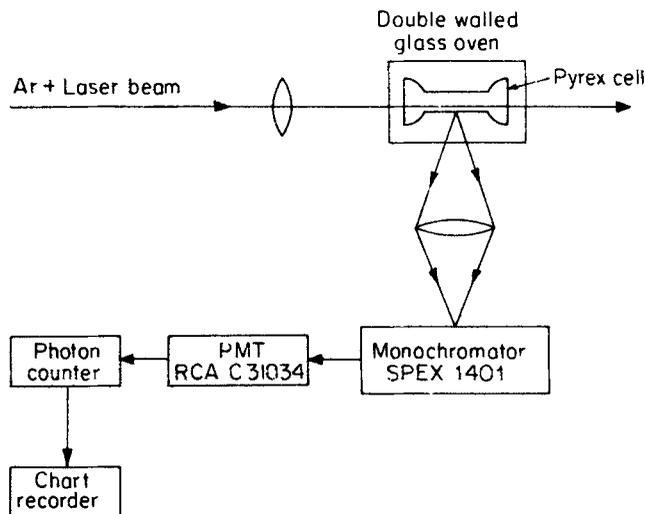


Figure 1. Experimental set-up for studying the laser-induced photodissociation of NaCs molecule.

proper insulation and temperature control. Prior to filling the pyrex cell its walls are degassed with a flame for sometime. The residual pressure in the cell is less than 10^{-5} torr before filling. The oven is heated with a nichrome heater wire, wound in such a way that one end of the cell is slightly cooler than the rest of the cell. The vapour pressure in the cell is determined by the temperature of this cooler end. The temperature of the cell is measured with a chromel alumel thermocouple. It was found that pyrex cells containing alkali metal vapour rapidly deteriorate as the temperature of the cell is raised above 250°C . Thus all our experiments were done at temperatures below 200°C . In equilibrium, Cs and Na coexist with Na_2 , Cs_2 and NaCs. At 180°C , for which the data are presented here, their number densities are estimated to be $7.4 \times 10^{14} \text{ cm}^{-3}$, $8.9 \times 10^{11} \text{ cm}^{-3}$, $2.2 \times 10^9 \text{ cm}^{-3}$, $1.5 \times 10^{12} \text{ cm}^{-3}$ and $1.5 \times 10^{11} \text{ cm}^{-3}$ respectively. The number densities of Na and Cs are calculated from the values of equilibrium constants taken from thermodynamic tables (Stull and Sinke 1956) whereas the number densities for molecules Na_2 , Cs_2 and NaCs are derived from the law of mass action (Kestin and Dorfman 1971). Various lines of CW argon ion laser (Spectra Physics 164) were used to photodissociate NaCs. Typical power for 5145, 5017, 4965, 4880, 4765, 4727 and 4579 Å laser line was 350, 35, 125, 300, 125, 18 and 20 mW respectively. The experiment consists of measuring the intensity of NaD light fluorescence as various lines of Ar^+ laser are incident on the cell, always maintaining the geometry of the experiment undisturbed. The experiment is done in three different parts. (i) Using a Na + Cs cell we study the NaD₁ and D₂ lines emitted in laser-induced photodissociation of both NaCs and Na_2 molecules. The laser not only causes photodissociation of Na_2 and NaCs but also produces a rich laser-induced fluorescence spectrum of stokes and antistokes lines emitted by Na_2 and NaCs. (ii) Na_2 present in the Na + Cs cell also gets photodissociated together with NaCs to produce NaD lines. However the proportion of NaD line signal from Na_2 is only a few percent of that from NaCs. To find out this proportion we used another cell containing only sodium vapour, mounted in a similar set-up as that of Na + Cs cell. Again, we studied the NaD lines and also the laser-

induced fluorescence from Na₂. (iii) To find the relative NaCs photodissociation cross-section, we studied the relative yield of NaD lines as the argon ion laser is tuned to its different wavelengths.

3. Results and discussion

The photodissociation of NaCs results in the production of Na in 3P state and Cs in 6S state. Intensity of *D*₁ (5896 Å) and *D*₂ (5890 Å) lines arising from the 3*P*_{1/2} and 3*P*_{3/2} states of Na respectively is monitored as the argon ion laser is tuned to its various wavelengths keeping the geometry undisturbed. A small fraction of fluorescence signal due to the photodissociation of Na₂ is also present in the cell. This also results in the production of Na(3P) atoms. However, as can be seen from the number densities mentioned above, the contribution of Na₂ to the intensity of NaD light emitted in photodissociation is insignificant as compared to that of NaCs. The minimum value of *v*' in *X*¹Σ_g⁺ ground state of Na₂ from which the molecule can get photodissociated is 30, 25, 23, 21, 17, 15, 11 for wavelength 5145, 5017, 4965, 4880, 4765, 4727 and 4579 Å respectively (Janson and Papernov 1982). The corresponding values of *v*' for the photodissociation of NaCs molecule in its ground state *X*¹Σ⁺ are 25, 20, 18, 15, 10, 8 and 1. This is because *D*₀ for Na₂ and NaCs are 0.72 eV and 0.57 eV respectively in their ground states. Because of the Boltzmann distribution, the fraction of NaCs molecules that can get photodissociated by any argon ion laser line is much higher than the corresponding fraction for Na₂ molecules. Experimentally, at 180°C a very bright yellow Na fluorescence is visible for vapour in a Na + Cs cell as any argon ion laser light is shone on it. For a different cell which has only Na vapour under identical conditions, the yellow fluorescence is very weak and barely visible. The laser-induced fluorescence spectrum of Na₂ with its stokes and antistokes lines is seen in both Na + Cs and Na cells. One could normalize the NaD light intensity from the photodissociation with respect to the intensity of a particular Na₂ stokes line. Figure 2 compares the results of photodissociation in a Na + Cs and Na cells, i.e. between parts (i) and (ii) of the experiment. When excited by 4880 Å Ar⁺ line, Na₂ dimers present in both the cells give rise to 5246 Å Na₂ stokes line which corresponds to *B*¹π_u (*v*' = 6, *J*' = 43) → *X*¹Σ_g⁺ (*v*" = 13, *J*" = 43) transition. As seen in figure 2, in a Na + Cs cell the NaD line intensity is more than 10 times the intensity of 5246 Å Na₂ stokes line. In a cell which has only sodium, it is the 5246 Å Na₂ line which is more than 30 times as intense as the NaD line. Thus in a Na + Cs cell, the contribution of NaCs to the NaD line is about 300 times the contribution of Na₂. Thus in a Na + Cs cell the contribution of Na₂ photodissociation to the NaD line intensity can be totally neglected.

NaD light intensity is always found to vary linearly with the incident laser power. This eliminates multiphoton processes and also effects of absorption saturation. The NaD light intensity also varies linearly with the ground state NaCs density. This further supports the view that NaD light is the result of photodissociation of NaCs molecule. The mechanism of excitation transfer from NaCs* to Na*(3P) on collision is totally unimportant. As shown by Kopeikina and Janson (1976) for number density *N*₀ (here Na in 3S state) less than 10¹⁴ cm⁻³, photodissociation dominates excitation transfer.

Figure 3 shows the NaD₁ and *D*₂ light intensity produced after the reaction,



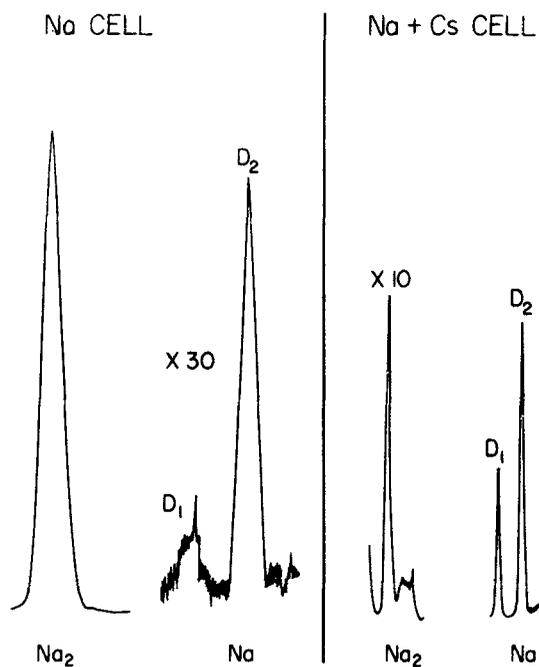


Figure 2. Comparison of NaD light intensity observed in separate experiments with Na and Na + Cs vapour cells. In both cases the Na₂ dimers present produce 5246 Å Stokes line which corresponds to the transition $B^1\pi_u (v' = 6, J' = 43) \rightarrow X^1\Sigma_g^+ (v'' = 13, J'' = 43)$.

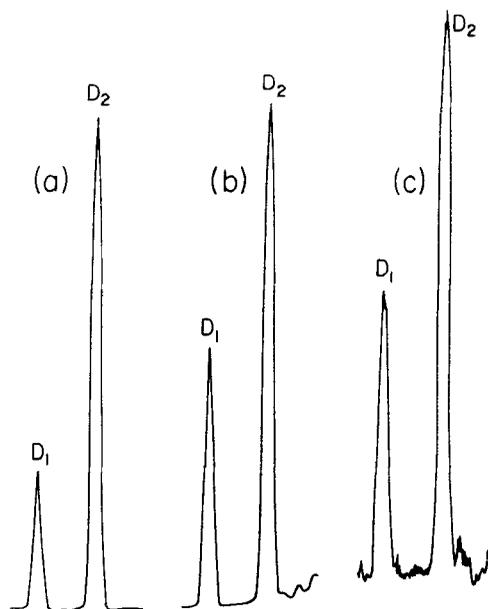


Figure 3. Yield of sodium D₁ (5896 Å) and D₂ (5890 Å) fluorescence due to photodissociation of NaCs molecules. Chart recorder trace (a), (b) and (c) is for 4579 Å, 4880 Å and 5017 Å laser light respectively. The intensity units are arbitrary.

In all our experiments the self-absorption of D light by Na vapour is found to be negligible. The ratio D_2/D_1 is thus reliable and due only to the primary process of photodissociation. It is seen that the ratio of intensities D_2/D_1 is always close to 2 for all wavelengths except for 4579 Å for which it is about 3.5. This could be compared to the total absence of D_1 light observed by Feldman and Zare (1976) in their Rb_2 work. Figure 4 shows the relative photodissociation cross section per photon for the various Ar^+ laser lines in the photo reaction mentioned earlier. The monotonic increase in the cross-section as the wavelength is reduced can be easily understood. This is because the minimum value of v'' from which photodissociation can take place also decreases as the wavelength is reduced. Thus a higher fraction of NaCs molecules is available for photodissociation for shorter wavelengths.

The photodissociation takes place in the continuum of $F^1\Sigma^+$ and $G^1\pi$ states, which are correlated with $3P$ state of Na atom. In the absence of any knowledge about the relevant potential energy curves of NaCs, it is not possible to be certain about the mechanism of photodissociation. Apart from direct excitation into the continuum of F and G states as in the case of Na_2 (Janson and Papernov 1982), for heavier alkali atoms the likelihood becomes higher that photodissociation can take place via some indirect process. In Rb for example (Feldman and Zare 1976), the argon ion laser excites the dimers to the $C^1\pi_u$ state followed by predissociation into the $B^1\pi_u$ state. Further information about the potential energy curves of NaCs should clarify our understanding about the photodissociation described here.

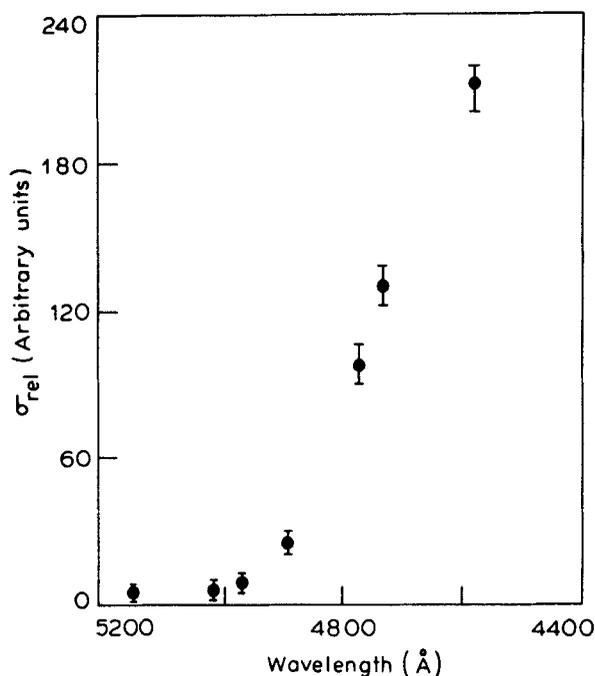


Figure 4. Relative photodissociation cross-section of NaCs molecule vs the argon ion laser wavelength. σ_{rel} is arbitrarily taken as 1 for 5145 Å wavelength. The error bars are mainly due to laser intensity fluctuation.

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