Pressure Shifts of the High Terms of the Absorption Series of Na, Rb, and Cs Produced by Hydrogen and Nitrogen

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The pressure shifts of the high terms of the principal series of Na, Rb, and Cs produced by commercially pure hydrogen and nitrogen were studied. Measurements were made for different concentrations of the perturbing gases up to a pressure of about 12 atmospheres (617°K) for hydrogen and 7.5 atmospheres (548°K) for nitrogen. The former produced a strong while the latter a very slight violet shift and the effective cross sections as calculated by Fermi's equations were found to be 14.0 cm^2/cm^3, and 2.0 cm^2/cm^3, respectively. For axially symmetrical molecules the values of effective cross sections calculated from Fermi-Reinsberg equations do not agree with those obtained by a direct electrical method.

THE displacement of the high members of the principal series of Na and K produced by nitrogen and hydrogen has been measured by Amaldi and Segrè.[1] The highest concentration of hydrogen they used was 5.37×10^{19} cm^{-3}, and that of nitrogen was 3.84×10^{19} cm^{-3}. About the same time Füchtbauer, Schulz, and Brandt[2] determined the displacement of the sodium high series members produced by nitrogen with a higher concentration, *viz.* 6.62×10^{19} cm^{-3} ($t=440$°C, $p=6.40$ atmos.). The effective cross section of nitrogen obtained by the former was 0.93 cm^2/cm^3 and that obtained by the latter was 5 cm^2/cm^3. In the present research the displacement of the high members of the absorption series of Na, Rb, and Cs was studied under different pressures of the foreign gas (H_2 or N_2) up to a concentration of about 14.3×10^{19} cm^{-3} ($t=617$°K, $p=12.0$ atmos.) for hydrogen, and 9.8×10^{19} cm^{-3} for nitrogen ($t=548$°K, $p=7.47$ atmos.).

Because of the fact that the constant shift (in cm^{-1}) of the high members of the absorption series depends on the nature of the perturbing atoms and is independent of the nature of the absorbing vapor, as has been shown both theoretically[3] and experimentally,[1, 2, 4] data obtained from the three alkalis (Na, Rb, and Cs) were averaged, and the mean result was compared with those obtained by different authors.

OBSERVATIONS AND RESULTS

The experimental procedure and apparatus were the same as those employed previously.[4] Commercially pure hydrogen and nitrogen (the purity was about 99.5 percent) were used. A high intensity hydrogen discharge tube was used for the background of the absorption spectrum of sodium, while for rubidium and caesium the carbon arc was used. Because of the fact that water cooling was applied at both ends of the absorption tube, the following experimental difficulty was experienced.[5] The cold gas at the ends of the tube and the hot gas at the central part caused convection, resulting in a higher gas density at the lower part of the absorption column. Consequently, the light traveling through the absorption tube will be refracted downward. In fact, whenever more gas was added to the absorption tube, the optical system had to be

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[1] E. Amaldi and E. Segrè, N. Cimento **11**, 145 (1934).

[2] C. Füchtbauer, P. Schulz and A. F. Brandt, Zeits. f. Physik **90**, 403 (1934).

[3] E. Fermi, N. Cimento **11**, 157 (1934).

[4] Ny Tsi-Zé and Ch'en Shang-Yi, Phys. Rev. **51**, 567 (1937).

[5] Indeed, this trouble would be entirely removed if the whole absorption tube were uniformly heated and MgO windows developed by R. T. Brice and J. Strong (J. Opt. Soc. Am. **25**, 207 (1935)) were used. One of the authors is doing this.

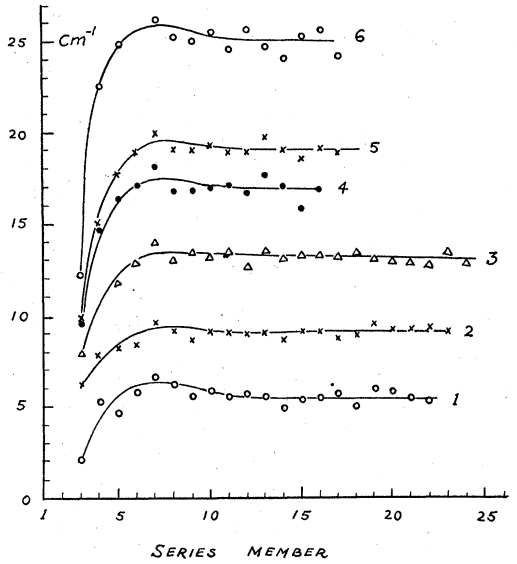

FIG. 1. The displacement of the Cs principal series perturbed by hydrogen. (Violet shift in cm^{-1} against series members.) Curve 1. $t=545°K$, $p=2.22$ atmos.; curve 2. $t=580°K$, $p=4.17$ atmos.; curve 3. $t=621°K$, $p=5.70$ atmos.; curve 4. $t=594°K$, $p=7.60$ atmos.; curve 5. $t=620°K$, $p=9.2$ atmos.; curve 6. $t=595°K$, $p=11.3$ atmos.

readjusted in order to allow the transmitted light to enter the slit of the spectrograph normally. This phenomenon was found to be negligibly small for helium and hydrogen, slight for neon, appreciable for argon, and most pronounced for nitrogen, in accordance with the above explanation that the light will be deviated more for heavier and more refractive gases.

Both for hydrogen and for nitrogen the shift first increases with the ordinal number of the lines in the series, then attains a weak maximum around the 7th member, and finally approaches a constant value at about the 14th.

Hydrogen produces a strong violet shift. Measurements were made for pressures up to 12.0 atmospheres ($t=617°K$) from the third member of the principal series up to about the 23rd. When the concentration of hydrogen was high, say a relative density greater than 3.5, the lines were rather diffused; hence for high concentrations the values were given only for members up to the 17th. Fig. 1 shows the results obtained when caesium was used as the absorbing atom.

Considerable trouble was met in the experiments with nitrogen. The refraction, as mentioned above, began to cause trouble when the pressure was increased to three atmospheres. When the pressure was as high as 7.5 atmospheres, the refraction of light and the increasing opacity of the alkali cloud rendered the transmitted light too weak to photograph.

Nitrogen made the high series lines of the alkalis much more diffuse than hydrogen, so for high concentrations of nitrogen the precision of

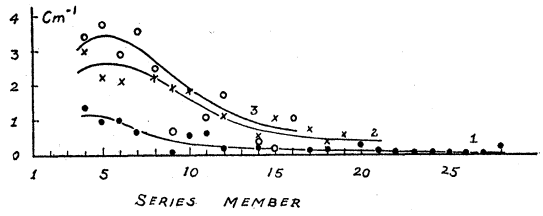

FIG. 2. The displacement of the Cs principal series perturbed by nitrogen. (Violet shift in cm^{-1} against series members.) Curve 1. $t=569°K$, $p=2.48$ atmos.; curve 2. $t=555°K$, $p=4.23$ atmos.; curve 3. $t=548°K$, $p=7.47$ atmos.

TABLE I. *The mean shifts of the high terms of the principal series of* Na, Rb *and* Cs *produced by hydrogen. (∇_ϵ and ∇_σ are the values calculated from Fermi's equations.)*

PRESSURE (ATMOS.)	TEMPERATURE	RELATIVE DENSITY	∇ (cm^{-1}) (VIOLET)	∇_ϵ (cm^{-1}) (RED)	∇_σ (cm^{-1}) (VIOLET)	SERIES MEMBERS	ALKALI
1.63	718°K	0.62	3.24	0.39	3.63	13–24	Na
2.25	609	1.01	5.01	0.74	5.75	13–22	Rb
2.22	545	1.12	5.47	0.85	6.32	13–22	Cs
3.21	720	1.22	6.26	0.95	7.21	13–20	Na
4.17	580	1.96	9.11	1.79	10.90	13–23	Cs
4.40	609	1.97	9.85	1.80	11.65	14–22	Rb
5.70	621	2.50	13.10	2.48	15.58	13–24	Cs
6.58	713	2.52	12.48	2.50	14.98	13–18	Na
8.55	725	3.22	15.45	3.47	18.92	13–18	Na
7.77	614	3.43	16.44	3.78	20.22	14–17	Rb
7.60	594	3.48	16.81	3.85	20.66	13–16	Cs
9.2	620	4.04	19.04	4.70	23.74	13–17	Cs
11.41	722	4.31	20.46	5.12	25.58	13–16	Na
11.3	595	5.18	24.8	6.54	31.3	13–17	Cs
12.0	617	5.31	24.4	6.77	31.2	13–17	Rb

TABLE II. *The mean shifts of the high terms of the principal series of* Na, Rb *and* Cs *produced by nitrogen. (∇_ϵ and ∇_σ are the values calculated from Fermi's equations.)*

PRESSURE (ATMOS.)	TEMPERATURE	RELATIVE DENSITY	∇ (cm^{-1}) (VIOLET)	∇_ϵ (cm^{-1}) (RED)	∇_σ (cm^{-1}) (VIOLET)	SERIES MEMBERS	ALKALI
2.17	728°K	0.81	0.04	1.27	1.31	14–18	Na
2.27	591	1.05	0.18	1.80	1.98	14–22	Rb
2.48	569	1.19	0.03	2.11	2.1	14–26	Cs
3.92	726	1.47	0.13	2.80	2.9	14–18	Na
4.22	580	1.98	0.2	4.16	4.4	14–19	Rb
4.23	555	2.08	0.3	4.45	4.7	14–21	Cs
6.61	723	2.50	0.2	5.69	5.9	14–17	Na
8.73	727	3.28	0.2	8.17	8.4	14–15	Na
7.28	580	3.42	0.3	8.64	8.9	14–16	Rb
7.47	548	3.72	0.4	9.66	10.1	14–16	Cs

measurement was greatly lowered, and determinations were made only for lines up to about the 17th member of the principal series. It produced a slight violet shift for about the first ten terms, then the shift decreased to very small values approaching the magnitude of the experimental error. Results obtained when caesium was used as the absorbing atom are shown in Fig. 2.

According to Fermi's theory the effective cross sections for the single atoms of perturbing gases can be deduced from the observation of the constant shifts of the high series lines of the alkalis.[6] Tables I and II summarize the results obtained from different determinations, where ∇ means the constant shifts of the high terms observed, ∇_ϵ the shift due to the polarization of the foreign atoms in the field of the core of the alkali atom, and ∇_σ the shift caused by the perturbation of the valence electron by the foreign atoms. Fig. 3 shows the relationship between the constant shifts of the high terms and the concentrations of the perturbing gases. From the slopes of these curves, which are 5.85 cm^{-1} (violet) per unit relative density and 2.2 cm^{-1} (violet) per unit relative density for hydrogen and nitrogen, respectively, the effective cross section for all the atoms in one cm^3 at one mm pressure and 0°C can at once be calculated. The results obtained in the present experiment were compared with those by different authors as shown in Table III.

Although Fermi's equations were derived for spherically symmetrical molecules; nevertheless, an extension of his treatment to axially symmetrical molecules as given by Reinsberg[7] shows that Fermi's equations can also be applied to them without any appreciable correction. But a comparison of the values of effective cross sections as found in this way with those extrapolated from Ramsauer and Kollath's curves[8] to very low electron velocity indicates that for spherically symmetrical molecules, the values obtained from spectroscopic observations agree fairly well with those obtained by the direct electrical method, while for axially symmetrical ones the values are apparently discrepant. This fact suggests that the theoretical treatment of the problem needs some further consideration.

TABLE III. *The effective cross sections in* cm^2/cm^3 *of hydrogen and nitrogen for electrons of very low velocity as measured by different authors.*

Gas	Amaldi and Segrè	Füchtbauer etc.	Wahlin	Ny and Ch'en
H_2	12.3	—	24.4	14.0
N_2	0.93	5	10	2.0

[6] The detailed method of calculation can be found elsewhere, such as the references cited in this paper.

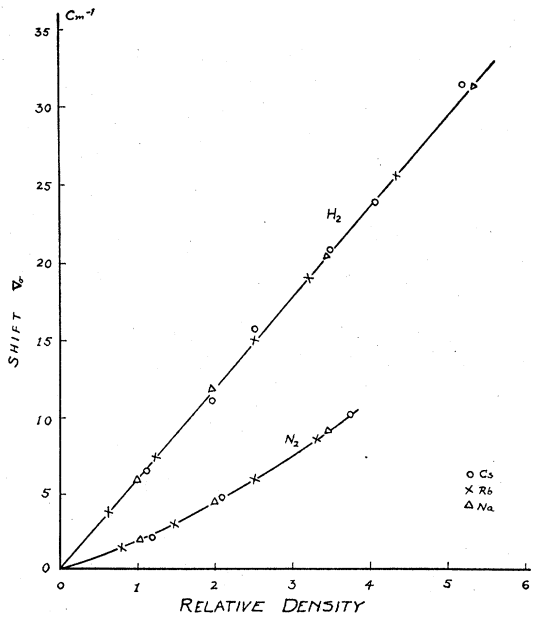

FIG. 3. Shift ∇_σ *vs.* the relative density of perturbing gas.

The authors wish to thank Professor W. V. Houston for his valuable help in writing the paper.

[7] C. Reinsberg, Zeits. f. Physik **93**, 416 (1935).
[8] C. Ramsauer and R. Kollath, Ann. d. Physik **3**, 536 (1929); **4**, 91 (1930). Also H. B. Wahlin, Phys. Rev. **37**, 260 (1931).