

Pressure Effects of Foreign Gases on the Sodium *D*-Lines

HENRY MARGENAU AND WILLIAM W. WATSON, *Sloane Physics Laboratory, Yale University*

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The effects of foreign gases (A, N₂ and H₂) on the *D*-lines of Na have been studied by means of a steel absorption chamber, in which the Na-vapor pressure is kept low while the foreign gas pressure varies between 0 and 17 atmospheres. Temperatures were such that true line contours could be photographed and photometrically evaluated. Results are: (1) The red shift of the absorption maximum varies linearly with the density of the perturbing gas.

(2) Study of the line contours reveals marked asymmetries, most pronounced near the base. Asymmetries are to the red in case of A and N₂, slightly to the blue for H₂. (3) Both *D*-lines show the same broadening and shift. (4) The effects can be accounted for theoretically by assuming a distance of closest approach between excited Na and the foreign gas molecules of about 9A. Quantitative results are summarized in Table I.

INTRODUCTION

IN studying the shape and position of spectral lines emitted or absorbed by an atom which is not in an isolated state, two conditions should be clearly distinguished: the optically active atom may be under the influence of perturbing neighbors of its own kind, or it may be perturbed by a foreign gas. Experimentally, very strong broadening and small shifts in the position of the lines are characteristic of the first named effect, while perturbation by foreign gases always produces relatively smaller broadening and larger shifts. The quantum mechanical forces responsible for the first effect are due to "resonance"; in the second case it is mainly the mechanism of nonstatic polarization which provides the forces of interaction, as was shown in an earlier paper¹ by one of the authors. Believing that theory at present furnishes more definite guidance in an experimental study of the effect due to foreign gases than it does in connection with resonance broadening, we have devoted this investigation entirely to the former problem. Absorption lines are chosen in preference to emission lines, of course, because of the difficulties attending the precise determination of the thermodynamic state in which emission occurs.

Much of the earlier work on problems similar to this was done with the main object of determining the "number of resonators" absorbing

the line in question (*f*-values).^{2,3} For this purpose, the exact position and the details of the shape of the line are inessential and have not been determined with great precision. Füchtbauer and Schell⁴ have measured the absorption of the *D*-lines in nitrogen and compared their results with the theory of Lorentz, which does not explain the most interesting and important features of the phenomenon, namely the asymmetries and the shifts. They also worked in a very limited pressure range, not exceeding 2 atmospheres. Minkowski⁵ obtained some interesting data on the shape of the *D*-lines perturbed by a large number of foreign gases from which the asymmetry of the lines is especially apparent. He finds that all gases except H₂ and He broaden predominantly toward the red, while the latter two produce noticeable blue asymmetries. Theory leads one to expect a shift toward the red in all these cases; hence there arises the question as to whether, in the case of H₂ and He, a blue asymmetry is coupled with a red shift. This will be verified presently, and a qualitative explanation will be given. Minkowski's measurements do not expose, however, the true contour of the absorption lines, for their centers were completely absorbed. His pressures are confined to

¹ H. Margenau, *Phys. Rev.* **40**, 387 (1932).

² C. Füchtbauer and Hofmann, *Ann. d. Physik* **43**, 96 (1914). (Work on Cs-lines.)

³ H. Bartels, *Ann. d. Physik* **65**, 143 (1921). (Cs-lines.)

⁴ Füchtbauer and Schell, *Phys. Zeits.* **14**, 1164 (1913).

⁵ R. Minkowski, *Zeits. f. Physik* **55**, 16 (1929).

values below one atmosphere. This pressure range was also studied by Korff,⁶ who used H₂ and He as perturbing gases.

Further papers deal more specifically with the effect of foreign gases on the integrated (total) absorption and demonstrate the existence of quenching. Different gases behave differently in reducing the total absorbed intensities, as was shown by Stuart,⁷ Kunze⁸ and others.

Very careful and significant measurements were made by Füchtbauer, Joos and Dinkelacker⁹ ten years ago. They observed the contours of the absorption curves for Hg 2537 in their entirety and produced an interesting set of data, suitable as a basis for theoretical analysis. Besides determining shift and half width, they also showed the quenching effect of several foreign gases. Their findings were first discussed from a theoretical point of view in reference one and proved to be in substantial agreement with current notions of intermolecular forces.

Meanwhile a complex of theories on the broadening of spectral lines has been developed. Confining attention only to those theories which have a direct bearing on the specific problem at hand, two principal methods of calculation appear to be prevalent. The first proceeds on the basis of an analysis of the potential energy curves¹⁰ representing the interaction between the active atom and its perturber. This method permits one, by applying the Franck-Condon principle together with statistical considerations, to account for the main experimental results.^{11, 12, 13} In the first of these papers, an evaluation of the intermolecular forces here encountered in terms of dispersion f -values was also given. The alternative mode of approach^{14, 15} considers the active atom as absorbing continuously, but with a varying frequency which

depends on the distance of the perturbers. The calculation is then a Fourier analysis of the electric moment of the atom, written as a function of the time. The former point of view leads to results capable at least of rough quantitative comparison with experiment and places emphasis on the main experimental features: shift and asymmetry of the lines. While our experimental results are independent of any chosen interpretation, the former method of reasoning will be employed in their discussion. It turns out that none of the observed features are contradictory to the basic assumptions of references 11 and 13.

To be of aid to any theory, the experimental data on pressure broadening must include observations on the entire absorption contour, which requires an adjustment of foreign gas pressure and temperature of absorbing gas for every exposure. The lines of an alkali metal were chosen for this investigation because both broadening and shift could be expected theoretically to be larger than for most other substances, which is verified. It seemed interesting, furthermore, to find out whether the two components of the Na-doublet suffer equal pressure effects or not. Finally, it remained to be seen what forces between the excited Na-atom and the gas molecule, together with the simple model used in references 11 and 13; would have to be assumed to account for the observed shifts and line contours. The interpretation also leads to an approximate value for the distance of closest approach between the excited Na-atom and the foreign molecule. Measurements at pressures greater than atmospheric appeared necessary to increase the accuracy of measurement. High pressures do not invalidate the application of theory in any essential way, for one can easily convince himself that the molecular forces even at the highest pressures used in this work remain approximately additive. An experimental verification of this assumption may be seen in the absence of departures from the linear dependence of shift and width on densities.

EXPERIMENTAL PROCEDURE

The absorption tube used in these experiments was a steel pipe 33 inches long, $1\frac{5}{8}$ inches outside diameter and with a 1 inch bore. Glass windows 1 cm thick were held on the ends by means of

⁶ S. A. Korff, *Astrophys. J.* **76**, 124 (1932).

⁷ H. A. Stuart, *Zeits. f. Physik* **32**, 262 (1925).

⁸ P. Kunze, *Ann. d. Physik* **8**, 500 (1931).

⁹ C. Füchtbauer, G. Joos and O. Dinkelacker, *Ann. d. Physik* **71**, 204 (1923).

¹⁰ First suggested qualitatively by Jablonski, *Zeits. f. Physik* **70**, 723 (1931).

¹¹ H. Margenau, *Phys. Rev.* **40**, 387 (1932).

¹² M. Kulp, *Zeits. f. Physik* **79** (1932).

¹³ H. Margenau, *Phys. Rev.* **43**, 199 (1933).

¹⁴ V. Weisskopf, *Zeits. f. Physik* **75**, 287; **77**, 398 (1932).

¹⁵ W. Lenz, *Zeits. f. Physik* **80**, 423 (1933).

overlapping nuts of $\frac{5}{16}$ inch steel threaded on to the tube. Considerable trouble was experienced in constructing gaskets which would continue to be pressure-tight after the absorption tube had been heated to 200°C and then cooled. This difficulty was almost completely overcome by the use of lead rings $\frac{3}{32}$ inch in thickness, their lateral expansion when compressed being hindered by short sections of thin-walled steel tubing which fitted tightly into the main tube and the end-nuts. An opening near one end, closed by a nut with a piece of annealed copper for a gasket, served for the introduction of the sodium. A side tube near the other end connected to the nitrogen, argon, or hydrogen tank, the vacuum pump, and the pressure gauge. The latter read to 200 lbs. full-scale and was carefully calibrated. The absorption tube could be kept at any desired temperature by means of a three-section electric furnace somewhat longer than the tube. A thermometer was placed in each section of the furnace.

In preparation for the taking of the spectrograms the apparatus was first evacuated and the tube heated with a blow-torch to free it of water vapor. The gas being used was then allowed to stream in slowly through a heated coil of copper tubing filled with copper filings. When atmospheric pressure was reached, metallic sodium was introduced into the tube through the small opening from which the gas was escaping all the while. In this way the pieces of sodium were but slightly oxidized on the surface. Next the tube was again evacuated, heated with the blow-torch until the sodium boiled, and then tipped so that the clean liquid sodium ran down its entire length. Gas was then admitted through the hot copper tube to atmospheric pressure, the valve to the vacuum pump closed, the furnace adjusted around the tube, and its temperature raised to about 200°C. Under these conditions the sodium vapor was so dense as to cause the *D*-lines to be very completely absorbed. The tube was then slowly filled with the foreign gas to a pressure of 200 lbs./in.² as read on the gauge. After taking the spectrogram at this highest pressure, the gas pressure and temperature were reduced and other spectrograms were taken at convenient pressure intervals. At each pressure the temperature of the furnace was adjusted so

that the absorption was less than total in the center of the *D*-lines in order that true line contours would be registered. With practice this adjustment could be checked by visual inspection of the lines.

A Pointolite lamp served as the source of continuous spectrum, a single lens being employed to produce a much-enlarged image of the tungsten bead on the slit of the spectrograph. The latter was a 21-foot concave grating in a stigmatic mounting giving a dispersion of 2.25Å per mm at 5890Å in the second order. The exposure times varied from 6 to 10 minutes. On each plate exposures of a half and a quarter of this time, all other variables being held constant, were placed as blackening marks for the purpose of calibrating the density gradations in the absorption lines. Both Eastman Hypersensitive Panchromatic and Eastman Type 4-D plates were used. The former were found to have a longer linear section for the density *vs.* log (*It*) curve and a lower threshold, thus necessitating but little correction to the microphotometer trace to get the true absorption curve, but their large plate grain proved troublesome. We therefore adopted the type 4-D emulsion together with a borax developer, the combination giving a very small plate grain. A more detailed determination of the characteristic curve of these plates, however, showed them to require care in calibrating the microphotometer deflections. A neon spectrum was superposed on a portion of the main exposure on each plate as a comparison. Ne has two lines 5881.896Å and 5902.475Å, one on either side of the *D*-lines which serve as convenient standards. Finally, on each spectrogram a fine scratch was drawn parallel to the spectral lines between the two Na lines, and its "wave-length" determined with the comparator by reference to the Ne standard lines, to serve as an additional reference point on the microphotometer traces.

Each spectrogram was run through a Koch-Goos recording microphotometer using the 1 : 40 ratio to give the maximum enlargement. Because of this enlargement two traces were necessary for each spectrogram, one covering the 5881 Ne line, the *D*₂ absorption band and the scratch above referred to, the other recording the region from the 5902 Ne line through the *D*₁ absorption band to about the center of the *D*₂ band. In

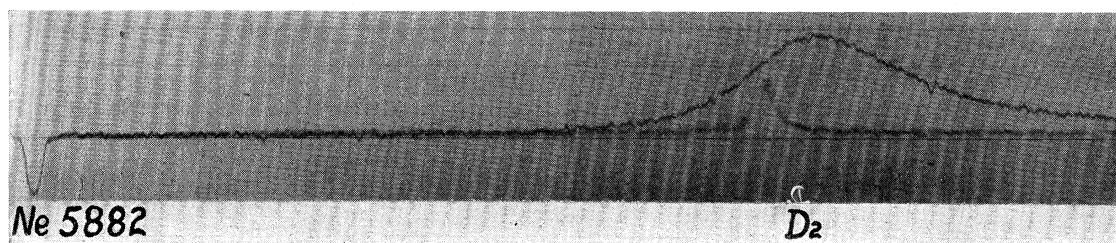


FIG. 1. Microphotometer traces of D_2 broadened by argon. *Small peak*: trace for an argon pressure of 1.85 atm.; *large peak*: trace for a pressure of 17.8 atm. Reference line (Ne, $\lambda 5881.896$), exactly superposed on the two traces, appears on extreme left. (Lower trace is slightly out of focus in the reproduction.)

addition the deflections of the microphotometer for the three blackening marks and for the clear portion of each plate were recorded. To illustrate the character of the microphotometer curves obtained, we give in Fig. 1 a superposition of two traces of the D_2 line perturbed by argon at relative densities d (cf. below) of 1.21 and 9.16, respectively. The large shift of the maximum of absorption to longer wave-length and the marked asymmetry of the absorption curve for the higher density of argon are to be noted.

For the computation a trace of each microphotometer curve was made on millimeter cross-section paper, smoothing out of course the slight irregularities due to plate grain. In each instance where necessary this curve was transformed into a true absorption intensity curve by means of the known photographic density curve. The wave-length dispersion on each of these traces being known from the interval between the peaks due to the two reference standards, the wave-length of the maximum of the absorption for each D -line was computed by interpolation. Drawing the base line beneath each absorption maximum for the position of the trace if no absorption were present, the levels for one-half and for one-quarter of the interval to the absorption peak were marked, the widths of the absorption band at these two points determined in millimeters, and the conversion to wave numbers made. These last measurements are the half-widths and quarter-widths referred to below. Since at the highest densities of the foreign gases the absorption on the red side of the D_2 -line is beginning to merge with the blue side of the D_1 -line, allowance for this overlapping was necessary in order to get the true line-widths.

EXPERIMENTAL RESULTS

It is clear that the effect of the foreign gases does not depend on their pressure, but on their concentration. A convenient unit of the concentration is the density of the amount of perturbing gas used in the experiment at 0°C and 1 atm. The density measured in this unit will be called "relative density." To convert pressures as read on the gauge into relative densities, two corrections had to be applied. First, because the gauge was slightly above room temperature with the gas in the absorption tube at approximately 200°C , account had to be taken of thermal transpiration. If the perturbing gas were ideal and equilibrium existed, this could be done by use of the simple formula: $P_1/P_2 = (T_1/T_2)^{1/2}$, where P_1 and T_1 are pressure and temperature in the absorption tube, P_2 and T_2 refer to the gauge. To test this relation, the tube was filled at room temperature and a reading of the pressure taken. After heating the tube the pressure was read again on the cool gauge, and finally the initial temperature was restored to insure that no leak had occurred. In this way the validity of the above relation was verified to within the experimental errors of pressure and temperature measurements, and the formula applied thereafter. The second step involved the reduction to density at 0°C and was made by means of van der Waals equation—although, except for the highest pressures, the deviation from the law for perfect gases is inappreciable.

The results indicate clearly that the two D -lines behave alike with respect to shift, width and asymmetry, as was concluded on theoretical grounds.¹¹ The shift, plotted against relative densities in Figs. 2 and 3, is seen to be proportional to the density of the perturbing gas, as

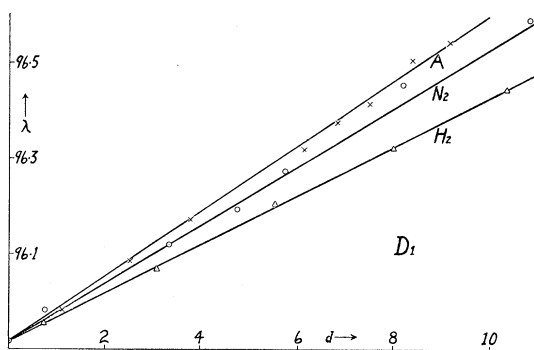


FIG. 2. Wave-length of maximum of D_1 vs. relative density of perturbing gas.

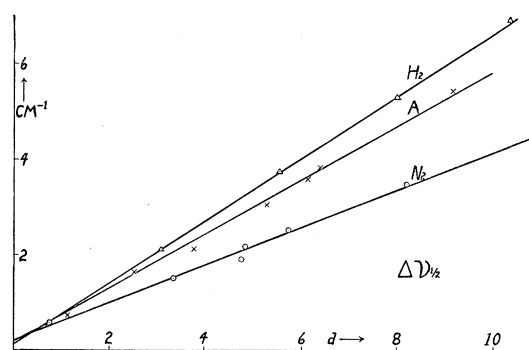


FIG. 4. Half widths (averages for D_1 and D_2) vs. relative density of perturbing gas.

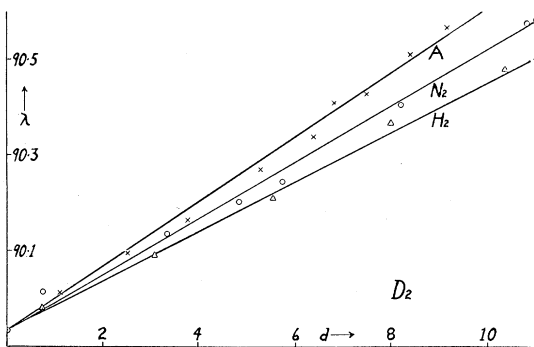


FIG. 3. Wave-length of maximum of D_2 vs. relative density of perturbing gas.

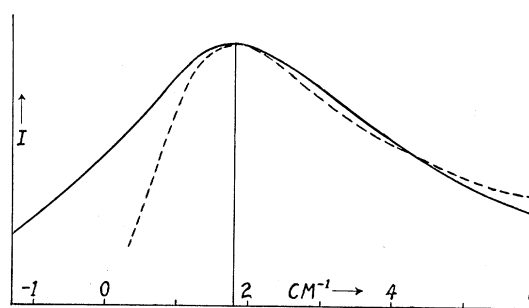


FIG. 5. *Solid curve*: Absorption contour of D_1 broadened by 17.8 atm. of argon pressure. *Dashed curve*: Corresponding theoretical curve.

was found by Füchtbauer and his collaborators for the Hg line. All shifts are to the red. Regarding the unperturbed position of the D -lines it may be noted that the values plotted in Figs. 2 and 3 are slightly different from those given by Wood and Fortrat¹⁶ (5889.933 and 5895.917 Å as against W. and F.'s 5889.963 and 5895.930 Å). Nevertheless our unshifted wave-lengths fall in line with the other points of the diagram distinctly better than do those of Wood and Fortrat. It may be, therefore, that a small constant error affects the absolute values of all the wave-lengths plotted in the figures. In Füchtbauer's⁹ experiment, the shift of the Hg-line was about 0.126 cm^{-1} per unit relative density of argon; the corresponding displacement for the Na-lines is 0.196 cm^{-1} . Because of the longer wave-length of the Na-lines, this makes the measured wave-length shift for the Na-lines more than 8 times as large as that for Hg, which

¹⁶ R. W. Wood and R. Fortrat, *Astrophys. J.* **43**, 73 (1916).

increases considerably the accuracy of measurement. An upper limit for the pressures used was set by the incipient overlapping of the D -lines. At 18 atmospheres, this became so strong that corrections became necessary, indicating the futility of continuing to greater densities, although this was originally planned.

The exact shape of the broadened lines is exhibited in Fig. 1 (uncorrected for plate characteristic) and Fig. 5 (solid curve, representing the absorption coefficient, i.e., $\text{const.} \times \log(\text{absorbed intensity})$) as a function of the wave number. In the case of N_2 and A, the asymmetries to the red are very pronounced; they grow especially strong near the base of the line. H_2 produces a slight but unmistakable asymmetry to the blue. Following the usual convention, we have chosen the "half width" to convey a measure of the broadening produced by the different gases. Half width is defined as the wave number or wave-length interval in which the absorption coefficient is equal to or greater than one-half

its maximum value. In Fig. 4, these half widths are plotted against relative densities. Since the corresponding values for D_1 and D_2 were found to be equal within the error of their determination, separate graphs for the two lines were thought unnecessary, hence the average half width was plotted in all cases. The best curves through the experimental points are straight lines.

To give an indication of the asymmetries, the ratio of the red "half" to the blue "half" of the half widths should be given. By these terms we wish to designate the two portions of the half width range on the two sides of the maximum. The ratio begins, as might be expected, with the value 1 at zero densities and grows to 1.3 and 1.45, respectively for N_2 and A at the highest pressures used in this experiment; for H_2 it falls to 0.96. Hydrogen, though producing the smallest shift, broadens most effectively in toto. It appears, however, that the broadening on the red side of the line alone maintains with respect to N_2 and A the same order as the shift. The large line width in the case of H_2 is best thought of as produced by additional broadening to the blue. A possible theoretical interpretation of this phenomenon will be considered later.

Comparing our results again with those of Füchtbauer, Joos and Dinkelacker on the Hg-line, we find that the D-lines are broadened by a given gas almost twice as strongly as is the Hg-line (using as a measure the half width intervals in wave numbers). Table I contains a summary of our data. $\Delta\lambda/d$ represents the shift of the line per unit relative density in A, $\Delta\nu/d$ the average of this shift for the 2 D-lines, expressed in wave numbers, and $\Delta\nu_{1/2}/d$ is the half width of the lines per unit relative density of the corresponding gas. The numbers are simply the slopes of the lines in Figs. 2 to 4. The variation of the total absorption ($\int(n\kappa)d\nu$) was not investigated because it depends very critically on the number of Na atoms within the absorption tube. This was difficult to determine

since deviations from exact equilibrium between Na-vapor and liquid in the large volume of our tube at high pressures may well be expected to occur.

THEORETICAL DISCUSSION OF RESULTS

Various assumptions have been made in the literature about the actual shape of pressure broadened lines. Among the simplest possible theoretical contours are the "dispersion" curve and the error curve. The asymmetries demonstrate, of course, that neither assumption is correct. Nevertheless it might be possible to characterize the general trend of the absorption contour by one of these two simple types; in fact this procedure has been largely followed by experimental investigators who, in stating line widths, assumed the line to be a simple dispersion curve in accordance with Lorentz' theory of broadening. This hypothesis is capable of being tested simply. Let us call the wave number range in which the absorption coefficient is equal to or larger than $\frac{1}{4}$ of its maximum value, the quarter width of the line, and denote it by $\Delta\nu_{1/4}$. Then the ratio $\Delta\nu_{1/4}/\Delta\nu_{1/2}$ is a simple characteristic for each of the two simple types of curve just mentioned. Experiment, too, gives a value for this ratio which is essentially independent not only of the density used (quarter widths are roughly proportional to the relative densities in our experiment) but even of the broadening gas. The values of this ratio were found to be 1.61, 1.59, 1.65, respectively, for A, N_2 and H_2 .—The dispersion curve has the form (ω is angular frequency):

$$I(\omega) = 1/[(\omega - \omega_0)^2 + 1/\tau^2];$$

it gives a half width $\Delta\omega_{1/2} = 1/\tau$, and a quarter width $\Delta\omega_{1/4} = 3^{1/2}/\tau$. Hence $\Delta\omega_{1/4}/\Delta\omega_{1/2} = 3^{1/2} = 1.73$. On the other hand, an error function

$$I(\omega) = \text{const. } e^{-(\omega - \omega_0)^2/a^2}$$

has a half width $\Delta\omega_{1/2} = a(\log 2)^{1/2}$ and a quarter width $\Delta\omega_{1/4} = a(\log 4)^{1/2}$, yielding a ratio $\Delta\omega_{1/4}/\Delta\omega_{1/2} = 2^{1/2} = 1.41$. The experimental ratio lies between these two values, indicating that neither assumption is strictly correct, even if asymmetries are disregarded.

A feature worthy of explicit mention is apparent from Fig. 1. The intensity in the high

TABLE I.

	$\Delta\lambda/d$		$\Delta\nu/d$	$\Delta\nu_{1/2}/d$
	D_1	D_2		
A	0.068A	0.068A	0.196 cm ⁻¹	0.57 cm ⁻¹
N_2	0.061A	0.059A	0.173 cm ⁻¹	0.39 cm ⁻¹
H_2	0.051A	0.052A	0.148 cm ⁻¹	0.65 cm ⁻¹

density curve at the point which corresponds to the maximum of the undisplaced line is surprisingly small. The effect of foreign pressures is not adequately described by referring to it as unsymmetrical broadening; the outstanding characteristic seems to be a very real displacement of the line. We feel, therefore, that any theory designed primarily to account for the broadening, and compelled afterwards to correct for asymmetries and displacements, misses the central part of the phenomenon. In the subsequent discussion we shall make use of the theoretical considerations proposed in the other papers,^{11, 13} which are free from this objection, and analyze the effect of argon on the D -lines in somewhat greater detail.

Following the reasoning in reference 13, we have attempted to fit the expression given in Eq. (17) of that paper to the experimental contour of the D -lines perturbed by 17.8 atmospheres of argon at a temperature of 250°C (relative density = 9.16). The result is given in Fig. 5, where the solid line represents the experimental curve, the dashed line being Eq. (17), with $R_1 = 8.5\text{A}$ and $\beta = 345$. This choice of constants produced the correct shift as well as the correct half width. The graphical evaluation of the theoretical curve is somewhat tedious, and it might be that a slightly different choice would have given a better fit. But the imperfection of the model (cf. below) used in the calculation would render further numerical refinement meaningless. R_1 is to be interpreted as the distance of closest approach between an excited Na-atom and the (unexcited) A-atom. The meaning of β is this: if the interaction energy between a normal Na-atom and an A-atom is given by $-a/R^6$, where R is the distance between the two measured in A-units (higher powers in $1/R$ are neglected!), and the corresponding energy between an excited Na-atom (3 2P -state) and A is $-b/R^6$, $\beta = b - a$. The value of β here obtained is about twice as great as that found by the use of f -values as outlined in reference 13, but a reasonable change in the choice of f 's would remove the discrepancy.

An application of these simple notions to the interaction between a Na-atom and an N_2 -molecule is probably more risky. It leads to a value between 9 and 10A for R_1 .

The meaning of the discrepancies in Fig. 5 is best understood if reference is made to the diagram in Fig. 6. Curve c gives the qualitative

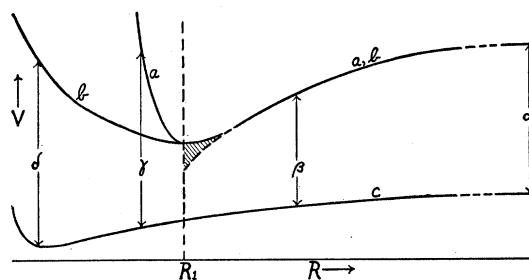


FIG. 6. Qualitative interaction curves demonstrating the mechanism of broadening and shift.

trend of the interaction energies between normal Na and a foreign gas atom or molecule as a function of the distance of separation, while curves a or b refer to an excited Na-atom. In the calculation, the upper curves have been replaced for simplicity by the dotted one, which rises vertically at R_1 . Hence in the simplified model, only transitions to the right of R_1 can occur, all of which have smaller energies than α , the transition at an infinite separation. The model can therefore not account for blue broadening. It also magnifies the extreme red transitions by inserting the shaded area into the diagram, which explains the divergence at the red end in Fig. 5. The relatively small blue broadening apparent in the experimental contours we wish to ascribe to transitions occurring to the left of R_1 , like γ .

For A and N_2 the upper curve is probably similar to a , while it is not unlikely that H_2 corresponds more nearly to b . For H_2 , therefore, our model is particularly inadequate. The situation is then approximately this: Since the average of all possible transitions has a frequency smaller than α , the center of gravity of the broadened line is displaced to the red. Nevertheless, the distribution of frequencies within the broadened line may well be nearly symmetrical if sufficient weight is assigned to the transitions of type δ ; or if the latter are particularly strong (the Boltzmann factor would render transitions at small values of R relatively more numerous) there can be a blue asymmetry superimposed on a red shift.

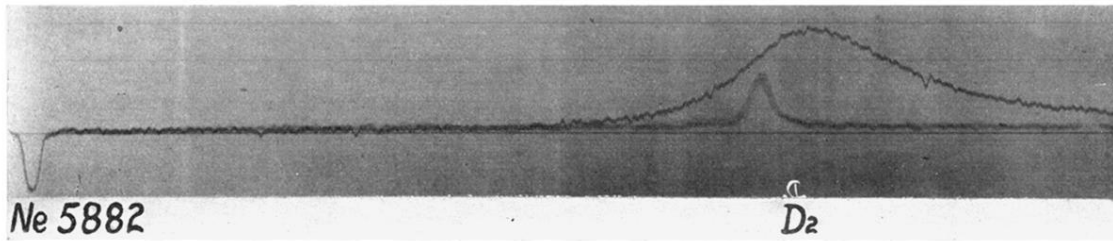


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