state should be ${}^4H_{3\frac{1}{2}}$, whereas if $4f5d^2$ is lower it should be ${}^4I_{4\frac{1}{2}}$. The J value of the lowest state which we have thus far found is $3\frac{1}{2}$, this possibly being ${}^4H_{3\frac{1}{2}}$. In any case the spectrum is not like that of La I, which Haspas' analysis purported to show.

Experimental g values have been determined for several of the levels. While these are not very precise they do show large departures from the theoretical g values, evidence of large interactions between the various levels. This perturbation is to be expected, since our term diagram, though far from complete, shows the greatest density of low levels yet observed. The fact that 13 low levels having J values of $3\frac{1}{2}$ have already been found means that at least 13 multiple terms lie within 8300 cm^{-1} of the lowest state. The large number of times this value of J is found shows also that some of the low levels belong to $4f5d^2$, since $4f5d6s$ can account for only eight at the most. The two configurations probably interact so strongly that exact electron configuration assignments will have little meaning.

The energy levels found are presented in Table II. The low levels are numbered from 1 up in order of energy, and the middle levels are numbered from 101 up.

Table III contains a list of the lines which have thus far been classified. Those wave-lengths given to hundredths of an angstrom only are taken from Exner and Haschek;[8] the remainder are M.I.T.-W.P.A. measurements. The second column contains the estimated intensity of the line as given by Klein[9] or by Exner and Haschek,[8] and, where known, King's temperature classification.

We record with gratitude assistance from a grant by the Rumford Committee of the American Academy of Arts and Sciences. We are particularly happy to acknowledge our debt to Colonel R. C. Eddy and the staff members of the W.P.A. project for their conscientious work on the wave-length determinations.

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[8] F. Exner and E. Haschek, *Die Spektren der Elemente bei normalen Druck* (Franz Deuticke, Leipzig, 1911).

[9] Ph. Klein, Zeits. f. wiss. Phot. **18**, 45 (1918).

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Pressure Effects of Homogeneous K Vapor in Absorption

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By use of the newly developed corrosion-resistant MgO windows, the K resonance lines in absorption of a homogeneous vapor, were obtained for pressures ranging from 0.001 to 20 mm Hg. The "dispersion" equation was generally adequate to describe the observed contours. The corresponding half-breadths were linear in the density, equal as between components, but of magnitude several times that predicted by the theory of the resonance interaction. The slight asymmetry which appeared at the highest pressure was attributed to van der Waals forces. But it is pointed out that, in contradistinction to the circumstance for Hg, a quantitative verification of the inverse sixth power law is probably not possible. The infrared bands of the K_2 molecule were also observed.

The strong asymmetries and shifts, characteristic of spectral lines arising from absorption by a metallic vapor in the presence of a foreign gas, have recently been the subject of extended investigation. The pressure effects in a homogeneous absorbing vapor,[1] with the typical marked symmetrical broadenings, are, however, not only less well understood, but their experimental study has been comparatively neglected. It is the purpose of this paper to describe an experimental investigation of the contours of the K resonance lines (λλ7664.9, 7699.0) for the latter case.

In what follows, it will be supposed that foreign gases are present in negligible quantity, so that the interactions among like particles only,

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[1] For a recent review article dealing with the general subject of pressure effects, see H. Margenau and W. W. Watson, Rev. Mod. Phys. 8, 22 (1936).

need be considered. Furthermore, the discussion will, for the most part, be pertinent only to the lowest (resonance) transitions of the atom, in absorption.

THEORY

The contour of a line otherwise determined by radiation damping, will be strongly modified in consequence of the presence of atoms in the vicinity of the absorbing one. The perturbations here involved arise by virtue of the existence of both resonance and van der Waals forces. For the resonance forces, the net change in the energy of the absorbing atom in the field of a single perturbing atom at distance R, is given by

$$\Delta\epsilon = \pm h(e^2 f/8\pi^2 m\nu_0)(1/R^3), \tag{1}$$

approximately,[2] where f is the oscillator strength of the transition of natural frequency ν_0. For the van der Waals forces, the corresponding equation is,[3] for not too small R,

$$\Delta\epsilon = -h(C/R^6), \tag{2}$$

where C is a constant of the transition, in general positive. Exact numerical evaluation of C has not been made. When more than one perturbing atom is involved, the $\Delta\epsilon$'s of (2) are additive. This is not true in the case of (1), and the precise nature of the relation is not known.

We shall not here concern ourselves with the effects that result from very close approaches[4] except to note that there is the possibility of the formation of molecular states as a consequence of the existence of a minimum in the potential energy of a configuration.

A rigorous application of the foregoing considerations to the determination of the absorption coefficient has not been made. But the approximate solutions are instructive. It will be convenient to discuss first the "statistical" distribution of frequencies, ignoring for the moment the contribution of the "velocity" effect.

The frequency actually absorbed is then related to the perturbation energy by $\nu - \nu_0 = \Delta\epsilon/h$, simply. The intensity at a given $\nu - \nu_0$ depends, of course, upon the statistical probability of the existence of a configuration capable of producing the corresponding $\Delta\epsilon$. Thus, the center of the line (small $|\nu - \nu_0|$) arises from the perturbations of many distant particles, and is of high intensity relative to the wings. But for larger $|\nu - \nu_0|$, the single encounter is determinative, because of the smaller probability of sufficiently close multiple approaches. Then, for moderately large $|\nu - \nu_0|$, the resonance perturbation prevails, because of the slower decay with distance of (1) in comparison to (2). But, as concerns the far part of one wing, the van der Waals force contributes strongly, and the line takes on the asymmetrical character of foreign gas broadening.[5] We turn now to quantitative considerations.

Margenau and Watson,[1] for the statistical distribution on the basis of resonance forces, obtained the familiar "dispersion" equation,[6]

$$\alpha x = \frac{A\Delta\nu_{\frac{1}{2}}/2\pi}{(\nu_0 - \nu)^2 + (\Delta\nu_{\frac{1}{2}}/2)^2}, \tag{3}$$

or, more properly, for $|\nu_0 - \nu| \gg \Delta\nu_{\frac{1}{2}}$,

$$\alpha x = (A\Delta\nu_{\frac{1}{2}}/2\pi)/(\nu_0 - \nu)^2, \tag{4}$$

for, as the authors have pointed out, (3) cannot hold at the line center[7] in view of the nonadditivity of the resonance interaction. The quantity A is the integrated absorption, and numerically equal to $(\pi e^2/mc)Nfx$ sec.$^{-1}$, where N is the number of atoms per cc, and x is the length of the absorbing column. They found, for the half-breadth,

$$\Delta\nu_{\frac{1}{2}} = (e^2 f/6m\nu_0)N \text{ sec.}^{-1}. \tag{5}$$

As indicated above, the van der Waals forces will, at sufficiently high pressures, result in a measurable intensity at the distant part of one wing (long wave-length for positive C). Kuhn[8]

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[2] See, for example, reference 1, p. 33.

[3] F. London, Zeits. f. Physik **63**, 245 (1930); Zeits. f. physik. Chemie **B11**, 222 (1930).

[4] For recent investigations in this connection, see H. Kuhn, Proc. Roy. Soc. **158**, 212 and 230 (1937); W. M. Preston, Phys. Rev. **51**, 298 (1937).

[5] Of course, in order to have a measurable intensity at these larger $|\nu - \nu_0|$, high density of the absorbing vapor is required.

[6] The absorption coefficient αx, is connected with the (observable) transmission I/I_0 by $I/I_0 = \exp[-\alpha x]$.

[7] This need not concern the experimenter, for because of the general practically complete absorption that occurs at the center of the line, the half-breadth is not directly measurable, but only the product $A\Delta\nu_{\frac{1}{2}}$ of (4). The circumstance is different for the case of a nonhomogeneous gas, since an additional parameter enters, *viz.*, the density of the foreign gas.

[8] H. Kuhn, Phil. Mag. **18**, 987 (1934). See also H. Margenau, Phys. Rev. **48**, 755 (1935).

has given

$$\alpha x = (2\pi ANC^{\frac{1}{2}}/3)/(\nu_0-\nu)^{\frac{3}{2}}. \tag{6}$$

It is apparent that, because of its slower decline with increasing $\nu_0-\nu$, (6) may overshadow (4).

Unfortunately, the above distributions are confused as a result of the velocity effect. In fact, at the center of the line, this latter is probably determinative. But as Kuhn and London[9] have shown in connection with the van der Waals forces, in the wings of the line the velocity effect contributes merely a "diffuseness;" one that is proportional to the square root of the velocity, approximately, and that decreases with increasing $\nu_0-\nu$. Thus (6) may, within the limits of its validity, be supposed to be satisfied the better the smaller the velocity and the larger the $\nu_0-\nu$. The same considerations can be extended to apply to the resonance case as given by (4), but certainly, the "diffuseness" decreases less rapidly with increasing $|\nu_0-\nu|$. This last may be seen as well, in connection with the Lorentz collision theory. This theory, as modified by Weisskopf,[10] also leads to (3), but (for the here more important case of resonance forces) the half-breadth is defined by

$$\Delta\nu_{\frac{1}{2}} = (e^2f/4\pi m\nu_0)N \text{ sec.}^{-1}. \tag{7}$$

This distribution, which may be considered as the limiting case of the velocity effect, falls off no more quickly with increasing $|\nu_0-\nu|$ than does (4). But the interpretation of Weisskopf's result is somewhat uncertain in view of the failure of the velocity to enter explicitly.

Recently, Furssow and Wlassow[11] have critically analyzed the foundations of the theory of resonance broadening discussed above. It suffices here only to point out that their method of attacking the problem again yields the dispersion Eq. (3), where now

$$\Delta\nu_{\frac{1}{2}} = (2e^2f/3\pi m\nu_0)N \text{ sec.}^{-1}. \tag{8}$$

It is to be noted that (5), (7) and (8) differ from one another only by a numerical factor.

To recapitulate, theory predicts for moderate pressures the distribution (4) for the wings of the line. The velocity effect will contribute strongly, but the dependence of αx upon frequency may remain approximately unchanged. The half-breadth given by (5) must then be considered only as the limiting value. At higher pressures, the line will exhibit an asymmetrical extension. This distant wing may be describable very nearly by (6), since the velocity effect is of less moment.

The foregoing discussion, although containing nothing new, seems appropriate here, in view of the absence of any recent consolidation of existing theoretical knowledge. It may well be interpreted in conjunction with the material of reference 4.

EXPERIMENT

Many investigators have confirmed the predictions of the radiation damping theory.[12] They noted deviation from constant half-breadth at pressures ranging from 0.001 to 0.01 mm Hg. This last fact permits estimation of the Lorentz collision diameter ρ,[13] found variously to be between 100 and 200A for the Na D lines.[14] These considerations are rather indirect.

By actually obtaining the absorption contours for higher pressures, the correctness of (3) was verified by Harrison and Slater[15] for the Na principal series, and again by Trumpy[16] and for Hg 2537 as well, and by Waibel[17] for the Cs principal series ($\rho \cong 100$A). But each found the half-breadths proportional to $N^{\frac{1}{2}}$. In these investigations, the pressure variation was, for the most part, small. Furthermore, some of the results may be questioned in view of the use of what is now known to be faulty technique, i.e.,

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[9] H. Kuhn and F. London, Phil. Mag. **18**, 983 (1934); H. Kuhn, Proc. Roy. Soc. **158**, 212 (1937). See also H. Margenau, reference 8.

[10] V. Weisskopf, Zeits. f. Physik **75**, 287 (1932). Kuhn (reference 8) has shown from considerations of a geometrical nature in connection with the mean free path of the collision process, that the half-breadth should increase somewhat more rapidly with N than indicated by (7).

[11] W. Furssow and A. Wlassow, Physik. Zeits. Sowjetunion **10**, 378 (1936).

[12] R. Minkowski, Zeits. f. Physik **36**, 839 (1926); W. Schütz, ibid, **45**, 30 (1927); M. Weingeroff, ibid, **67**, 679 (1931); S. A. Korff, Astrophys. J. **76**, 124 (1932).

[13] This is a convenient measure of the magnitude of the pressure effect. As is well known, the Lorentz collision theory leads to (3), with $\Delta\nu_{\frac{1}{2}} = N\rho^2\bar{v}$ sec.$^{-1}$, where $\bar{v}$ is the mean relative velocity of the colliding pairs.

[14] The value $\rho \cong 50$A is yielded for Hg from the data on the quenching of resonance radiation of W. Orthmann and P. Pringsheim, Zeits. f. Physik **46**, 160 (1927).

[15] G. R. Harrison, Phys. Rev. **25**, 768 (1925); G. R. Harrison and J. C. Slater, Phys. Rev. **26**, 176 (1925).

[16] B. Trumpy, Zeits. f. Physik **34**, 715 (1925); **40**, 594 (1927).

[17] F. Waibel, Zeits. f. Physik **53**, 459 (1929).

the employment of a foreign gas in the absorption cell, to retard diffusion of the vapor to the (cold) windows. It appears that a systematic study of the pressure effects in a homogeneous atomic absorbing vapor has not been made. In particular, the dependence of the half-breadth upon density has not been resolved experimentally to accord with theory.

This is excepting a recent investigation by Kuhn[18] of Hg 2537 for pressures yielding van der Waals forces. He confirmed (6) for the long wave-length wing, and determined the constant C. Interesting conclusions were drawn as to the nature of the potential energy curves.

Experimenters have invariably been hampered by the inability of the conventional windows (quartz or glass) of the absorption cell to chemically withstand the hot vapors, particularly as to the alkali metals. This difficulty was eliminated in the present instance by the use of the newly developed corrosion-resistant MgO windows.[19] They showed no sign of attack throughout the experiment (K vapor up to 500°C).

PROCEDURE

The source used was a high intensity tungsten incandescent lamp with replaceable filament. The absorption cell consisted of a copper cylinder of internal and external diameters of approximately 1.5 cm and 2.5 cm, respectively. Two lengths were used, 0.2 cm and 15 cm. The cell fitted snugly into a cylindrical resistance-heating-element of 31 cm length, both being enclosed in a vacuum-tight water-cooled steel cylinder having glass end-windows. MgO windows, of diameters of about 2 cm, could be pressed, one at either end, against the absorption cell, and this under vacuum, by virtue of a head, threaded, and containing a sylphon, forming one end of the outermost cylinder. A seal at the windows resulted from the collapse of the thin ring turned at either end of the soft copper cell.

A thermocouple yielded the temperature. It was calibrated *in situ* from the melting points of strips of appropriate metals placed within the cell.

Prior to use, the cell, and the potassium, were independently heated under vacuum to release foreign gases. For each tube-length, and at increasing cell temperature settings, a series of spectrograms was obtained with an astigmatic grating (2.64A/mm dispersion in first order). Eastman type I–R plates were used, with exposure times of the order of a few hours.

Each plate was calibrated from the image of a pair of step-weakeners placed just before it, one on either side of the absorption doublet. The transmission of the step-weakeners was previously determined photographically, *in situ*, using a constant intensity source in conjunction with a high speed rotating sector of variable aperture placed before the slit. A trace of the plates was obtained on a Krüss microphotometer having magnification ratios up to 40 : 1.

All contours were tested graphically for fit to (4). At lower pressures, some deviation is to be expected because of the Doppler effect, and because of the finite resolving power of the spectrograph. And at higher pressures, uncertainty resulted from incipient overlapping of the members of the doublet. This then, was a sufficient reason for using a long tube and a short tube, respectively, for the two cases. At the highest pressure (20 mm), the lines were completely overlapped, and accordingly were treated as a single line of strength equal to the sum of the components, a reasonably valid procedure for large $|\nu_0-\nu|$. In addition, the outer wings for the higher pressures were tested for fit to the equation

$$\alpha x = \text{const } (N^2 fx)(\nu_0-\nu)^{-a}, \tag{9}$$

where a, a positive constant, is to be determined.

Vapor pressure data for potassium are rather incomplete. Fiock and Rodebush,[20] for a lower limit of 680°K, found

$$\log_{10} \text{p} = -4433/T + 7.183, \tag{10}$$

where p is the vapor pressure in mm Hg, and T is the absolute temperature. This formula, when extrapolated to lower temperatures, yields pressures only in approximate agreement with those given by other observers; but the latter show considerable disagreement among themselves. For the sake of definiteness, (10) was used here throughout.[21] The density then follows from

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[18] H. Kuhn, Proc. Roy. Soc. **158**, 230 (1937).

[19] J. Strong and R. T. Brice, J. O. S. A. **25**, 207 (1935).

[20] Fiock and Rodebush, J. Am. Chem. Soc. **48**, 2522 (1926).

[21] A. R. Gordon, J. Chem. Phys. **4**, 100 (1936), has determined the molecular concentration. At 800°K there is only a 2 percent formation of molecules.

$N=9.70\times 10^{18}p/T$. It is probable that (10) yields too small a pressure. Hence, although the relative values of the half-breadths here determined cannot be seriously in error, the absolute values may be a little high.

In evaluating the constant A of (4) for each line, the density N was determined as in the foregoing paragraph, the tube-length x was measured directly, and the oscillator strengths were assumed to have the values $f_s=\frac{2}{3}$, $f_l=\frac{1}{3}$, where s and l refer to the short and long wave-length component, respectively.

Discussion

With the exception of the higher pressures, the dispersion formula (4) was adequate to describe the observed contours, thus confirming the theory of the resonance interaction. The half-breadths were determined for each line from the measured value of $A\Delta\nu_{\frac{1}{2}}$, in conjunction with the known value of A. In Table I is given $(\Delta\nu_{\frac{1}{2}})_s/N$ and $(\Delta\nu_{\frac{1}{2}})_l/N$ (cm³/sec.) for each pressure. No differentiation is there made explicitly as to wing, or as to tube-length. The value given parenthetically for $p=20$ mm, is the average for each wing of the completely overlapped line.

The ratios of the half-breadths, as between the components, are shown in the last column.[22] They are scattered uniformly over the whole pressure range about a mean of 1.05. The theory of the resonance interaction has not been refined sufficiently to deal with fine structure. Hence it is not possible to compare theory and experiment in this connection.*

TABLE I. *Observed half-breadths.*

T	p	N	$(\Delta\nu_{\frac{1}{2}})_s/N \times 10^7$	$(\Delta\nu_{\frac{1}{2}})_l/N \times 10^7$	$(\Delta\nu_{\frac{1}{2}})_s/(\Delta\nu_{\frac{1}{2}})_l$
444	1.58×10^{-3}	3.45×10^{13}	2.0	2.3	0.9
461	3.67	7.73	2.0	2.2	0.9
463	4.05	8.47	6.4	6.4	1.0
481	9.18	1.85×10^{14}	3.2	2.8	1.1
498	1.90×10^{-2}	3.71	2.9	2.8	1.0
516	3.89	7.31	2.7	2.7	1.0
518	4.20	7.87	3.1	2.6	1.2
545	1.11×10^{-1}	1.98×10^{15}	4.5	4.1	1.1
555	1.56	2.73	2.2	2.2	1.0
584	3.89	6.47	4.3	4.2	1.0
593	5.09	8.32	3.2	2.4	1.3
633	1.51×10^{0}	2.31×10^{16}	2.4	2.8	0.9
664	3.21	4.69	3.6	3.7	1.0
696	6.47	9.03	3.1	2.4	1.3
755	2.00×10^{1}	2.62×10^{17}	(2.5)		

The linear dependence of the half-breadths upon N, though evident from the table, is best seen graphically.[23] A plot of $\log_{10}(\Delta\nu_{\frac{1}{2}})$ (without regard to component) against $\log_{10} N$ is given in Fig. 1. The points fit a line of unit slope reasonably well over the entire range.[24] The dashed line represents the theoretical value of $\log_{10}\Delta\nu_{\frac{1}{2}}$ for radiation damping, which should be the limiting value of the half-breadths with decreasing pressures. Observations in this region were not obtained. But agreement with other observers as to the pressure at which "deviation" from natural breadth occurs (see above), is not precluded (here at 0.001 mm, about).

The average value of $\Delta\nu_{\frac{1}{2}}/N$ (both components) is 3.2×10^{-7} cm³/sec., which is about $3/f$, $6/f$, and $2/f$ times that value given by (5), (7), and (8), respectively. Since, in any case, $f\leq 1$, a considerable discrepancy exists, one which can hardly be attributable to experimental error. The mean value of the Lorentz collision diameter[13] is $\rho=2.0\times 10^{-6}$ cm, in approximate agreement with the results of other observers for Na.

The interpretation of the observed contours at higher pressures is difficult, because of overlapping of the lines, as noted, because of the nonlinear characteristics of the plate, and because of overlapping of the wings of the lines upon the step-weakener images.

The application of (9) yielded a value of the exponent a, usually somewhat greater than 2. Accordingly, for pressures above about a mm, the half-breadths determined by the use of (4) (listed in Table I) are only approximately correct. The completely overlapped contour for $p=20$ mm yielded, from (9), $a_s=2.5$ and $a_l=2.0$, about. This result for the long wave-length wing is hardly a confirmation of (6). But its smaller value, as compared to that for the short wave-

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[22] The difference in the wave-lengths of the components may be disregarded.

* *Note added in proof.* Dr. W. V. Houston has recently extended the theory to include fine structure. He shows that the component half-breadths should indeed be equal. See abstract of paper presented at the 217th meeting of the American Physical Society (to appear shortly in this publication).

[23] A dependence upon velocity is hardly to be observed unless the temperature be variable independently of N.

[24] Some prior (unpublished) results showed deviations at the lower end. But this may presumably be explained away, as arising from a faulty manner of thermocouple calibration then used.

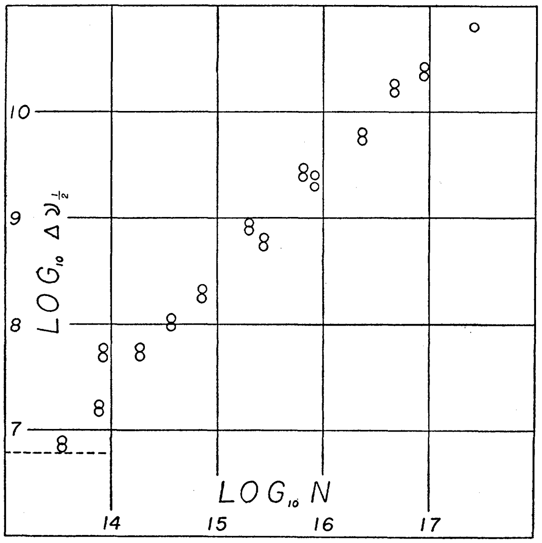

FIG. 1. Showing the linearity of $\Delta\nu_{\frac{1}{2}}$ in N.

length wing, may be attributable to the influence of the van der Waals interaction.

Superimposed upon the long wave-length wing of the much broadened line there appeared a discrete structure, clearly visible only for the plate corresponding to $p=20$ mm. This spectrum was identified as being the infrared bands of K_2,[25] the molecules arising from a weak chemical bond.[26]

A comparison of our K contour at $p=20$ mm, to the microphotometer trace of Kuhn[18] for Hg at $p=7.7$ mm, indicates that the latter exhibits a greater long wave-length asymmetry despite only about $\frac{2}{3}$ the density, but that the broadening (with allowance for a factor N^2fx, and for the difference in wave-length), is considerably less. This result is not surprising, for the resonance forces are expected, theoretically, to be of great importance for K.[27] Kuhn obtained $C=5.4\times10^{-32}$. Then, for Hg, the perturbation energy of (2) is equal to that of (1) ($f\leqq 1/35$) for $R=9$A, about. But, for K, if we assume the same value of C, and use $f=\frac{1}{3}$, the corresponding distance is only about 3A. This result cannot be correct. But it shows that the neglect of the resonance forces for R values even only slightly greater than that corresponding to the potential minimum, is probably unjustified. Furthermore, in order to separate the effects, higher pressures are required for K, as compared to Hg. Using the above value of C, and $R=4$A, (2) yields $\nu_0-\nu=400$ cm^{-1} (240A). This is within the range of out contour for $p=20$ mm. Now (2) is not likely to be valid for much smaller R values, but if the true value of C for K is appreciably greater than that for Hg, the effect of the van der Waals forces may possibly be separable from that of the resonance forces, and for values of $\nu_0-\nu$ greater than those at which occurs a measurable absorption in the present experiment. But in any case, the statistical contour (6) is less readily observable for K, because of the greater masking of the velocity distribution in view of relatively greater speeds of the atoms. It is to be conceded that these last conclusions may be straining the available experimental data. But it seems likely that accurate quantitative determination of the constant C of the van der Waals interaction for K, is hardly to be expected by this method. The circumstance for Cs, however, is more favorable.

The authors wish to express their considerable indebtedness to Drs. I. S. Bowen and W. V. Houston for their many helpful suggestions, to Dr. R. T. Brice for his having kindly supplied the MgO windows, and to Mr. K. Watanabe for valuable assistance.

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[25] For their analysis, see W. O. Crane and A. Christy, Phys. Rev. **36**, 421 (1930).

[26] The existence of van der Waals type molecules for the alkalis has been demonstrated by H. Kuhn, Zeits. f. Physik **76**, 782 (1932), in connection with the higher members of the principal series. Their presence was not here in evidence.

[27] Confirmation of this is forthcoming from comparison of our value of ρ to that given in reference 14 for Hg. For, assuming $N_K=N_{Hg}$, $(\Delta\nu_{\frac{1}{2}})_K/(\Delta\nu_{\frac{1}{2}})_{Hg}\cong(\rho_K)^2/(\rho_{Hg})^2=(200/50)^2=16$.