SHAPE OF THE Hg 2537 Å RESONANCE LINE IN THE PRESENCE OF $Hg(6^3P_1)$–$Hg(6^1S_0)$ INTERACTIONS

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The shape of the Hg 2537 Å absorption resonance line in pure mercury vapour has been investigated over the spectral range between $\tilde{\nu}_0$ — 1800 cm^{-1} and $\tilde{\nu}_0 + 500$ cm^{-1} for Hg vapour having densities from 1.34×10^{16} to 3.50×10^{18} atoms/cm^3, and temperature from 386.2 to 564.4 K, respectively. Results obtained for the short-wave wing are worthy of particular notice. If the absorption coefficient $k(\Delta\tilde{\nu})$ in the long-wave wing is proportional to N^2 (N — Hg number density) then the short-wave wing absorption coefficient is proportional to N, which indicates that pressure broadening does not influence the blue wing of the Hg 2537/Hg. Hence it follows that the difference potential for $Hg(6^3P_1)$–$Hg(6^1S_0)$ interactions is negative over the whole range under investigation. The interaction constant for the potential of van der Waals type has been derived from red wing measurements. Experimental results and calculated constants, together with those reported by other authors are collected in the tables.

1. Introduction

The investigations presented in the paper concern the influence of $Hg(6^3P_1)$–$Hg(6^1S_0)$ interactions on the shape of the mercury resonance line — 2537 Å. Measurements in pure mercury vapour have been performed in order to include the self-broadening contribution to the absorption coefficient observed in the presence of neutral atoms (Ar or Ne). Interesting results, especially for the short-wave wing, as well as a divergence of opinions about the self-broadening of Hg 2537 Å line [1–4] were helpful in writing this paper. The results of the line profile measurements are shown in the figures as $k(\Delta\tilde{\nu})/N^2$ and $k(\Delta\tilde{\nu})/N$-dependences, on logarithmic and log-log scales, for both wings and for different densities of mercury vapour corresponding to different temperatures. For the long-wave wing, in the range of van der Waals forces, the interaction constants ΔC_6^0 and ΔC_6^1 for two distinct potential curves $\Delta V^0(r)$ and $\Delta V^1(r)$, arising from the splitting of the excited $Hg(6^3P_1)$ state into substates with two quantum numbers $\Omega = 0$ and $\Omega = \pm 1$, have been determined assuming

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that only one of the two curves is attributed to the red wing. $\Delta V(r)$ means the difference of the potentials $V^i(r)$, $V^f(r)$ for the initial (ground) and final (excited) states of the system: $\Delta V(r) = V^f(r) - V^i(r)$.

As yet, there is no consistency in opinions about which transitions are responsible for forming the red wing. Kuhn [1] has assumed that both transitions are effective, but the contribution of the transitions connected with $\Omega = \pm 1$ is probably much smaller than that with $\Omega = 0$. Losen and Behmenburg [2] have made the assumption that the red wing is formed exclusively by transitions with $\Omega = \pm 1$, and the blue wing by transitions with $\Omega = 0$. Grycuk [5] has also maintained that the red wing is formed by transitions connected with $\Omega = \pm 1$ only. (The cases discussed above refer to the far long-wave wing, for $|\Delta\tilde{\nu}| > 10^2$ cm^{-1}). The ΔC_6 value derived from experimental results is closely connected with the problem which of the two transitions has been attributed to form the red wing. Comparison presented in Table III shows that the ΔC_6 value obtained in this work is grater than the values obtained by other authors. Grycuk and Pałucha [5] have come to the similar conclusion.

2. *Experimental details and measurements*

The measurements of the broadened absorption line profile were performed using the experimental arrangement described in detail in the previous papers [7, 8]. A high pressure discharge xenon lamp XBO (100 W) was used as the background source. The spectrum was obtained by applying a PGS-2 spectrograph with photoelectrical detection (a EMI 6256 S photomultiplier connected to a self registering recorder GIBI).

Different densities of mercury vapour were obtained by changing the temperature in the electric furnace in which the cell (20 cm long and 2 cm in diameter) containing a drop of the mercury was placed. The furnace was a part of the thermostat arrangement securing

TABLE I

T [K]	386.2	420.3	457.3	488.9	530.5	564.4
p [mm Hg]	0.532	2.48	10.1	28.2	90.1	204.0
N [10^{17} atoms/cm^3]	0.134	0.572	2.14	5.59	16.5	35.0

a very good stability of temperature, with an accuracy equal to 0.2 K. The practical resolving power of the spectrograph was greater than 22000 in the first-order spectrum, dispersion — 7.38 Å/mm. The dispersion of the spectrum registered on the recorder tape was equal to 0.553 Å/mm. In order to have the line shape readable in a wide spectral range, the measurements were performed for 6 different temperatures of the absorption cell ranging from 386.2 to 564.4 K, corresponding to 6 different densities of saturated mercury vapour.

Table I contains the experimental data for a temperature (T), pressure (p), and Hg density (N) in the absorption cell.

Each series of measurements was performed 10 times in order to check the reproducibility of the results and to eliminate accidental effects. The measurements have covered the spectral range of $(\tilde{\nu}_0 - 1800 < \tilde{\nu} < \tilde{\nu}_0 + 500)\ \mathrm{cm}^{-1}$, where $\tilde{\nu}_0$ — the wave number corresponding to the center of the unperturbed resonance line.

The spectral distribution of the absorption coefficient $k(\Delta\tilde{\nu})$ in the line wings was derived from measurements of the spectral distribution of the intensity transmitted by the absorption cell, once with mercury in it ($I(\Delta\tilde{\nu})$, at an elevated temperature) and once without mercury ($I_0(\Delta\tilde{\nu})$, at room temperature), $k(\Delta\tilde{\nu})$ was then obtained from the well known relation

$$k(\Delta\tilde{\nu}) = (1/l) \ln (I_0(\Delta\tilde{\nu})/I(\Delta\tilde{\nu})). \tag{1}$$

3. Discussion of the results

In order to analyse the experimental results it is convenient to present them in figures as the relations $k(\Delta\tilde{\nu})/N^2$ and $k(\Delta\tilde{\nu})/N$, on logarithmic and log-log scales. Such a presentation of the results is a good illustration of whether the line wing has been pressure broadened or not. Moreover, by plotting these relations on a log-log scale, one can find the spectral range in which the difference potential is of the type

$$\Delta V(r) = -C/r^n, \tag{2}$$

and determine the value of n as well. The assumption that the interactions between the atoms are described by relation (2) leads to the following formula for the spectral distribution of the absorption coefficient in the line wings:

$$k(\Delta\tilde{\nu}) = AN^2(\Delta\tilde{\nu})^{-(n+3)/n}, \tag{3}$$

where A is constant within the limits of the validity of formula (2). On a log-log scale, relation (3) assumes the shape of a straight line with a slope $-p = -\dfrac{n+3}{n}$. For a potential of the van der Waals type, $n = 6$ and $p = 3/2$. The defining of the spectral range limits, where the slope of the red wing is equal $-3/2$, is necessary for determining the true difference potential directly from far wing measurements, without relying on any particular model function. The direct method has been reported by Behmenburg [6].

3.1. The short-wave wing

In figures 1 and 2 the spectral distributions of the absorption coefficient in both wings of the Hg 2537/Hg line and for different densities of the Hg atoms have been plotted in the form of relations $k(\Delta\tilde{\nu})/N^2$ and $k(\Delta\tilde{\nu})/N$, respectively. The behaviour of the blue wing, with changing mercury density, clearly differs from that for the red wing. If the absorption coefficient in the red wing ($\Delta\tilde{\nu} < 0$) is proportional to N^2 (in Fig. 1 the experimental points corresponding to different densities are on the same curve), in the blue wing ($\Delta\tilde{\nu} > 0$), there is no such proportionality (in Fig. 1 the curves formed by points obtained for different N are distinctly displaced from each other). Instead, the experimental points for the blue

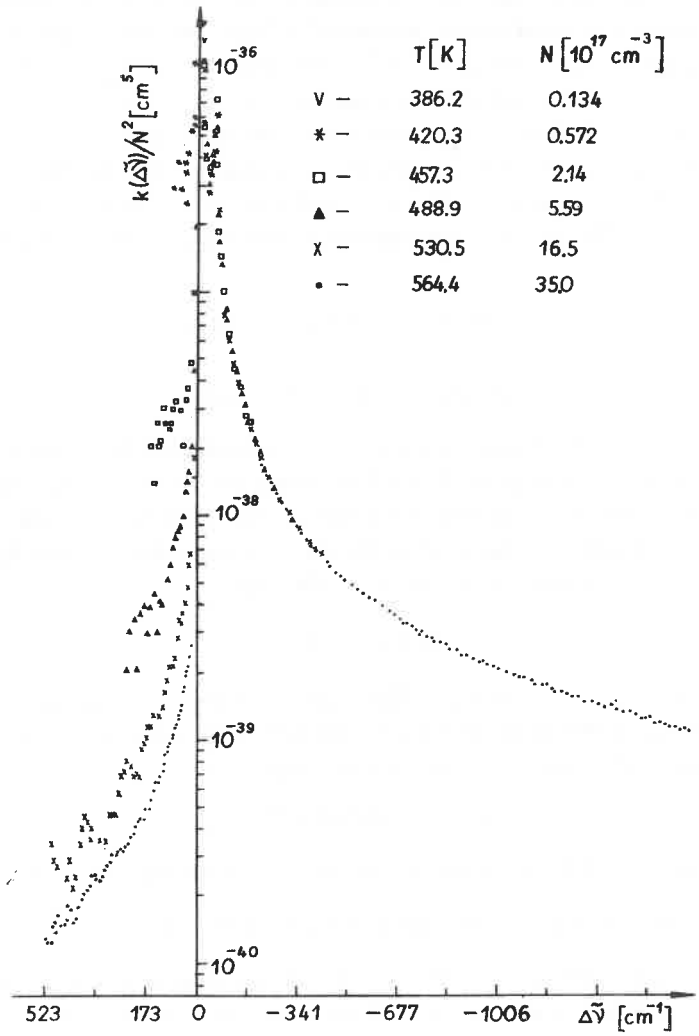

Fig. 1. Shapes of the self-broadened Hg-absorption line 2537 Å for the various densities ($k(\Delta\tilde{\nu}) \sim N^2$ for $\Delta\tilde{\nu} < 0$)

wing form one curve if they have been plotted as a function of $k(\Delta\tilde{\nu})/N$ (Fig. 2). Therefore, the absorption coefficient in the blue wing is proportional to N and not N^2. It shows that there is no pressure broadening towards short-wave lenghts and that the difference potential for $Hg(6^3P_1)$ — $Hg(6^1S_0)$ interactions is negative over the whole range under investigation.

The differences between the blue and red wings described above are also visible in figures 3, 4 and 5, where the red (Fig. 3) and blue (Figs 4, 5) wings are shown separately on a log-log scale for different Hg densities.

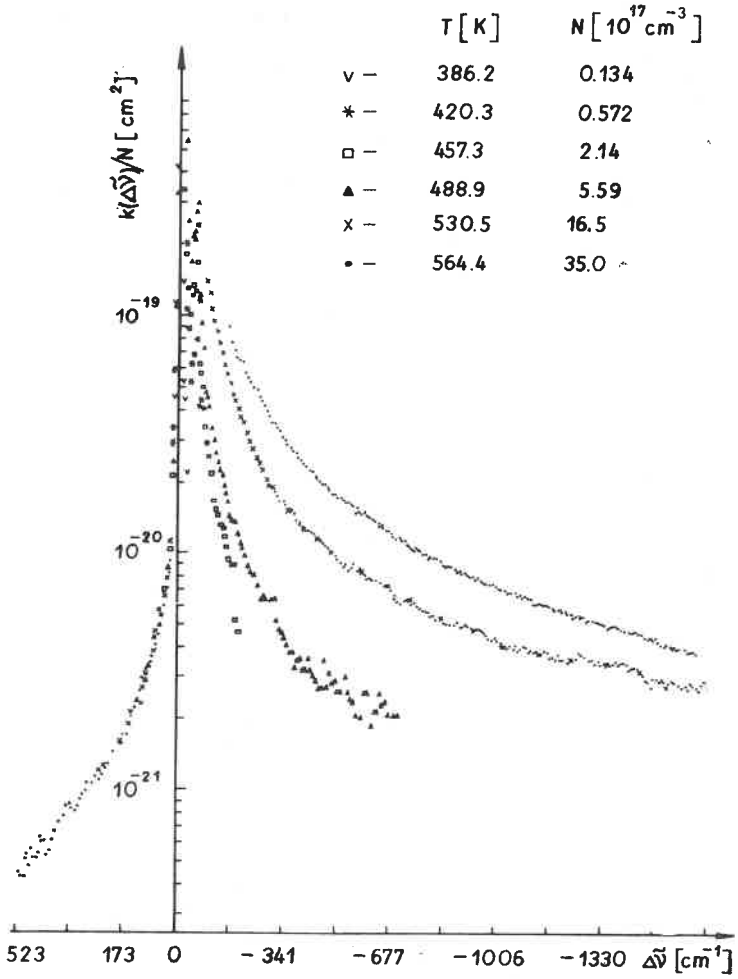

Fig. 2. Shapes of the self-broadened Hg-absorption line 2537 Å for the various densities ($k(\Delta\tilde{\nu}) \sim N$ for $\Delta\tilde{\nu} > 0$)

In papers [1, 2] the results for the blue wing obtained for different densities have been plotted on a common experimental curve $k(\Delta\tilde{\nu})/N^2$. However Kuhn [1] has mentioned that his measurements were hardly accurate enough to prove the proportionality of $k(\Delta\tilde{\nu})$ to N^2. The measurements of Losen and Behmenburg [2] for the blue wing covered a relatively narrow density range of $(1.065\text{–}3.36) \times 10^{18}$ atoms/cm^3, which is probably the reason for the absence of any noticeable displacement of the points for different N on the $k(\Delta\tilde{\nu})/N^2$--plot. One ought to stress that the results presented here relate to a wider range of densities, between 1.34×10^{16} and 3.50×10^{18} atoms/cm^3. Perrin–Lagarde and Lennuier [3] have argued that $k(\Delta\tilde{\nu})$ is proportional to N^2, but they have not given clear information about the density range in which that dependence had been studied.

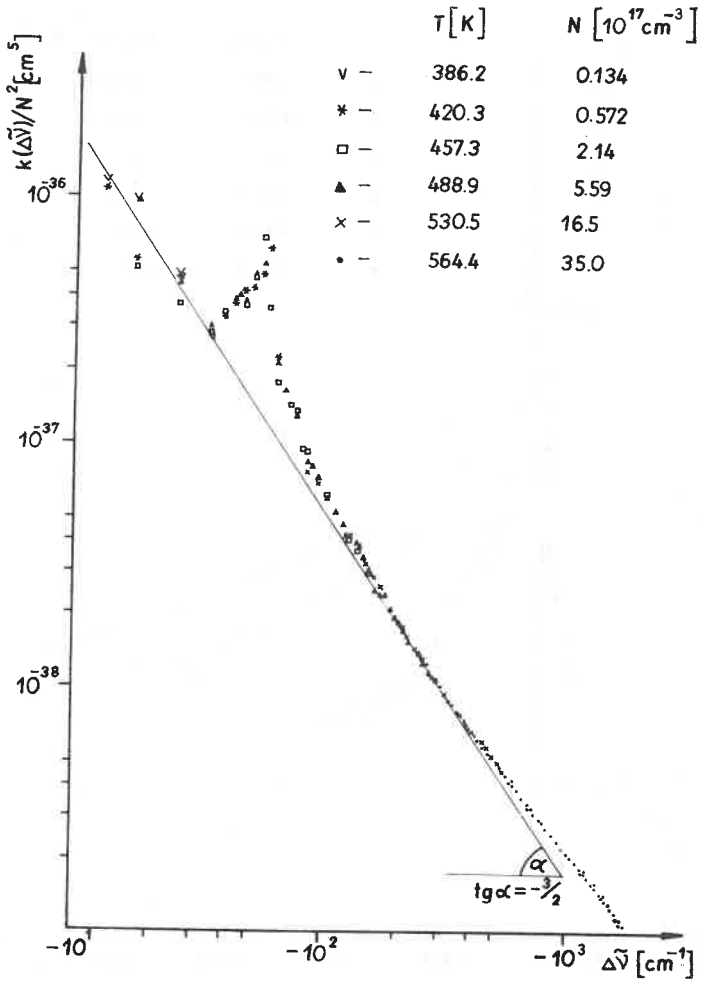

Fig. 3. Red wing of the self-broadened Hg-absorption line 2537 Å

It is shown in figures 4 and 5 that two rectilinear parts can be distinguished in the blue wing plotted on a log-log scale. Two straight lines whose slopes are

$$\operatorname{tg}\alpha_1 = -2 \quad \text{for} \quad \Delta\tilde{\nu} \lesssim 26\ \text{cm}^{-1}$$

and

$$\operatorname{tg}\alpha_2 = -1 \quad \text{for} \quad \Delta\tilde{\nu} \gtrsim 26\ \text{cm}^{-1}.$$

seem to be a good approximation of the experimental wing. It has been reported in papers [1] and [2] that the decrease of the blue wing was much faster than the inverse square of $\Delta\tilde{\nu}$. On the other hand, the authors of the paper [3] have also distinguished two straight

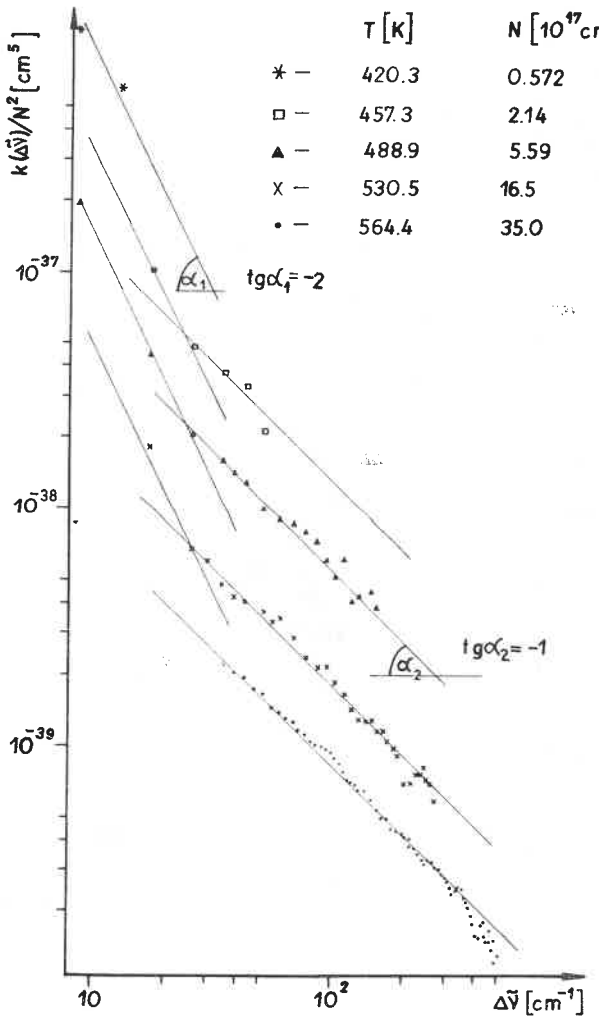

Fig. 4. Blue wing (the reduced absorption coefficient $k(\Delta\tilde{\nu})/N^2$) of the self-broadened Hg-2537 Å line for the various densities of the Hg atoms

lines, but with the slopes of $-11/3$ and $-9/2$ and crossing at $\Delta\tilde{\nu} = 1.5\ \mathrm{cm}^{-1}$. The results relating to the blue wing of the Hg 2537/Hg line, obtained by different authors have been collected in Table II.

3.2. The long-wave wing

The spectral distributions of the absorption coefficient in the red wing have been plotted against $\Delta\tilde{\nu}$ in figures 1, 2 and 3 (the last plot is on a log-log scale).

The measurements have covered the spectral range between -10 and $-1800\ \mathrm{cm}^{-1}$. The quantitative comparison of these results shows that they are in very good agreement

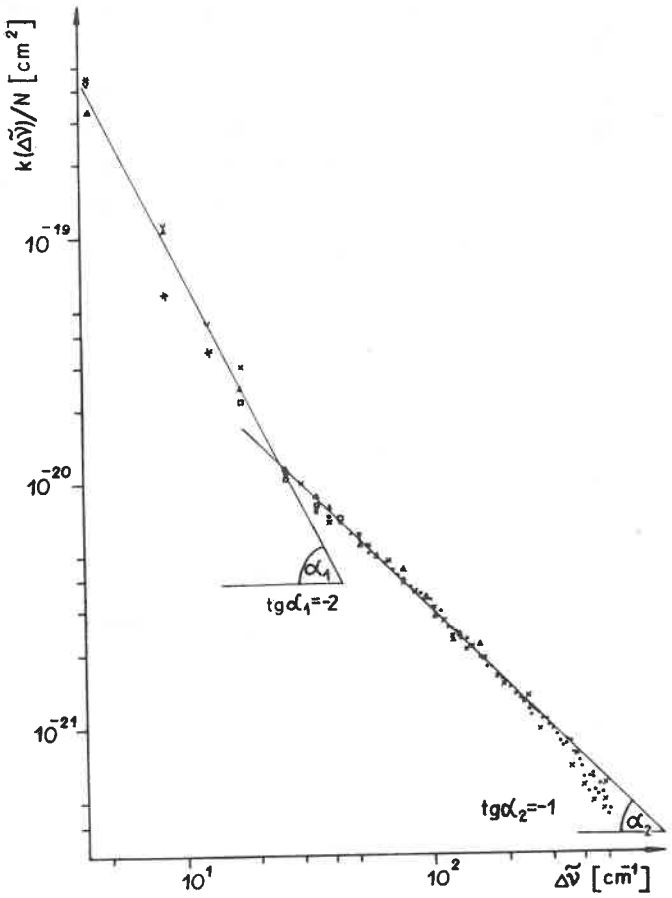

Fig. 5. Blue wing of the self-broadened Hg-absorption line 2537 Å

with those presented by Losen and Behmenburg [2] (deviations within 3 %) in the common for both papers spectral region (-100 to -1800) cm^{-1}. From Fig. 3 the spectral range in which interactions of the van der Waals type have the main influence on the shape of the red wing has been determined as well as the constants ΔC_6 for two possible difference potentials responsible for the red wing: $\Delta V^0(r)$ if the red wing is formed by electronic transitions 6^1S_0–6^3P_1 with $\Omega = 0$, or $\Delta V^1(r)$ if with $\Omega = \pm 1$.

It has been found that the rectilinear part of the wing, with a slope exactly equal to $-3/2$, is limited to values of $\Delta\tilde{\nu}$ between -220 and -350 cm^{-1}. Near -60 cm^{-1} the large discrete Hg_2 band has appeared, of which the long-wave wing extends up to about -220 cm^{-1} (this is in agreement with the results obtained by Grycuk and Pałucha [5]), increasing the value of the absorption coefficient in relation to the further rectilinear part of the wing. For $|\Delta\tilde{\nu}| > 350$ cm^{-1} a decrease of the absorption coefficient is slower than for the "$-3/2$" region.

TABLE II

Blue wing	I Kacprzyk	II Kuhn*	III Losen and Behmenburg*	IV Perrin–Lagarde and Lennuier
1. Investigated spectral region [cm^{-1}] [GHz]	$8 < \Delta\tilde{\nu} < 500$ $120 < \Delta\tilde{\nu} < 15000$	$\sim 5 < \Delta\tilde{\nu} < 30$ $\sim 150 < \Delta\nu < 900$	$\sim 23 < \Delta\tilde{\nu} < 100$ $\sim 700 < \Delta\nu < 3000$	$\Delta\tilde{\nu} < 50$ $\Delta\tilde{\nu} < 1500$
2. Density [atoms/cm^3] Temperature [K]	1.34×10^{16}—3.50×10^{18} 386.2—564.4		1.065×10^{18}—3.36×10^{18} 513.0—562.9	10^{16}—10^{19}
3. Shape of the function describing a wing $k(\Delta\tilde{\nu})$	$k(\Delta\tilde{\nu}) \simeq BN(\tilde{\nu}-\tilde{\nu}_0)^{-2}$ for $\Delta\tilde{\nu} \lesssim 26\ cm^{-1}$, $k(\Delta\tilde{\nu}) \simeq CN(\tilde{\nu}-\tilde{\nu}_0)^{-1}$ for $\Delta\tilde{\nu} \gtrsim 26\ cm^{-1}$	$k(\Delta\tilde{\nu}) \sim N^2(\tilde{\nu}-\tilde{\nu}_0)^{-4.2}$ uncertain because of insufficient accuracy of measurements	$k(\Delta\tilde{\nu}) \simeq CN^2(\tilde{\nu}-\tilde{\nu}_0)^{-3.7}$ very short interval of densities	the Lorentzian form with the width $\sim N$ for $\Delta\nu < 45$ GHz ($\Delta\tilde{\nu} < 1.5\ cm^{-1}$) $k(\Delta\nu) = CN^2(\nu-\nu_0)^{-11/3}$ for $45 < \Delta\nu < 210$ GHz ($1.5 < \Delta\tilde{\nu} < 7.0\ cm^{-1}$) $k(\Delta\nu) = CN^2(\nu-\nu_0)^{-9/2}$ for $210 < \Delta\nu < 1500$ GHz ($7.0 < \Delta\tilde{\nu} < 50\ cm^{-1}$)
4. Values of the proportionality coefficients for $[k(\Delta\tilde{\nu})] = cm^{-1}$ $[N] = cm^{-3}$ and a) $[\Delta\tilde{\nu}] = GHz$ b) $[\Delta\tilde{\nu}] = cm^{-1}$	b) $B = 6.8\times10^{-18}$ b) $C = 3.0\times10^{-19}$	only qualitative comparison is possible	b) $C = 2.55\times10^{-34}$	a) $B = 7.82\times10^{-29}$ b) $B = 3.00\times10^{-34}$ a) $C = 603\times10^{-29}$ b) $C = 13.6\times10^{-34}$

* The values collected in the rows 1,3 and 4 are calculated in the present paper on the basis of the graphs reported in [1, 2].

TABLE III

Red wing	I Kacprzyk	II Kuhn	III Losen and Behmenburg	IV Perrin-Lagarde and Lennuier
1. Investigated spectral region [cm^{-1}] [GHz]	$10 < \lvert\Delta\tilde{\nu}\rvert < 1800$ $300 < \lvert\Delta\nu\rvert < 54000$	$\sim 9 < \lvert\Delta\tilde{\nu}\rvert < 1000$ $\sim 270 < \lvert\Delta\nu\rvert < 30000$	$100 < \lvert\Delta\tilde{\nu}\rvert < 10^4$ $3000 < \lvert\Delta\nu\rvert < 3\times10^5$	$\lvert\Delta\tilde{\nu}\rvert < 333$ $\lvert\Delta\nu\rvert < 10^4$
2. Density of Hg [atoms/cm^3] Temperature [K]	1.34×10^{16}—3.50×10^{18} 386.2—564.4		2.62×10^{17}—3.36×10^{18} 463.9—562.9	10^{16}—10^{19}
3. Shape of the function describing a wing $k(\Delta\tilde{\nu})$	$k(\Delta\tilde{\nu}) \simeq AN^2(\tilde{\nu}_0-\tilde{\nu})^{-3/2}$ for $(220 < \lvert\Delta\tilde{\nu}\rvert < 350)$ cm^{-1}, for $\lvert\Delta\tilde{\nu}\rvert > 350$ cm^{-1} the slope of the wing decreases	$k(\Delta\tilde{\nu}) \sim N^2(\tilde{\nu}_0-\tilde{\nu})^{-3/2}$ for $(9 < \lvert\Delta\tilde{\nu}\rvert < 160)$ cm^{-1} or $k(\Delta\tilde{\nu}) \sim N^2(\tilde{\nu}_0-\tilde{\nu})^{-1.6}$ for $(9 < \lvert\Delta\tilde{\nu}\rvert < 1000)$ cm^{-1}	in the spectral region $(-100, -1800)$ cm^{-1} the quantitative comparison of the results $k(\Delta\tilde{\nu})/N^2$ with those given in column I is in agreement with an accuracy of 3%	the Lorentzian form with the width $\sim N$ for $\lvert\Delta\tilde{\nu}\rvert < 4.5$ cm^{-1} ($\lvert\Delta\nu\rvert < 135$ GHz) and $k(\Delta\tilde{\nu}) = AN^2(\tilde{\nu}_0-\tilde{\nu})^{-3/2}$ for $8 < \lvert\Delta\tilde{\nu}\rvert < 28.3$ cm^{-1} ($240 < \lvert\Delta\nu\rvert < 850$ GHz)
4. Values of the proportionality coefficients for $[k(\Delta\tilde{\nu})] = cm^5$, $[N] = cm^{-3}$ and a) $[\Delta\nu] = GHz$ b) $[\Delta\tilde{\nu}] = cm^{-1}$	b) $A = 5.44\times10^{-35}$	only qualitative comparison is possible		a) $A = 8.98\times10^{-33}$ b) $A = 5.465\times10^{-35}$

5. Values $k(\Delta\tilde{\nu})/N^2$ for $\Delta\nu = -300\ \mathrm{cm}^{-1}$ [cm^5]		$\sim 1.08\times10^{-38}$		$\sim 1.11\times10^{-38}$	$\sim 1.105\times10^{-38}$
6. Constant for van der Waals potential ΔC_6 a) [eV Å^6] b) [$\mathrm{s}^{-1}\ \mathrm{cm}^6$]	$\Omega = 0$	a) 1477 ± 12 b) $(35.7\pm0.3)\times10^{-32}$	a) 223.3		a) 177.8
	$\Omega = \pm 1$	a) 369 ± 3 b) $8.93\pm0.08)\times10^{-32}$	b) 5.4×10^{-32}	a) 270 ± 50 b) $(6.5\pm1.2)\times10^{-32}$	b) 4.3×10^{-32}

For $\Delta\tilde{\nu}$ in the neighbourhood of the center of the line ($\Delta\tilde{\nu} = 0$), (also for the short-wave side), the accuracy of the results is less than for the far wings because of the steep run of the recorded profiles in this region, and that is why the deviations of the experimental points near the center of the line are relatively large in figures 3, 4, 5.

The results referring to the red wing are collected in Table III. For comparison, the Table also contains the results obtained by other authors [1–3]. The very good agreement of the absorption coefficient $k(\Delta\tilde{\nu})/N^2$, given exemplarily for $\Delta\tilde{\nu} = -300\ \mathrm{cm}^{-1}$, is visible[1].

Nevertheless, the essential differences between the ΔC_6 values are noticeable, especially the value of ΔC_6 in column IV which is about two times less than that in column I for $\Omega = \pm 1$. One of the reasons for the differences is probably the divergence of interpretations of the Hg 2537/Hg red wing (see Introduction). Perrin–Lagarde and Lennuier have not given any information about the interpretation assumed by them.

4. Remarks

In the present paper the temperature effects in the wings of the investigated line have been ignored. Such effects were noticeable, especially in the behaviour of the red Hg_2 molecular band ($-60\ \mathrm{cm}^{-1}$) and many smaller bands occurring in both wings of the line (Figs 1, 2, 4). This problem as well as that relating to the determination of the true difference potential $\Delta V(r)$ for $Hg(6^3P_1)$–$Hg(6^1S_0)$ interactions are being studied and will be presented in the next paper.

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[1] The values given in columns III and IV are calculated in the present paper on the basis of the graph reported in [2] and from the formula describing a red wing for the "$-3/2$" region (see the row 3) reported in [3], respectively.