Resonance Broadening and Oscillator strength of the Mercury Absorption Line 1850 Å

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(Z. Naturforsch. 30 a, 445—450 [1975]; received December 19, 1974)

A new method for the determination of $f$-values of resonance transitions from wing-measurements of selfbroadened resonance absorption lines is described. The method is applied to the mercury resonance transition $6^1S_0 \rightarrow 6^1P_1$, $\lambda$ 1850 Å. The resulting $f$-value of 1.08 ± 0.05 agrees well with those obtained from other methods.

I. Introduction

For the derivation of interaction potentials from measurements of the near resonance absorption spectrum of a gaseous mixture containing an absorbing and a perturbing gas, a knowledge of selfbroadening of the absorption line is necessary. This would be of particular importance in case of a resonance transition, where, because of the large oscillator strength, resonance broadening will in general contribute considerably to the spectrum.

In addition, measurements of resonance broadening would yield a possibility of testing line broadening theories, since at least in simple cases the resonance interaction constant may be calculated from perturbation theory. On the other hand, after having proved the reliability of the broadening theory, the interaction constant and thus the oscillator strength of the line may be derived from line profile measurements. Such a method for the determination of radiative transition probabilities may with advantage be applied to lines in the visible spectral range, ending on a resonance level, whereas the resonance transition (to the ground state) lies in the extreme UV. Based on this idea, Vaughan has determined the $f$-value of the He resonance line $\lambda$ 584 Å ($1^1S \rightarrow 2^1P$) from measurements of the halfwidths of the He-emission lines $\lambda$ 7281 Å ($2^1P \rightarrow 3^1S$) and $\lambda$ 6678 Å ($2^1P \rightarrow 3^1D$).

In this paper we propose a method of determining $f$-values of resonance transitions from far wing measurements of self broadened resonance absorption lines. Its applicability relies essentially on the validity of the quasistatic theory of line broadening.

The method was tested for the case of the Hg absorption line $\lambda$ 1850 Å ($6^1S_0 \rightarrow 6^1P_1$). One reason, among others, for choosing this line was, that its far wings do not interfere with those of neighbouring multiplet components (as is the case with the alkali doublets). Measurements were carried out with saturated Hg vapor, contained in a 10 cm long absorption cell, at two different Hg number densities, namely $1.37 \times 10^{18}$ and $5.85 \times 10^{18}$ cm$^{-3}$, corresponding to temperatures of 388.2 and 421.2 K respectively. At these densities absorption coefficients could be measured with good accuracy in the range between 30 and 400 cm$^{-1}$ wave number distance from the unperturbed resonance line. In this range and under the experimental conditions quoted above the binary approximation of the quasistatic theory, on which the evaluation of the oscillator strength is based, may assumed to be valid, as will be shown.

The $f$-value of the Hg resonance transition, obtained in this way, is 1.08 ± 0.05. It agrees well with the values $1.17 \pm 0.06$ and $1.12 \pm 0.04$, obtained from zero field level-crossing (Hanle-effect) measurements.

II. Theory

For the interaction between two neutral atoms one obtains in the dipole-approximation from perturbation theory up to second order

$$V(r) = -\frac{C_3}{r^3} - \frac{C_6}{r^6} - \ldots$$

(1)

$r$ being the internuclear distance. If both atoms are different the coefficient $C_3$ of the first order term is zero. If, on the other hand, both atoms are alike but in different electronic states, resonance interaction will occur, i.e. $C_3 \neq 0$. For the special case (which...
we consider) that one atom is in the ground state with angular momentum quantum number \( L = 0 \) and one in the resonance state with \( L = 1 \), one obtains for \( C_3 \) the expression:

\[
C_{3|M|} = \gamma_{|M|} \frac{e^2 \hbar}{4 \pi m v_0} f_{ge} \tag{2}
\]

with \( \gamma_0 = -2, \quad \gamma_1 = 1 \)

\((e, m \) charge and mass of the electron, \( v_0, f_{ge} \) frequency and oscillator strength of the resonance line, respectively, \( \hbar \) Planck's constant). The dependence of \( C_{3|M|} \) on the orientation quantum number \( M \) with respect to the internuclear axis leads to an asymmetric splitting of the resonance state.

On the other hand, additional information on the constants \( C_{3|M|} \) and \( f_{ge} \) may be obtained from the absorption coefficient \( k(\Delta v) \) as function of the frequency in the wings of the self-broadened resonance line. As will be shown below, the quasi-static theory of line broadening relates \( k(\Delta v) \) to the quantities \( C_{3|M|} \) and \( f_{ge} \) as parameters by

\[
k(\Delta v) = f_{ge} g(\Delta v, C_{3|M|}) .
\]

In principle then \( C_{3|M|} \) and \( f_{ge} \) may be obtained from measurements of \( k(\Delta v) \) and using the relation (2).

According to the binary approximation of the quasi-static theory of line broadening, the absorption coefficient at the distance \( \Delta r \) of the radiation frequency \( v \) from the resonance frequency \( v_0 \) is proportional to the probability of finding the perturber at internuclear distances \( r_{|M|} \) from the radiating atom, where it just produces the frequency perturbation \( \Delta v \):

\[
k(\Delta v) d(\Delta v) = \sum_{|M|} K_{|M|} W[r_{|M|}(\Delta v)] . \tag{3}
\]

Here the summation has to be taken over all adiabatic states \( |M| \), into which the excited atomic state splits in the field of the perturber. The constant \( K_{|M|} \) is given by

\[
K_{|M|} = \frac{\pi e^2}{mc} g_{|M|} g_j f_{ge} N \tag{4}
\]

\((g_j, g_{|M|} \) statistical weights of the excited state and its substates, respectively, \( c \) velocity of light, \( N \) number density of absorbing atoms). The probability density \( W(r) \) is in the case of thermal equilibrium given by

\[
W(r) = 4 \pi r^2 n(r) \exp \left\{ -\int_0^r 4 \pi r^2 n(r) \, dr \right\} , \tag{5}
\]

\[
n(r) = n_0 \exp \left\{ - V_0(r)/kT \right\} I(r) \tag{6}
\]

\((n_0 \) perturber number density, \( k \) Boltzmann constant, \( T \) absolute temperature, \( V_0(r, \) ground state interaction potential, \( I(r) \) number of free pairs relative to the total number of pairs free and bound\(^9\)). \( r_{|M|}(\Delta v) \) is the inverse function of \( \Delta v_{|M|}(r) \), which in turn is related to the difference \( V_{|M|}(r) = V_{|M|}(r) - V_0(r) \) of the adiabatic potentials for the excited and ground state of the system respectively by

\[
\Delta v_{|M|}(r) = (1/h) V_{|M|}(r) . \tag{7}
\]

The function \( k(\Delta v) \) may then be calculated in principle from (1) and (3) to (7). The calculation simplifies considerably in the special case of the selfbroadened Hg absorption line \( \lambda 1850 \, \AA \) \( ^{6s}S_0 \rightarrow ^{6p}P_1 \) considered. In this case, as will be shown in Chapt. V, the following assumptions are fulfilled: (a) The line wings are exclusively formed by either one of the Hg-transitions \( \Delta M = 0 \) and \( \Delta |M| = 1 \). Then the sum in (3) reduces to a single term for each wing. (b) The second order term \( \sim r^{-6} \) in (1) is negligibly small compared to the resonance term \( \sim r^{-3} \) in the spectral range investigated. (c) The function \( g(r) \equiv \exp \left\{ -\frac{4 \pi r^2 n(r) \, dr}{kT} \right\} \) in (5) and the function \( f(r) \equiv \exp \left\{ - V_0(r)/kT \right\} I(r) \) in (6) are nearly constants close to unity. Under these assumptions one then obtains:

\[
k(\Delta v)/N^2 = \frac{2 \pi c^2}{3 m c f_{ge}} g_{|M|} C_{3|M|} g_j \hbar \Delta v^{-2} . \tag{8}
\]

The proportionality of \( k(\Delta v) \) to \( \Delta v^{-2} \) is characteristic for pure resonance interaction. \( k(\Delta v) \) is symmetric with respect to \( \Delta v = 0 \) because the product \( g_j C_{3|M|} \) is independent of \( |M| \); this follows from (2) since \( g_{|M|} \) takes the values 1 and 2 for \( |M| = 0 \) and 1 respectively.

From the measurement of \( k(\Delta v) \) we then obtain by means of (8) the value of the product \( C_{3|M|} f_{ge} \) and by using (2) finally the \( f_{ge} \)-value:

\[
f_{ge} = \frac{3 m c^2}{e^2} \bar{v}_0^{-1/2} \left( \frac{k(\Delta v)}{N^2 \Delta v^2} \right)^{1/2} . \tag{9}
\]

where \( \Delta v \) has been replaced by \( c \Delta \bar{v} \).

**III. The Experimental Arrangement**

Details of the experimental arrangement will be published elsewhere\(^9\). Here we restrict ourselves to describing the main features of the apparatus.
1. Optics

The measurements of the absorption spectrum in the vicinity of the Hg line $\lambda 1850$ Å was performed using a conventional single beam arrangement. Radiation from a continuous background source (commercial deuterium lamp) was passed through an absorption tube, then spectrally selected and measured photoelectrically. The total light path was kept under vacuum at less than $10^{-4}$ torr.

Spectral selection was achieved by means of a 0.5 meter McPherson grating monochromator of 16.4 Å/mm dispersion in first order. Slit widths were chosen to 10 μ, corresponding to an effective apparatus width of about 0.25 Å.

Intensity measurements were performed using an EMI photomultiplier of type 9783/B, the output voltage of which across a load resistor was registered by means of a Siemens Kompensograph III.

A weak emission line from a low pressure Hg-discharge lamp was used as frequency reference. The wavelength calibration of the monochromator was checked by measuring the distance of the mercury emission line $\lambda 1942.32$ Å (ion line) from the resonance line $\lambda 1849.68$ Å #10.

2. Absorption Tube

The absorption tube consisted of a quartz cell 10 cm long and 4 cm in diameter. Hg was distilled into the cell, after it had been outgassed for 6 hours under a vacuum of about $10^{-6}$ torr; thereafter it was melted off. The cell was inserted into an oven, which itself was placed into the vacuum chamber. With the oven temperatures up to 450 K could be produced. Maximum change of temperature during the time of measurement (about 15 min) was 0.3 K; the maximum error of temperature measurement was 1.5 K, corresponding to an error of number density of about 5% at 450 K.

3. Measurement of the Absorption Profile

The absorption coefficient was determined from independent measurements of the radiation intensity $I_0(\Delta \nu)$ and $I(\Delta \nu)$ transmitted by the absorption cell without Hg-vapor (room temperature and with Hg-vapor in it (elevated temperature) respectively. After corrections due to the stray-light and dark current $k(\Delta \nu)$ was obtained from the well known relation $I(\Delta \nu) = I_0(\Delta \nu) \exp \{-k(\Delta \nu)l\}$, $l$ being the length of the absorption cell. The intensity of the radiation from the current stabilized Deuterium lamp and the gain of the multiplier were sufficiently constant, so that during a given run the measurements of fractional transmission were accurate to 0.5% near unit transmission. This was controlled by checking, whether in the far blue wing the measured functions $I(\Delta \nu)$ and $I_0(\Delta \nu)$ merged into each other, after they had been addjusted in the far red wing at the beginning of the run.

The wings of the absorption line were measured with saturated mercury vapor at densities $1.37 \times 10^{16}$ and $5.85 \times 10^{16}$ cm$^{-3}$ corresponding to temperatures of 388.2 and 421.2 K respectively.

IV. Results

Figure 1 shows the wavelength dependence of the intensity arriving at the photomultiplier. The signal-to-noise ratios indicated by the trace are typical of the data used to obtain the absorption coefficients cited in this paper. Because of the distortion of the absorption profile by the apparatus profile we use only data for which the wavelength shift from the line center was greater than about 3 times the apparatus width of 0.25 Å.

The measured absorption coefficients had to be corrected for the contribution of the radiation damping. Assuming, that the collision broadened part $k_{\text{coll}}(\Delta \nu)$ may be represented by a dispersion profile $\sim \Delta \nu^{-2}$ over the relevant spectral range and that the observed profile $k_{\text{tot}}(\Delta \nu)$ may be obtained by folding $k_{\text{coll}}(\Delta \nu)$ into the part $k_{\text{rad}}(\Delta \nu)$ produced by radiation damping, one obtains

$$k_{\text{coll}}(\Delta \nu) = k_{\text{tot}}(\Delta \nu) - k_{\text{rad}}(\Delta \nu) \quad (10)$$

Using the well known expression for $k_{\text{rad}}(\Delta \nu)$ one finds, that $k_{\text{rad}}/k_{\text{tot}}$ amounts to about 0.22 and 0.05 at $N = 1.37 \times 10^{16}$ and $5.84 \times 10^{16}$ cm$^{-3}$ respectively.

The absorption coefficient data are shown in Figure 2. There the reduced absorption coefficient, defined by the measured absorption coefficient $k(\Delta \nu)$ divided by the square of the Hg density $N$, is plotted as function of the wavenumber distance from the line center.

Within the error bounds, the absorption coefficient $k$ at a certain $\Delta \nu$ is found to be proportional to $N^2$. Furthermore with good accuracy a proportionality of $k$ to $\Delta \nu^{-2}$ is observed in both wings of the line.

V. Discussion

1. Comparison of the Observed $k(\Delta \nu)$ with Theory

It is seen, that the proportionality of $k(\Delta \nu)$ to $N^2$, as expected from theory, is experimentally veri-
Fig. 1. Wavelength dependence of intensities transmitted by the absorption cell without Hg vapor \((I_0, \text{room temperature})\) and with Hg vapor in it \((I, \text{elevated temperature})\). The \(I_0\)-curve is dash-dotted to indicate, that it is an independent recording obtained by adjustment of the \(I_0\)-signal to the \(I\)-signal at \(\lambda=1960\,\text{Å}\) (zero absorption). The adjustment was achieved by controlling the amplification of the recorder.

2. The Assumptions of the Binary Approximation of the Quasistatic Theory

2.1. The Condition of Stationary Phase

This condition defines in the case of a monotonic potential function a limiting frequency \(|\Delta \omega_L|\), so that for \(|\Delta \omega| \gg |\Delta \omega_L|\) this condition is fulfilled. In case of resonance interaction \(|\Delta \omega_L|\) is given by

\[
|\Delta \omega_L| = \left( \frac{3}{2} \right)^{3/2} \left( \frac{\hbar}{C_{3/10}} \right)^{1/2} \frac{1}{E_{\text{r}}}.
\]

With \(C_{3/10}\) given by (2) and \(E_{\text{r}} = 4.35 \times 10^4\) cm\(^{-1}\) one obtains for \(|\Delta \omega_L|^M \geq |\Delta \omega_L|^M / c 2\pi / c 2\pi / c 2\pi\) for \(M = 0\) and \(M = \pm 1\) respectively. The above condition is thus well fulfilled in the range \(400 \geq |\Delta \phi| / \text{cm}^{-1} \geq 30\) investigated in this paper.

2.2. The Assumption of Binary Interaction

This assumption is fulfilled, if the exponent

\[
g(r) = \exp \left\{ - \int_0^r r^2 n(r)dr \right\}
\]

in (5) is close to...
Fig. 2. Reduced absorption coefficient as function of the wavenumber distance from the line center in both wings of the line at different Hg-number densities. Double logarithmic plot.

unity. For an estimation of the lower bound of $g(r)$ we use from literature the semiempirical potential function $V^e(r)$ for the Hg-Hg-system. With $kT = 3.35 \times 10^{-2}$ eV one obtains

$$n_{\text{max}} \approx 2 \times n_0 \approx 1.2 \times 10^{-7} \text{Å}^{-3}.$$ 

With $r_{\text{max}} = 16.9$ Å from

$$|\Delta \tilde{r}|_{\text{min}} = \frac{C_{30}}{\hbar c} \frac{1}{r_{\text{max}}^3} = 30 \text{ cm}^{-1},$$

one then finds $(1 - 2.4 \times 10^{-3}) \leq g(r) \leq 1$.

2.3. The Criterium of Adiabaticity

The criterium for collisions to be adiabatic with respect to the internuclear axis leads to the existence of a critical frequency $\Delta \omega_{\text{cr}}$, so that in the range $|\Delta \omega| \gg |\Delta \omega_{\text{cr}}|$ $M$-mixing collisions are negligible. In case of resonance interaction $|\Delta \omega_{\text{cr}}|$ is given by

$$|\Delta \omega_{\text{cr}}^{M}| = \left(\frac{\hbar}{\Delta C_3}\right)^{3/2} \frac{C_{31}[M]}{\hbar} \left(\frac{\hbar \bar{v}}{\Delta C_3}\right)^{3/2}$$

with $\Delta C_3 = C_{31} - C_{30}$.

In our special case the values for $|\Delta \omega_{\text{cr}}^{M}| = |\Delta \omega_{\text{av}}^{M}|$ are $0.03$ and $0.015 \text{ cm}^{-1}$ for $M = 0$ and $M = \pm 1$ respectively. The above condition is thus fulfilled within the spectral range under investigation.
3. The f-value of the Hg transition $6^1S_0 \rightarrow 6^1P_1$

The f-value of the Hg transition $6^1S_0 \rightarrow 6^1P_1$ obtained from the method described in this paper, namely $f = 1.08 \pm 0.05$, agrees well with the values $1.17 \pm 0.06$\(^5\) and $1.12 \pm 0.04$\(^6\) from Hanle-effect measurements. From interferometric measurements of the dispersion of mercury vapor in the range between 1890 and 2800 Å, interpreted by means of a 3-term dispersion formula, a f-value of $1.19 \pm 0.02$ was found\(^{13}\).

The good agreement of our f-value with those obtained by other methods excludes possible systematic errors in our determination of the mercury atom densities from temperature measurements via the vapor pressure curve.

4. Range of Applicability of the Method

The agreement shows furthermore, that the quasi-static theory seems to be reliable for the determination of resonance interaction constants from wing measurements of absorption lines. Thus the suggested method for the determination of oscillator strengths should generally be applicable to strong dipole transitions (large f-values). For transitions between multiplet states rather than singlet states considered in this paper only a slight generalization of equation (2) is necessary. For transitions with smaller f-values, on the other hand, where the second order interaction term influences considerably the $k(\Delta r)$-function in the quasistatic validity range, the simple formula (8) cannot be used for the evaluation of the oscillator strength. In this case rather a numerical computation of $k(\Delta r)$ is necessary, starting from a two term potential function and using the expressions (5) and (6) for $W(r)$ in their full generality. The f-value may then be evaluated by means of a proper procedure of adjustment of the computed to the measured function $k(\Delta r)$. For transitions with very small f-values (e.g. intercombination lines), however, the method should be used with caution. In this case the part of the line profile, where resonance interaction still contributes measurably, is shifted towards the line center, where the quasistatic theory becomes increasingly invalid.

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