Interaction Potentials of Hg-Ar from Temperature Dependent Absorption Spectra

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The temperature dependence of the absorption spectrum $k(\tilde{\nu})$ of Hg-Ar-mixtures in the range 30–1000 cm^{-1} about the center of the Hg-line at $\tilde{\nu}_0 = 39425\ \mathrm{cm}^{-1}$ ($\lambda_0 = 2536.5$ Å) has been investigated in the temperature interval 473–1273 K. The measurements were carried out at number densities 1.0×10^{17}–$9.1 \times 10^{18}\ \mathrm{cm}^{-3}$ for Hg and 9.4×10^{18}–$9.7 \times 10^{18}\ \mathrm{cm}^{-3}$ for Ar. Potentials for the Hg-Ar-system in the thermal energy range originating from the Hg-states 6^1S_0 and 6^3P_1 have been deduced from the data. It turned out that they differ considerably from Lennard-Jones-functions. By comparison of the observed spectra with calculations on the basis of quantummechanical theory of collisional line broadening it is concluded that transitions from free translational states of Hg-Ar-pairs as well as bound and quasi-bound vibrational states of the Hg-Ar-molecule contribute to the formation of the satellite structure on the short wavelength side of the Hg-line.

1. Introduction

The spectra of mercury-noble gas systems, in particular of mercury-Argon, have for a long time been the object of numerous investigations; in particular, halfwidth, shift and the wings of the Hg-absorption line λ 2537 Å ($6^1S_0 \rightarrow 6^3P_1$), as well as the structures superimposed to the wing continua (satellites) have been studied in detail [1–4]. Aim of these studies was to derive from the experimental data the molecular potentials involved. Potentials of these systems are of considerable interest because they are known to be possible candidates for excimer lasers [5]. So far, however, only the dependence of the spectra on number densities has been investigated with the result that simple two-term model potentials of the Lennard-Jones type seem to be sufficient for unique interpretation of the data.

On the other hand it is well known that much more information on the potentials may be obtained from the temperature dependence of the spectra; even a pointwise mapping of the real potentials is possible under certain conditions, without relying on any assumptions regarding their analytical representation [6, 7]. This method has already been successfully applied to alkali-noble gas fluorescence spectra [7], and it was demonstrated that real potentials considerably deviate from the simple Lennard-Jones form. In addition, good overall agreement was found with calculated pseudopotentials of Baylis [8] and Pascal and Vandeplanque [9].

Since such calculations are much more difficult and have not been performed so far for Hg-noble gas systems, it appeared desirable to obtain informations experimentally from temperature dependent spectra. In addition, it is hoped that such experiments may contribute to the understanding of the satellites joining the short wavelength side of the Hg-2537 Å line.

In this paper systematic measurements of the temperature dependence of the far wings of the Hg-absorption line 2537 Å perturbed by Ar are reported for the first time. The measurements were performed at Ar-number densities around $10^{19}\ \mathrm{cm}^{-3}$ at temperatures in the range 473–1273 K. By temperature independent variation of the Hg-number densities (1.0×10^{17} to $9.1 \times 10^{18}\ \mathrm{cm}^{-3}$) the spectra could be scanned in the range $20 \leqq |\Delta\tilde{\nu}|/\mathrm{cm}^{-1} \leqq 1000$ of the red wing and $20 \leqq |\Delta\tilde{\nu}|/\mathrm{cm}^{-1} \leqq 500$ of the blue wing of the line ($\Delta\tilde{\nu}$ wave number distance from line center). Potentials evaluated from the measurements have been confronted to the Lennard-Jones-model potentials obtained recently from near wing data ($1 \leqq |\Delta\tilde{\nu}|/\mathrm{cm}^{-1} \leqq 400$) by Lennuier et al. [4].

2. Theory

2.1. Classical Quasistatic Theory

According to the nearest neighbour approximation of the classical quasistatic theory of collisional line broadening (QST) [1] the absorption $k(\Delta\omega)\,\mathrm{d}(\Delta\omega)$ at $\Delta\omega \equiv \omega - \omega_0$ (ω radiation frequency, ω_0 resonance frequency of the atomic oscillator) is proportional to the probability $W(r)\,\mathrm{d}r$ of finding the

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perturbing atom at the internuclear distance r from the optical atom, producing the frequency perturbation $\Delta\omega$:

$$k(\Delta\omega)\,\mathrm{d}(\Delta\omega) = C\,W(r)\,\mathrm{d}r\,. \tag{1}$$

In Eq. (1) $\Delta\omega(r)$ is related to the difference of the adiabatic molecular potentials $V_{\mathrm{e}}^{\Omega}(r) - V_{\mathrm{g}}(r)$ for the excited and ground state by

$$\hbar\,\Delta\omega(r) = V_{\mathrm{e}}^{\Omega}(r) - V_{\mathrm{g}}(r) \equiv \Delta V^{\Omega}(r)\,. \tag{2}$$

For the probability density function $W(r)$ we assume

$$W(r) = n_0\,4\pi\,r^2 \exp\{-V_{\mathrm{g}}(r)/KT\} \tag{3}$$

where n_0 denotes the perturber number density. The constant C in Eq. (1) is given by

$$C = \pi\,r_{\mathrm{e}}\,c\,(g_{\Omega}/g_{\mathrm{J}})\,f_{\mathrm{eg}}\,N \tag{4}$$

where r_{e} = classical electron radius, c = light velocity, g_{Ω}, g_{J} = molecular and atomic statistical weights, f_{eg} = oscillator strength, N = number density of the optical atoms.

In deriving Eq. (1) for $k(\Delta\omega)$ the conditions of the validity of the QST were assumed to be fulfilled:

1) $r(\Delta\omega)$ is a real solution of $\Delta V^{\Omega}(r) - \hbar\Delta\omega = 0$;
2) $\mathrm{d}r(\Delta\omega)/\mathrm{d}(\Delta\omega)$ is not too large, which implies, that the line center and satellite regions have to be excluded;
3) collisional mixing between different substates Ω' of the excited state e is negligible, i.e., the collisions are assumed to be adiabatic with respect to the internuclear axis.

In addition, the following assumptions have been made in the derivation of Eq. (1):

4) $r(\Delta\omega)$ is unique;
5) only a single upper molecular state Ω' contributes to the spectrum;
6) the contribution of bound-free- and bound-bound-transitions to the part of the spectrum under consideration may be negligible;
7) f_{eg} is independent of r.

Substituting Eqs. (2), (3) and (4) into Eq. (1) one obtains the following expression for the temperature dependent absorption spectrum:

$$k(\Delta\omega, T) = G(\Delta\omega)\,B(\Delta\omega, T)\,, \tag{5}$$

$$G(\Delta\omega) = 4\pi\,n_0\,C\,r^2(\Delta\omega)\,\frac{\mathrm{d}r(\Delta\omega)}{\mathrm{d}(\Delta\omega)}\,,$$

$$B(\Delta\omega, T) = \exp[-V_{\mathrm{g}}(r(\Delta\omega))/kT]\,,$$

where $G(\Delta\omega)$ is independent of temperature.

2.2. *Quantum-mechanical Approach*

The simple classical theory outlined above may be generalized for cases in which assumptions 1)—3) of 2.1 are not fulfilled. This generalization has been carried out on the basis of the quantum-mechanical, quasimolecular approach to the theory of collisional broadening theory [10] by Sando and Wormhoudt [11] and by Baylis and Szudy [12]. It should be noted, however, that the results may also be obtained from exact Fourier analysis of the collisionally perturbed classical oscillator [13]. Szudy and Baylis arrive at the following expression for the absorption coefficient:

$$\begin{aligned} k(\Delta\omega) = C\,&\frac{4\pi\,n_0\,\xi^2}{\xi^2 + (\gamma/2)^2} \\ &\cdot \sum_{c} \frac{(\mathrm{Re}(r_{\mathrm{c}}))^2 \exp\{-V_{\mathrm{g}}(\mathrm{Re}(r_{\mathrm{c}}))/kT\}}{|\Delta V'(r_{\mathrm{c}})/\hbar|} \\ &\cdot |36\pi\,z_{\mathrm{c}}|^{1/2}\,L(z_{\mathrm{c}})\,, \end{aligned} \tag{6}$$

$$z_{\mathrm{c}} = \tfrac{1}{2}(\mu/KT)^{1/3}[\Delta V'(r_{\mathrm{c}})/\hbar]^2\,|\Delta V''/\hbar|^{-4/3}\,,$$

$$\xi = \Delta\omega - \Delta\,,$$

γ, Δ = halfwidth, shift respectively of the collisional Lorentz profile.

$L(z_{\mathrm{c}})$ is a universal line shape function defined and tabulated in Ref. [12]; the symbols $\langle ' \rangle$ and $\langle '' \rangle$ denote first and second derivatives respectively. The Condon points (r_{c}) are solutions of $V(r_{\mathrm{c}}) = \hbar\,\xi$, which in general are complex.

In case of a Lennard-Jones potential

$$V(r) = \hbar\,\varepsilon\,[(r_0/r)^{12} - 2(r_0/r)^6]$$

one obtains for r_{c}:

$\Delta\omega \leqq \varepsilon$ (quasistatic wing):

$$(r_{\mathrm{c}})_{1,2} = r_0[1 \pm (1 + \xi/\varepsilon)^{1/2}]^{-1/6}\,; \tag{7}$$

$\Delta\omega > \varepsilon$ (antistatic wing):

$$r_{\mathrm{c}} = r_0\,|\varepsilon/\xi|^{1/12}\,e^{\pm i\theta}\,,$$

$$\Theta = \tfrac{1}{6}\arccos|\varepsilon/\xi|^{1/2}\,.$$

2.3. *Determination of Potentials*

From the measured temperature dependent spectra $k(\Delta\omega, T)$ the potentials may be evaluated as follows (see also Ref. [7]): The ground state potential $V_g(\Delta\omega)$ is obtained from the slopes of $\ln k(T^{-1})|_{\Delta\omega}$ for different $\Delta\omega$, using Equation (5). The difference potential $\Delta V(r) = \hbar\Delta\omega(r)$ is obtained from the spectrum $k(\Delta\omega, T=\infty)$ found by extrapolation of the $k(\Delta\omega, T)$-data, using the relation

$$\int_{\Delta\omega_0}^{\Delta\omega} k(\Delta\omega, \infty)\,\mathrm{d}(\Delta\omega) = \frac{4\pi}{3}\, n_0\, C\,(r^3 - r_0{}^3) \tag{8}$$

obtained by integration of Equation (5). The remaining arbitrary integration constant $r_0 \equiv r(\Delta\omega = \Delta\omega_0)$ in Eq. (8), however, cannot be determined from this experiment, since near the integration limits $r = 0$, $\Delta\omega = \infty$ the classical QST loses its validity. It therefore has to be established by comparison with other data. Since there are no atomic beam scattering results available for the nercury-noble gas systems we have used as reference the semiempirical Heller potential [14]:

$$V_{g,\mathrm{H}} = H_1 \exp\{-r/H_2\} - H_3\, r^{-6} - H_4\, r^{-8} - H_5\, r^{-10} - H_6\, r^{-12}\,, \tag{9}$$

$$\begin{aligned} H_1 &= 6601\ \mathrm{eV}, & H_4 &= 257.8\ \mathrm{eV\AA^8}\,, \\ H_2 &= 0.28\ \mathrm{\AA}, & H_5 &= 1055\ \mathrm{eV\AA^{10}}, \\ H_3 &= 66.09\ \mathrm{eV\AA^6}, & H_6 &= 5409\ \mathrm{eV\AA^{12}}\,. \end{aligned}$$

If $V_g(r)/KT \ll 1$, i.e. if the corresponding parts of the spectrum display small temperature gradients, large uncertainties arise in the determination of $V_g(r)$. Nevertheless in this case the difference potential $\Delta V^{\Omega}(r)$ and thus $V_e^{\Omega}(r)$ may be evaluated with sufficient accuracy, if $V_g(r)$ is known from other data:

$$\int_{\Delta\omega_0}^{\Delta\omega} k(\Delta\omega, T)\,\mathrm{d}(\Delta\omega) = 4\pi\, C\, n_0 \int_{r_0}^{r} r^2 \exp[-V_g(r)/KT]\,\mathrm{d}r\,. \tag{10}$$

The starting point $\Delta\omega_0(r_0)$ in (10) may be obtained in the following way. According to the Boltzmann-factor the $k(\Delta\omega, T)$-curves intersect at a common point $\Delta\omega_S$, corresponding to the zero of $V_g(r)$; also, there exists a point $\Delta\omega_M$ of maximum temperature gradient $\mathrm{d}k(\Delta\omega, T)/\mathrm{d}T|_{\Delta\omega}$, corresponding to the minimum of $V_g(r)$. From measurements of $k(\Delta\omega)$ at two widely differing temperatures $\Delta\omega_0(r_0)$ may then be determined from the observed $\Delta\omega_S$ or $\Delta\omega_M$.

2.4. Contribution of Molecular Transitions to the Spectrum

In general, the absorption coefficient k at a given $\Delta\omega$ is composed of transitions $g \to e, \Omega$ of free atoms (free-free transitions) and of molecules (bound-bound and bound-free transitions), the relative contribution of the latter to $k(\Delta\omega)$ depending on the Franck-Condon factors $F(\Delta\omega)$. The situation may arise, that in a given spectral range $F(\Delta\omega)$ is so small, that the spectrum is almost exclusively formed by free-free transitions. In this case the probability density function $W(r)$, given by Eq. (3), has to be multiplied by the relative number of free pairs [3]:

$$I(r) = \frac{2}{\sqrt{\pi}} \sqrt{x_0}\, \exp(-x_0) + (1 - \operatorname{erf} \sqrt{x_0})$$

$$x_0 = \frac{|V_g(r)|}{kT}\,. \tag{11}$$

Correspondingly, in order to obtain the absorption spectrum, the right hand side of Eq. (5) has to be multiplied by $I(\Delta\omega, T) = I(r)$.

3. Experimental Details

3.1. Optics

The measurements of the Hg-absorption spectra between 2200 Å and 3000 Å were performed using a conventional single beam arrangement. Continuous background radiation from a Deuterium lamp was passed through an absorption cell, then spectrally selected and measured photoelectrically. Spectral selection and scanning was achieved by means of a 0.75 meter Spex scanning monochromator of ≈ 11 Å/mm dispersion in first order; slit widths were chosen to 25 μ, yielding an effective instrumental width of ≈ 0.4 Å. Wavelength measurements were performed with reference to the self reversal free emission line λ 2536.52 Å from a low pressure Hg-discharge lamp. The dispersion of the monochromator was determined by means of additional Hg-emission lines.

3.2. Absorption Cells

The measurements were performed with a cell of window material Suprasil I with 10 and 30 cm in length and 4 cm in diameter. The cell was mounted inside a directly heated ceramics tube of 1 m length, which was part of a commercial oven (Heraeus ROK/A8/100) for production of temperatures up to 1300 K.

For production of unsaturated Hg-vapor of known number density weighted drops of Hg were introduced into the evacuated cell and heated to temperatures above those necessary for complete vaporization. Temperature control and measurement was performed, using Pt-PtRh-thermocouples with uncertainties of ± 10 K.

3.3. Measurement of the Absorption Spectra

The absorption coefficient

$$k(\lambda) = \frac{1}{l} \times \ln I_0(\lambda)/I(\lambda)$$

was determined from independent measurement of the radiation intensities $I_0(\lambda)$ and $I(\lambda)$ transmitted by the absorption cell without Hg-vapor (room temperature) and with vapor in it (elevated temperature) respectively. A sensitive criterium for the reliability of the measurements was to test whether the $I_0(\lambda)$ and $I(\lambda)$ spectra, after allowing for an adjustment factor, merged into each other in the spectral regions of zero absorption.

By a preliminary experiment the temperature behaviour of the cell window transmission spectrum $T_w(\lambda)$ was investigated. It turned out that apart from an irreversible decrease by typically 20% in the UV-region during the first heating up procedure, T_w changed only by a few percent between 300 and 1200 K. There was, however, some evidence, that ΔT_w at 3000 Å differed by 1–2% from ΔT_w at 2200 Å. Account for this instrumental effect was taken by adjusting $I_0(\lambda)$ to $I(\lambda)$ in different zero absorption regions, namely around 2400 Å or 3000 Å, in studying respectively the spectra on the short or long wavelength side of the 2537 Å line.

In order to cover spectral regions of widely differing absorption, measurements were carried out at 3 different number densities, namely 1.0×10^{17}, 4.3×10^{18}, 9.1×10^{18} cm^{-3}, in combination with absorption lengths of 10 and 30 cm.

The intensity of the radiation from the current stabilized Deuterium lamp and the gain of the photomultiplier were sufficiently constant during a given run, so that intensity measurements were accurate to 0.5%.

3.4. Data Acquisition and Processing

Scanning of the spectrum was achieved by continuously driving the monochromator wavelength (velocity S) and simultaneously punching (punch frequency F) the multiplier voltage signals on stripes. The wavelength interval $\Delta\lambda$ between two punched signals is thus $\Delta\lambda = S/F$. F was typically 1 s^{-1}, $S = 1$ Å/min. For reduction of noise 10 individual intensity values were collected for averaging. The absolute wavelength was determined from the peak intensity position of the emission line λ 2536.52 Å with an uncertainty of $\Delta\lambda \approx 0.015$ Å. Averaging of the intensity values, assignment of the averaged values to absolute wavelengths and evaluation of the reduced absorption coefficients was performed using a Hewlett-Packard computer 9830 A.

4. Results and Their Interpretation

4.1. The Red Wing of the Hg-line 2537 Å

At temperatures up to 600 K, Kuhn's law $k(\Delta\tilde{\nu}) \sim |\Delta\tilde{\nu}|^{-3/2}$ has been reconfirmed to be valid in the range $30 < |\Delta\tilde{\nu}|/\text{cm}^{-1} < 200$. For $|\Delta\tilde{\nu}| > 200$

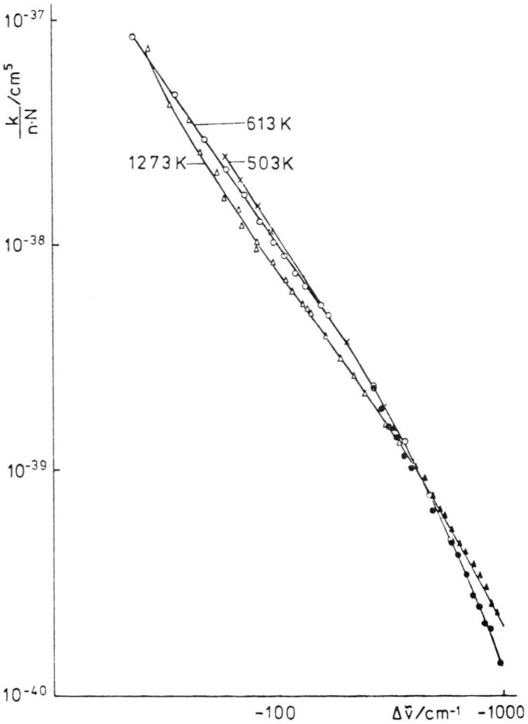

Fig. 1. Temperature dependence in the red wing of the Hg line λ 2536.52 Å perturbed by Ar. k = absorption coefficient corrected for self broadening.

	N [cm^{-3}]	n [cm^{-3}]	l [cm]	T [K]
×	2.94×10^{17}	1.33×10^{19}	10.3	503
○	2.94×10^{17}	1.33×10^{19}	10.3	613
●	3.96×10^{18}	9.86×10^{18}	10.0	613
△	2.94×10^{17}	1.33×10^{19}	10.3	1273
▲	3.96×10^{18}	9.86×10^{18}	10.0	1273

cm^{-1}, however, $k(\Delta\tilde{\nu})$ decreases stronger than $\sim|\Delta\tilde{\nu}|^{-3/2}$. At higher temperatures, on the other hand, $k(\Delta\tilde{\nu})$ is seen to deviate considerably from Kuhn's law over the total $\Delta\tilde{\nu}$-range investigated (Figure 1). Regarding the temperature dependence, the T-gradient is observed to be largest at $\Delta\tilde{\nu}_{\mathrm{M}} \approx -90\ \mathrm{cm}^{-1}$; furthermore, the $k(\Delta\tilde{\nu},\ T)$-curves intersect at a common point $\Delta\tilde{\nu}_{\mathrm{S}} \approx -400 \pm 50\ \mathrm{cm}^{-1}$. This behaviour of $k(\Delta\tilde{\nu},\ T)$ is in agreement with theoretical prediction (Eq. (5)) and reflects that of the ground state potential.

Determination of Potentials

1. Ground State Potential

Since the overall effect of temperature on $k(\Delta\tilde{\nu})$ was observed to be rather small, it was not expected to obtain detailed information on $V_{\mathrm{g}}(r)$. Nevertheless, from the observed maximum value of $|\mathrm{d}k/\mathrm{d}T|$ the depth ε_{g} of $V_{\mathrm{g}}(r)$ could be determined fairly accurately. With the value of the ratio k_{613}/k_{1273} of absorption coefficients at $T=613$ and 1273 K, measured at $\Delta\tilde{\nu}=-90\ \mathrm{cm}^{-1}$, Eq. (5) yields for ε_{g} the value ≈ 0.029 eV. This value agrees well with the value 0.0296 eV of the Heller potential. The agreement also shows that the observed temperature dependence of the spectrum is governed by the Boltzmann-factor; this can be seen by a comparison of the experimental with calculated values of k_{613}/k_{1273} given in the table below. This means, that the spectrum is formed by transitions both from bound and free states in an equilibrium distribution.

Table 1.

Experiment	Calculation	Calculation
k_{613}/k_{1273} at 90 cm^{-1}	$B(613)/B(1273)$ at $r_{\mathrm{m}}=3.35$ Å	$\dfrac{B(613)\times I(613)}{B(1273)\times I(1273)}$ at $r_{\mathrm{m}}=3.35$ Å
1.33 ± 0.05	1.34	1.13

2. Difference Potential

Because of the small temperature effect on $k(\Delta\tilde{\nu})$ the difference potential $\Delta V^{\Omega}(r)$ was evaluated according to Eq. (10) using as ground state potential the Heller potential $V_{\mathrm{g,H}}(r)$, given by Equation (9). Furthermore it was assumed, that this part of the spectrum is formed exclusively by transitions from the ground state to the $m=0$ substate of the excited state $6^3\mathrm{P}_1$ of the Hg-atom, corresponding to the molecular state $\Omega=0$ of Hg $6^3\mathrm{P}_1$-Ar $3^1\mathrm{S}_0$ with statistical weight $g_{\Omega}=1$. This assumption seems to be justified in view of an analysis of measurements in the spectral range $2<|\Delta\tilde{\nu}|/\mathrm{cm}^{-1}<400$ (at little varying temperatures around 350 K), reported recently by Lennuier et al. [4]. As starting point of the integration in Eq. (10) was chosen the observed intersect of the $k(\Delta\tilde{\nu},\ T)$-curves, corresponding to the zero of the Heller potential:

$$|\Delta\tilde{\nu}_0| = |\Delta\tilde{\nu}_{\mathrm{S}}| = 400 \pm 50\ \mathrm{cm}^{-1}\,,$$
$$V_{\mathrm{g,H}}(r=r_0) = 0 \rightarrow r_0 = 2.93\ \text{Å}\,.$$

The difference potential $\Delta V^0(r)$ evaluated under these conditions is plotted in Figure 5.

The validity of the Heller potential $V_{\mathrm{g,H}}(r)$ used in evaluating the difference potential $\Delta V^0(r)$ may by tested indirectly in several ways. First, from $V_{\mathrm{g,H}}(r)$ and $\Delta V^0(r)$ the maximum temperature gradient should occur at $|\Delta\tilde{\nu}_{\mathrm{M}}| \approx 140 \pm 20\ \mathrm{cm}^{-1}$. The observed $|\Delta\tilde{\nu}_{\mathrm{M}}|$-value, $90 \pm 10\ \mathrm{cm}^{-1}$, however, is significantly smaller. Furthermore, a Van der Waals potential may be adjusted to the pointwise mapped $\Delta V^0(r)$ at large r and the resulting $(C_6{}^0)_{\mathrm{exp}}$-value compared to theoretical $C_6{}^0$-values. With an adjustment at $r=3.90$ Å, corresponding to $|\Delta\tilde{\nu}| = 50\ \mathrm{cm}^{-1}$, one obtains

$$(C_6{}^0)_{\mathrm{exp}} = (2.2 \pm 0.2) \times 10^1\ \mathrm{eV\text{Å}^6}\,.$$

This is considerably smaller than

$$(C_6{}^0)_{\mathrm{theor}} = 3.3 \times 10^1\ \mathrm{eV\text{Å}^6}\,,$$

recently obtained by second order perturbation calculation [4]. These deviations certainly indicate insufficiencies of the Heller potential. It should be noted, however, that the differences between the C_6-values may also partly be due to contributions of higher multipole terms in $\Delta V^0(r)$ no longer negligible at $r=3.90$ Å.

4.2. The Blue Wing of the Hg-line λ 2537 Å

The absorption spectrum (Figs. 2, 3) contains two satellites SI and SII, well known from literature, and a steeply decreasing continuum joining to the short wavelength side of SII.

The intensity of both satellites was found to decrease with increasing temperature; for example, the maximum of SII was found to decrease by $(17 \pm 1)\%$ if T increases from 473 to 1273 K; also.

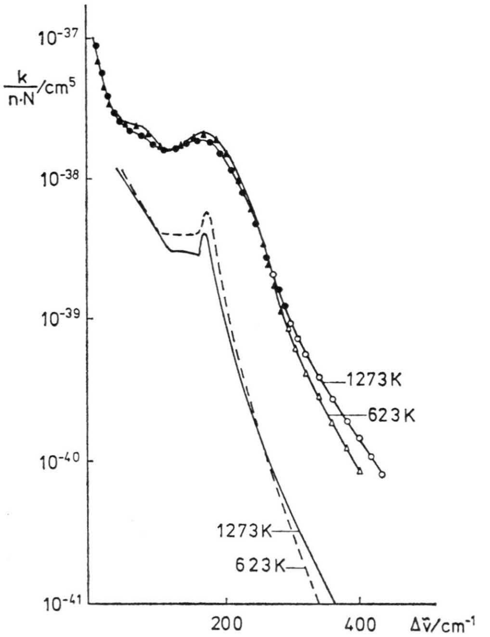

Fig. 2. Temperature dependence in the blue wing of the Hg line λ 2536.52 Å perturbed by Ar.

Measurements

	N [cm^{-3}]	n [cm^{-3}]	l [cm]	T [K]
△	3.96×10^{18}	9.86×10^{18}	10.0	623
▲	1.0×10^{17}	9.7×10^{18}	30.0	623
○	3.96×10^{18}	9.86×10^{18}	10.0	1273
●	1.0×10^{17}	9.7×10^{18}	30.0	1273

Calculations

According to Eq. (6), for

$$V(r) = h\,c\,\varepsilon((r_0/r)^{12} - 2(r_0/r)^6)$$

with $\varepsilon = 200$ cm^{-1}; $r_0 = 3.15$ Å.

---- 623 K; —— 1273 K.

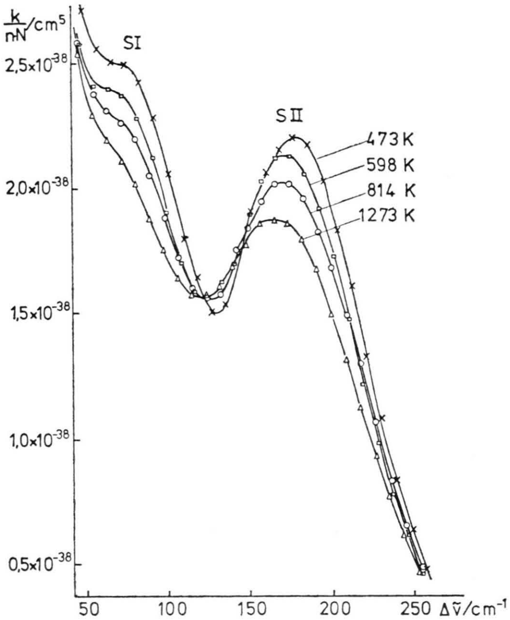

Fig. 3. Temperature dependence of the satellite structure in the blue wing of the Hg line λ 2536.52 Å perturbed by Ar.
$N = 1.0 \times 10^{17}$ cm^{-3}; $n = 9.7 \times 10^{18}$ cm^{-3}; $l = 30$ cm.

this maximum was observed to shift by (8 ± 2) cm^{-1} towards the line center (Figure 3). Beyond SII the continuous absorption profiles $k(\Delta\tilde{\nu}, T)$ were found to intersect at a common point, $\Delta\tilde{\nu}_S = 260 \pm 20$ cm^{-1}.

Like in the red wing, this point was related to the zero of $V_g(r)$. It follows then that the region $|\Delta\tilde{\nu}| > |\Delta\tilde{\nu}_S|$ of the spectrum is formed by transitions from free states and quasi-bound states, whereas in the region $|\Delta\tilde{\nu}| < |\Delta\tilde{\nu}_S|$ also transitions from bound states contribute to the spectrum.

4.2.1. On the Nature of the Satellites

Michels and De Kluiver [2] have interpreted the satellites as bands of weakly bound Hg-Ar-molecules. In particular they have attributed the outermost satellite SII to transitions from the vibrational state $v'' = 0$. From the shape of SII, reflecting the vibrational wavefunction of this state, they have deduced the potential $V_e(r)$ of the excited molecule Hg$\,6^3$P$_1$-Ar$\,3^1$S$_0$:

$$V_{e,M}(r) = M_1 \exp(-r/M_2) - M_3\,r^{-6} - M_4\,r^{-8}\,,$$

$$M_1 = 510.7 \text{ eV}\,, \qquad M_3 = 82.67 \text{ eVÅ}^6\,,$$

$$M_2 = 0.404 \text{ Å}, \qquad M_4 = 1204 \text{ eVÅ}^8\,.$$

This interpretation of the satellites in terms of bound-bound and bound-free transitions seems to be contradictory to that given earlier by Kuhn [1], who proposed them to be formed by transitions of free pairs. From an analysis of the observed temperature dependence it may be seen, however, that both mechanisms do contribute to the generation of the structure: If it were exclusively due to transitions from bound molecular states, the absorption should be proportional to the occupation density of the ground state vibration rotational levels; the change of absorption with temperature should then reflect this occupation density. Using the formulas given in Ref. [2] we have calculated the density change of the states $v'' = 0, 1$ for a temperature increase from 473 to 1273 K. Comparison of the result of these calculations to the

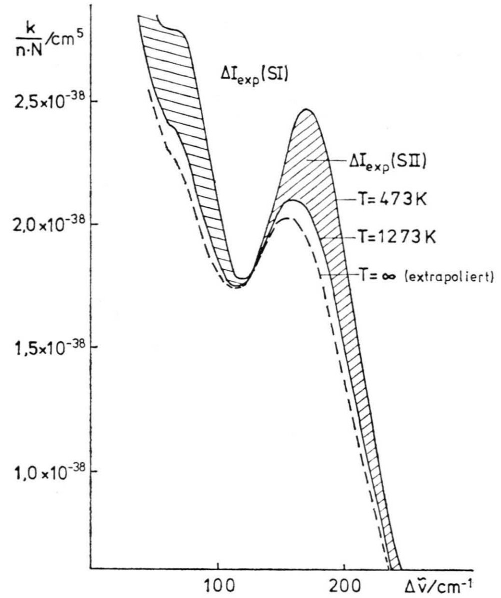

Fig. 4. On the interpretation of the satellites in the blue wing of Hg 2536.52/Ar in terms of molecular bands.

observed temperature dependence of $k(\varDelta\tilde{\nu}, T)$ yielded the spectrum $k(\varDelta\tilde{\nu}, \infty)$ to be expected at $T = \infty$ by extrapolation (Figure 4). From the shape of $k(\varDelta\tilde{\nu}, \infty)$ the following conclusions may be drawn: 1. Because of the almost complete vanishing of the inner satellite SI this satellite may be interpreted as pure molecular band. 2. From the fact that there remains a residual hump at ≈ 150 cm^{-1}, one must conclude that satellite SII cannot be exclusively formed by molecular transitions, but must be partially due to free-free transitions in the neighbourhood of an extremum in a difference potential. This conclusion is consistent with the fact that the difference potential, $\varDelta V_{\mathrm{M}}(r) = V_{\mathrm{e,M}}(r) - V_{\mathrm{g,H}}(r)$, derived from the shape of SII, exhibits a maximum of height ≈ 210 cm^{-1} (Fig. 5): If a Lennard-Jones-6-12-function is adjusted to this, the generalized theory of collisional line broadening (Eq. (6)) predicts a satellite at ≈ 160 cm^{-1}, which is in excellent agreement with observation.

4.2.2. The Free-Free Portion of the Spectrum

In an earlier investigation [3] the region $\varDelta\tilde{\nu} > \varDelta\tilde{\nu}_{\mathrm{S}}$ of the spectrum has been tentatively interpreted as quasistatic wing (validity of condition 1) of the QST, see 2.1). In order to test this assumption we have tried to evaluate the ground state potential $V_{\mathrm{g}}(r)$ from the experimental $k(\varDelta\tilde{\nu}, T)$-curves, using the method described in 2.3. Because of the physically unreasonable shape of the resulting $V_{\mathrm{g}}(r)$ it had to be concluded, however, that QST is not applicable to this part of the spectrum.

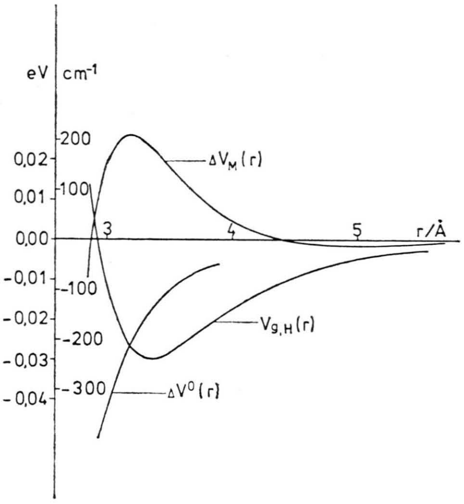

Fig. 5. Potentials of mercury-Argon interaction. $V_{\mathrm{g,H}}(r)$ Heller potential of ground state interaction, Eq. (9); $\varDelta V_{\mathrm{M}}(r)$ difference potential from the shape of the blue satellite SII, $\varDelta V^0(r)$ difference potential from the far red wing of the Hg line λ 2536.52 Å perturbed by Ar.

We have therefore tried to give an interpretation of the spectrum beyond satellite SII ($\varDelta\tilde{\nu} > \varDelta\tilde{\nu}_{\mathrm{SII}}$) in terms of an antistatic wing, related to the maximum in the difference potential $\varDelta V_{\mathrm{M}}$. For this purpose the free-free portion of the spectrum was calculated according to the generalized collisional line broadening theory, Eqs. (6), (7), assuming a Lennard-Jones function adjusted to $\varDelta V_{\mathrm{M}}$. The spectra obtained with $\varepsilon = +200$ cm^{-1} and $r_0 =$ 3.15 Å for $T = 473$ and 1273 K are seen in Figure 2. Comparison with experiment (see table below) shows that good agreement exists regarding the position $\varDelta\tilde{\nu}_{\mathrm{SII}}(T)$ of the outer satellite SII. Also, the position of intersect $\varDelta\tilde{\nu}_{\mathrm{S}}$ of the $k(\varDelta\tilde{\nu}, T)$-curves, namely $(\varDelta\tilde{\nu}_{\mathrm{S}})_{\mathrm{theor}} = 250$ cm^{-1}, compares well with the experimental value 260 ± 20 cm^{-1}.

Table 2.

T [K]	$\varDelta\tilde{\nu}_{\mathrm{SII}}$ [cm^{-1}]		$(k/Nn)_{\mathrm{SII}}[10^{-38}\,\mathrm{cm}^5]$	
	exp.	theor.	exp.	theor.
473	185 $\pm$ 2	183.5	2.2 $\pm$ 0.1	0.7
1273	172.5 $\pm$ 2	180	1.8 $\pm$ 0.1	0.43

Regarding the intensity of SII, on the other hand, there is only agreement with respect to sign and magnitude of its change with temperature. The calculated shape and intensity level, however, differ considerably from observation. In particular, the calculated absorption coefficient for free-free transitions in the range $\Delta\tilde{\nu} > \Delta\tilde{\nu}_{\mathrm{SII}}$ is by more than a factor 3 smaller than observed. Therefore, the spectrum in this region must be predominantly due to bound states and/or quasi-bound states existing within the rotational barrier of the effective potential. The outer wing of SII in the range $\Delta\tilde{\nu} > \Delta\tilde{\nu}_{\mathrm{S}}$, corresponding to $r < r_0$, where bound states cannot exist, should then mainly be formed by transitions from such quasi-bound states. These latter should also contribute to the satellite region, since the residual hump at $T = \infty$ (Fig. 4) cannot be due to stable molecules. Calculations of the spectrum taking into account free, bound and quasi-bound states are under way.

4.2.3. Assignment of the Potential $\Delta V_{\mathrm{M}}(r)$

The difference potential $\Delta V_{\mathrm{M}}(r)$, obtained from the shape of SII, may be identified with $\Delta V^1(r)$ for two reasons: 1. $\Delta V_{\mathrm{M}}(r)$ displays a minimum of depth $-10\ \mathrm{cm}^{-1}$ at 5.0 Å (s. Fig. 5) and should thus produce a satellite on the long wavelength side of the parent line. Such a red satellite has actually been observed at $\Delta\tilde{\nu} = -(10 \pm 1)\ \mathrm{cm}^{-1}$ and associated to transitions to the excited molecular state $\Omega = 1$ [4]. 2. The potential $\Delta V^0(r)$, obtained from the far red wing, is purely attractive in the r-range where $\Delta V_{\mathrm{M}}(r)$ is repulsive, passing through a maximum (see Figure 5). It should be noted that $\Delta V_{\mathrm{M}}(r) \equiv \Delta V^1(r)$ differs at small r considerably from the Lennard-Jones-6-12-function $\Delta V_{\mathrm{LJ}}{}^1(r)$ proposed [4] to account only for the near red wing including the red satellite mentioned above.

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