

SATELLITE BAND ACCOMPANYING THE Hg-RESONANCE LINE BROADENED BY He

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The satellite band produced by helium on the short wavelength side of the Hg-resonance line $\lambda 2537 \text{ \AA}$ was interpreted as a result of the continuous absorption (due to bound-free transitions) of the HgHe Van der Waals molecules. The results of the calculations of the shape of the HgHe-absorption band are presented. The calculations were performed assuming the eigenfunctions of the discrete vibrational-rotational levels of the HgHe molecule in the form of the Morse-Pekeris functions. The wave functions of the continuous levels in the neighbourhood of classical turning points were approximated by means of Airy's integrals. It is shown that a satisfactory agreement between the calculated shape of the HgHe-absorption band and the shape of the satellite band is achieved if the rotational effects and the effects of the decomposition of the HgHe molecules are taken into account.

1. Introduction

Many experiments have shown that in the spectra of metallic vapours (such as mercury and the alkali metals) mixed either with rare gases, or *e.g.* H_2 or N_2 , diffuse bands, usually called satellites, appear. Most observations have been made on resonance lines and showed that satellites occur both on the short wavelength side (blue satellites) as well as on the long wavelength side (red satellites) of these lines. The existence of such bands was first observed in fluorescence by Oldenberg [1] and then by Kuhn [2] and Preston [3]. In absorption, systematic experimental investigations of satellites of alkali metal lines produced by various gases were carried out by Chen and his collaborators [4, 5], [6] who found satellites on both sides of the fine structure components. Michels *et al.* [7]–[10], Robin and Robin [11] and Granier and Granier [12] investigated the satellites on the short wavelength side of the Hg-resonance line $\lambda 2537 \text{ \AA}$ at very high rare gas pressures. They found that the number of satellites, both blue and red, depends on the nature of both the radiating and perturbing atoms. There is, however, an essential difference between these two kinds of satellites. Namely, the blue satellites are observed for all perturbing gases provided the pressure is high enough; their intensity increases with the increase in pressure. On the other hand, the appearance

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of red satellites is typically a low-pressure phenomenon (below half an atmosphere); they disappear entirely at higher pressures. Moreover they are produced only by heavier rare gases. Helium and neon used as perturbers do not produce any red satellites, whereas they do give rise to strong blue ones.

Different approaches have been used in attempts to explain the origin of satellites. The hypothesis put forward by Preston [3] and modified by Jefimenko [13] ascribes the formation of satellites to transitions between potential curves of complicated shape (with additional minima and maxima) at different distances. Recently, Breene [14] has shown that such minima and maxima can be due to the intersection of potential curves of different electronic states and that satellites result from the Jabłoński pressure broadening theory [24] when the Born–Oppenheimer approximation breaks down. Another concept interprets the satellites as due to the existence of the vibrational levels of the Van der Waals molecule formed by the radiating and perturbing atoms (Klein and Margenau [15], Michels *et al.* [10], Mahan and Lapp [16]). One more possibility of explaining the satellites, which ignores altogether the existence of vibrational levels, has recently been reported by Hindmarsh and Farr [17], [18] and Kieffer [19]. Their interpretation concerns only the red satellites and is based on the quasi-static theory of pressure broadening of spectral lines given by Margenau¹ [20]. Applying the Lennard–Jones potential to this theory, they have shown that at low foreign gas pressures additional intensity maxima, which were interpreted by them as red satellites, appear on the long wavelength side of the line. Experiments performed by McCartan and Hindmarsh [25] on the potassium line $\lambda 4047 \text{ \AA}$ broadened by krypton yielded a satisfactory agreement of the measured positions of the red satellites with those predicted theoretically.

The present work deals mainly with the blue satellites and its purpose is to show that the origin of these is primarily due to the existence of quantized vibrational-rotational states of the Van der Waals molecules. All the considerations given below concern the Hg-resonance line $\lambda 2537 \text{ \AA}$ broadened by helium but there is no doubt that they are generally applicable to other such perturbed systems (*cf.* [10]).

2. The HgHe molecule

In an earlier paper [26], hereafter referred to as I, the pressure broadening theory of Jabłoński [21], [22] was applied to calculations of shape and shift of the Hg-resonance line $\lambda 2537 \text{ \AA}$ perturbed by helium under assumption of the Lennard–Jones (12–6) potential. For helium densities less than 150 Amagat a very good agreement between the calculated and experimental intensity distribution was obtained over the whole frequency range of the broadened line. However at very high densities of helium (above 200 Amagat) the agreement is violated on the short wavelength side of the line due to the appearance of a satellite band with a maximum shifted by 225 cm^{-1} with respect to the unperturbed frequency (39424 cm^{-1}) [7]. In I the view that the origin of this band cannot be due to Van der Waals HgHe molecules

¹ It can be shown that the Margenau theory follows from the pressure broadening theory given by Jabłoński [21]–[24] in the asymptotic case when (1) the classical form of the Franck–Condon principle is applied and (2) in the limit $\bar{v} \rightarrow 0$, \bar{v} being the mean relative velocity of atoms.

was expressed. This view was based on very rough calculations, which led to the conclusion that the energy of even the lowest vibrational state would exceed the dissociation energy of such molecules. This was in accordance with the qualitative considerations of Kuhn and Oldenberg [27] who also excluded the possibility of the formation of HgHe molecules because of the small polarizability of the He-atom. In a recent paper [28], hereafter referred to as II, the preliminary results of a more accurate analysis were reported which showed that contrary to the opinion given in I Hg and He atoms can form molecules and that mainly these molecules are responsible for the origin of the satellite band in question.

The ground molecular state of HgHe corresponding to the atomic states Hg (6^1S_0) + He(1^1S_0) is the $^1\Sigma^+$ state with $\Omega = 0$ (Ω being the quantum number of the projection of the total electronic angular momentum on nuclear axis). During the collision of the Hg-atom in the 6^3P_1 state with the He-atom in the 1^1S_0 state two molecular excited states $^3\Sigma^+$ with $\Omega = \pm 1$ and $^3\Pi_0$ with $\Omega = 0$ result. The potential curves for these states are given in II.

The values E_v of the energy of vibrational levels can be approximately determined from the Kramers condition (cf. [29])

$$2 \int_{r_1}^{r_2} [2\mu(E_v - V(r))]^{1/2} dr = \left(v + \frac{1}{2}\right) h \quad (1)$$

where v is the vibrational quantum number, μ the reduced mass of the pair of atoms, $V(r)$ the interaction energy as a function of the distance r between the atoms and r_1 and r_2 are the r 's at the classical turning points. The interaction energy was assumed in the form of the Lennard-Jones (12-6) potential:

$$V(r) = C_{12} \cdot r^{-12} - C_6 \cdot r^{-6} \quad (2)$$

where the constants C_6 and C_{12} for the ground electronic state $^1\Sigma^+$ as well as for both potential curves corresponding to $\Omega = 0$ and $\Omega = \pm 1$ of the excited states $^3\Pi_0$ and $^3\Sigma^+$ determined in I are given in Table I. This table also contains the energies E_v calculated numerically from Eq. (1). It turned out that there exist two vibrational levels ($v'' = 0; 1$) for the ground

TABLE I
Force constants and vibrational energies of the HgHe molecule

State	Lennard-Jones potential				Morse potential				
	C_6 [eV·Å ⁶]	C_{12} [eV·Å ¹²]	E_v [cm ⁻¹]		ϵ [cm ⁻¹]	r_e [Å]	β [Å ⁻¹]	E_v [cm ⁻¹]	
			$v = 0$	$v = 1$				$v = 0$	$v = 1$
$^1\Sigma^+$	13.2	5430	-37.0	-7.1	64.8	3.059	1.960	-36.4	-5.0
$^3\Pi_0$ ($\Omega=0$)	13.6	8760	-22.1	—	42.6	3.296	1.818	-21.4	—
$^3\Sigma^+$ ($\Omega = \pm 1$)	15.9	27900	—	—	18.2	3.899	1.538	—	—

electronic state of HgHe, only one ($v' = 0$) for the excited state ${}^3\Pi_0$ ($\Omega = 0$) and none for ${}^3\Sigma^+$ ($\Omega = \pm 1$).

The E_v values were also computed using the Morse potential

$$V(r) = \varepsilon\{\exp[-2\beta(r-r_e)] - 2\exp[-\beta(r-r_e)]\}, \quad (3)$$

where ε is the depth of the potential well, r_e the position of its minimum and β a constant. The values of these parameters were determined by comparing the Morse potential and the Lennard-Jones potential (Eq. (2)) and their second derivatives for the minimum of the functions. This procedure leads to the following relationships:

$$\begin{aligned} \varepsilon &= \frac{C_6^2}{4C_{12}}, \quad r_e = \left(2\frac{C_{12}}{C_6}\right)^{1/6}, \\ \beta &= 3\left(32\frac{C_6}{C_{12}}\right)^{1/6}. \end{aligned} \quad (4)$$

It was stated that the Morse potential with these parameters agrees well with that of Lennard-Jones in the most important region, *i.e.* in the neighbourhood of the minimum. The discrepancies between them appear only at large interatomic distances [28] (*cf.* also [30]).

The eigenvalues, E_v , of vibrational levels for the Morse potential can be calculated (in cm^{-1}) from the formula

$$E_v = \omega_e \left(v + \frac{1}{2}\right) - x_e \omega_e \left(v + \frac{1}{2}\right)^2, \quad (5)$$

where

$$\omega_e = \frac{\beta}{\pi c} \left(\frac{\varepsilon h}{2\mu}\right)^{1/2}, \quad x_e \omega_e = \frac{h\beta^2}{8\pi^2 c \mu}, \quad (6)$$

c being the vacuum velocity of light.

The values E_v calculated from Eq. (5) are given in Table I. They differ only slightly from those obtained for the Lennard-Jones potential from Eq. (1), the difference being 0.6 cm^{-1} for the $v'' = 0$ vibrational level, 2.1 cm^{-1} for $v'' = 1$ and 0.7 cm^{-1} for $v' = 0$ ($\Omega = 0$ of the ${}^3\Pi_0$ state).

As was shown in II for the HgHe molecule, a continuous absorption should appear due to the transitions from the discrete levels ($v'' = 0$ and $v'' = 1$) of the ground electronic state to the levels in the range of continuous energies connected with the repulsion branches of the potential curves ($\Omega = 0, \pm 1$) of the excited states ${}^3\Sigma^+$ and ${}^3\Pi_0$ (bound — free transitions). The minima of the potential curves of the excited electronic states are shifted towards larger distances with respect to the minimum of the ground state potential curve, so that their repulsion branches lie above the minimum of the ground state. Thus, according to the Franck-Condon principle, the transitions from the vibrational levels v'' of the ground state to the continuous levels connected with repulsion branches of the potential curves of the excited states will give absorption bands with frequencies on the short wavelength side of the Hg-resonance line. It is thus possible to interpret the blue satellite band of the Hg-line as due to the continuous absorption of HgHe.

The concentration N_{HgHe} of the HgHe molecules can be calculated from the equilibrium constant

$$\mathcal{K}_{\text{Hg, He}} = \frac{\tilde{N} \cdot N_{\text{HgHe}}}{N_{\text{Hg}} \cdot N_{\text{He}}}, \quad (7)$$

where \tilde{N} is the Avogadro number, N_{Hg} the concentration of all (free and bonded) Hg-atoms and N_{He} the concentration of He-atoms. According to Stogryn and Hirschfelder [31], the equilibrium constant can be expressed as

$$\mathcal{K}_{\text{Hg, He}} = -2[B_b(T)]_{\text{Hg, He}}, \quad (8)$$

$[B_b(T)]_{\text{Hg, He}}$ being the part of the second virial coefficient for the gaseous mixture of Hg and He atoms, which is directly connected with the existence of the HgHe Van der Waals molecules (T is the temperature). From Eqs (7) and (8) we have

$$\kappa \equiv \frac{N_{\text{HgHe}}}{N_{\text{Hg}}} = -\frac{2[B_b(T)]_{\text{Hg, He}}}{\tilde{N}} N_{\text{He}}. \quad (9)$$

Introducing the so-called reduced second virial coefficient

$$B_b^*(T^*) = \frac{1}{\alpha} B_b(T), \quad (10)$$

where

$$\alpha = \frac{2}{3} \pi \tilde{N} \left(\frac{C_{12}}{C_6} \right)^{1/2}, \quad T^* = \frac{4 C_{12}}{C_6} T, \quad (11)$$

Eq. (9) becomes

$$\kappa = -\frac{4}{3} \pi \left(\frac{C_{12}}{C_6} \right)^{1/2} N_{\text{He}} [B_b^*(T^*)]. \quad (12)$$

The reduced coefficients $B_b^*(T^*)$ were calculated by Stogryn and Hirschfelder for potentials of the Lennard-Jones (12—6) type and tabulated for a wide range of reduced temperatures T^* . Substituting the values of $B_b^*(T^*)$ determined by them into Eq. (12), the values of κ were calculated for different helium densities². For a helium density of 1 Amagat, Eq. (12) gives the value $\kappa = 2.3 \times 10^{-4}$, which explains the fact that at lower densities the satellite band is not observed.

The concentration $N_{\text{Hg}}^{(f)}$ of the free (unbonded) mercury atoms is given by

$$N_{\text{Hg}}^{(f)} = (1 - \kappa) N_{\text{Hg}}. \quad (13)$$

Hence the ratio of the concentration of the HgHe molecules to the concentration of the free Hg-atoms is

$$\frac{N_{\text{HgHe}}}{N_{\text{Hg}}^{(f)}} = \frac{\kappa}{1 - \kappa}. \quad (14)$$

² It should be noted that the contribution from metastable states (denoted by $B_m(T)$ in [31]) is also taken into account in Eq. (12).

This ratio determines the relative intensity of the continuous (satellite) band to the atomic line.

The shape of the satellite band for a helium density of 271.2 Amagat is shown in Fig. 1 (curve *S*). It was determined as the difference between the measured absorption coefficient [7] and the absorption coefficient of the broadened line calculated in I on the basis of the Jabłoński theory (curve 2). Curve 2 differs in absolute values from that reported in I be-

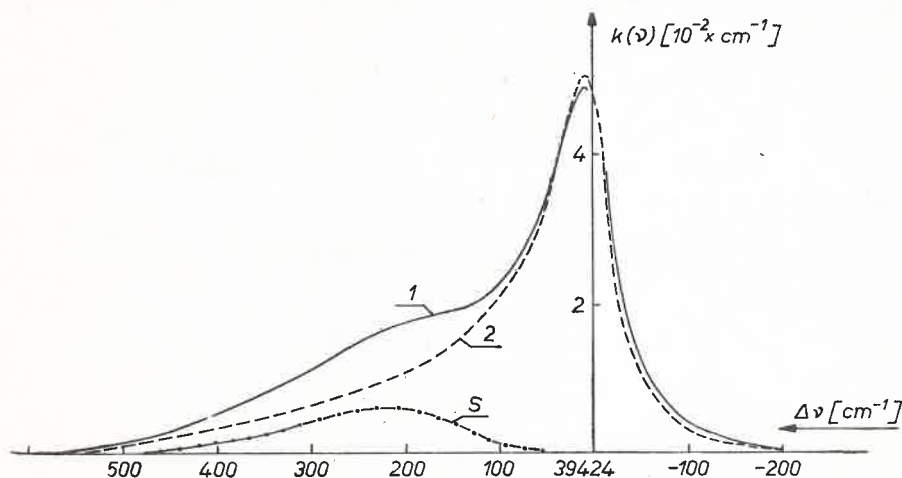


Fig. 1. Shape of Hg-resonance line $\lambda 2537 \text{ \AA}$ broadened by helium for density 271.2 Amagat. Curve 1 – experimental shape [7], curve 2 – theoretical shape [26]; S – shape of satellite band

cause it was re-calculated with account taken of the corrected value of the concentration of the mercury atoms given by Eq. (13). For a helium density of 271.2 Amagat Eq. (14) yields $\frac{N_{\text{HgHe}}}{N_{\text{Hg}}^{(f)}} = 0.11$. It was assumed that the Hg-atoms bonded with He-atoms do not contribute to the formation of the Hg-resonance line and that they are responsible for the arising of the satellite band only.

3. The shape of the satellite band

A. Theoretical

Continuous absorption in diatomic molecules is due to transitions from the discrete vibrational-rotational levels (v'', J) with the energies $E_{v'', J}$ to the continuous levels with the energies E'_J . The radial eigenfunctions $\psi_{v'', J}(r)$ and $\psi_{E'_J}(r)$ of these levels are solutions of the Schrödinger equation

$$\frac{d^2\psi}{dr^2} + \frac{2\mu}{\hbar^2} \left[E - V(r) - \frac{\hbar^2 J(J+1)}{2\mu r^2} \right] \psi = 0. \quad (15)$$

Both the wave functions $\psi_{v'', J}$ of the discrete levels and the wave functions $\psi_{E'_J}$ of the continuous ones are normalized to unity. Such a normalization of the wave functions $\psi_{E'_J}$ means

that the continuous states are treated as discrete with a certain density of levels $\rho_{E'_J} = \frac{dv'}{dE_{v',J}}$.

The boundary condition for the wave functions $\psi_{E'_J}(R) = 0$ (R being the radius of a large sphere around the radiating atom) leads to the following formula for the density of levels [24]:

$$\rho_{E'_J} = \left(\frac{2\mu}{\hbar^2 E'_J} \right)^{1/2} R. \quad (16)$$

If the quantum-mechanical form of the Franck-Condon principle is applied, the absorption coefficient $k(v'', J; E'_J)$ corresponding to the transitions $(v'', J) \rightarrow E'_J$ is given by the formula [35], [24]:

$$k(v'', J; E'_J) = \frac{8\pi^3}{3hc} \nu N_{v'',J} d_e^2 \left| \int_0^\infty \psi_{v'',J}(r) \psi_{E'_J}(r) dr \right|^2 \rho_{E'_J}, \quad (17)$$

where $N_{v'',J}$ is the concentration of the molecules in the discrete state (v'', J) , ν the absorbed frequency and d_e the electronic part of the dipole momentum which can be expressed by means of the oscillator strength f as

$$d_e^2 = \frac{3he^2 f}{8\pi^2 m c \nu_0}. \quad (18)$$

Here, e and m are the charge and mass of the electron, and ν_0 is the unperturbed frequency.

The effective potential $V_J(r)$ in the wave equation (15), *i. e.* interaction energy $V(r)$ together with the centrifugal potential is

$$V_J(r) = V(r) + \frac{\hbar^2 J(J+1)}{2\mu r^2}. \quad (19)$$

Let r_J be the classical turning point for the continuous levels E_J connected with the repulsion branches of the potential curves. Now the definition

$$F_J = - \left[\frac{d}{dr} V'_J(r) \right]_{r=r_J}, \quad (20)$$

is introduced, $V'_J(r)$ being the effective potential for the excited electronic state. Assuming the potential curves of the excited electronic states ${}^3\Sigma^+$ and ${}^3\Pi_0$ to be of the Lennard-Jones type we have

$$V'_J(r) = C_{12} \cdot r^{-12} - C_6 \cdot r^{-6} + \frac{\hbar^2 J(J+1)}{2\mu r^2}, \quad (21)$$

where the constants C_{12} and C_6 were determined in *I* both for $\Omega = 0$ (${}^3\Pi_0$ state) and for $\Omega = \pm 1$ (${}^3\Sigma^+$ state) (see Table I). On introducing a new variable

$$\xi = \gamma_J^{1/2} (r - r_J), \quad (22)$$

where

$$\gamma_J = \frac{4\pi\mu c}{\hbar} F_J, \quad (23)$$

then the solution of the Schrödinger equation (15) valid in the neighbourhood of the classical turning point r_J can be written as a good approximation in the form (cf. [32], [33])

$$\psi_{E_J'}(r) = \left(\frac{2}{R}\right)^{1/2} \left(\frac{p_\infty}{\gamma^{1/2}}\right)^{1/2} \Phi(-\xi), \quad (24)$$

where $p_\infty = (2\mu E_J')^{1/2}$. In this equation $\Phi(x)$ denotes the Airy integral (cf. [29]). For $r \gg r_J$ and $r \ll r_J$ the wave function given by Eq. (24) becomes identical with the quasi-classical (W. K. B.) wave function.

Substituting Eq. (24) into Eq. (17) and using Eqs (18) and (16) we obtain

$$k(v'', J; E_J') = \frac{\pi e^2}{mc^2} f N_{v'', J} A_{v'', J; E_J'}^2 \quad (25)$$

where

$$A_{v'', J; E_J'} = F_J^{-1/2} \int_{-\infty}^{+\infty} \psi_{v'', J}(\xi) \Phi_{E_J'}(-\xi) d\xi, \quad (26)$$

and $\psi_{v'', J}(\xi)$ is the wave function of the discrete vibrational-rotational level (v'', J) of the ground state expressed as a function of the variable ξ .

For the ground electronic state of HgHe the interaction potential $V(r)$ was approximated by means of the Morse potential (Eq. (3)) with parameters given by Eq. (4). Pekeris [34] has shown that the solutions $\psi_{v'', J}(r)$ of the wave equation (15) with this potential and the rotational term included ($J \neq 0$) can be presented in a good approximation in the form

$$\psi_{v, J}(r) = C_{v, J} \exp \left[-\frac{1}{2} Z_J(r) \right] [Z_J(r)]^{1/2} L_{v+b_v(J)}^{b_v(J)}(r), \quad (27)$$

where

$$Z_J(r) = 2d_J \exp[-\beta(r-r_e)] \quad (28)$$

and

$$b_v(J) = k_J - 2v - 1. \quad (29)$$

The coefficients d_J and k_J are given by

$$d_J = \frac{1}{\beta \hbar} [2\mu(\epsilon + C_2(J))]^{1/2}, \quad (30)$$

$$k_J = \frac{2\mu}{\beta^2 \hbar^2 d_J} (2\epsilon C_1(J)), \quad (31)$$

where

$$C_1(J) = \frac{\hbar^2 J(J+1)}{2\mu r_e^2} \left(\frac{4}{\beta r_e} - \frac{6}{\beta^2 r_e^2} \right), \quad (32)$$

$$C_2(J) = \frac{\hbar^2 J(J+1)}{2\mu r_e^2} \left(\frac{3}{\beta^2 r_e^2} - \frac{1}{\beta r_e} \right). \quad (33)$$

In Eq. (27), $L_{v+b_v(J)}^{b_v(J)}(r)$ are the generalized Laguerre polynomials

$$L_{v+b}^b(r) = \frac{e^z}{v! z^b} \frac{d^v}{dz^v} [e^{-z} z^{v+b}],$$

$$z \equiv z_J(r); \quad b \equiv b_v(J), \quad (34)$$

and $C_{v',J}$ is the normalizing constant.

The energy $E_{v',J}$ of the vibrational-rotational levels (in cm^{-1}) can then be calculated from the formula [34], [35]

$$E_{v',J} = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + B_v J(J+1) - D_v J^2(J+1)^2, \quad (35)$$

where

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right),$$

$$D_v = D_e + \beta_e \left(v + \frac{1}{2} \right),$$

$$B_e = \frac{\hbar}{2\mu c r_e^2}, \quad D_e = \frac{4B_e^3}{\omega_e^2},$$

$$\alpha_e = \frac{6(\omega_e x_e B_e^3)^{1/2}}{\omega_e} - \frac{6B_e^3}{\omega_e},$$

$$\beta_e = D_e \left(8x_e - \frac{5\alpha_e}{B_e} - \frac{\alpha_e^2 \omega_e}{24B_e^3} \right), \quad (36)$$

and ω_e and x_e are the same as in Eq. (6).

The energy E'_J of the continuous level connected with the repulsion branches of the potential curves $\Omega = 0$ and $\Omega = \pm 1$ of the excited states ${}^3\Pi_0$ and ${}^3\Sigma^+$ of the HgHe molecule can be written as

$$E'_J = V'(r_J) + \frac{\hbar^2}{2\mu r_J^2} J(J+1), \quad (37)$$

r_J being the classical turning point for a given J .

B. Results

In the first approximation rotations are neglected ($J = 0$). In this case $c_1(0) = 0$ and $c_2(0) = 0$ (see Eqs (32) and (33)), so the functions $\psi_{v',J=0}$ given by Eq. (27) are now identical with the usual eigenfunctions of the Morse oscillator [36]. Substituting these functions into Eq. (26) the absorption coefficients $k_{J=0}(\Delta\nu)$ ($\Delta\nu$ being equal to $\frac{1}{hc} (E'_{J=0} - E_{v',0})$) corre-

sponding to the transitions from the vibrational levels $v'' = 0$ and $v'' = 1$ to the continuous levels $E'_{J=0}$ were calculated using the ODRA 1003 computer. The populations $N_{v'', J=0}$ of the vibrational levels were determined on the basis of Eq. (12). It was assumed that the value f of the oscillator strength of HgHe molecule is the same as for the Hg-atom ($f = 0.0255$). The shape of the absorption band (pure vibrational) of HgHe determined in this way is given in Fig. 2 (curve 1), where it is compared with the satellite band (curve 2). The position of the maximum of the calculated band falls at a frequency $\Delta\nu_m = 164 \text{ cm}^{-1}$ with respect to the unperturbed frequency ($\nu_0 = 39424 \text{ cm}^{-1}$) of the Hg-line, that of the satellite at $\Delta\nu_s = 225 \text{ cm}^{-1}$. As can be seen from Fig. 2 there are also large discrepancies between the

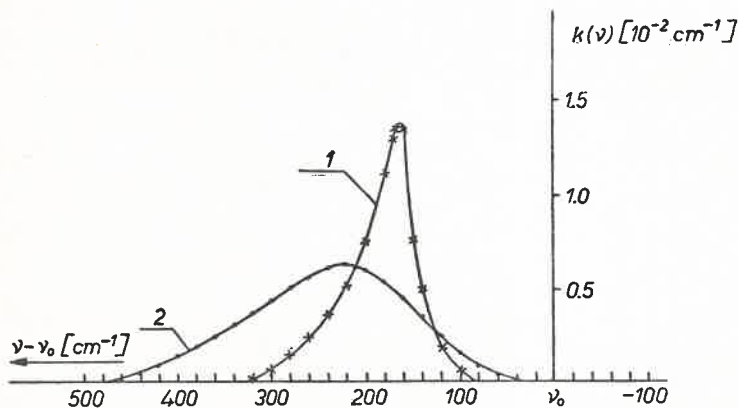


Fig. 2. Calculated shape of purely vibrational continuous absorption band of HgHe molecule (curve 1). Curve 2 - satellite band

calculated shape of the absorption band of HgHe and the expected shape of the satellite band if the rotational effects are neglected. These discrepancies are too large to be explained only by the change in the value of the oscillator strength. Thus, inclusion of rotation is necessary for an improvement in the theoretically derived shape of the band.

On including rotation ($J \neq 0$), the absorption coefficient $k_{v''}(\Delta\nu)$ corresponding to the transitions from all vibrational-rotational levels (v'', J) according to Eq. (25) is given by

$$k_{v''}(\Delta\nu) = \frac{\pi e^2}{mc^2} f \sum_{J=0}^{J_{\max}(v'')} N_{v'', J} A_{v'', J; E'_J}^2 \quad (38)$$

where the summation is over all quantum numbers J for which the molecule exists in the ground electronic state with a given v . The value $J_{\max}(v'')$, *i. e.* the largest value of J for which the level (v'', J) is a discrete one, was determined in the usual manner by considering the curves of the effective potential $V_J(r)$ (Eq. (19)) (*cf.* [35]). The typical shape of these effective potential curves is such that, apart from the minimum corresponding to the equilibrium position r_e , there is at larger r a maximum due to the existence of the centrifugal term $\frac{\hbar^2 J(J+1)}{2\mu r^2}$ in Eq. (19). Thus, there are also rotational levels above the dissociation

limit which are separated by this centrifugal potential barrier from the dissociated states. In Fig. 3 the energies E_{\max} of the maxima of the effective potential curves of the ground state of HgHe are plotted as a function of $J(J+1)$. The energies $E_{v'',J}$ of the vibrational-rotational levels for $v'' = 0$ and $v'' = 1$ calculated from Eq. (35) are also plotted in Fig. 3 as a function of $J(J+1)$ where they are denoted by $v'' = 0$ and $v'' = 1$. From the intersections of the curve E_{\max} with the curves $v'' = 0$ and $v'' = 1$, the values $J_{\max}(v'')$ were found to be equal to $J_{\max} = 11$ for $v'' = 0$ and $J_{\max} = 4$ for $v'' = 1$. The absorption coefficient $k(\Delta\nu)$ corresponding to the transitions from the vibrational-rotational levels (v'', J)

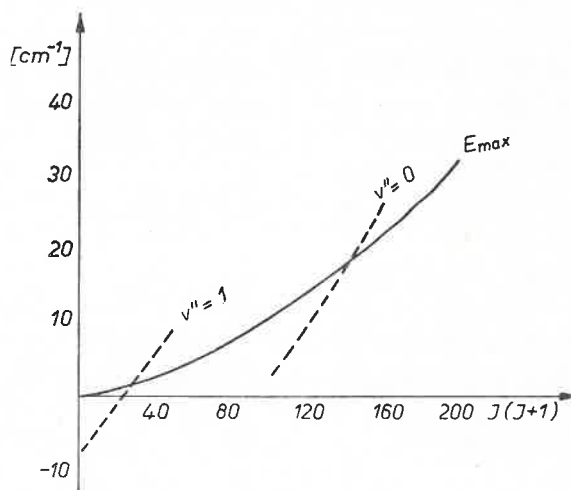


Fig. 3. Limiting curve of dissociation for ground state of HgHe molecule (for explanation see text)

with $J \leq J_{\max}(v'')$ were calculated from Eq. (43), the populations $N_{v'',J}$ being determined from Eq. (12). The integrals A_{v'',J,E'_J} (Eq. (26)) were computed numerically on the Odra 1003 using the wave functions $\psi_{v'',J}(r)$ of the discrete levels in the form of Eq. (27). The Airy integrals were taken from Tables given by Smirnov [37]. The shape of the absorption band of HgHe obtained by the above method is represented in Fig. 4 (curve 1), where it is compared with the shape of the satellite band curve 3). It is seen that the inclusion of rotation significantly improves the results of the calculations giving the shape of the absorption band which is now in better agreement with the shape of the satellite band on the short wavelength side of the Hg-line. The maximum of the calculated band falls at a frequency $\Delta\nu_m = 195 \text{ cm}^{-1}$ (with respect to the unperturbed frequency of the Hg-line) which differs by 30 cm^{-1} from the position 225 cm^{-1} of the maximum of the satellite band.

A somewhat better agreement between the calculated shape of the HgHe-band and the satellite band can be achieved if one more correction is made, that is, inclusion of the diffuseness of the higher rotational levels due to predissociation by rotation. This effect is a result of passage through the centrifugal potential barrier (tunnel effect) and leads to decomposition of molecules in the vibrational-rotational states $E_{v'',J}$ (cf. [35]). On the basis of semi-

-classical considerations, the lifetime $\tau_p(v'', J)$ with respect to such a decomposition of the molecule in the state $E_{v'', J}$ was found to be given by [38] (cf. also [35])

$$\tau_p(v'', J) = \tau_0(v'', J) \exp \left\{ \frac{2}{\hbar} \left| \int_{r_2}^{r_3} [2\mu(E_{v'', J} - V_J(r))]^{1/2} dr \right| \right\}, \quad (39)$$

where

$$\tau_0(v'', J) = 2 \int_{r_1}^{r_3} \left[\frac{2}{\mu} (E_{v'', J} - V_J(r)) \right]^{-1/2} dr. \quad (40)$$

is the classical period of oscillation of the particle with mass equal to the reduced mass μ of the molecule in the potential well (between the turning points r_1 and r_2 corresponding to the energy $E_{v'', J}$), r_3 being the third turning point at the potential barrier ($r_1 < r_2 < r_3$).

For $v'' = 0$ in the HgHe there are three levels ($J = 9; 10; 11$) and for $v = 1$ only one ($J = 4$) which can decay in this manner. The numerical calculations for Eq. (39) yield the following values of $\tau_p(v'', J)$ in seconds:

- a) $v'' = 0$: $\tau_p = 3.1 \times 10^{-8}$ for $J = 9$; $\tau_p = 2.8 \times 10^{-11}$ for $J = 10$ and $\tau_p = 1.7 \times 10^{-12}$ for $J = 11$;
 b) $v'' = 1$: $\tau_p = 2.1 \times 10^{-12}$ for $J = 4$.

For HgHe molecules one more cause of decomposition of these molecules, namely, collisions should be taken into account because of the small depth of potential well. This collision decomposition leads to the diffuseness of all vibrational-rotational levels (v'', J). The

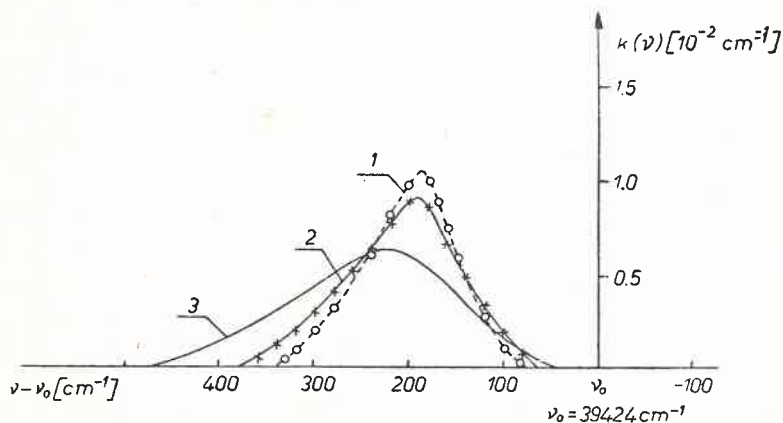


Fig. 4. Calculated HgHe-absorption band with inclusion of rotational effects. Curve 1 - without inclusion of decomposition of HgHe molecule (due to collisions and predissociation by rotation). Curve 2 - with inclusion of decomposition; curve 3 - satellite band

effects of tunneling and collision decomposition of Van der Waals molecules have recently been studied by Bouchiat *et al.* [39] in their interpretation of relaxation phenomena for optically polarized Rb atoms in a rare gas. The lifetime τ_c of a molecule due to collisions can be approximately calculated from the formula

$$\frac{1}{\tau_c} = \pi r_c^2 N_{\text{He}} \bar{v}, \quad (41)$$

where \bar{v} is the relative velocity. For the helium density of 271.2 Amagat and temperature $T = 340^\circ\text{K}$ τ_c is equal to 0.73×10^{-12} sec.

The influence of these effects on the shape of the absorption band was approximately estimated by assuming Lorentzian distributions for the contours of the diffuse levels with half-width $\gamma(v'', J)$ equal to $\frac{1}{\tau_p(v'', J)} + \frac{1}{\tau_c}$. The resulting absorption coefficient $k_{v'', J; E_J}(\Delta\nu)$ corresponding to the transitions from the diffuse levels (v'', J) was then calculated as the convolution of the absorption coefficient distributions (for sharp levels) given by Eq. (25) with these Lorentzian distributions according to the formula

$$k_{v'', J; E_J}(\Delta\nu) = \frac{\pi e^2}{mc^2} f N_{v'', J} \int_{-\infty}^{+\infty} \frac{\gamma(v'', J)}{2\pi} \frac{A_{v'', J; E_J}^2(\Delta\nu')}{(\Delta\nu - \Delta\nu')^2 + \left(\frac{\gamma(v'', J)}{2}\right)^2} d(\Delta\nu'). \quad (42)$$

After summation over all $J \leq J_{\max}$ as in Eq. (38), the resultant absorption coefficient distribution $k(\Delta\nu)$ was determined. The shape of the absorption band of HgHe including the above corrections is represented in Fig. 4 by curve 2. As can be seen, the calculated shape of the HgHe-band is in satisfactory agreement with that of the satellite band. The origin of the discrepancy between the position of the maximum of the continuous band of HgHe ($\Delta\nu_m = 195 \text{ cm}^{-1}$) and the maximum of the satellite band ($\Delta\nu_s = 225 \text{ cm}^{-1}$) can be ascribed to a pressure shift of the maximum of the HgHe-band.

Finally the contribution of the HgHe-spectrum of the transitions from the discrete levels $v'' = 0$ and $v'' = 1$ of the ground electronic state to the discrete level $v' = 0$ of the excited state ${}^3\Pi_0$ ($\Omega = 0$) was calculated. One of these transitions ($v'' = 1 \rightarrow v' = 0$) corresponds to frequencies on the long wavelength side of the Hg-line; namely the frequencies of the purely vibrational transitions are given by $\Delta\nu = 15 \text{ cm}^{-1}$ for $v'' = 0 \rightarrow v' = 0$ and $\Delta\nu = -17 \text{ cm}^{-1}$ for $v'' = 1 \rightarrow v' = 0$. The intensities of the vibrational lines corresponding to them were determined using the Morse oscillator eigenfunctions both for the $v'' = 0; 1$ and $v' = 0$ levels (Eq. (27) with $J = 0$), computing the overlap integrals $A_{v'', v'} = \int \psi_{v''}(r) \times \psi_{v'}(r) dr$. It turned out that for a density of helium of 271.2 Amagat, the intensity of these vibrational lines relative to the total intensity of the continuous band on the short wavelength side of the Hg-line is equal to 2×10^{-2} for $v'' = 0 \rightarrow v' = 0$ and 5×10^{-3} for $v'' = 1 \rightarrow v' = 0$. Although the existence of bands on the long wavelength side of the Hg-line would be useful in explaining some of the discrepancies between the measured and calculated intensity distributions in this region (see Fig. 1), the above magnitudes are too small for this. This is the result of a small overlap of the wave functions of the discrete levels due to the fact that the potential curves of the excited states are shifted to larger distances with respect to the potential curve of the ground state. Thus for the Hg-He system no red satellites are expected what is in accord with observations.

It should also be noted in conclusion that calculations based on the concept proposed by Hindmarsh and Farr [17] do not predict any red satellites for Hg-He.

4. Summary

On the basis of the results of the calculations given above for Hg-He system, one can conclude that the origin of the blue satellites is mainly due to continuous absorption (or emission) connected with the bound — free transitions between the discrete and continuous levels of the Van der Waals molecules. It is necessary, in general, to take into account the role of the bound — bound transitions (between different discrete vibrational levels) of these molecules. In many cases they may contribute strongly to the intensity of these bands. Apart from them, however, it seems that the contribution from bound — free transitions is always the most important. On the other hand the bound — bound transitions may be responsible to some extent for the origin of the red satellites, but it is clear that they cannot be treated as the only cause for the appearance of the red satellites. An explanation of the appearance of the red satellites should probably be sought along lines based on concepts such as those proposed by Hindmarsh and Farr [17], [18] and Kieffer [19] or Breene [14].

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