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The investigation of the satellite rainbow in the spectra of diatomic molecules

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Abstract. A refinement of the theoretical model for the description of the shape of a satellite rainbow in the spectra of diatomic molecules, based on the uniform Airy approximation, is presented. The satellite rainbow in the red wing of the caesium 852.1 nm line has been measured by means of classical absorption spectroscopy and excellent agreement with the calculated shape is found. The method for the quasistatical singularity position determination from the position of the minimum of the first derivative of the reduced absorption coefficient is proposed. The first derivative of the experimentally determined reduced absorption coefficient with respect to wavelength gives the position of the quasistatical singularity of the satellite rainbow to be 857.32 ± 0.02 nm, while our theoretical calculations predict its position at 857.36 nm.

1. Introduction

The appearance of a satellite rainbow in the spectra of diatomic molecules is due to the existence of the extrema in the curve describing the difference between the electronic energies of the initial and the final adiabatic state of an optical transition. In order to explain this phenomenon, Holstein (1950) suggested the Airy approximation of the characteristic integrals within the theory of a classical oscillator. Using the JWKB formalism Sando and Wormhoudt (1973) applied the transient Airy approximation in order to describe the spectral region in the vicinity of the classical singularity. Szudy and Baylis (1975) proposed, also using the JWKB formalism, the non-coherent uniform Airy approximation while Bieniek and Streeter (1983), as well as Vicharelli and Collins (1985), used the coherent uniform approximation which includes the contribution arising from the interference of the Condon points. The shape of the satellite rainbow in the case when non-radiative mixing of one of the electronic states of an optical transition with some other energetically close electronic state exists was investigated by Devderiani and Sebyakin (1989) using the Landau–Zener model.

All of the theoretical models mentioned above, including the simple one that is going to be presented here, comprise many common charactertics, one requiring to be emphasized in particular. Namely, the first derivative of the temperature-averaged linear absorption or emission coefficient with respect to frequency exhibits divergence at the position corresponding to the extreme in the difference potential curve of the respective transition. This can be exceptionally useful in the otherwise tricky (Exton and Snow 1978, Ferray *et al* 1980) problem of the reconstruction of the shape of the difference potential based on the experimentally determined continuous spectra.

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The validity of the proposed theoretical model, as well as the accuracy of the determination of the difference potential extreme based on the feature mentioned above, has been tested in the case of resonance broadening of the first caesium resonant doublet, which has so far been widely investigated experimentally and theoretically (Gregory 1942, Chen and Phelps 1968, Niemax and Pichler 1974, Movre and Pichler 1977, 1980, Niemax *et al* 1979, Veza *et al* 1980). The satellite rainbow in the red wing of the caesium 852.1 nm line has been chosen for study because it is easily attainable experimentally and allows the interatomic potential curves, in the long-range region, to be determined with satisfactory precision.

2. Theory

The simple approximation for description of the satellite rainbow which is going to be presented here is based on the well known Holstein Fourier integral approach. In order to achieve a correct description of the real physical situation within this model, a series of conditions have to be fulfilled. Here, it is supposed that the interaction of the electromagnetic field with the molecule is weak enough to allow the optical transition probability to be calculated in the first order of the perturbation. In addition, it is presumed that the atomic vapour densities are low enough so that the major contribution to the spectrum comes from transitions among electronic states of diatomic molecules or from short-living collisional quasimolecules formed by nearest-neighbour atoms. The motion of the atomic nuclei is described by classical trajectories which is correct to the extent to which the dominant contribution to the spectra arises from the free–free transitions. The rotation of the electronic dipole moment of the optical transition in the collisional frame leads to the splitting of the spectrum into three branches: P, Q, R (Spielfiedel *et al* 1989). This effect can be neglected if the interval of the internuclear separation relevant for the formation of the spectrum falls in the region of large internuclear distances. Finally, it is assumed that the optical transitions take place at internuclear separations much larger than the turning point R_t, and therefore the contributions to the spectrum arising from two half-collisions are non-coherently added.

With these conditions being fulfilled, the linear absorption coefficient can be expressed in the form:

$$k(\omega)=N^2\frac{2\pi\omega}{3c\hbar g_i}\sum_{\alpha,\beta}\langle|\overline{\mathfrak{J}_{\alpha\beta}(\omega)}|^2\rangle_{\mathrm{AV}} \tag{1a}$$

where

$$\overline{\mathfrak{J}_{\alpha\beta}(\omega)}=\int_{-\infty}^{\infty}\mathrm{d}t\,\overline{D_{\alpha\beta}(t)}\,\mathrm{e}^{\mathrm{i}f(\omega,t)} \tag{1b}$$

$$f(\omega,t)=\frac{1}{\hbar}\int_{-\infty}^{t}\mathrm{d}t'\,\Delta_{fi}(t')-\omega t \tag{1c}$$

and ω is the frequency of the absorbed radiation, N is the atom number density, g_i is the statistical weight of the initial state, while the summation extends over all degenerate substates of the initial $|i\alpha\rangle$ and final $|f\beta\rangle$ states. The limits of the time integral (1b) are $\pm\infty$, which correspond to the beginning and the end of one half-collision, respectively. $\overline{D_{\alpha\beta}(t)}$ is the matrix element of the electrical electronic dipole moment of the molecule given by:

$$\overrightarrow{D_{\alpha\beta}(t)} = \sum_j \langle i\alpha | e\mathbf{r}_j | f\beta \rangle \tag{2}$$

where $\mathbf{r}_j$ denotes the position of the electron, and summation extends over all electrons in the molecule. Δ_{fi} is the difference in the adiabatic electronic energies V_f and V_i of the final and the initial state. The statistical average $\langle\,\rangle_{\mathrm{AV}}$ over the particle assembly corresponds to summation over the impact parameters b and to averaging over the initial kinetic energies E. In the case of the canonical distribution of the energies in the system this averaging is expressed by:

$$\langle\ldots\rangle_{\mathrm{AV}} = \frac{4}{(kT)^{3/2}}\left(\frac{2\pi}{\mu}\right)^{1/2}\int_W^{\infty} \mathrm{d}E\, E\varepsilon^{-E/kT}\int_0^{\infty}\mathrm{d}b\, b \tag{3}$$

where μ is the reduced mass of the diatomic molecule, T is the temperature of the gas, k is the Boltzmann constant and W is the greater of 0 and V_i.

The main task in the evaluation of relation (1a) is the determination of the Fourier integral $\overrightarrow{\mathfrak{J}(\omega)}$. The dominant contribution to the integral $\overrightarrow{\mathfrak{J}(\omega)}$ comes from the neighbourhood of the stationary points t_s, the positions of which are determined by the equation:

$$\Delta_{fi}(t_s) = \hbar\omega. \tag{4}$$

Because the internuclear distance R is a function of time $(R = R(t))$, equation (4) determines the position of the Condon point $R_c = R(t_s)$, too. Subsequent to the expansion of the phase (relation (1c)) in power series around stationary points t_s and retaining only terms up to quadratic, one obtains a quasistatical expression for linear absorption coefficient (Movre and Pichler 1979):

$$k(\omega) = N^2\frac{4\pi^2 e^2\hbar}{mc}\sum_c f(R_c)\frac{R_c^2}{|\Delta'_{fi}(R_c)|}\exp(-V_i(R_c)/kT) \tag{5}$$

where $\Delta'_{fi}(R_c) = (\mathrm{d}\Delta_{fi}(R)/\mathrm{d}R)_{R=R_c}$, and $f(R_c)$ is the molecular oscillator strength:

$$f(R_c) = \frac{2m\omega}{3\hbar e^2 g_i}\sum_{\alpha,\beta}|\overrightarrow{D_{\alpha\beta}(R_c)}|^2. \tag{6}$$

The summation involves all real Condon points. In evaluation of relation (5), $W \ll kT$ is assumed.

If several real Condon points exist, relation (5) is applicable if there is no interference among them. In the neighbourhood of the difference potential extreme two Condon points come close together, and the derivatives of the difference potentials tend to zero which yields a non-physical result for the extreme position (quasistatical singularity). In the case where only one extreme in the difference potential is present, the classically allowed region includes two real Condon points, for which the Franck–Condon principle is satisfied. In order to evaluate the asymptotic value of the integral (1b), the method of uniform mapping (Connor and Marcus 1971), developed within catastrophe theory (Connor 1976), has been applied, which enables the correlation of the stationary points t_1 and t_2 to be appropriately included. Following the procedure of Connor and Marcus (1971), we have obtained the asymptotic form of the integral $\overrightarrow{\mathfrak{J}(\omega)}$:

$$\overrightarrow{\mathfrak{J}_{\alpha\beta}(\omega)} = (2\hbar)^{1/2}\pi\zeta^{1/4}\,\mathrm{e}^{\mathrm{i}A(\omega)}\left\{\frac{\overrightarrow{D_{\alpha\beta}(R_1)}}{(v_r(R_1)|\Delta'_{fi}(R_1)|)^{1/2}}\left(\mathrm{Ai}(-\zeta)-\mathrm{i}\sigma_1\frac{\mathrm{Ai}'(-\zeta)}{\zeta^{1/2}}\right)\right.$$
$$\left.+\frac{\overrightarrow{D_{\alpha\beta}(R_2)}}{(v_r(R_2)|\Delta'_{fi}(R_2)|)^{1/2}}\left(\mathrm{Ai}(-\zeta)-\mathrm{i}\sigma_2\frac{\mathrm{Ai}'(-\zeta)}{\zeta^{1/2}}\right)\right\} \qquad (7)$$

where

$$A(\omega)=\tfrac{1}{2}(f(\omega,t_1)+f(\omega,t_2)) \qquad (8a)$$

$$\zeta(\omega)=(\tfrac{3}{4}\sigma_1(f(\omega,t_2)-f(\omega,t_1)))^{2/3} \qquad (8b)$$

$$\sigma_j=\mathrm{sign}(\Delta'_{fi}(t_j)) \qquad j=1,2. \qquad (8c)$$

$\mathrm{Ai}(-\zeta)$ and $\mathrm{Ai}'(-\zeta)$ are the Airy function and its first derivative, respectively, and

$$v_r(R_j)=\frac{2}{\mu}[E(1-b^2/R_j^2)-V_i(R_j)]^{1/2} \qquad (9)$$

are the radial velocities at the Condon points.

The contributions of the Condon points are formally separated in relation (7), with their correlation being comprised in function $\zeta(\omega)$. Substituting relation (7) into (1*a*) one obtains:

$$k(\omega)=\frac{4\pi^3e^2\hbar}{mc}\left(\frac{f(R_1)}{|\Delta'_{fi}(R_1)|}\mathscr{K}_1(\omega,T)+\frac{f(R_2)}{|\Delta'_{fi}(R_2)|}\mathscr{K}_2(\omega,T)\right.$$
$$\left.+2\frac{F(R_1,R_2)}{(|\Delta'_{fi}(R_1)\Delta'_{fi}(R_2)|)^{1/2}}\mathscr{K}_{12}(\omega,T)\right) \qquad (10)$$

where $\mathscr{K}_j$ $(j=1,2)$ is given by

$$\mathscr{K}_j(\omega,T)=\tfrac{1}{2}\left(\left\langle\frac{\zeta^{1/2}\,\mathrm{Ai}^2(-\zeta)}{v_r(R_j)}\right\rangle_{\mathrm{AV}}+\left\langle\frac{\mathrm{Ai}'^2(-\zeta)}{v_r(R_j)\zeta^{1/2}}\right\rangle_{\mathrm{AV}}\right) \qquad (11a)$$

$\mathscr{K}_{12}$ is equal to

$$\mathscr{K}_{12}(\omega,T)=\tfrac{1}{2}\left(\left\langle\frac{\zeta^{1/2}\,\mathrm{Ai}^2(-\zeta)}{(v_r(R_1)v_r(R_2))^{1/2}}\right\rangle_{\mathrm{AV}}-\left\langle\frac{\mathrm{Ai}'^2(-\zeta)}{\zeta^{1/2}(v_r(R_1)v_r(R_2))^{1/2}}\right\rangle_{\mathrm{AV}}\right) \qquad (11b)$$

and R_j $(j=1,2)$ are real Condon points $(R_1<R_2)$. The function $F(R_1,R_2)$ is defined in analogy with molecular oscillator strengths:

$$F(R_1,R_2)=F(\omega)=\frac{2m\omega}{3\hbar e^2g_i}\sum_{\alpha,\beta}\overrightarrow{D_{\alpha\beta}(R_1)}\,\overrightarrow{D_{\alpha\beta}(R_2)}. \qquad (12)$$

The integration over impact parameter b in expressions (11) can be restricted to the interval comprising the real values of the radial component of the relative motion. This restriction determines the maximal impact parameter B_j $(j=1,2)$ for which the nuclei reach the Condon points R_j $(j=1,2)$. Therefore the relation (9) gives:

$$B_j=R_j\left(\frac{E-V_i(R_j)}{E}\right)^{1/2}. \qquad (13)$$

Thus, the corresponding upper limits of the integrals in the relations (11) are B_1 for $\mathscr{K}_1$ and $\mathscr{K}_{12}$, and B_2 for $\mathscr{K}_2$.

If the conditions

$$\frac{R_2-R_1}{R_2}\ll 1 \qquad \text{and} \qquad \left|\frac{V_i(R_1)-V_i(R_2)}{kT}\right|\ll 1 \tag{14}$$

are satisfied, then $v_r(R_2)\simeq v_r(R_1)$. The same conditions applied to the function $\zeta(\omega)$ yield the following approximate expression for $\zeta(\omega)$:

$$\begin{aligned}\zeta(\omega)&=\left(\frac{3\sigma_1}{4\hbar}\int_{t_1}^{t_2}\mathrm{d}t(\Delta_{fi}(t)-\hbar\omega)\right)^{2/3}\\&=\left(\frac{3\sigma_1}{4\hbar}\int_{R_1}^{R_2}\frac{\mathrm{d}R}{v_r(R)}(\Delta_{fi}(R)-\hbar\omega)\right)^{2/3}\\&\simeq\left(\frac{3\sigma_1}{4\hbar\bar{v}_r}\int_{R_1}^{R_2}\mathrm{d}R(\Delta_{fi}(R)-\hbar\omega)\right)^{2/3}\end{aligned} \tag{15}$$

with $\bar{v}_r=v_r(R_1)$ being used in the evaluation of $\mathcal{K}_1$ and $\mathcal{K}_{12}$ and $\bar{v}_r=v_r(R_2)$ in the evaluation of $\mathcal{K}_2$.

According to Szudy and Baylis (1975), the partial integration reduces the averaging over the statistical assembly to the single integral, and relations (11) obtain the following form:

$$\mathcal{K}_j(\omega,T)=3R_j^2\exp(-V_i(R_j)/kT)\sqrt{\pi z}\,(L(z)+H(z)/z) \tag{16a}$$

$$\mathcal{K}_{12}(\omega,T)=3R_1^2\exp(-V_i(R_1)/kT\sqrt{\pi z}\,(L(z)-H(z)/z). \tag{16b}$$

The functions $L(z)$ and $H(z)$ are given by:

$$L(z)=\int_0^\infty \mathrm{d}t\,\mathrm{e}^{-1/t^3}\frac{[\mathrm{Ai}(-zt)]^2}{t^2} \tag{17}$$

$$H(z)=\int_0^\infty \mathrm{d}t\,\mathrm{e}^{-1/t^3}\frac{[\mathrm{Ai}'(-zt)]^2}{t^3}. \tag{18}$$

The features of the function $L(z)$ were discussed by Szudy and Baylis (1975), while the function of the form $H(z)/z$ appeared for the first time in the work of Vicharelly and Collins (1985). The functions $L(z)$, $H(z)$ and $H(z)/|z|$ are shown in figure 1. The

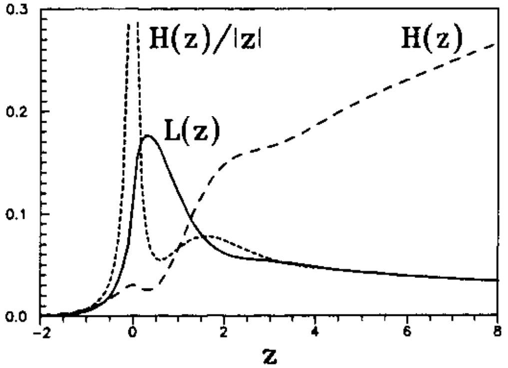

Figure 1. The shape of the functions $L(z)$ (equation (17)), $H(z)$ (equation (18)) and $H(z)/|z|$.

substitution of relations (16) into (10) yields the final expression for the absorption coefficient:

$$k(\omega)=\frac{12\pi^3e^2\hbar}{mc}N^2\sqrt{\pi z}\left[\left(\frac{R_1^2f(R_1)}{|\Delta'_{fi}(R_1)|}\exp(-V_i(R_1)/kT)+\frac{R_2^2f(R_2)}{|\Delta'_{fi}(R_2)|}\exp(-V_i(R_2)/kT)\right)\right.$$
$$\times\left(L(z)+\frac{H(z)}{z}\right)+2\frac{R_1^2F(R_1,R_2)}{(|\Delta'_{fi}(R_1)\Delta'_{fi}(R_2)|)^{1/2}}\exp(-V_i(R_1)/kT)$$
$$\left.\times\left(L(z)-\frac{H(z)}{z}\right)\right] \tag{19}$$

where the function $z=z(\omega)$ is given by:

$$z(\omega)=\left(\frac{\mu}{2kT}\right)^{1/3}\left(\frac{3\sigma_1}{4\hbar}\int_{R_1}^{R_2}\mathrm{d}R(\Delta_{fi}(R)-\hbar\omega)\right)^{2/3}. \tag{20}$$

The first term in the square bracket in relation (19) describes the contribution of the two Condon points. In the case when $z(\omega)$ is large, i.e. when the phase difference between points R_1 and R_2 is large, the first term assumes the quasistatical form. The second term describes the interference of the Condon points, and it vanishes for large phase differences.

In the neighbourhood of the extreme, the difference potential Δ_{fi} and the dipole moment $\overrightarrow{D_{\alpha\beta}}$ can be approximated with a quadratic (Sando and Wormhoudt 1973) and linear expansion, respectively:

$$\Delta_{fi}(R)=\hbar\omega_0+\tfrac{1}{2}\Delta''_{fi}(R_0)(R-R_0)^2 \tag{21a}$$

$$\overrightarrow{D_{\alpha\beta}(R)}=\overrightarrow{D_{\alpha\beta}(R_0)}+\frac{\mathrm{d}\overrightarrow{D_{\alpha\beta}(R_0)}}{\mathrm{d}R}(R-R_0) \tag{21b}$$

with R_0 being the position of the extreme, and $\hbar\omega_0=\Delta_{fi}(R_0)$.

Using this approximation the analytical continuation of the difference potential and the dipole moment into the region of complex Condon points can be done. Thus, the simple expression for the linear absorption coefficient in the neighbourhood of the quasistatical singularity is obtained:

$$k(\omega)=\frac{24\pi^3\sqrt{2\pi}\,e^2\hbar^{2/3}}{mc}\left(\frac{\mu}{kT}\right)^{1/6}\frac{R_0^2f(R_0)}{|\Delta''_{fi}(R_0)|^{2/3}}\exp(-V_i(R_0)/kT)$$
$$\times\left\{L(z)+2\left|\frac{\mathrm{d}\overrightarrow{D(R_0)}/\mathrm{d}R}{\overrightarrow{D(R_0)}}\right|^2\left(\frac{\hbar}{\Delta''_{fi}(R_0)}\right)^{2/3}\left(\frac{kT}{\mu}\right)^{1/3}H(z)\right\} \tag{22}$$

where $z(\omega)$ has the simple form

$$z(\omega)=(\omega-\omega_0)\left(\frac{\hbar\mu}{kT\Delta''_{fi}}\right)^{1/3}. \tag{23}$$

The existence of the first term in the braces in the relation (22) has already been published (Szudy and Baylis 1975), but the second term has not yet appeared in the literature explicitly. This term equals zero if the electrical dipole moment happens to be constant in the vicinity of the extreme. However, the extreme in the difference potential usually arises in the region of crossing of two diabatic states. Therefore, the dipole moment of the adiabatic state in the vicinity of the crossing changes in value or in direction, which can have the influence on the absorption coefficient.

As was shown by Szudy and Baylis (1975), the first derivative of $L(z)$ diverges in the vicinity of $z=0$:

$$\lim_{z\to 0}\frac{\partial L}{\partial z}=2\,\mathrm{Ai}(0)\,\mathrm{Ai}'(0)\ln|z| \tag{24}$$

while $H(z)$ exhibits a local maximum in $z=0$. Therefore, the first derivative of the absorption coefficient, $\mathrm{d}\ell(\omega)/\mathrm{d}\omega$ diverges in the vicinity of the classical singularity

$$\frac{\mathrm{d}\ell(\omega)}{\mathrm{d}\omega}\propto\ln|z(\omega)| \qquad |z|\to 0. \tag{25}$$

As can be seen the divergence of the linear absorption coefficient at the position of the classical singularity obtained in the quasistatical approximation is no longer present in the Airy approximation, while the divergences of the first and all higher derivatives of the linear absorption coefficient still remain.

The characteristic of the linear absorption coefficient expressed by relation (25) is not necessarily related to the quadratic approximation of the difference potential curve. Investigating the spectra arising from the transition into the states among which non-adiabatic mixing of Landau-Zener type exists, Devderiani and Sebyakin (1989) approximated the shape of the difference potential in the neighbourhood of the extreme with one branch of the hyperbola. Their model in the adiabatic limit yields the linear absorption coefficient corresponding to relation (22) with the characteristic feature described by relation (25).

3. Experiment

The experimental set-up for the absorption measurements is shown in figure 2. The tungsten lamp was used as a continuous light source. The parallel beam was transmitted through the absorption cell and focused on the 10 μm entrance slit of the monochromator (1 m McPherson model 2051, instrumental profile 0.02 nm). The output of the photomultiplier (RCA S-20) was fed to the lock-in amplifier (SR 510) connected

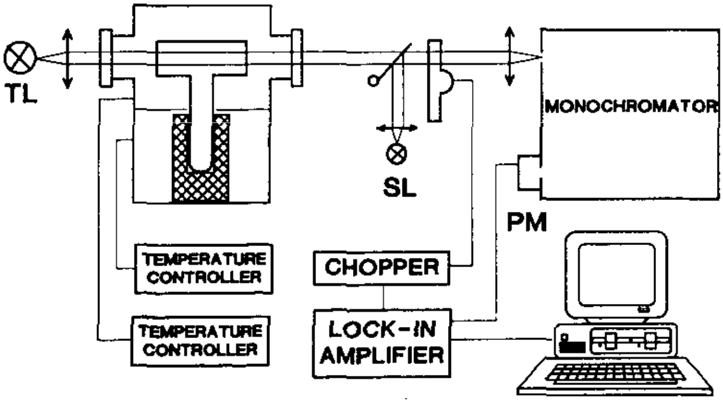

Figure 2. Experimental set-up: TL, tungsten lamp; SL, spectral lamp; PM, photomultiplier.

to the computer via an IEE488 interface. The reference signal for the lock-in amplifier was supplied by a chopper (SR 540) operated at 1 kHz frequency. The spectra were collected automatically with an average rate of 75 points/nm. The glass absorption cell (13.2 cm long, 2.8 cm in diameter) was situated in a two-chamber oven with separate heating systems. The temperature control in both chambers was realized by use of HAAKE (type 24 and 32) controllers supplied with Pt resistance thermometers attached to the walls of the oven. The temperature of the bath as well as of the cell was measured by calibrated Fe–constantan thermocouples, glued to the glass walls with high temperature cement (Astroceram) of good thermal conductivity. The bath was enclosed in a massive metal block in order to ensure temperature stability of the bath. The temperature stability of the bath and the cell was ±0.1 K and ±0.2 K, respectively. The temperature of the bath was always kept about 30 K lower than that of the absorption cell, in order to prevent caesium atoms from depositing on the cell windows. The absorption cell temperature was varied in the range from 550 K to 600 K.

The reduced absorption coefficient $k(\lambda)/N^2_{\mathrm{Cs}}$, N_{Cs} being the number density of caesium atoms, was obtained using the value for N_{Cs} determined from the absorption coefficient of the self-broadened blue wing of the caesium 852.1 nm line, according to the relation (Movre and Pichler 1977, 1980):

$$N_{\mathrm{Cs}}=\left(\frac{3mc^3k}{\Pi e^2 f\lambda_0^2 C_3}\right)^{1/2}\frac{\Delta\lambda}{\lambda} \tag{26}$$

where k is the linear absorption coefficient, f is the atomic oscillator strength, C_3 is the effective constant for the Cs-Cs resonant interaction, λ_0 is the wavelength of the centre of the line and $\Delta\lambda$ is the wavelength separation from the line centre. For values of C_3 and f, we have used those obtained by Niemax *et al* (1979) and Link (1966), respectively, which yields the caesium number density:

$$N_{\mathrm{Cs}}=2.05\times10^{16}(k(\mathrm{cm}^{-1}))^{1/2}\Delta\lambda(\mathrm{nm}). \tag{27}$$

The spectroscopically determined values for N_{Cs} were compared to those obtained from the caesium vapour pressure curve (Nesmeyanov 1963) and the relative error in the determination of N_{Cs} was found to be at most ±2%. The spectrum of the tungsten lamp was measured at room temperature both prior to and after completing the measurement at elevated temperature, in order to control and account for possible alteration of the intensity of the continuum. The overall uncertainty in the presented results for the reduced absorption coefficient, comprising the errors due to N_{Cs} uncertainty and alteration of the continuum, was estimated to at most ±5%.

The speed of the wavelength scan of the monochromator was checked by collecting the spectrum of the spectral lamp in the range from the Rb 780.2 nm to the Cs 894.9 nm line. The maximum error in the determination of the wavelength separation from the line centre was found to be ±0.001 nm.

4. Results and discussion

The red wing of the Cs 852.1 nm absorption line is formed by the optical transitions from 0_u^+, 1_u and 0_g^- electronic molecular states originating from the $6^2S_{1/2}+6^2S_{1/2}$ asymptote, to the excited electronic states 1_g, 0_u^+, 1_u and 0_g^- ending in the $6^2S_{1/2}+6^2P_{3/2}$ asymptote. The difference potential curve for the transition $0_g^-\rightarrow 1_u$ exhibits a shallow minimum which causes the occurrence of the asymmetry of the red wing at a distance of ≈0.25 nm from the 852.1 nm line centre (Niemax *et al* 1979). Since our interest has been focused on the wing shape at larger distances from the line centre, where this transition does not influence the line profile, it is not taken into consideration. All the potential curves and corresponding absorption oscillator strengths in the long-range region have been calculated following the procedure given by Umanskij and Nikitin (1969). The electrostatic interaction has been taken into account up to the dipole-quadrupole term in the multipole expansion, while the influence of the exchange interaction has been neglected. As for values of the C_3 constants for the resonant dipole-dipole interaction, we have used the semiempirical results of Niemax *et al* 1979. The values of the C_6 constants for the dispersion dipole-dipole contribution, as well as the C_8 constants for the dispersion and induction dipole-quadrupole interaction, have been taken from the work of Bussery and Aubert-Frécon (1984). Figure 3(*a*) displays the calculated difference potential curves corresponding to the transitions: 0_u^+, $1_u \rightarrow 1_g$; 0_u^+, $1_u \rightarrow 0_g^-$ and $0_g^- \rightarrow 0_u^+$. The curves shown are assigned with the label of the corresponding excited electronic state, while the energy zero is identified with the asymptote of the $6^2S_{1/2}+6^2P_{3/2}$ state. The difference potential curves related to the transitions to the 0_u^+ and 1_g states are monotonically attractive in the frequency range of interest, and are dominantly governed by the resonant interaction. The curve related to the transition to the 0_g^- state exhibits a minimum ($-72.2\ \mathrm{cm}^{-1}$) at the internuclear distance of 1.33 nm, both the depth and the position of which are strongly affected by dispersion contributions to the interatomic interaction.

The absorption oscillator strengths corresponding to the transitions mentioned, plotted against interatomic separation, are shown in figure 3(*b*). As one can see, the value of the oscillator strength of the 0_u^+, $1_u \rightarrow 0_g^-$ transition does not depend on the

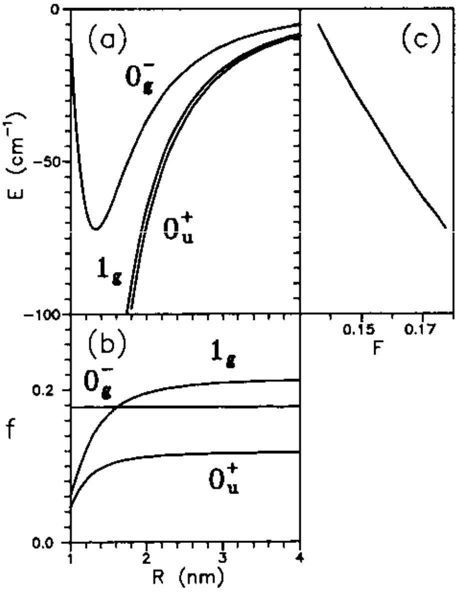

Figure 3. (*a*) The calculated difference potential curves corresponding to the transitions: 0_u^+, $1_u \rightarrow 1_g$; 0_u^+, $1_u \rightarrow 0_g^-$ and $0_g^- \rightarrow 0_u^+$. The curves shown are assigned with the label of the corresponding excited electronic state, while the energy zero is identified with the asymptote of the $6^2S_{1/2}+6^2P_{3/2}$ state; (*b*) oscillator strengths for the transitions in the 0_g^-, 1_g and 0_u^+ states; (*c*) relationship between the oscillator strength like function *F* (described in the text—relation (12)) and the energy of the 0_g^- difference potential.

interatomic separation R, leading to the conclusion that the value of the dipole moment does not depend on the interatomic separation either. However, in the body-fixed frame, the dipole moment orientation of this transition changes as a consequence of the wavefunction of the adiabatic 0_g^- state being an R-dependent linear combination of the diabatic $^3\Pi_g(0_g^-)$ and $^3\Sigma_g^+(0_g^-)$ states. This causes the oscillator strength-like function F (relation (12)) to change depending on the energy of the absorbed photon (figure 3(*c*)). The fact that the F function, if properly treated, turns out to be a scalar product instead of a product of scalars (which has usually slipped the attention of the authors dealing with the shape of satellite rainbows) can appreciably influence the interference of the Condon points.

Figure 4(*a*) shows experimental results for the reduced linear absorption coefficient in the red wing of the Cs 852.1 nm line, obtained at several temperatures in the range from 550 K to 600 K. The differences among the displayed wing profiles were not caused by temperature variation, but merely by uncertainty in the caesium number density determination. The argument in favour of the above statement is as follows. There are two ways in which the temperature can affect the wing profile: through the Boltzmann factor and due to the temperature dependence of the function $z(\omega)$ (relation (20)). The depth of the ground state potential in the range of interest is much smaller than the mean kinetic energy kT of the molecules at this temperature, so that the Boltzmann factor remains close to unity in the whole relevant range of temperatures and internuclear separations. Particularly, for the internuclear separation of 1.33 nm, corresponding to the position of the extreme in the 0_g^- potential, the ground state potential depth amounts to 10.2 cm^{-1}, which yields the Boltzmann factor change of 0.1% for temperature variation in the interval from 550 K to 600 K. The contribution to the temperature alteration of the wing profile due to $z(\omega)$ has been estimated to be no more than 1% for the same temperature interval. Consequently, it is obvious that the effects of the temperature influence are not discernible in the overall experimental error declared above. The theoretical result for the reduced linear absorption coefficient

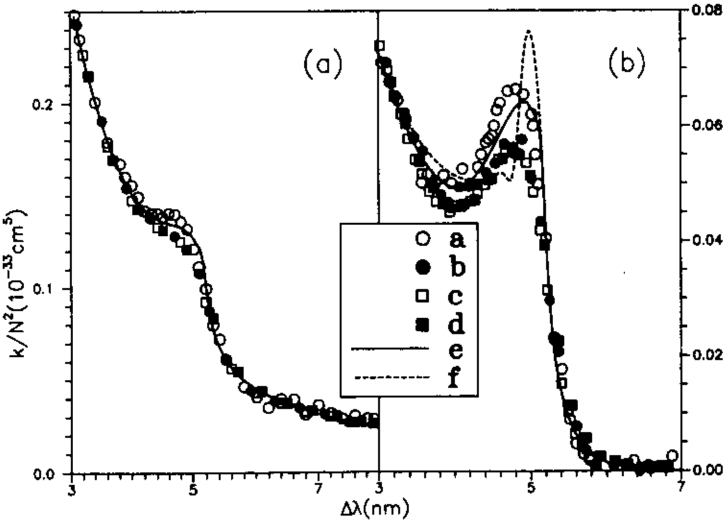

Figure 4. Comparison of experimental and calculated results for (*a*) reduced linear absorption coefficient, (*b*) contribution of 0_g^- state to the linear absorption coefficient. a, $T_c = 553.8$ K; b, $T_c = 575.8$ K; c, $T_c = 586.6$ K; d, $T_c = 598.8$ K; e, theory (present results); f, theory (Szudy and Baylis 1975).

in the red wing of the Cs 852.1 nm line is shown in the same figure with a full curve. The theoretical profile has been calculated for the temperature $T = 575$ K. The profile shown includes the contributions from the transitions to 1_g and 0_u^+ states, which are simple resonant contributions calculated according to the quasistatical approximation (relation (5)), and the contribution from the transition to the 0_g^- state responsible for the satellite formation and calculated according to relations (19) and (22). Excellent agreement between the experiment and the theoretical prediction is clearly displayed in figure 4(*a*). Being convinced, to the extent of the agreement displayed in figure 4(*a*), of the properness of the calculated contributions to the wing profile, especially those of the simple resonant ones, we have subtracted them from the experimentally determined data shown in figure 4(*a*), thereby obtaining solely the shape of the satellite, which is shown in figure 4(*b*). The theoretical shape of the satellite alone is displayed with the full curve. The discussion given above for figure 4(*a*) remains valid here as well. For comparison, the theoretical result of Szudy and Baylis (1975) is also shown. As one can see, the theory of Szudy and Baylis (1975) results in a very narrow and high satellite shape, differing considerably from the experiment, while the shape of the satellite obtained on the basis of the theory given in section 2 fits the experimental data within the experimental error.

As expressed in section 2, the divergence of the first derivative of the absorption coefficient occurs at the position of the quasistatical singularity. The numerical derivatives of the experimental and theoretical data shown in figure 4(*a*) and (*b*) are given in figure 5(*a*) and (*b*), respectively. The pronounced minima in the derivatives of the reduced linear absorption coefficients with respect to the wavelength separation from

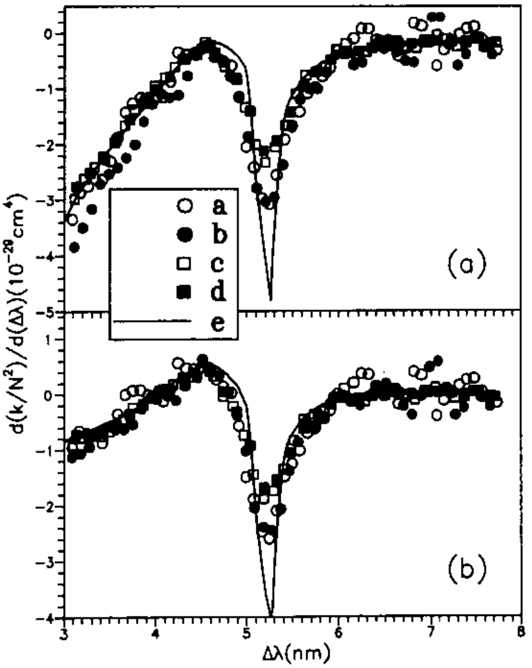

Figure 5. Numerical derivatives with respect to wavelength of experimental and theoretical data for (*a*) reduced linear absorption coefficients, (*b*) contribution of 0_g^- state to the linear absorption coefficient. a, $T_c = 553.8$ K; b, $T_c = 575.8$ K; c, $T_c = 586.6$ K; d, $T_c = 598.8$ K; e, theory (present results).

the line centre exist at the position of the quasistatical singularity. The numerical derivatives of the theoretical results exhibit finite minima rather than divergences due to the finite step chosen for obtaining the numerical derivatives. The theory predicts the position of the quasistatical singularity to be 5.26 nm away from the line centre, while the experiment gives 5.22 ± 0.02 nm, which yields the depth of the minimum of the corresponding difference potential as $71.5 \pm 0.3\ \mathrm{cm}^{-1}$. Our calculated value is $72.2\ \mathrm{cm}^{-1}$, as has been mentioned above. The position of the derivative minimum does not depend on whether the wing profile itself (figure 4(*a*)), or only the satellite contribution (figure 4(*b*)), is considered. Moreover, the derivative of the raw intensity data with respect to wavelength separation from the line centre exhibits the minimum at the very same position, as shown in figure 6. The position of the minimum is not temperature dependent, as predicted by theory. For the sake of visual clarity the number of data points presented is much smaller than the actual one, so that the position of the derivative minimum has been determined with an accuracy greater than figure 5 suggests at first sight (see section 3). Particularly, the accuracy of the experimental determination of the position of the classical singularity was limited by the instrumental profile (0.02 nm) of the monochromator.

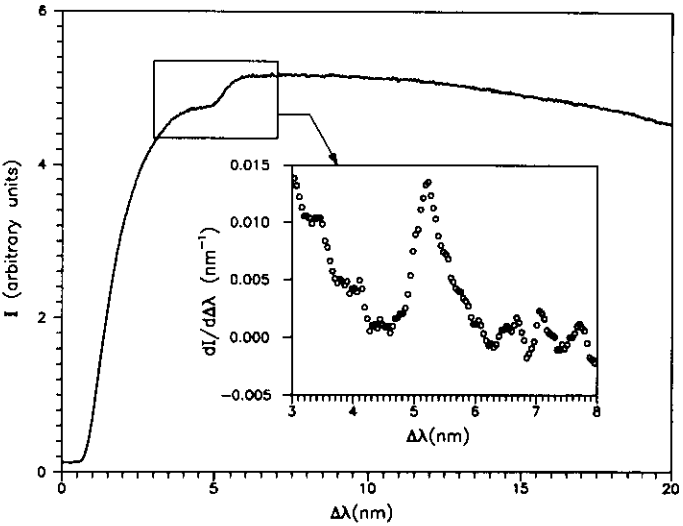

Figure 6. The transmitted light intensity profile of the red wing of the caesium 852.1 nm line obtained at temperature $T = 553.8$ K. The numerical derivative of the intensity profile with respect to the wavelength separation from the line centre is shown in the inset.

The usual method for determining the quasistatical singularity position from the experimental data has so far been that proposed by Carrington and Gallagher (1974), stating that it should coincide with the position corresponding to 65% of the satellite maximum height. A certain degree of arbitrariness is inherent in this method since one, being left with the data presented in figure 4(*a*) faces the problem of the estimation of satellite maximum, which is subject to an error. Even knowing the satellite contribution to the spectrum alone, this method is questionable because it is based upon the assumption of invariability of the dipole moment with regard to both value and direction, which does not need to be the truth. The fair analysis of our experimental data in such a manner could not yield an accuracy, regarding the quasistatical singularity position, better than 0.1 nm.

5. Conclusion

Here we have presented a simple theoretical model for the description of the satellite rainbow in the spectrum of a diatomic molecule. Experimental verification has been achieved for the case of the satellite in the red wing of the caesium 852.1 nm line. To our knowledge, no better agreement between the theoretically predicted shape of a satellite and the experimentally observed one has been published so far. The orientational dependence of the dipole moment has been rigorously taken into account, which certainly contributes a great deal to the excellent agreement with the experimental results. Also, the method of determining the quasistatical singularity position from the derivative of the linear absorption coefficient has been justified, turning out to be at least half of one order of magnitude more accurate than the customary one (Carrington and Gallagher 1974). It has to be emphasized that by using this method the position of the quasistatical singularity can be determined, with the same reliability, from whether the satellite contribution alone, the wing profile or simply the raw intensity data. The method proposed can be as well applied in the case of discharge emission or laser-induced fluorescence, provided that the moelcules in the excited states are thermalized. The accuracy of the quasistatical singularity position determination can be further improved in laser absorption measurements, thus eliminating the restriction imposed by the instrumental profile of the monochromator.

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