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Far wings of the $6s\Sigma - 5d\Sigma$ and $6s\Sigma - 7s\Sigma$ transitions in Cs–He: influence of non-adiabatic effects

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Abstract. The far wings of $6s\Sigma - 5d\Sigma$ and $7s\Sigma$ transitions of the Cs–He system have been calculated using the semiclassical model of Szudy and Baylis and the recent potentials and the oscillator strengths of Pascale. In spite of real improvements with respect to previous calculations, important differences remain with the experimental profile in a spectral region which corresponds to the vicinity of the pronounced avoided crossing between the $5d\Sigma$ and $7s\Sigma$ potential curves. Non-adiabatic transitions which occur between the two states are probably responsible for that disagreement.

1. Introduction

Satellites often appear in the far wings of spectral lines because of the existence of extrema in the energy difference between the potentials of the upper and lower states of the transition. They cannot be interpreted by the quasi-static theory (QS). To treat the satellite region semiclassical approaches have been developed (Sando and Wormhoudt 1973, Szudy and Baylis 1975). But their use is restricted to the case where the levels involved in the transition are only slightly perturbed by neighbouring levels and when the dipole moment of the transition is constant or slowly varying with the internuclear distance (Visticot et al 1981b). In the vicinity of an avoided crossing between two potential energy curves, this condition is generally not fulfilled. In particular there is an exchange between the characteristics of the states at the avoided crossing which may lead to a dramatic variation of the dipole moment. Moreover, in the case of a pronounced avoided crossing, non-adiabatic transitions may occur which are not taken into account at all in these semiclassical models.

The far wings of the $6s\Sigma - 7s\Sigma$ and $6s\Sigma - 5d\Sigma$ transitions in the Cs–He system are examples of such a situation. The wings of the corresponding dipole-forbidden atomic transitions have been observed experimentally (Sayer et al 1978, Tam 1978). They do not overlap with wings of other transitions and the study of the quasi-static part of these lines has provided accurate information about the potentials and the variation of the dipole moment with the internuclear distance (Ferray et al 1980). It has been shown that, contrary to the prediction of previous theoretical calculations of adiabatic potentials and oscillator strengths (Pascale and Vandeplanque 1974, Pascale 1977, Czuchaj and Sienkiewicz 1979, Czuchaj 1979), the two states $7s\Sigma$ and $5d\Sigma$ are strongly interacting. Recently $l$-dependent pseudopotential molecular structure calculation of the alkali–helium systems has been performed which substantially improves the comparison with experimental data and previous theoretical results (Pascale 1982, 1983).
In particular it reproduces quite well the potentials and induced oscillator strengths for the Cs–He 6s–5D transition which have been deduced from the experiment by means of the quasi-static theory.

The purpose of this work is to try to extend the comparison between experiment and theory for Cs–He to the region where the quasi-static theory fails. For that we have used the recent potentials and oscillator strengths calculated by Pascale (1982, 1983) and the unified Franck-Condon (UFC) model of Szudy and Baylis (1975) to calculate the shape of the blue satellite of the 6sΣ–7sΣ transition and to compare it with the experiment. The calculation has in fact been performed for all the 6sΣ–7sΣ and 5dΣ wings. In the crossing region, the UFC model, as well as the quasi-static theory, fails because it assumes transitions between isolated levels. However some qualitative arguments can provide information about the validity of the potentials.

2. Theories for far-wing line broadening

2.1. Quasi-static theory

The qs theory has been widely used to interpret the far wings of atomic lines. One of the reasons is because of its simplicity: the absorption or emission coefficient is related to the interatomic potentials and dipole moment by a simple relation which allows one to draw quantitative information from the wings. Gallagher (1975) applied it to the wings of resonance alkali lines perturbed by rare gases and Sayer et al. extended it to the forbidden caesium lines 6s–7S and 5D where the variations of the dipole moment are very large (Sayer et al. 1979, 1980, Ferray et al. 1980). The qs theory is a classical theory based upon the Franck-Condon principle which assumes that there is no change in kinetic energy or relative position of the atoms during the radiative transition. The energy $h\nu$ of the photon therefore corresponds to the difference between the adiabatic potentials $V$ of the upper (u) and lower (l) states at the interatomic distance $R$:

$$ h\nu = V_u(R) - V_l(R) = \Delta V(R). $$

(1)

This equation relates the frequency $\nu$ to $R$. In the qs theory the absorption coefficient $\alpha$ can be expressed as (Gallagher 1975, Sayer et al. 1979):

$$ \alpha_{qs} = \frac{32\pi^4 n_p n_l \nu}{3c} \sum_i \frac{R_i^2 D^2_i(R_i)}{\Delta V'(R_i)} \exp \left( -\frac{V_l(R_i)}{kT} \right) $$

(2)

where $n_l$ and $n_p$ are the densities of absorbers and perturbers, $\Delta V'$ is the first derivative of $\Delta V$ with respect to $R$ and the summation is performed over the various Condon points determined by equation (1).

The qs theory supposes that the trajectories can be treated classically and this classical path approximation is generally considered as valid if the interatomic potential does not vary appreciably over the de Broglie wavelength of the absorber–perturber pair (Allard and Kielkopf 1982). This approximation is therefore less valid for a light perturber such as helium, and Drummond and Gallagher (1974) have attributed the difficulty that they had in interpreting the wings of the resonance line of the Rb–He pair to a failure of this classical theory. However a recent quantal calculation of the red wing of the resonance line of the Na–He pair has shown that the quasi-static theory gives good results even for helium (Pontius and Sando 1983).
In equation (2) it can be seen that \( \alpha_{qs} \) diverges when \( \Delta V' \) is equal to zero, i.e. when there is an extremum in the potential difference \( \Delta V \). In that case a relatively large region in \( R \) contributes to a narrow band of frequency, consequently velocity and interference effects neglected in the \( qs \) theory are important. The intensity of the wing tends to increase and generally a maximum or a shoulder, called satellite, appears in the spectrum.

2.2. UFC model

In order to treat the satellite region, Sando and Wormhoudt (1973) proposed a model assuming a quadratic potential difference \( \Delta V \). Later on Szudy and Baylis (1975) generalised it to describe the whole profile of the line. This model, called the unified Franck–Condon model, is derived under the assumption of the Born–Oppenheimer approximation considering the absorption between two isolated adiabatic states. It leads to an absorption coefficient in the wings expressed as (Szudy and Baylis 1975, Visticot et al 1981b):

\[
\alpha_{UFC} = \frac{64\pi^{9/2}n_{p}n_{p}e}{c} \sum \frac{R^{2}D^{2}(R)}{\Delta V'(R)} \exp\left(-\frac{V_i(R)}{kT}\right)|Z|^{1/2}L(Z). \tag{3}
\]

The main difference with the \( qs \) absorption coefficient comes from the universal function \( L \) defined by (Sando and Wormhoudt 1973, Szudy and Baylis 1975):

\[
L(Z) = \int_{0}^{\infty} dx x^{-2}|\text{Ai}(-Zx)|^{2} \exp(-x^{-3}) \tag{4}
\]

where \( Z \) depends on the first and second derivatives of \( \Delta V \):

\[
Z = \frac{1}{2} \left( \frac{\mu}{kT} \right)^{1/3} \left( \frac{\Delta V'(R)}{\hbar} \right)^{2} \left| \frac{\Delta V''(R)}{\hbar} \right|^{-4/3}. \tag{5}
\]

When \( Z \) becomes large \( L(Z) \) approaches the asymptotic form \((36\pi Z)^{1/2}\) and \( qs \) and \( UFC \) absorption coefficients become identical.

In equation (3) the dipole moment is expressed as a function of \( R \). It does not appear in the article of Szudy and Baylis because they have considered a constant dipole moment. Nevertheless, it is possible to introduce \( D(R) \) if its variations are not too fast (Visticot et al 1981b).

Let us also recall that the \( UFC \) model was derived under the assumption of absorption between isolated levels. Consequently it cannot be used to describe the region of an avoided crossing and, to our knowledge, there is no semiclassical treatment which has been used in such a situation.

3. Shape of the potentials and oscillator strengths

Figure 1 shows the calculated adiabatic potential curves and oscillator strengths used in the present calculation (Pascale 1982, 1983). In particular, figure 1(a) shows the pronounced avoided crossing between the \( 7s\Sigma \) and \( 5d\Sigma \) potential curves. Such an avoided crossing explains the large cross section of about 5 Å² measured by Sayer et al for the transfer from the \( 7S \) state to the \( 5D \). Indeed a Landau–Zener calculation at 650 K gives a cross section of 6 Å² in good agreement with the experimental
Far wings of Cs–He

Figure 1. Plot of the potentials and oscillator strengths of the Cs–He pair calculated by Pascale (1982, 1983). (a) Potential of the excited 5dΣ (full curve) and 7sΣ (broken curve) states; the mixed lines are tentative potentials which give a better agreement with the experimental wings. (b) Difference between these potentials and the 6sΣ ground-state potential. The arrows labelled S0 to S3 indicate extrema leading to satellites. (c) Oscillator strength for the 6sΣ–5dΣ (full curve) and 6sΣ–7sΣ (broken curve) transitions. The dotted curves give the oscillator strength of the transition from the ground state to the diabatic 5d (upper curve) or 7s (lower curve) states of figure 1(d). (d) Diabatic potentials (dotted) obtained from the adiabatic curves (mixed).

determination considering the rather large uncertainty of the measurement. A more rigorous quantum-mechanical calculation (Pascale 1985) has led to a cross section of 5.4 Å², confirming the validity of the Landau–Zener calculation for this particular transition. At the avoided crossing there is an exchange between the characteristics of the 7sΣ and 5dΣ states and this clearly appears in figure 1(c) where at R = 6.6 au, the position of the avoided crossing, the oscillator strength f(R) varies by more than one order of magnitude.

In figure 1(b) are plotted the differences between the potentials of the excited states and the ground state. According to the Franck–Condon principle (see equation (1)), this gives the spectral range of the wings. Several extrema are predicted which are called Sₙ(ₙ = 0–3) and satellites are expected for these frequencies.
4. Comparison between calculated and experimental far-wing profiles

In figure 2 is presented the wing calculated with the potentials and induced oscillator strengths of Pascale by using the UFC model (see equation (3)). The calculation has been performed for the whole profile of the wing, even for the parts where, as we said previously, the assumptions are not fulfilled. This will be discussed later on.

The calculated wing of the 6S–5D transition extends from 14 500 to 17 800 cm\(^{-1}\) and is ended by a satellite \(S_0\). The wing of the 6S–7S transition lies between the two satellites \(S_2\) and \(S_3\) (17 800–18 800 cm\(^{-1}\)).

![Figure 2. Experimental absorption profile of the far wings of the 6sΣ-7sΣ and 6sΣ-5dΣ Cs-He transitions obtained by Ferray et al (1980) (full curve) and comparison with the calculation using the UFC model of Szudy and Baylis (1979) and the potentials and oscillator strengths of Pascale (1982, 1983) (broken curve). The vertical arrows show the positions of the dipole-forbidden transitions 6S\(_{1/2}\)-7S\(_{1/2}\) and 6S\(_{1/2}\)-5D\(_{5/2}\). The three arrows \(S_0, S_2, S_3\) indicate the positions of the satellites of the calculated profile. The dotted curve is the result of a UFC calculation with the tentative potential presented in figure 1(a).](image)

In figure 2 the calculated spectrum is also compared with the experimental determination of Ferray et al (1980). For \(\Delta V < 17 000\) cm\(^{-1}\) there is very good agreement for both the shape and the intensity of the wing. In this part of the spectrum the UFC model is identical to the QS model. This agreement simply confirms what has been found when comparing the potentials and oscillator strengths calculated by Pascale with those deduced from the experimental investigation (Pascale 1982, 1983).

The blue satellite \(S_3\), due to a hump on the 7sΣ potential curve, is also observed experimentally but there is a disagreement concerning its location and intensity. Figure 3 magnifies the comparison between calculated and experimental satellite profiles. The calculated maximum lies at about 160 cm\(^{-1}\) from the unperturbed 6S–7S transition instead of 90 cm\(^{-1}\) in the experiment. This would mean that the calculated hump of the 7sΣ curve is too high by almost a factor of two. Moreover, the intensity of the calculated satellite is too large by nearly a factor of three. A possible explanation could be an overestimation of the induced oscillator strength calculated by Pascale,
but, without changing this oscillator strength, a shift of about 2 au of the position of the maximum of $\Delta V$ could give the same variation of the intensity.

Using the same method as in previous work (Visticot et al. 1981a, b) we have tried to reproduce the experimental satellite by changing the potential of the excited $7s\Sigma$ state and the best result is given in figure 3. The corresponding $7s\Sigma$ potential curve is presented in figure 1(a). It has the same asymptotic behaviour as the Pascale's potential curve and the value of the maximum of $\Delta V$ has been adjusted to agree with the experimental result. The intensity is also in better agreement because the maximum of $\Delta V$ occurs at larger interatomic distance (13.5 au instead of 11.5 au for Pascale's potential). The width is close to what is observed experimentally. However there is a large asymmetry which does not appear in the experiment. This asymmetry is inherent to the UFC relation (equation (3)) and remains whatever the $\Delta V(R)$ is. This suggests some limits in the ability of the UFC model to reproduce the experiment.

If we come back to figure 2, the last part remaining to be discussed is the region of the avoided crossing. In this region, where the satellites $S_0$ and $S_2$ appear, the UFC model is expected to fail. Consequently the profile given by the calculation for $S_0$ and $S_2$ could not be compared with the experimental profile determined by Ferray et al. All that can be said is that the overlap between the wings of the $6s\Sigma-7s\Sigma$ and $6s\Sigma-5d\Sigma$ transitions is predicted to be at about 17 850 cm$^{-1}$. Concerning the experimental profile, Sayer et al. (1978) and later Ferray et al. (1980) deduced from their investigation that this overlap should be around 17 500 cm$^{-1}$. Consequently this would mean that the calculated avoided crossing has to be shifted to a lower energy (about 350 cm$^{-1}$).

As a summary we present in figure 1(a) a tentative drawing of how the calculated potential curves should be modified to better reproduce the experiment. In figure 2 is

Figure 3. Blue satellite of the $6s\Sigma-7s\Sigma$ transition. The experimental profile (full curve) is compared with the calculation with the UFC model in absolute (left-hand side) and relative (right-hand side) scale. Two calculations are presented: the first with the potentials of Pascale (broken curve) and the second with the estimate $7s\Sigma$ potential presented in figure 1(a) (dotted curve). The position of the unperturbed $6S-7S$ forbidden transition is also indicated.
also shown the calculated profile of the wings using these curves and the UFC model. The agreement with experiment is obviously improved, but some differences remain. They are mainly localised in the avoided crossing region where the UFC model fails and in the region around $18\,300\,\text{cm}^{-1}$ where the experimental absorption coefficient is much less intense.

5. Temperature dependence of the wings

In figure 4 the temperature dependence of the wings is shown by plotting the quantity $U = -d\ln(\alpha)/d(1/kT)$ against the frequency $\Delta V$. When the quasi-static theory is valid and only one Condon point contributes to the profile, $U$ represents the potential of the ground state (see equation (2)). The dependence calculated with the tentative potentials of figure 1(a) and the UFC model is compared with the experimental determination of Ferray et al (1980).

![Figure 4. Temperature dependence of the far wings. The derivative $U = -d\ln\alpha/d(1/kT)$ is plotted against the frequency. The experimental points (○) are compared with the calculation with the tentative potentials given in figure 1(a) using the UFC model of Szudy and Baylis (1975).](image)

If we consider first the calculated temperature dependence, from $14\,500$ to $17\,400\,\text{cm}^{-1}$, in the wing of the $6s\Sigma-5d\Sigma$ transition, $U$ increases from 0 to about $500\,\text{cm}^{-1}$ which corresponds to a variation of $R$ from infinite to $7.2\,\text{au}$ close to the location of the avoided crossing. Around $17\,500\,\text{cm}^{-1}$, as we have already noticed, the UFC model is not valid and the variation of $U$ is not meaningful and for $\Delta V > 17\,600\,\text{cm}^{-1}$ the profile corresponds to the wing of the $6S-7S$ transition. Between $17\,600$ and $18\,000\,\text{cm}^{-1}$ $U$ still increases. In this region two Condon points contribute to the profile but the inner point has a much higher oscillator strength (see figure 1). For higher frequencies the exponential term due to the repulsive form of the ground state reduces the importance of the inner point and $U$ decreases to be close to zero at the position of the satellite $S_3$ arising at large interatomic distance ($R \sim 13.5\,\text{au}$).

The agreement between experimental and calculated temperature dependence is good. The only discrepancy at the limit of the error bars occurs around $17\,500\,\text{cm}^{-1}$ where the experimental points are lower than the calculated ones but there the
calculation is expected to fail. This seems to confirm that the overlap between the wings of the $6s\Sigma-7s\Sigma$ and $6s\Sigma-5d\Sigma$ transitions effectively occurs in this region.

6. Discussion of the avoided crossing region

The UFC model considers the absorption between isolated adiabatic states and consequently is not suitable to describe the avoided crossing region. On the other hand we have considered the case of diabatic potentials and oscillator strengths. The real profile is probably a compromise between these two extreme cases. In figure 1(d) are given the diabatic curves of the potentials and in figure 1(c) the corresponding oscillator strengths. These curves are deduced from the adiabatic potentials and oscillator strengths by using the method described by Faist and Levine (1976). It appears that the diabatic 5d state has a much higher oscillator strength than the other and the main part of the absorption will be due to this state.

Figure 5 gives the result of a quasi-static calculation using the diabatic states. As expected this profile does not exhibit any peculiar structure in the avoided crossing region (around 17 500 cm$^{-1}$). This approximation would be justified if the probability of diabatic transition is nearly unity, because, in this case, the diabatic 5d state could be considered as isolated. On the other hand, if this diabatic transition probability is very low, the adiabatic approximation should be valid. In an intermediate situation the two contributions have to be taken into account.

Very recently O'Callaghan et al (1985) proposed a semiclassical model to describe the absorption or emission of radiation in an avoided crossing region. It is based on the well known Landau-Zener approximation, assuming a straight line trajectory to describe the relative motion of the system. The profile is obtained by multiplying the

![Figure 5](image_url)

**Figure 5.** Absorption profile in the region of the avoided crossing. The experimental profile (full curve) is compared with a quasi-static calculation using diabatic potentials (broken curve). The results of the model of O'Callaghan et al (1985) are given for three values of the distance between the adiabatic curves (---, 330 cm$^{-1}$; ---, 600 cm$^{-1}$; and ---, 845 cm$^{-1}$).
quasi-static profile of the diabatic states by a function. This function depends on the slopes of the diabatic potentials at the crossing and on the coupling, that is to say, on the closest distance between the two adiabatic curves at the crossing. As was proposed by O’Callaghan et al. (1985) we have tried using the diabatic potentials of figure 1(d) and keeping their slopes constant to vary the coupling between the states. Moreover for each value of the distance we have calculated the Landau-Zener cross section for the transfer between the 7s and 5D states. In figure 5 we present the resulting profiles for three values of this distance: 330, 600 and 845 cm$^{-1}$, corresponding respectively to cross sections of 33, 12.8 and 2.5 A$^2$. As for the experimental spectrum, there is a minimum at the crossing and two maxima on both sides, the amplitude of which depend strongly on the distance. If the model can reproduce the experimental spectrum qualitatively, the quantitative agreement is not very good because the maxima appear a little further than observed. The experimental ratio between maximum and minimum suggests a larger distance between the two adiabatic states than calculated by Pascale (95 cm$^{-1}$). This is not incompatible with the transfer cross section because a distance of about 700 cm$^{-1}$ gives the same value as 95 cm$^{-1}$. Indeed this results from the Landau-Zener relation which predicts a maximum transfer cross section for an intermediate coupling giving a transfer probability of $\frac{1}{2}$. The same cross section can result from a strong or a weak coupling. However, to better reproduce the experimental spectrum, a more accurate calculation of the profile in the avoided crossing region appears desirable. It should provide accurate information about the coupling between the states.

7. Conclusion

By using the UFC model of Szudy and Baylis (1975) we have calculated the wings and the temperature dependence of the 6sΣ–7sΣ and 6sΣ–5dΣ transitions of the Cs–He pair with the recent adiabatic potentials and oscillator strengths of Pascale (1982, 1983). In spite of an important improvement of these potentials and oscillator strengths with respect to previous determinations (Pascale and Vandeplanque 1974, Pascale 1977, Czuchaj and Sienkiewicz 1979, Czuchaj 1979) some disagreements remain. It suggests that the avoided crossing between the 7sΣ and 5dΣ states is predicted at too high an energy by about 350 cm$^{-1}$ and the hump in the 7sΣ state is also too high (~70 cm$^{-1}$).

Concerning the region of the avoided crossing between the 7sΣ and 5dΣ states, no quantitative comparison can be made at the present time. Indeed the adiabatic models generally used to describe the far wings fail. A new model including the non-adiabatic effects is needed and its application to this transition where accurate experimental data are available would certainly provide useful information on the interaction between the states.

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