INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS B: ATOMIC, MOLECULAR AND OPTICAL PHYSICS

J. Phys. B: At. Mol. Opt. Phys. **35** (2002) 2469–2475 PII: S0953-4075(02)31621-3

Semiclassical analytical approach to the description of quasimolecular optical transitions

A Devdariani[1], E Bichoutskaia[3], E Tchesnokov[1], T Bichoutskaia[2], D S F Crothers[3], E Leboucher-Dalimier[4], P Sauvan[4] and P Angelo[4]

[1] Institute of Physics, St Petersburg University, St Petersburg 198904, Russia
[2] Radiophysics Research Institute, St Petersburg University, St Petersburg 198904, Russia
[3] Theoretical and Computational Physics Research Division, The Queen's University of Belfast, Belfast BT7 1NN, UK
[4] Physique Atomique dans les Plasmas Denses, LULI UMR7605, CNRS-Ecole Polytechnique-CEA-Université Paris VI, 75252 Paris Cedex 05, France

Received 5 December 2001
Published 24 May 2002
Online at stacks.iop.org/JPhysB/35/2469

Abstract

A formula was obtained that describes asymptotically forbidden quasimolecular optical transitions in the frame of the semiclassical approach. It is particularly relevant for the weak extrema in the difference between the ground- and excited-state interaction potentials. When averaged over impact parameters and velocity distribution the formula agreed reasonably well with the recent experimental data for the Ca($4^1S \rightarrow 3^1D$) + He transition.

This paper is devoted to the problem of analytical descriptions of quasimolecular optical transitions which are asymptotically forbidden at large interatomic distances R.

It is well known that spectral line shapes (SLS) produced by the allowed atomic transitions show mainly Lorentzian distributions with far wings attributed to collisions with buffer gas atoms (Sobelman 1979). In contrast, little is known about the SLS for transitions caused by a pair of colliding atoms and which are forbidden at large R values (asymptotically forbidden transitions). A typical example for such transitions, which can be referred to as quasimolecular optical transitions, is optical depopulation of metastable atoms, especially those of the second group and of rare gases. The analytical description of asymptotically forbidden transitions presents great difficulties in view of the considerable difference in the behaviour of the potential energy curves and the optical transition moments, which are required to complete the SLS calculation. For instance, the transition moments in this situation cannot be approximated by constant values as in the case of allowed transitions.

However, in many cases the quasimolecular optical transitions result from a change of angular momentum during the collision (Devdariani 1993) due to predominantly short-range repulsion. Here, potential energy curves and optical transition probability (or radiation width $\Gamma(R)$) can be reasonably approximated by exponential functions. It should be noted that

an exponential approximation fits naturally into the description of quasimolecular optical transitions in highly ionized plasmas (Devdariani *et al* 1996). Our study has revealed that a general formula which covers the central part of the spectral line, the extremum vicinity and the far wings, and also takes into account the fast exponential change in the state radiative width, can be obtained with the use of the Morse potential for the potential energy difference. The Morse approximation has been also used (Sato 1995) for spectral simulations.

The required formula for the transition amplitude (in atomic units) with a frequency shift $\Delta\omega = \omega - \omega_0$, where ω_0 is the position of the excited level in the limit of separated atoms, has been obtained in the framework of first-order perturbation theory:

$$b(\Delta\omega) = -\mathrm{i}\int_{t_0}^{\infty} \sqrt{\frac{\Gamma(t)}{2\pi}} \exp\left[-\mathrm{i}\int_{t_0}^{t} (\Delta U - \Delta\omega)\,\mathrm{d}t'\right]\mathrm{d}t, \tag{1}$$

where $t_0 \to -\infty$, $\Delta U(R) = U^*(R) - U_0(R)$ and where $U^*(R)$ and $U_0(R)$ are potential energy curves for the excited and ground states with an accidental degeneracy as $R \to \infty$, and $R(t)$ is a classical trajectory. The approach can be considered as a Fourier-transform of a transition dipole moment calculated with time-dependent quasimolecular wavefunctions. According to the discussion above we use a Morse potential for the potential energy difference:

$$\Delta U(R) = d(2\mathrm{e}^{-\alpha_R(R-R_{\mathrm{ex}})} - \mathrm{e}^{-2\alpha_R(R-R_{\mathrm{ex}})}), \tag{2}$$

where d, R_{ex} are the potential barrier height and the position of its extremum, respectively, and where an exponential approximation to the radiation width is given by

$$\Gamma(R) = \gamma_R \mathrm{e}^{-2\beta_R(R-R_{\mathrm{ex}})}, \tag{3}$$

where α_R, β_R and γ_R are constant values. In addition, the approximation (2) allows us to treat the problem of SLS features produced by weak extrema, which cannot be solved within the limits of the parabolic approximation for ΔU (Szudy and Baylis 1997). For the straight-line trajectories at zero impact parameter for which $R = vt$, the transition amplitude is given by:

$$b(\Delta\omega) = -\frac{\mathrm{i}}{\alpha}\sqrt{\frac{\gamma}{2\pi}}\, x^{\mathrm{i}\Omega}\Gamma(-\mathrm{i}\Omega) D_{\mathrm{i}\Omega}(2x\mathrm{e}^{-\frac{3\mathrm{i}\pi}{4}}) \exp\left(\mathrm{i}\varphi + \mathrm{i}x^2 - \frac{\pi\Omega}{4}\right), \tag{4}$$

where

$$\alpha = \alpha_R v, \qquad \beta = \beta_R v, \qquad \gamma = \gamma_R \mathrm{e}^{2\beta_R R_{\mathrm{ex}}}, \qquad x = \sqrt{\frac{\mathrm{d}}{\alpha}},$$
$$\Omega = \frac{\Delta\omega + \mathrm{i}\beta}{\alpha}, \qquad \varphi = \int_{t_0}^{\infty} \Delta U\,\mathrm{d}t + \Delta\omega\frac{R_{\mathrm{ex}}}{v}$$

is a real phase, Γ is a gamma function and $D_p(z)$ is a parabolic cylinder function which may be expressed in terms of regular Kummer hypergeometric functions (Abramowitz and Stegun 1970):

$$D_{\mathrm{i}\Omega}(2x\mathrm{e}^{-\frac{3\mathrm{i}\pi}{4}}) = 2^{\frac{\mathrm{i}\Omega}{2}}\mathrm{e}^{-\mathrm{i}x^2}\sqrt{\pi}\left(\frac{M(-\frac{\mathrm{i}\Omega}{2}, \frac{1}{2}, 2\mathrm{i}x^2)}{\Gamma(\frac{1-\mathrm{i}\Omega}{2})} - 2^{\frac{3}{2}}x\mathrm{e}^{-\frac{3\mathrm{i}\pi}{4}}\frac{M(\frac{1-\mathrm{i}\Omega}{2}, \frac{3}{2}, 2\mathrm{i}x^2)}{\Gamma(-\frac{\mathrm{i}\Omega}{2})}\right), \tag{5}$$

where we define:

$$M(a, b, y) = 1 + \frac{a}{b}y + \frac{a(a+1)}{b(b+1)}\frac{y^2}{2!} + \cdots. \tag{6}$$

First we note that for small values of x, the transition amplitude (4) may be simplified to:

$$b(\Delta\omega) = -\frac{\mathrm{i}}{2\alpha}\sqrt{\frac{\gamma}{2\pi}}\left(\frac{x^2}{2}\right)^{\frac{\mathrm{i}\Omega}{2}}\Gamma\left(-\frac{\mathrm{i}\Omega}{2}\right)\exp\left(\mathrm{i}\varphi - \frac{\pi\Omega}{4}\right). \tag{7}$$

In the limit of small values of x such that $\alpha x^2 e^{\alpha_R R_{ex}} \to 0$ and the quantity $\alpha x^2 e^{2\alpha_R R_{ex}}$ is finite, expression (7) describes the transition amplitude for the spectra produced by an exponential potential energy term with $C = de^{2\alpha_R R_{ex}}$ in place of x^2 (Devdariani *et al* 1977). According to (7) the SLS is non-symmetrical. The blue wing of the profile is produced by optical transitions in the classically forbidden region and its intensity decreases as $\exp(-\pi\Delta\omega/\alpha)$, whereas the red wing results from transitions in the classically allowed region with the intensity declining as $-1/\Delta\omega$. The central part of (7), where $|\Delta\omega/\alpha| < 1$, is determined by

$$\left|\Gamma\left(-\frac{i\Omega}{2}\right)\right|^2 = \left|\Gamma\left(\frac{\beta}{2\alpha} - i\frac{\Delta\omega}{2\alpha}\right)\right|^2.$$

Both parameters α and β are atomic values which do not include the interaction with light and they are mainly governed by the exchange interaction, that is $\beta/\alpha \sim 1$; consequently

$$|b(\Delta\omega)|^2 \sim \left|\Gamma\left(\frac{\beta}{2\alpha} - i\frac{\Delta\omega}{2\alpha}\right)\right|^2 \approx \frac{\pi}{1 + \frac{1}{8}(\frac{\Delta\omega}{\alpha})^2}. \tag{8}$$

Strictly speaking the last expression holds for $\alpha = \beta$ only, but, in any case, typically we have $|b(\Delta\omega)|^2 \sim |\Gamma(\alpha/2\beta)|^2 \sim 1$ at the maximum of the spectral distribution. Therefore, we conclude that the SLS of asymptotically forbidden quasimolecular transitions is rather flat and its central part is close to the Lorentzian distribution with velocity-dependent FWHM $\Delta\omega_{1/2} = (\sqrt{8}/\pi)\alpha_R v$.

The SLS produced by asymptotically allowed quasimolecular transitions can be described by equation (1) with the radiation width $\Gamma(t)$ approximated by its atomic value Γ_0. The value Γ_0 is to be included in the exponent of equation (1) in order to account for radiation depopulation during the collision. This leads at once to the sharp Lorentzian distribution with a velocity-independent half-width (Devdariani *et al* 1996), because in this case $\Gamma_0/2\alpha \ll 1$ and

$$|b(\Delta\omega)|^2 \sim \left|\Gamma\left(\frac{\Gamma_0}{2\alpha} - i\frac{\Delta\omega}{2\alpha}\right)\right|^2 \approx \frac{1}{(\frac{\Gamma_0}{2\alpha})^2 + (\frac{\Delta\omega}{2\alpha})^2}. \tag{9}$$

In general, simulations reveal that for $x \leqslant 2.5$ only a few terms in equation (5) are necessary to get a perfect description for the SLS including the region of oscillations due to the occurrence of two saddle points in the integral (1) under the approximation (2) or, in other words, of two Condon points (Szudy and Baylis 1997). Figure 1 shows the results for spectrum simulations calculated on the basis of equations (4)–(6) for $\beta/\alpha = 0.54$ and various small values of x, along with the limiting case of equation (7).

In order to apply the results obtained with the use of equation (4) to the experimental data in gas cell conditions with the temperature T, one needs to average a spectrum $|b(\Delta\omega)|^2$ over the impact parameters ρ and kinetic energies E of colliding atoms, assuming a Maxwellian distribution over the energies. The approach of averaging the spectral profiles of type (1) has already been discussed (Bichoutskaia *et al* 2001). It has been shown that the intensity of radiation I and the absorption coefficient K are proportional to the average profile

$$\langle|b(\Delta\omega, T)|^2\rangle = \frac{1}{2}\int_0^\infty e^{-t}\left|b\left(\Delta\omega, v = \sqrt{\frac{2kTt}{\mu}}\right)\right|^2 dt, \tag{10}$$

where T is the temperature and μ is the reduced mass of the colliding atoms. For the absorption coefficient we have:

$$K = \frac{g(\Omega^*)}{g(\Omega)} p(\Omega) A(R_0, T) \cdot S(\omega, T), \tag{11}$$

where the factor

$$S(\omega, T) = \frac{\lambda^2}{4}\exp\left(\frac{\Delta\omega}{kT}\right)\langle|b(\omega)|^2\rangle \tag{12}$$

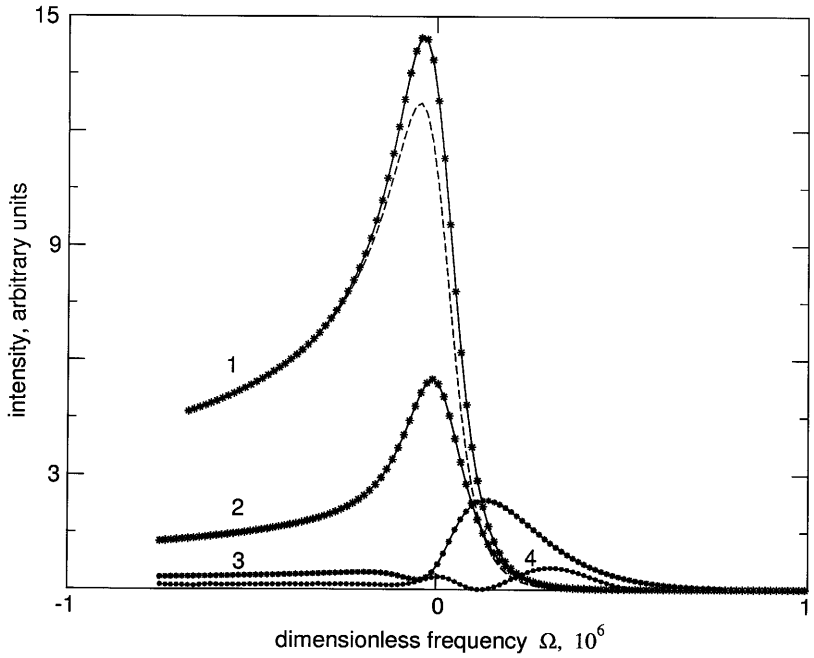

Figure 1. Spectrum profiles for $|b(\Delta\omega)|^2$ for asymptotically forbidden quasimolecular transitions with the use of the Morse potential (2) as a difference potential function for different values of parameter x: 1: 0.12, 2: 0.4, 3: 1.2, 4: 2.5. Stars, $*$, represent numerical calculations in the Fourier-approach; lines are analytical results, solid using formulae (4)–(6) and broken using formula (7).

determines the shape of the spectral line; $p(\Omega) = g(\Omega)/g(J)$ is the probability of the formation of quasimolecules with projection Ω in the ground state; $g(\Omega^*)$ (or $g(\Omega)$) is a statistical coefficient of the quasimolecular state with projection Ω^* (or Ω). The factor

$$A(R_0, T) = \pi v R_0^2 \exp\left(-\frac{U^*(R_0)}{kT}\right) \tag{13}$$

defines the spectrum intensity. The absorption coefficient (11) has been derived from the assumption that the radial velocity of the relative movement of the atoms is a constant in the vicinity of a point R_0 which is the most significant region of the spectrum. In our case the centre of the non-adiabatic region is naturally taken as the point R_0, where quasimolecular states produced by the $4s4p\,^1P$ and $4s3d\,^1D$ atomic states are fully mixed by the Ca–He interaction. Note that $R_0 = 7$ in the case of the $m = 0$ projection and $R = 3.6$ for $m = 1$, see also Bichoutskaia *et al* (2001) for an extended discussion.

As a specific example we have chosen the reaction

$$\mathrm{Ca}(4s3d,\,^1D) + \mathrm{He}(1^1S_0) \leftrightarrow \mathrm{Ca}(4s^2,\,^1S_0) + \mathrm{He}(1^1S_0) + \hbar\omega_0, \tag{14}$$

where $\omega_0 = 21\,850\ \mathrm{cm}^{-1}$. The reason is that this reaction has been investigated both experimentally and theoretically (Bichoutskaia *et al* 2001) for absorption in a semiclassical approach based on a numerical calculation of the transition amplitude (1). A previous study of the potential energy curves and radiation widths involved (Bichoutskaia *et al* 2000) led to the following parameters: $\alpha_R = 0.59$, $\beta_R = 0.32$, $\gamma_R = 2.77 \times 10^{-10}$, $d = 10^{-3}$, $R_{\mathrm{ex}} = 8.2$ and $R_0 = 7.0$. For the temperature $T = 1000$ K used in the experiments $\bar{x} = \sqrt{d/\bar{\alpha}} = 1.2$ ($\bar{\alpha} = \alpha_R\sqrt{8kT/\pi\mu}$).

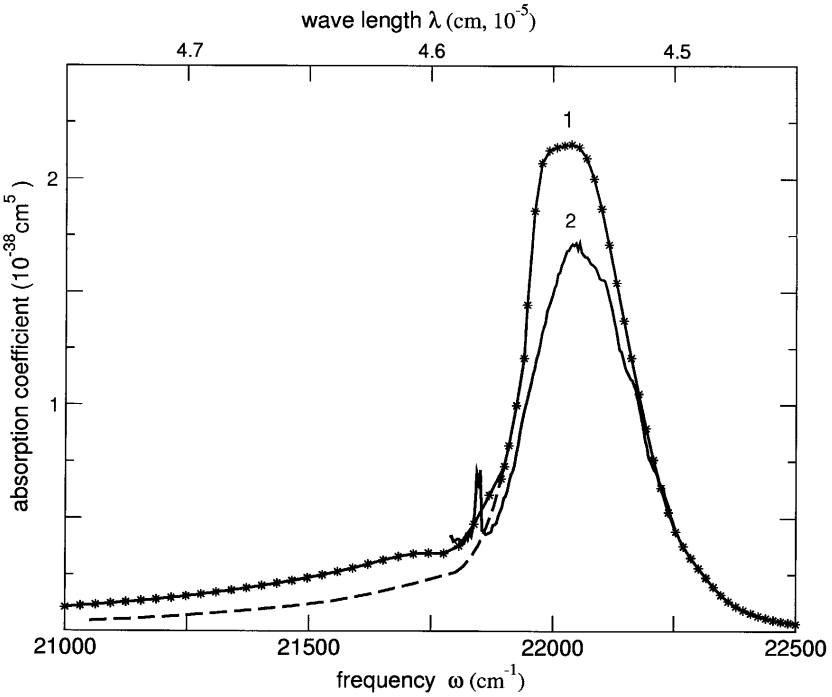

Figure 2. Absorption spectrum for the asymptotically forbidden Ca($4s^2$, $^1S_0 \rightarrow$ 4s3d, $^1D_2$)–He quasimolecular transition. Curve 1 shows calculations using the analytical formula (4), averaged over the impact parameters and the energies of colliding particles (10)–(13) (the broken line is the same, but with substitution of $R_0 \rightarrow R_C$); stars represent numerical calculations in the Fourier-approach and curve 2 is the experimental data of Bichoutskaia *et al* (2001).

Figure 2 shows analytical estimates (4)–(6), (10)–(13) for the absorption spectrum of the forbidden optical transition Ca($4s^2$, $^1S_0 \rightarrow$ 4s3d, $^1D_2$)–He (solid curve 1) and the experimental spectral line of Bichoutskaia *et al* (2001) (solid curve 2). As one can see, the results are in good agreement not only regarding shape, but also regarding absolute value. On the scale of figure 2 the analytical results for the spectrum coincide with the accurate calculation in the semiclassical Fourier-approach using the numerical procedure of Bichoutskaia *et al* (2001), indicated by stars. We note that the rough estimates of the FWHM mentioned above give $\Delta\omega_{1/2} = 129\ \mathrm{cm}^{-1}$ in contrast to the experimental value 250 cm^{-1}. In order to indicate the influence of the parameter R_0 on the spectrum profile in the region of a real Condon point R_C (the red wing of the spectrum) we have performed the calculations replacing the fixed parameter R_0 by a different value of R_C for each frequency. The broken line in figure 2 represents the results of the refined calculation, which do not affect the profile shape near the maximum.

Figure 3 demonstrates the influence of spectrum averaging, i.e. substitution of $\langle|b(\Delta\omega, T)|^2\rangle$ by $|b(\Delta\omega, v = \sqrt{8kT/\pi\mu})|^2$ in the expression for radiation intensity

$$I(\Delta\omega, T) = 2p(\Omega^*)A(R_0, T)\langle|b(\Delta\omega, T)|^2\rangle, \tag{15}$$

for different values of d; all other parameters are identical to those for the Ca–He case. The results of spectrum averaging are depicted in figure 3 by solid lines for three selected heights of potential barrier $d = 1\times10^{-4}$, 1×10^{-3} and 6×10^{-3} (for comparison the dotted curve shows the non-averaged spectrum calculated with formula (4)). One can see that the spectrum averaging leads to the smoothing of oscillations, but it preserves the main characteristic peculiarities of

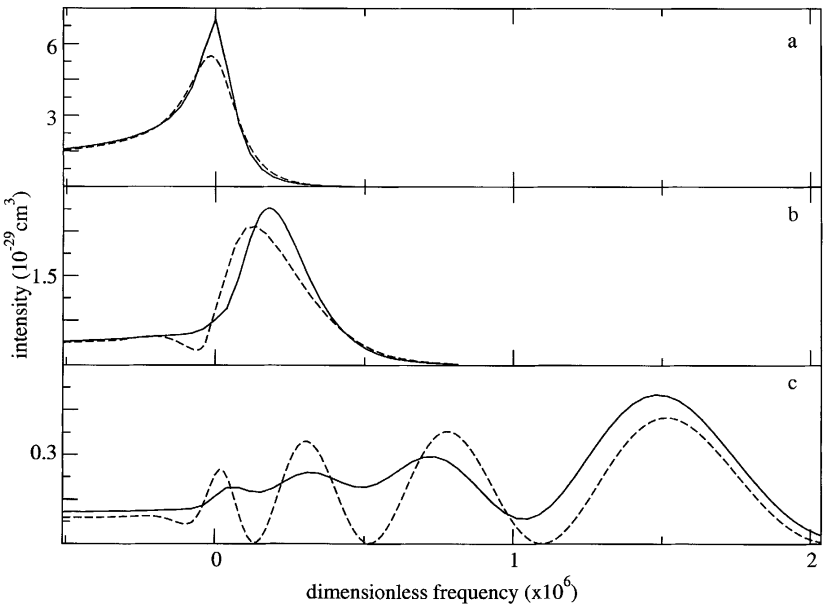

Figure 3. The effect of spectrum averaging on the emission spectral line for asymptotically forbidden quasimolecular transitions with the use of the Morse potential (2) as a difference potential function for different values of d: a: 1×10^{-4}, b: 1×10^{-3}, c: 6×10^{-3} and $T = 1000$ K. Dashed curves are calculations based on a formula using the general formulae (4)–(6) for a and b and on a formulae (4), (16) for c, solid curves represent averaged contours of the spectral line (10), (15).

the spectrum. It should be stressed that equations (5) and (6) do not apply in the case of higher potential barriers ($\bar{x} > 2.5$) and consequently a great number of oscillations. We found that an asymptotic expression given by Gunninen and Makarov (1962), namely

$$D_{i\Omega}(z) = \exp\left(-\frac{z^2}{4} - \frac{\Omega^2}{2z^2}\right) z^{i\Omega} - \frac{\sqrt{2\pi}}{\Gamma(-i\Omega)} \exp\left(\frac{z^2}{4} + \pi\Omega + \frac{(1+i\Omega)^2}{2z^2}\right) z^{-i\Omega-1}, \tag{16}$$

where $z = 2xe^{-\frac{3i\pi}{4}}$, was appropriate to calculate the profiles in this case. In the case of $\bar{x} > 2.5$ the width of the distribution is determined by d rather than by α and the spectrum intensity decreases respectively.

In conclusion we have obtained the semiclassical formula (4) that describes the SLS of asymptotically forbidden quasimolecular transitions. The formula has been derived with the use of the Morse potential for the potential energy difference and is particularly useful for describing weak extrema in potential energy curve differences, which are typical for atoms in metastable states. The far wings of the spectrum are also sensitive to the behaviour of the potential energy curves; however in the case of forbidden transitions the influence of the long-range interaction is negligible due to the small value of the radiation width. It is found that the intensity distribution is rather flat and close to the Lorentzian shape in the central part of the spectral line. The FWHM varies in proportion to the collision velocity and is inversely related to the radius of the exchange interaction of the atoms. Being averaged over impact parameters and velocity distributions the formula agrees reasonably well with the recent experimental data for the Ca(4^1S $\rightarrow$ 3^1D) + He transition.

Acknowledgments

The research has been supported by RFBR (Grant N99-03-33168a) and INTAS (Grant N99-00039). Support by the Royal Society, NATO and the Foreign and Commonwealth Office Chevening Fellowship is gratefully acknowledged by EB.

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