EU approach to the description of collisionally induced optical transitions of diatoms

R. M. Beuc*, M. Movre

Institute of Physics, Bijenicka c. 46, HR-10000 Zagreb, Croatia

Abstract. We have applied the extended uniform (EU) formula to the model recently proposed by Devdariani *et al.* Our results demonstrate that the unified Franck-Condon theory is capable to describe asymptotically forbidden but collisionally induced transitions.

1 Introduction

In a recent paper by Devdariani et al. [1], a formula was obtained that describes asymptotically forbidden quasimolecular optical transitions in the frame of the semiclassical approach. The main difficulty in the analytical description of asymptotically forbidden transitions is the consequence of the simple fact that the transition moments in this situation cannot be approximated by constant values as in the case of allowed transitions. However, potential energy curves and optical transition probability (or radiation width) usually can be reasonably approximated by exponential functions and 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 [1].

Our approach is based on a refinement of the uniform Airy approximation as presented by Beuc and Horvatic [2] (extended uniform (EU) formula [3]). The main point is careful treatment of the phases corresponding to the relevant Condon points and the resulting interference effects which in the same time take care of the variable transition moment in the vicinity of an extremum in the curve describing the difference between the electronic energies of the initial and the final states of the optical transition.

Bieniek et al. [4] have analyzed analogous processes of ionizing collisions in complex potentials within uniform JWKB stationary-phase techniques. Their numerical results are in excellent agreement with fully quantal, complex-potential computations.

*Corresponding author. E-mail address : beuc@ifs.hr (R. M. Beuc)

2 Model, methods and results

Model difference potential is of the form $\Delta U(R) = d[2exp(\alpha(R\text{-}Ro))\text{-}exp(2\alpha(R\text{-}Ro))]$ and radiation width is $\Gamma(R)=\gamma\, exp[-\beta(R\text{-}Ro)]$. For the straight-line trajectories at zero impact parameter $R(t)=Ro+vt$, the exact solution for absorption probability is expressed through parabolic cylinder function [1]. Using either the method of stationary phase or saddle point method, the relevant integral can be approximated as the sum over the stationary/saddle-point contributions. Extended uniform formula [2] corrects these contributions for infinities, and correction function is expressible through Airy functions and their first derivatives, the argument being defined either through local or uniform mapping, respectively [3].

Some of our results are shown in Fig. 1. Dimensionless parameters are defined as $V=d/\alpha v$ and $\Omega= \Delta\omega/d$, where $\Delta\omega$ is detuning from the line center.

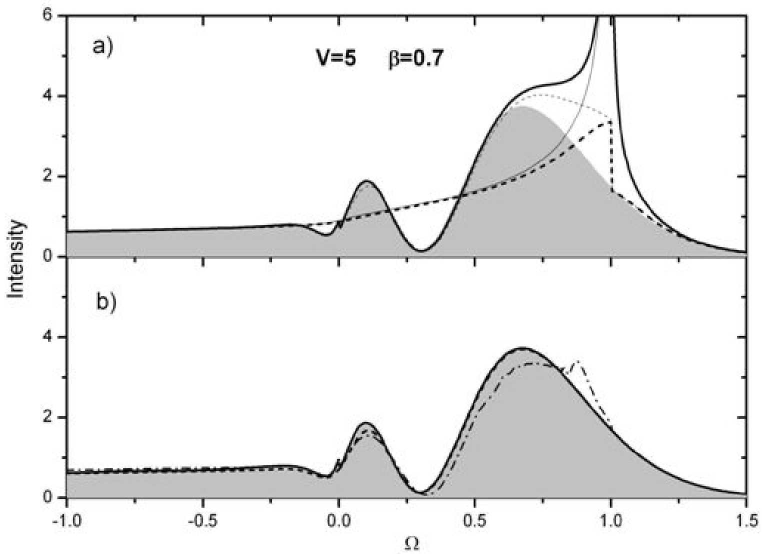

Figure 1 : a) *Comparison of quasistatic approximation (full lines - stationary points; broken lines - saddle points) with exact spectrum (shaded). Thick curves – coherent approximation; thin curves - incoherent approximation.* ***b)*** *Comparison of Airy approximation (dash-dot line: stationary points - local mapping; full line: stationary points - uniform mapping; broken line: saddle points), with exact spectrum (shaded)*

3 Conclusions

The main characteristics of spectrum are described with coherent stationary point approximation, which besides the usual incoherent contributions (simple quasistatic spectrum) contains in addition all interference terms. Airy correction function which removes singularity is important only in the neighborhood of the extremum. Even in the case of variable transition dipole moment, stationary point method gives correct results.

For model parameters d = 200 cm^{-1} (barrier height) and α^{-1} = 5 bohr (barrier half width), the dimensionless parameter $V=d/\alpha v$ changes from 1 (for H_2 at 3000 K) to 11, 36, and 64 000 for Cs_2 at 3000, 300, and 10^{-4} K (cold collisions), respectively.

Our approach is thus applicable for the range of typical situations. Even the simplified formula using the modified correction functions (where only the asymptotic form is used for Ai´ functions) which are numerically stable and easier to implement, gives reliable results. Therefore, our results demonstrate that the unified Franck-Condon theory is capable to describe asymptotically forbidden but collisionally induced transitions.

References

[1] A. Devdariani, E. Bichoutskaia, E. Tchesnokov, T. Bichoutskaia, D. S. F. Crothers, E. Leboucher-Dalimier, P. Sauvan and P. Angelo, J. Phys. B.: At. Mol Opt. Phys. 35 (2002) 2469-2475

[2] R. Beuc and V. Horvatic, J. Phys. B: At. Mol. Opt. Phys. 25 (1992) 1497-1510

[3] J. Szudy and W. Baylis, Phys. Rep. 266, 127-227 (1996)

[4] R. J. Bieniek, M. W. Müller and M. Movre, J. Phys. B: At. Mol. Opt. Phys. 23 (1990) 4521-4538