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II. Non adiabatic theory of collisions in a radiative field. Semi-classical limit : Ar + O case

A. Spielfiedel, E. Roueff and N. Feautrier

Département Atomes et Molécules en Astrophysique, Observatoire de Paris, Section de Meudon, 5 place Jules Janssen, 92195 Meudon Principal Cedex, France

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Abstract. — The semi-classical limit of the non adiabatic theory of collisions in a radiative field detailed in paper 1 is applied to the numerical calculation of the collision induced emission cross section of the O(2 1S) + Ar → O(1 1D) + Ar + hν transition of oxygen perturbed by argon. This problem was previously studied in the close coupling quantal approach by Julienne (1982) [2] whose available quantal results are taken as reference. The numerical results are discussed in terms of trajectories and coupling localizations and the spectroscopic branches effect first pointed out by Julienne is qualitatively reproduced.

Classification
Physics Abstracts
34.50

1. Introduction.
Atomic scattering in the presence of a radiation field has been developed recently both experimentally and theoretically. In the preceding paper [1], we have discussed both the quantal and the semi-classical limits of light induced atomic scattering and the various approximations which can be used in the case of asymptotically forbidden transitions. This paper presents a close coupling semi-classical calculation of the profile of the collision induced emission of metastable O(2 1S) state of oxygen perturbed by argon. This problem was previously thoroughly studied in the close coupling quantal approach by Julienne (1982) [2] whose results are taken as a reference. So we use the same interaction potentials and coupling elements as Julienne [2] and we derive the semi-classical limit of the quantal
equations for both the dynamical and radiative couplings. Numerical results are subsequently discussed in terms of trajectories and coupling localizations.

2. Quantal close coupling theory.

We briefly outline the quantal scattering formalism for radiatively assisted collisions where the total molecule + radiation field wave function at total energy $E$ is expanded as a product basis set of the type

$$\Psi = |JMp\rangle \otimes |n_{\lambda}\rangle$$

(1)

where $|JMp\rangle$ is an eigenstate of the molecular Hamiltonian $H_M$ including electronic and nuclear motions and $|n_{\lambda}\rangle$ an eigenstate of the radiation field Hamiltonian $H_R$ ($n_{\lambda}$ is the number of radiative oscillators at wavelength $\lambda$).

The total Hamiltonian of the matter-radiation system

$$H' = H_M + H_R + H_{MR}$$

involves also the coupling between the radiation and the molecule $H_{MR}$.

The quantum numbers $J$, $M$ and $p$ respectively represent the total molecular angular momentum (including electronic and rotational motions), its space-fixed projection along an arbitrary axis and parity $\pm 1$ with respect to inversion of all coordinates. Julienne [2] has shown that the extension of the usual scattering theory to radiatively assisted collisions leads to the following coupled equations for the radial functions after the usual partial wave expansion of the molecular wave function:

$$\left[ \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + E - v_M^{\|} - n\hbar \nu \right] \cdot F_{ii}(R) = \sum_i H_{MR}^{ii} \cdot F_{if}(R)$$

$$\left[ \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + E - v_M^{\|} - (n \pm 1) \hbar \nu \right] \cdot F_{if}(R) = \sum_i v_M^{if} \cdot F_{if}(R) + H_{MR}^{if} \cdot F_{if}(R).$$

(2)

The labels $i$ and $f$ respectively stand for the initial and final molecular states connected by the radiative transition. We consider here the case where the coupling elements vanish asymptotically (the atomic transition is forbidden) so that the usual scattering formalism can be applied.

The above equations are relevant to the $2^1S \rightarrow 1^1D$ transition of oxygen perturbed by argon where the initial state ($v_M^{\|}$) is non degenerate and where, in the final state, non adiabatic coupling ($v_M^{\perp}$) occurs leading to off diagonal elements in the molecular Hamiltonian $H_M$.

The $S$ matrix is determined from the asymptotic forms of the amplitudes $F$.

The asymptotic wave functions are well described in a Hund's case (e) basis where the atomic quantum numbers and the relative orbital angular momentum $\ell$ commute with the molecular Hamiltonian. However, the coupling elements are more readily expressed in a Hund's case (a) molecular basis $|JM\rangle$ for non Born-Oppenheimer terms as well as for the radiative coupling. Subsequently transforming these expressions in the asymptotic Hund's case (e) basis leads to three different coupled equations systems for each ($P$, $Q$, $R$) branch where radiative as well as non adiabatic rotational couplings are readily calculated.

Table I recalls the corresponding matrices for the $O(1S) \rightarrow O(1D)$ transition induced by collisions with argon atoms in the Hund's case (a) coupling scheme.
Table Ia. — *Quantal electronic rotational coupling matrix elements evaluated in Hund's case (a).* $X = J(J + 1)$ where $J$ is the angular momentum. $i, f$ respectively indicate the initial, the final state. $B = \frac{\hbar^2}{2 \mu R^2}$ where $\mu$ is the Ar + O reduced mass, $R$ the internuclear distance.

<table>
<thead>
<tr>
<th>State</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma^+$</td>
<td>$(U_0 \Sigma + BX_i)$</td>
</tr>
<tr>
<td>$^1\Pi$</td>
<td>$\begin{pmatrix} U_\Pi + B(X_f + 4) &amp; 2B \sqrt{X_f - 2} \ -2B \sqrt{X_f - 2} &amp; U_\Delta + B(X_f - 2) \end{pmatrix}$</td>
</tr>
</tbody>
</table>

Table Ib. — *Quantal reduced radiative coupling matrix elements evaluated in Hund's case (a).* $J_i = J$ is the initial state angular momentum. $\mathcal{C}_0, \mathcal{C}_1$ are respectively the $\Sigma-\Sigma, \Sigma-\Pi$ electronic transition dipole moments [2].

<table>
<thead>
<tr>
<th>Transition</th>
<th>$V_{if} = (J_i \parallel d \parallel J_f)$</th>
<th>Branch</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma-^1\Sigma$</td>
<td>0</td>
<td>$Q(J_f = J)$</td>
</tr>
<tr>
<td>$^1\Sigma-^1\Pi$</td>
<td>$+ \mathcal{C}_1$</td>
<td>$Q(J_f = J)$</td>
</tr>
<tr>
<td>$^1\Sigma-^1\Delta$</td>
<td>0</td>
<td>$Q(J_f = J)$</td>
</tr>
</tbody>
</table>

| | $\begin{pmatrix} U_\Sigma + B(X_f + 6) & -B \sqrt{12X_f} & 0 \\ -B \sqrt{12X_f} & U_\Pi + B(X_f + 4) & 2B \sqrt{X_f - 2} \\ 0 & -2B \sqrt{X_f - 2} & U_\Delta + B(X_f - 2) \end{pmatrix}$ | |

<table>
<thead>
<tr>
<th>$^1\Sigma$</th>
<th>$^1\Pi$</th>
<th>$^1\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma$</td>
<td>$^1\Pi$</td>
<td>$^1\Delta$</td>
</tr>
</tbody>
</table>

$J_f = J + 1$ \hspace{1cm} $J_f = J - 1$
3. Semi-classical theory.

In paper I [1], we have established the general formulation of the semi-classical theory obtained as the large total angular momentum \( J \) limit of the quantal equations for non adiabatic collisions in the presence of a radiative field.

We have in particular derived a semi-classical analogue to the different (quantal) spectroscopic branches of a radiative transition in terms of different components of the rotation matrices involved in the generalized \( S \) matrix expression.

The induced emission coefficient in the presence of an electromagnetic radiation of field intensity \( \Phi (\text{photons. cm}^{-2}. \text{s}^{-1}) \) and pulsation \( \omega \) is expressed in terms of the generalized cross section \( \sigma (\omega) \) [2]:

\[
k_{\text{em}}(\omega) = \frac{8 \pi}{\lambda^2} \frac{\langle \sigma (\omega) \cdot v \rangle_{av}}{\Phi}
\]

where \( \langle \cdot \rangle_{av} \) indicates an average over the relative velocities.

The semi-classical radiative cross section is then given by the following expression [1]:

\[
\sigma (j_i \leftarrow j_i \varepsilon_i q) = \frac{2}{2j_i + 1} \cdot \frac{1}{3} \int_{-\infty}^{\infty} b \ db \cdot \sum_{pM_{ji}} \left| \langle j_i M_{ji} | S^p_{\omega} | j_i M_{ji} - p \rangle \right|^2
\]

where \( p = 0, 1, -1 \) corresponds to branch \( Q, P, R \) respectively.

\( b \) is the usual impact parameter, \( j_i \) and \( j_f \) are the total initial and final atomic quantum numbers of the emitting oxygen atom, \( M_{ji} \) is the final angular momentum projection in the rotating molecular basis for asymptotically vanishing radiative coupling (forbidden atomic transition \( \text{O}(2 \cdot 1S) \rightarrow \text{O}(1 \cdot 1D) \)).

The \( S^p_{\omega} \) matrix is then obtained from the integration of the usual first order derivative coupled equations where non adiabatic coupling as well as radiative coupling is obtained from standard procedures detailed in paper I.

The time dependent total wave function is expanded over the various atomic (molecular) substates and the various \( S \) matrix elements are extracted from the asymptotic limit of the different final states according to the specific initial condition that the oxygen atom is in the \( 1S \) state.

Table II gives the corresponding coupling matrix in the Hund’s case (a) molecular basis for the three different \( P, Q, R \) branches collision induced transitions for each parity.


A well known difficulty encountered in the integration of the first order semi-classical coupled equations is the choice of the trajectory since the different potentials imply different trajectories. This has led many authors (Masnou-Seeuws 1970 [3], Roueff 1977 [4], Spielfiedel et al. 1979 [5]) to choose a rectilinear trajectory which is a good approximation at relatively large incident energies.

In paper I, we have introduced a local wave number \( K_i \) involving an average potential \( U_0(R) \):

\[
K_i^2 = k_i^2 \left[ 1 - \frac{J_0(J_0 + 1)}{k_i^2 R^2} - \frac{2 \mu}{\hbar^2 k_i^2} \cdot U_0(R) \right].
\]
Table IIa. — *Semi-classical electronic rotational coupling matrix elements evaluated in Hund's case (a).* \( \dot{\theta} \) is the time derivative of the internuclear axis rotation angle \( \theta \).

<table>
<thead>
<tr>
<th>State</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^1D + ^1S )</td>
<td>(- (- \gamma)) parity</td>
</tr>
<tr>
<td>( ^1\Pi )</td>
<td>( \begin{pmatrix} U_{\Pi} + \frac{E_b^2}{R^2} &amp; - \dot{\theta} \ - \dot{\theta} &amp; U_{\Delta} + \frac{E_b^2}{R^2} \end{pmatrix} )</td>
</tr>
<tr>
<td>( ^1\Delta )</td>
<td></td>
</tr>
</tbody>
</table>

Table IIb. — *Semi-classical reduced radiative coupling matrix elements evaluated in Hund's cases.* \( \Omega, \Theta \) are phase factors defined in [1].

Table of transitions:

<table>
<thead>
<tr>
<th>Transition</th>
<th>( T_{if} )</th>
<th>Branch</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^1\Sigma^1\Sigma )</td>
<td>0</td>
<td>( Q )</td>
</tr>
<tr>
<td>( ^1\Sigma^1\Pi )</td>
<td>( + \Theta_1 )</td>
<td></td>
</tr>
<tr>
<td>( ^1\Sigma^1\Delta )</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( ^1\Pi^1\Sigma )</td>
<td>( - \frac{\Theta_0}{\sqrt{2}} e^{+i\left(\theta + \frac{\pi}{2}\right)} )</td>
<td>( P )</td>
</tr>
<tr>
<td>( ^1\Pi^1\Pi )</td>
<td>( + \Theta_1 \cdot e^{+i\left(\theta + \frac{\pi}{2}\right)} )</td>
<td></td>
</tr>
<tr>
<td>( ^1\Pi^1\Delta )</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( ^1\Delta^1\Sigma )</td>
<td>( + \frac{\Theta_0}{\sqrt{2}} e^{-i\left(\theta + \frac{\pi}{2}\right)} )</td>
<td>( R )</td>
</tr>
<tr>
<td>( ^1\Delta^1\Pi )</td>
<td>( + \frac{\Theta_1}{\sqrt{2}} e^{-i\left(\theta + \frac{\pi}{2}\right)} )</td>
<td></td>
</tr>
<tr>
<td>( ^1\Delta^1\Delta )</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
Consequently each channel $i$ involves a different trajectory and a different turning point $R_i$. Aubert and Le Sech (1976) [6] have introduced the « common turning point » method which has the further advantage to give the correct asymptotic form in each channel: $e^{i k_i R}$. We briefly recall the derivation of the corresponding equations.

The quantal coupled equations:

$$\left[ \frac{d^2}{dR^2} + k_i^2 \frac{J_i(J_i + 1)}{R^2} - \frac{2 \mu}{\hbar^2} \cdot U_i(R) \right] \cdot F_i(R) = \frac{2 \mu}{\hbar^2} \sum_{j \neq i} V_{ij} \cdot F_j(R)$$

are rewritten in the following form:

$$\left[ \frac{d^2}{dR^2} + K_i^2 \right] \cdot F_i(R) = \left[ \frac{2 \mu}{\hbar^2} \left( U_i - U_0 \right) + \frac{J_i(J_i + 1)}{R^2} \frac{J_0(J_0 + 1)}{R^2} + k_i^2 \cdot g_i(R) \right] \cdot F_i(R) +$$

$$+ \frac{2 \mu}{\hbar^2} \sum_{j \neq i} V_{ij} \cdot F_j(R) \quad (7)$$

where

$$K_i^2 = k_i^2 \left[ 1 - \frac{J_0(J_0 + 1)}{k_0^2 R_0^2} - \frac{2 \mu}{\hbar^2 k_0^2} \cdot U_0(R) \right]. \quad (8)$$

For each channel

$$g_i(R) = \left[ \frac{J_0(J_0 + 1)}{R^2} + 2 \mu \cdot U_0(R) \right] \left( \frac{1}{k_i^2} - \frac{1}{k_0^2} \right) \quad (9)$$

$k_0$ denotes an « average » wave number relevant to the mean potential $U_0$. This expression involves now the same turning point $R_0$ defined by:

$$\left[ 1 - \frac{J_0(J_0 + 1)}{k_0^2 R_0^2} - \frac{2 \mu}{\hbar^2 k_0^2} \cdot U_0(R_0) \right] = 0. \quad (10)$$

The semi-classical equations are then derived in the limit of large quantum numbers of the quantal equations as described in paper I.

Diagonal terms are taken away by introducing specific phase factors in the semi-classical amplitudes which preserves the correct asymptotic form.

$$b_i = a_i \cdot \exp \left[ \int_{R_0}^{R} h_i(R') \cdot dR' \right] \quad (11)$$

with

$$h_i(R) = \frac{\mu}{\hbar^2 K_i} \cdot (U_i - U_0) + \frac{J_i(J_i + 1) - J_0(J_0 + 1)}{2 K_i R^2} + \frac{k_i^2}{2 K_i} \cdot g_i(R) \quad (12)$$

The following semi-classical coupled equations are then obtained:

$$i \frac{db_i}{dR} = \frac{\mu}{\hbar^2} \sum_{j} \frac{V_{ij}}{\{ k_i k_j \}^{1/2}} \cdot b_j \cdot \exp \left[ i \int_{R_0}^{R} \{ K_j - K_i - h_j(R') + h_i(R') \} \cdot dR' \right]. \quad (13)$$
Now we introduce the time variable $dt = \frac{\mu}{\hbar K_0} \cdot dR$ with

$$K_0^2 = k_0^2 \left[ 1 - \frac{J_0(J_0 + 1)}{k_0^2 R^2} - \frac{2 \mu}{\hbar^2 k_0^2} \cdot U_0(R) \right].$$

The time dependent coupled equations become:

$$i \hbar \frac{db_i}{dt} = \sum_j \frac{k_0}{\{k_i k_j\}^{1/2}} \cdot V_{ij} \cdot b_j \cdot \exp \left[ i \int_{t_0}^t \frac{hK_0}{\mu} \cdot dt' \left\{ K_j - K_i - h_j(t') + h_i(t') \right\} \cdot dR' \right].$$

If one can assume that $k_0 = \{k_i k_j\}^{1/2}$, we obtain the coupled equations of paper I. Otherwise, additional corrective phase factors are introduced.

We then make the following change of variable introducing the curvilinear abscissa $s$:

$$\frac{dt}{ds} = \frac{\mu}{\hbar K_0} \cdot \frac{\sqrt{1 - \frac{J_0(J_0 + 1)}{k_0^2 R^2} - \frac{2 \mu}{\hbar^2 k_0^2} \cdot U_0(R)}}{\sqrt{1 - \frac{2 \mu}{\hbar^2 k_0^2} \cdot U_0(R)}}.$$  \hspace{1cm} (16)

In this way, we avoid numerical difficulties arising at the classical turning point. The coupled equations are then solved numerically by the Merson algorithm [7].

5. Results and discussion.

We first study the problem involved in the choice of the potential that is to be used for the common trajectory. Only one $^1\Sigma$ potential is correlated to the initial $O(2\,^1S)$ state whereas three molecular potentials $^1\Pi, \, ^1\Pi, \, ^1\Delta$ are correlated to the final $O(1\,^1D)$ state.

Figures 1a, 1b, 1c, 1d respectively show for several impact parameters the trajectories derived from using each of these four potentials in turn as common potential.

We can see that the general shapes of the trajectories are similar:

- small deflection angles are observed for impact parameters $b$ smaller than 6$ a_0$ thereby showing the extent of the classically forbidden region;
- for impact parameters beyond 12$ a_0$, the trajectories become roughly linear which indicates the range of the potentials.

We thus expect that the choice of the common potential defining the common turning point [6, 9] is not critical in this specific case. However this condition is no warrant whether the semi-classical approach will yield good quantitative results or not.

Figure 2 shows the time evolution of the probability of induced emission $P_{E}^{B}$ in a specific branch B for several impact parameters $b$ at different detuning frequencies $\Delta$ in cm$^{-1}$. The incident kinetic energy $E$ is 300 cm$^{-1}$. $P_{E}^{B}(\Delta, b, t) = \sum_{t} |a_{P}^{B}(\Delta, b, t)|^2$ where $a_{P}^{B}(\Delta, b, t)$ is the probability amplitude of the final state obtained in the semi-classical close coupling common trajectory method.

Time $t = 0$ corresponds to the classical turning point relevant to the $O(1\,^1S)$ $\Sigma$ common potential. Vertical lines show the two Franck-Condon (FC) times $\pm t_{FC}^{\Sigma}$ pertaining to each
Fig. 1. — Trajectories respectively yielded by the successive use as common potential of the upper state $\Omega ('S) \Sigma$ potential (Fig. 1a), the lower states $\Omega ('D) \Sigma$, $\Pi$, $\Delta$ potentials (Figs. 1b, 1c, 1d). The impact parameter $b$ varies from 0.5 to 11.5 $a_0$ by 1 $a_0$.

existent FC distance in an adiabatic calculation. The solid line corresponds to the $\Sigma-\Pi$ transition, the dashed line to the $\Sigma-\Sigma$ transition.

For each detuning, we present four different impact parameters (curves a, b, c, d correspond to impact parameter values $b = 4.5$, 5.5, 6.1, 7.2 $a_0$ respectively). Each graph shows the emission probability of the three spectroscopic branches P, Q, R versus time $t$. Every one of them presents the same variation.

For negative times, the probability is very small. Then it starts oscillating and building up in a region centered round the turning point (time 0) before reaching a different final value according to the spectroscopic branch for positive times. This region is more or less extended depending on the detuning as shown in figures 2, 3, 4. In the blue wing ($\Delta = + 60 \text{ cm}^{-1}$, Figs. 2a, 2b, 2c, 2d), Franck-Condon points exist for the smaller impact parameters (2a, 2b, 2c). In that case, the final value of the probability is mostly reached for $t = + t_{\text{FC}}^*$ (outgoing passing through the FC point). So the transition takes place mainly at the FC points. For the higher impact parameter shown here (Fig. 2d), the FC points fall in the classically forbidden region, the probability only presents a large oscillation around the turning point and the final probability is very small. In the red wing ($\Delta = - 50 \text{ cm}^{-1}$, Figs. 4a, 4b, 4c, 4d), no FC point exist either and the situation is quite similar to figure 2d. Thus, in both wings, although for different reasons, the transition is « localized » since the final probability is reached in a time whose order of magnitude is much smaller than a typical collision time duration $\Delta T_c \approx 0.6 \times 10^{-12} \text{ s}$. On the contrary, in the line center ($\Delta = + 1 \text{ cm}^{-1}$, Figs. 3a, 3b, 3c, 3d), the emission transition is not well localized.
Fig. 2, 3, 4. — Individual time evolution of the probability $P^\beta(\Delta, b, t)$ as a function of time $t$ in seconds for impact parameter $b = 4.5 \ a_0$ (a), $b = 5.5 \ a_0$ (b), $b = 6.1 \ a_0$ (c), $b = 7.2 \ a_0$ (d) and detuning $\Delta = + 60 \ cm^{-1}$ (Fig. 2), $\Delta = + 1 \ cm^{-1}$ (Fig. 3), $\Delta = - 50 \ cm^{-1}$ (Fig. 4). $E = 300 \ cm^{-1}$. B stands for the spectroscopic branch P, Q, R. All three spectroscopic branches are shown.
So this time analysis leads us to expect that in the blue wing the result will be close to a quasistatic calculation whereas significant departures from the quasistatic profile are to be expected in the line center. We also expect the red wing intensity to be very small in the present calculation.

In figure 5, we study the total opacity functions $b \cdot P_E(\Delta, b)$ summed over the three branches versus the impact parameter $b$ for three different detunings ($\Delta = +60, +1, -50 \text{ cm}^{-1}$). The incident kinetic energy is 300 cm$^{-1}$.

$$b \cdot P_E(\Delta, b) = \sum_b \int_{-\infty}^{\infty} b \cdot P^B_E(\Delta, b, t) \cdot dt.$$ 

The aim of the present analysis is to show what impact parameter range contributes to the cross section which can give some insight on the resulting shape of the total profile. In addition to the fully non adiabatic calculation (Fig. 5a), two other semi-classical calculations (Figs. 5b, 5c) based on the same molecular potentials are reported:

- a close coupled calculation (Fig. 5b) in the usual rectilinear trajectory approximation. In that particular case, the potentials are replaced by a repulsive barrier for $R$ lower than the upper state turning point $R_t = 5.8 a_0$ to ensure that the classically forbidden region is just so;
- a common trajectory calculation (Fig. 5c) in an « adiabatic » approximation (Julienne 1983 [8]) assuming no interaction between the final states. In that case, the total cross section is simply a sum of the separate cross sections respectively relevant to the $\Sigma-\Sigma$ and $\Sigma-II$ transitions.

In the following, the notation CCC, RCC and CBO is used to denote respectively: the common trajectory (CCC) and rectilinear (RCC) non adiabatic calculations and the latter the Born-Oppenheimer results (CBO).

Figure 5a (CCC results) shows that:
- the dominant impact parameters for the blue wing are smaller than for the line center;
- the dominant impact parameters for the line center extend over a broader range than for the blue wing;
- the red wing is virtually inexistent.

All three facts are consistent with our previous time analysis.

By comparing respectively the blue wing and line center curves in figure 5b (RCC calculation) to figure 5a, one can see that taking into account to some extent the curvature of the trajectories in the CCC calculation by means of the turning point method [6, 9] mostly results in increasing the relative contribution of the smaller impact parameters especially in the blue wing. However, for the red detuning, the RCC opacity function (Fig. 5b) is much higher than the CCC result which indicates extremely strong trajectory effects in the red wing.

If one compares now figure 5c (CBO result) to figure 5a, it can be seen that the blue wings are quite similar in both calculations whereas the line centers are very different namely that the CCC peak is much reduced compared to the CBO result. So the rotational couplings in the CCC emission opacity function actually have little effect on the nearly quasistatic blue wing whereas the non adiabatic line center is strongly decreased. This confirms the trend expected from the time analysis.

Finally, one can also compare the CCC result to the quantal calculation by Julienne 1982 (Fig. 10, [2]) which is our reference for this test case. Qualitatively, we see that the last peak of the opacity function appears to be missing for the blue detuning ($\Delta = +60 \text{ cm}^{-1}$, $J \approx 50$ i.e. $b \approx 6.7 a_0$) and at the line center ($\Delta = +1 \text{ cm}^{-1}$, $J \approx 55$ i.e. $b \approx 7.3 a_0$). However, this mostly affects the blue wing so that we expect our calculated blue wing profile to be lower
Fig. 5. — Total opacity function $b \cdot P_E(\Delta, b)$ summed over the three spectroscopic branches as a function of the impact parameter $b$ for $E = 300 \text{ cm}^{-1}$ and detuning $\Delta = +60 \text{ cm}^{-1}$ (dashed line), $\Delta = +1 \text{ cm}^{-1}$ (solid line), $\Delta = -50 \text{ cm}^{-1}$ (dotted line). Semi-classical calculations are shown: CCC (Fig. 5a), RCC (Fig. 5b), CBO (Fig. 5c).

than the quantal result. For the red detuning ($\Delta = -50 \text{ cm}^{-1}$), the dominant angular momentum range is also around $J = 55$. Since the equivalent impact parameter range contribution is vanishing in our semi-classical calculation, our red wing is extremely small compared to the quantal result. The difference arises from the contribution of the classically forbidden region: indeed, in our calculation, the common potential (upper $^1\Sigma$ state) is more repulsive than the $\Sigma$ and $\Pi$ final lower states so that the effective common turning point occurs
at higher internuclear distances than the lower states would yield and the Franck-Condon points fall in the classically forbidden region for higher impact parameters.

In figure 6, we report our RCC and CCC semi-classical profiles together with the close coupled (Q) and adiabatic (QBO) quantal calculations by Julienne [2] and the quasistatic approximation (QS) [2]. From the opacity function analysis, we know that the strong discrepancy between the RCC and CCC red wing intensities arises from important trajectory effects. However, the near blue wing (20-50 cm⁻¹) intensities appear relatively insensitive to such trajectory effects since both semi-classical calculations are very close. From the opacity function analysis, we also know that the blue wing intensity is not sensitive to rotational couplings whereas the line center is strongly non adiabatic. This trend is confirmed by the reference Q and QBO quantal profiles by Julienne [2] in the blue wing and the line center. Now we compare our semi-classical profiles to the reference quantal calculations [2] : in the line center (Δ = -10, +10 cm⁻¹), our CCC result is much closer to the quantal close coupled profile (Q) than the RCC result which indicates that the common turning point treatment [6, 9] takes correctly into account the curvature of the trajectories and the rotational couplings. However, as expected from the previous time and opacity function analyses, the agreement is not so good in the line wings where we explore the short internuclear region of the potentials close to the classically forbidden region. In the red wing the discrepancy between the semi-classical and the quantal close coupling results further indicates that the important rotational couplings involving the lower ¹Σ, ¹Π and ¹Δ potentials are effective for R values around the common turning point so that their contribution to the cross section is vanishing in our semi-classical calculation. In the blue wing, as expected, our CCC result is significantly lower than

Fig. 6. — Total radiative cross section PE(Δ) as a function of detuning Δ for E = 300 cm⁻¹. The detuning Δ is in cm⁻¹ and the profile in 10⁻⁷ a₀². Several profiles are shown : This work : semi-classical close coupled calculations either with a common trajectory (CCC : ×) or a rectilinear trajectory (RCC : +). Reference (Julienne 1982 [2]) : quantal close coupled calculation (Q : bold faced solid line), quantal two state Born-Oppenheimer approximation (QBO : solid line), quasistatic calculation (QS : dashed line).
the quantal result. Consequently, in both wings, the preceding remarks lead us to attribute the discrepancy to the contribution of the classically forbidden region.

Finally, figure 7 shows the relative contributions of the semi-classical equivalent of the P, Q, R spectroscopic branches to the total CCC profile together with the reference quantal results by Julienne 1982 [2]: since we have shown [1] that we can interpret the spectroscopic branches in terms of the rotation of the internuclear axis during the collision, it is not surprising that our semi-classical treatment reproduces qualitatively the branch effect first pointed out by Julienne [2, 8] in the predominantly case (e) line center and near wing region of the profile: namely, the individual branches are shifted according to the relevant case (e) selection rules by amounts proportional to the angular momentum change Δℓ: so the P branch (Δℓ = −1, −3) is shifted several cm⁻¹ to the red, the R branch (Δℓ = +1, +3) to the blue and the Q branch is not much shifted (Δℓ = ±1).

Fig. 7. — Total relative cross section $P_E(Δ)$ and individual contributions $P_E^B(Δ)$ from the three spectroscopic branches as a function of detuning Δ for $E = 300$ cm⁻¹. Units are the same as in figure 6. Two types of close coupled calculations are shown: This work (dotted line curves): semi-classical calculation with a common trajectory. B = P', Q', R'. Reference (solid line curves): quantal calculation by Julienne 1982 [2]. B = P, Q, R.

Conclusion.

In this work, we have numerically applied the semi-classical radiatively assisted collisions theory for both scattering and radiative couplings. Our calculations are based on the same potential and radiative coupling values as Julienne 1982 [2] whose available Ar + O quantal calculations are thus used as reference in the discussion of the results. This test case which allowed us to build the numerical codes was not suitable to obtain good quantitative results (except in the line center) since quantal effects related to the classically forbidden region are
especially important in the wings. However, our aim was rather to study qualitatively this test transition and we have shown that the various versions of the semi-classical treatment are useful to gain some insight into the physical processes involved stressing some aspects of the non localization of the transition and the trajectory and rotational coupling effects.

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