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To cite this version:
D. Vienne-Casalta, J. Margerie. Rare gas collisional perturbation of the (6 3D1, 6 1D2) levels of mercury: a theoretical estimate II. Journal de Physique, 1982, 43 (1), pp.31-36. <10.1051/jphys:0198200430103100>. <jpa-00209380>

HAL Id: jpa-00209380
https://hal.archives-ouvertes.fr/jpa-00209380
Submitted on 1 Jan 1982

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Rare gas collisional perturbation of the $(6^3D_1, 6^1D_2)$ levels of mercury: a theoretical estimate II

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(Reçu le 18 mai 1981, révisé le 14 septembre, accepté le 18 septembre 1981)

Résumé. — Dans le cadre de la théorie d'Omont et Gay, les auteurs évaluent les effets (relaxations et transferts) des collisions de gaz rares contre des atomes de mercure dans l'un des deux niveaux très voisins $6^1D_2$ et $6^3D_1$. Le calcul est fait d'abord en champ magnétique nul. Un calcul précédent (J. Physique 41 (1980) 503) avait été effectué avec le mauvais signe de la partie anisotrope du potentiel effectif; il est repris ici avec le signe correct. Les résultats des deux calculs sont comparés avec les données expérimentales disponibles. Par ailleurs, le même modèle a permis de calculer un grand nombre de sections efficaces de transfert entre les sous-niveaux de $(6^1D_2, 6^3D_1)$ en fonction du champ magnétique dans le domaine 0-100 kG. Ces calculs en champ non nul ont été faits pour les collisions avec l'argon, à 295 K. On discute l'origine physique des effets prédits.

Abstract. — In the framework of the Omont-Gay theory, the authors calculate the effects (relaxations and transfers) of rare-gas collisions against mercury atoms in either of two very close levels $6^1D_2$ and $6^3D_1$. Zero external magnetic field is first considered. A previous calculation (J. Physique 41 (1980) 503), which was carried out with the wrong sign of the anisotropic part of the effective potential, is now performed with the right sign. The results of both calculations are compared with available experimental data. On the other hand, the authors have computed, in the same model, a number of transfer cross-sections among the eight sublevels of $(6^1D_2, 6^3D_1)$ as a function of the magnetic field in the 0-100 kG range. These non zero field calculations have been performed for argon perturbers, at 295 K. The physical origin of the various predicted effects is discussed.

Introduction. — In a recent publication [1], hereafter referred to as I, J. C. Gay and ourselves performed a theoretical study of the relaxation and transfer of tensorial quantities in either of two very close $(\delta E = 2.982 \text{ cm}^{-1})$ levels $6^1D_2$ and $6^3D_1$ of mercury by collisions against rare-gas atoms in zero magnetic field. The work described in I used the Omont-Gay approach [2-6]: impact approximation; atoms described quantum mechanically for their internal state but classically for their relative motion; rectilinear trajectories with constant relative velocity $v$; neglect of wavefunction overlap and electron exchange between collision partners; restriction of the problem to an 8-dimensional subspace (the 5 sublevels of $6^1D_2$ and the 3 sublevels of $6^3D_1$) by use of an effective potential $V_{eff}$ which describes the action of $V^2/AE$ within this subspace. $AE$ is some average energy denominator and $V$ is the electrostatic interaction between the electrons and protons of one atom and the electrons and protons of the other one. $V_{eff}$ is developed as an asymptotic expansion in negative powers of the internuclear distance $R$

$$V_{eff} = C_6 R^{-6} + C_8 R^{-8} + C_{10} R^{-10} + \cdots$$ (II, 1)

where $C_6 R^{-6}$ is the familiar Van der Waals potential (1). In I, numerical calculations were performed both with $V_{eff1} = C_6 R^{-6}$ and with $V_{eff2} = C_6 R^{-6} + C_8 R^{-8}$.

The agreement with the experiment, although not perfect, was found to be considerably better with potential $V_{eff2}$ than with $V_{eff1}$.

In the concluding remarks of I, we mentioned the project of experimentally studying the transfers between sublevels of $6^1D_2$ and $6^3D_1$ while tuning their energy interval between $\delta E$ and zero by a suitable external magnetic field. We have recently performed calculations in order to decide whether such an experiment would be worthwhile. In the course of these new calculations, we discovered that a numerical mistake had unfortunately vitiated a substantial part

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Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphys:0198200430103100
of the conclusions of I: In solving equations (12), the tensorial part $V_{\text{eff}}$ of the effective potential was replaced by:

$$V_{\text{eff}} = - V_{\text{eff}}$$  \hspace{1cm} (II, 2)

which amounts to change the sign of the anisotropic part of the interaction, i.e. to modify the relative energetic position of levels $\Sigma, \Pi$ and $\Delta$ of the pseudomolecule formed by the colliding atoms.

The aim of the present paper is to correct our mistake of I for the zero field case and to present the results of our high magnetic field calculations. The reader is referred to I for the discussion of the model, the notations and most equations ($^1$). In section 1 below, we calculate the zero-field relaxations and transfers with the correct $V_{\text{eff}}$ and we compare the results with available experimental data. In section 2, we describe our non zero field computations and we attempt a physical interpretation of the predicted effects.

1. Zero field relaxations and transfers. — 1.1 Calculation results. — We have performed the same numerical calculations as in I, but with the correct sign of the interaction potential, i.e. the sign consistent with data of table I and with formulas in the appendix of I. Nothing has to be altered in sections 1 and 2 of I except that figure 3 is only qualitatively correct and that some $\frac{J^2}{J'}$s or $\frac{J^2}{J''}$s may differ from 1.0 by as much as 0.2. Table II of paper I must be replaced by table A below. For ease of discussion, table B compares a few selected data obtained with both correct and incorrect signs of potential $V_{\text{eff}}$: Figure 4 of paper I is also wrong and should be replaced by figure 1 opposite.

![Fig. 1](image)

**Fig. 1.** Thermal dependence of mercury-argon cross-sections with the correct sign of the interaction potential. (Broken lines: calculation with $C_6 R^{-6}$ effective potential, full lines: calculations with $C_6 R^{-6} + C_8 R^{-8}$ potential.)

Table A. — Comparison of calculated zero field results (with the correct sign of potential $V_{\text{eff}}$) and experimental data. Temperature = 295 K. In the 7 first columns, cross-sections are in $\text{A}^2$. Experimental data are from references [7] (columns 1, 3 and 5 to 9) and [8] (columns 2 and 4). Results of reference [8] have been multiplied by $\pi$ because of a difference in the definition of cross-sections.

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_{11}(0)$</th>
<th>$\sigma_{11}(1)$</th>
<th>$\sigma_{22}(0)$</th>
<th>$\sigma_{22}(1)$</th>
<th>$\sigma_{12}(0)$</th>
<th>$\sigma_{12}(1)$</th>
<th>$\sigma_{12}(2)$</th>
<th>$\sigma_{12}(0)$</th>
<th>$\sigma_{12}(2)$</th>
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</thead>
<tbody>
<tr>
<td>He</td>
<td>Calc.1 79</td>
<td>76</td>
<td>62</td>
<td>85</td>
<td>17</td>
<td>-1.1</td>
<td>-2.4</td>
<td>-1.1</td>
<td>-2.4</td>
</tr>
<tr>
<td></td>
<td>Exp. 219(26)</td>
<td>220(22)</td>
<td>272(19)</td>
<td>239(24)</td>
<td>67(10)</td>
<td>-7.0(1.5)</td>
<td>-9.2(1.6)</td>
<td>-10(10)</td>
<td>-10(10)</td>
</tr>
<tr>
<td>Ne</td>
<td>Calc.1 141</td>
<td>133</td>
<td>109</td>
<td>151</td>
<td>27</td>
<td>.0</td>
<td>-4.1</td>
<td>0</td>
<td>-15</td>
</tr>
<tr>
<td></td>
<td>Calc.2 260</td>
<td>246</td>
<td>227</td>
<td>280</td>
<td>49</td>
<td>-7.7</td>
<td>-7.9</td>
<td>-16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Exp. 197(14)</td>
<td>223(22)</td>
<td>245(17)</td>
<td>251(25)</td>
<td>70(10)</td>
<td>-6.5(1.2)</td>
<td>-15(3)</td>
<td>-22(22)</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>Calc.1 377</td>
<td>295</td>
<td>216</td>
<td>297</td>
<td>46</td>
<td>.8</td>
<td>-7.2</td>
<td>2(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Calc.2 437</td>
<td>413</td>
<td>375</td>
<td>479</td>
<td>69</td>
<td>.5</td>
<td>-11.1</td>
<td>1(1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Exp. 341(24)</td>
<td>393(39)</td>
<td>404(28)</td>
<td>408(41)</td>
<td>104(19)</td>
<td>.0(3)</td>
<td>-17(3)</td>
<td>0(0)</td>
<td></td>
</tr>
<tr>
<td>Kr</td>
<td>Calc.1 364</td>
<td>338</td>
<td>285</td>
<td>394</td>
<td>51</td>
<td>1.9</td>
<td>-8.0</td>
<td>4(4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Calc.2 542</td>
<td>511</td>
<td>467</td>
<td>597</td>
<td>69</td>
<td>1.6</td>
<td>-11.0</td>
<td>2(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Exp. 445(31)</td>
<td>581(36)</td>
<td>505(35)</td>
<td>597(60)</td>
<td>151(25)</td>
<td>-9(2)</td>
<td>-19(4)</td>
<td>-6(6)</td>
<td></td>
</tr>
<tr>
<td>Xe</td>
<td>Calc.1 367</td>
<td>432</td>
<td>369</td>
<td>512</td>
<td>57</td>
<td>2.9</td>
<td>-8.8</td>
<td>5(5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Calc.2 660</td>
<td>623</td>
<td>569</td>
<td>733</td>
<td>71</td>
<td>3.0</td>
<td>-11.6</td>
<td>4(4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Exp. 523(36)</td>
<td>723(72)</td>
<td>583(41)</td>
<td>660(66)</td>
<td>164(22)</td>
<td>-18(4)</td>
<td>-23(5)</td>
<td>-11(11)</td>
<td></td>
</tr>
</tbody>
</table>

Table A. — Comparison of calculated zero field results (with the correct sign of potential $V_{\text{eff}}$) and experimental data. Temperature = 295 K. In the 7 first columns, cross-sections are in $\text{A}^2$. Experimental data are from references [7] (columns 1, 3 and 5 to 9) and [8] (columns 2 and 4). Results of reference [8] have been multiplied by $\pi$ because of a difference in the definition of cross-sections.
Table B. — Comparison of some calculated zero field cross-sections (in Å²) with correct \((V_{\text{eff}})\) and incorrect \((V'_{\text{eff}})\) effective potentials : calculation 2. For comparison, the experimental values of \(12\sigma^{(0)}\) \((900\,\text{K})/12\sigma^{(0)}\) \((295\,\text{K})\) are 0.84 and 1.20 with helium and xenon perturbers respectively.

<table>
<thead>
<tr>
<th>Perturber</th>
<th>Temperature</th>
<th>Potential used</th>
<th>(11_{\sigma}^{(1)})</th>
<th>(11_{\sigma}^{(2)})</th>
<th>(22_{\sigma}^{(1)})</th>
<th>(22_{\sigma}^{(2)})</th>
<th>(12_{\sigma}^{(0)})</th>
<th>(12_{\sigma}^{(1)})</th>
<th>(12_{\sigma}^{(2)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>295 K</td>
<td>(V'_{\text{eff}})</td>
<td>170</td>
<td>150</td>
<td>147</td>
<td>181</td>
<td>38</td>
<td>-1.1</td>
<td>-5.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(V_{\text{eff}})</td>
<td>170</td>
<td>160</td>
<td>149</td>
<td>181</td>
<td>42</td>
<td>-1.3</td>
<td>-6.1</td>
</tr>
<tr>
<td>He</td>
<td>900 K</td>
<td>(V'_{\text{eff}})</td>
<td>144</td>
<td>135</td>
<td>126</td>
<td>153</td>
<td>32</td>
<td>-0.9</td>
<td>-5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(V_{\text{eff}})</td>
<td>144</td>
<td>135</td>
<td>126</td>
<td>153</td>
<td>34</td>
<td>-1.0</td>
<td>-5.1</td>
</tr>
<tr>
<td>Xe</td>
<td>295 K</td>
<td>(V'_{\text{eff}})</td>
<td>660</td>
<td>623</td>
<td>569</td>
<td>733</td>
<td>71</td>
<td>3.0</td>
<td>-11.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(V_{\text{eff}})</td>
<td>677</td>
<td>598</td>
<td>618</td>
<td>694</td>
<td>167</td>
<td>4.9</td>
<td>-21.0</td>
</tr>
<tr>
<td>Xe</td>
<td>900 K</td>
<td>(V'_{\text{eff}})</td>
<td>557</td>
<td>534</td>
<td>478</td>
<td>614</td>
<td>87</td>
<td>0.9</td>
<td>-14.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(V_{\text{eff}})</td>
<td>569</td>
<td>522</td>
<td>508</td>
<td>594</td>
<td>148</td>
<td>-1.1</td>
<td>-20.4</td>
</tr>
</tbody>
</table>

It appears that our error of I did not alter noticeably the relaxation cross-sections of orientation or of alignment inside level \(6\,^3\Delta(1)\) and inside level \(6\,^1\Sigma(2)\) \((\sigma^{(0)})\). On the other hand, it affected severely the transfers between \(6\,^3\Delta\) and \(6\,^1\Sigma\) : \(12\sigma^{(1)}\) is smaller for potential \(V'_{\text{eff}}\) than for potential \(V_{\text{eff}}\), and the relative difference is greater for heavy perturbers and low temperatures. For instance, in calculation 2, \(-58\%\) for xenon at 295 K but \(-6\%\) only for helium at 900 K. This has consequences for the predicted thermal dependence of \(12\sigma^{(0)}\). With wrong potential \(V'_{\text{eff}}\), \(12\sigma^{(0)}\) was found to be a decreasing function of the temperature, like the relaxation cross-sections (Fig. 4 of I for argon and similar results for the other perturbers). On the other hand, with correct potential \(V_{\text{eff}}\), the thermal behaviour of \(12\sigma^{(0)}\) is predicted to depend on the foreign gas : with helium and neon, one expects a decreasing function in the 295-900 K domain, with xenon, an increasing function. A flat maximum of \(12\sigma^{(0)}\) is foretold in the same temperature range for krypton in calculation I and for argon in calculation 2.

\(12\sigma^{(2)}\) is similarly affected by the sign of the tensorial part of the interaction, so that the degree of alignment transfer \(12\sigma^{(2)}\) \((\Delta(28))\) was little affected by the incorrect use of \(V'_{\text{eff}}\) instead of \(V_{\text{eff}}\) \((\text{last columns of tables II and A})\). \(12\sigma^{(1)}\) remains close to zero, whatever the sign of the effective potential.

1.2 COMPARISON WITH EXPERIMENT. — Tables A and B show that the agreement with experiment has unfortunately not been improved on the whole by correcting our error in the sign of \(V'_{\text{eff}}\). The agreement for the values of \(11\sigma^{(2)}, 22\sigma^{(1)}, 22\sigma^{(2)}\) and \(12\sigma^{(2)}\) which was already good (calculation 2 and experimental values from \([7]\) and \([8]\)) is not spoilt. Similarly, both with the correct and the incorrect sign of \(V'_{\text{eff}}\), the orientation relaxation cross-sections of \(6\,^3\Delta\) are predicted \(-20\) to \(-30\%\) too big and the orientation transfer rates \(12\sigma^{(1)}\) are calculated to be nearly zero for all perturbers which is in agreement with the observation only in the case of argon.

The observables for which the right and the wrong calculations differ significantly in their comparison with available experimental information are the population transfer cross-sections \(12\sigma^{(0)}\) and their thermal dependences. We are sorry to observe that the population transfer cross-sections \(12\sigma^{(0)}\) which were nicely predicted by calculation 2 using \(V'_{\text{eff}}\) become definitely too small with the correct \(V_{\text{eff}}\). On the other hand, S. A. Arbajji et al. \([7]\) have found \(12\sigma^{(0)}\) to be a decreasing function of temperature for some perturbers and an increasing function for some other ones, in general agreement with the result of the correct calculation (see table B) while the incorrect calculation of reference \([1]\) predicted \(12\sigma^{(0)}\) to be a decreasing function of temperature, whatever the perturber.

A more complete comparison between experiment and the present theory may be found in reference \([7]\).
2. Effect of an external magnetic field. — 2.1 CALCULATION PROCEDURE. — As in I, we consider three frames of reference: the «molecular» Oxyz, the «standard» OXYZ (see Fig. 2 of I) and the laboratory frame OX1 Y1 Z1. Let \( \varphi, \theta, \eta \) be the Euler angles for the rotation which carries OXYZ on OX1 Y1 Z1. For the same reason as in I, we neglect the influence of nuclear spin and we start from the set of intermediate coupling eigenvectors \( |1^3D_1, M\rangle \) and \( |1^3D_2, M\rangle \) (for short \( |J, M\rangle \) in the standard frame (equation (9)). We obtain the corresponding kets \( |J, m\rangle \) in the OX1 Y1 Z1 frame by use of the rotation matrix \( R^{(J)}(\varphi, \theta, \eta) \)

\[
| J, m \rangle = \sum_{M} | J, M \rangle R^{(J)}_{M,m}(\varphi, \theta, \eta).
\]

If a magnetic field B is applied along the Z1 axis, it mixes \( |1^3D_1, m\rangle \) and \( |1^3D_2, m\rangle \) for a given m. Except for \( m = \pm 2 \), the corresponding mixtures \( |J, m\rangle \) are obtained, as functions of B, by the diagonalization of a \( 2 \times 2 \) matrix \( (3) \). The \( \tilde{J} \) labels are chosen to be equal to the \( J \)'s by continuity for vanishing magnetic field values. Let the transformation matrix \( T \) be defined by:

\[
| \tilde{J}, m \rangle = \sum_{J} | J, m \rangle T_{j_m,j_m}.
\]

With the mercury wavefunctions developed on the new \( | \tilde{J}, m \rangle \) basis, equation (12) must be replaced by:

\[
\frac{i\hbar}{\hbar} \frac{d|a_{j,m}\rangle}{dt} = \sum_{m'} \langle \tilde{J}, m | \mathcal{U}_{\text{eff}} | \tilde{J}, m' \rangle \times \exp\left(\frac{i}{\hbar}(E_{j,m} - E_{j,m'})t\right) |a_{j,m'}\rangle.
\]

with:

\[
\mathcal{U}_{\text{eff}} = T_{(b)} R_{(\varphi, \theta, \eta)} V_{\text{eff}} R_{(\varphi, \theta, \eta)} T_{(b)}.
\]

\( R_{(\varphi, \theta, \eta)} \) being the \( 8 \times 8 \) rotation matrix for a space, easily constructed from \( R_{(1)}^{(1)} \) and \( R_{(2)}^{(2)} \).

In the zero field problem (I and section 1 of present paper), we could use, instead of relation (12), its counterpart (12) in the standard frame OXYZ. As mentioned in I, it splits into two independent sets of four coupled differential equations. From the solution of these equations, it was easy to obtain the S-matrix in the laboratory frame OX1 Y1 Z1 for any orientation \( (\varphi, \theta, \eta) \) of OXYZ with respect to OX1 Y1 Z1. When B is different from zero, we could still use relations (12) but the Zeeman hamiltonian would then have to be included in \( V_{\text{eff}} \), with the result that, even in the standard frame, the differential system would not generally split into two subsystems.

Moreover, one would have to perform on the resultant S-matrix transformations by the \( R_{(\varphi, \theta, \eta)} \) and \( T_{(\theta)} \) matrices of equation (II, 6). Instead of this complicated procedure, we preferred to use relations (II, 5) which generally form one single set of eight coupled differential equations. Whatever the calculation method used, the laboratory frame S-matrix no longer depends in a simple way on Euler angles \( \varphi \) and \( \theta \). The \( \eta \) dependence, however, remains trivial [5],

\[
S_{j_m,j_m}(\eta) = e^{i(m-m')\eta} S_{j_m,j_m}(\eta = 0).
\]

All numerical computations are therefore performed with \( \eta = 0 \). But they must be worked out for various values of \( \varphi \) and \( \theta \) : we used 5 and 7 values of these parameters respectively \( (4) \). The unitarity and unimodularity of \( S \) are used here, as in zero field, to get tests of numerical accuracy. Designating for short the \( |J, m\rangle \)'s by \( |J\rangle \), \( |k\rangle \), ..., we define relaxation and transfer coefficients \( \gamma^{(j)}(kk') \) by an equation similar to (18) but using for the Liouville space a « Zeeman basis » [4] instead of the irreducible tensorial basis of I. The \( \gamma^{(j)}(kk') \) are calculated from:

\[
\gamma^{(j)}(kk')(\eta) = \delta_{jk} \delta_{k'k} - \langle j | S | k \rangle \langle k' | S^\dagger | j \rangle >_{\text{Ang}}.
\]

where \( \langle \cdot \rangle_{\text{Ang}} \) denotes angular averaging. In fact, we are primarily interested in the relaxations and transfers of populations (not of coherences between different sublevels). Thus, we restricted our final calculations \( (5) \) to the \( \gamma^{(j)}(kk') \), written for short \( \gamma^{(j)}(k) \), with the following properties [5],

\[
\sum_{j} \gamma^{(j)(k)} = 0 \quad (\forall k)
\]

\[
\gamma^{(j)(k)} \text{ real}
\]

\[
\gamma^{(j)(k)} = \gamma^{(j)(k)}
\]

which correspond respectively, for the Zeeman basis, to equations (21), (22) and (23) and have similar physical meanings. From the \( \gamma^{(j)(k)} \) one could easily obtain the corresponding cross-sections \( \sigma^{(j)(k)} \) by equations (24) and (25). However, calculations in the presence of a magnetic field are much longer than in zero field and, in order to reduce computation times, we have fixed the relative velocity of collision partners at its average value \( v > \) and, therefore, approximated \( \gamma^{(j)(k)} \) by \( \sigma^{(j)(k)}(\langle v \rangle) \) \( (6) \) as already done by Gryenberg et al. [9]. We verified that such a procedure has only a small influence on the results.

\( (4) \) For \( \varphi \), the symmetry of the problem allows the range to be limited to \( 0 \leq \varphi \leq \pi/2 \) [5]. For \( \theta \), however, the whole domain \( 0 \leq \theta \leq \pi \) must be retained.

\( (5) \) The same techniques would easily yield relaxation and transfer coefficients for coherences, if necessary.

\( (6) \) The velocity dependent cross-sections \( \sigma' \) are defined by relation (24) with the upper sign if \( j = k \) (relaxation) and the lower one if \( j \neq k \) (transfer).
of the zero field calculations of I and of section 2 of the present paper and we hope this remains true in the presence of an intense magnetic field.

In order to save computer time, we performed calculations only for argon perturbers, at 295 K and with potential \( V_{\text{eff2}} \) (which is more successful than \( V_{\text{eff1}} \) for the interpretation of zero field experimental data). We have also, for the same economy reason, deliberately limited somewhat too drastically the range of \( q \) values for which the calculation was performed, with, as a consequence, systematic errors which may amount to 10 or 20 \( \% \) \(^{(1)} \). However, since the same calculation procedure has been used throughout section 2, the variations of the \( \sigma^{(j)}(\theta) \)'s with the magnitude of \( B \) should not be affected noticeably by this inaccuracy.

2.2 CALCULATION RESULTS. — Figures 2a to f show, as functions of \( B \), some of the calculated population relaxation and transfer cross-sections \(^{(8)} \). We plot on the same graph \( \sigma^{(J,m)}(J',m') \) and \( \sigma^{(J,-m)}(J',-m') \) which are equal in zero magnetic field because of time reversal invariance. Zero field is in the middle of the graph, with \( \sigma^{(J,-m)}(J',-m') \) to its left and \( \sigma^{(J,m)}(J',m') \) to its right. These figures are typical, they are qualitatively similar to the 15 other ones not printed here. They show that:

a) All \( \sigma \)'s are slowly varying functions of \( B \), with no « accident » at the location of the level crossings (arrows on figures 2e and f).

b) In the low \( B \) region, the only large transfer cross-sections (\( \sim 100 \AA^2 \)) are between sublevels belonging both to the same fine structure level (\( \Delta J = 0 \)) and they don’t involve too large a change in \( m \) (\( |\Delta m| = 1 \) or 2). Examples may be seen on figures 2b and c, counterexamples on figures 2e and f (\( J \neq J' \)) or 2d (\( \Delta m = 4 \)).

c) As one shifts towards higher \( B \) values, remark b) above progressively loses its validity. In the 50-100 kG domain, some of the \( \Delta J \neq 0 \) transfer cross-sections become as big as the largest \( \Delta J \neq 0 \) transfer cross-sections (see Fig. 2e).

d) For still higher \( B \) values, one observes a general decreasing tendency of all relaxation and transfer cross-sections: A few \( \sigma \)'s are still increasing functions of \( B \) around 100 kG (for example \( \sigma^{(2,2)}(1,1) \) of figure 2e). Calculations performed for \( B = 200 \) and 500 kG showed that even these « refractory » \( \sigma \)'s finally decrease with \( B \) like most other ones already do around 100 kG.

\( \theta \) Thus, numerical results of the present section 2 are not directly comparable to those of section 1 in which calculations were performed with higher accuracy.

\( \theta \) Let us mention that detailed balance symmetrization of the results \(^{(10)} \) is neglected here, as it was in I, since \( kT \) is much larger than the energy differences among the 8 sublevels of interest.

\( \theta \) This critical field only differs from the one introduced in equation (9) of [5] by a numerical factor of the order of unity.
where $g_f$ is some Landé factor (taken as 1.0 below), $R$ the gas constant, $T$ the temperature, $M^*$ the reduced atomic mass of the collision partners and $\sigma$ the cross-section under investigation (taken as 100 Å² below). We thus find $B_a = 87$ kG, which explains why crossing effects are not visible on figures 2e, 2f and similar: they are much too broad.

b) The $\Delta J = 0$ «pseudo-selection-rule» in low fields arises from the fact that the perturbation of Hg by the rare gas atom is spin independent (10) and that no transfer at all would take place between $^6 3D_1$ and $^6 1D_2$ if the coupling was pure $L$-$S$. Since the intermediate coupling parameter $\beta$ (equation (9)) is 0.59 instead of 0.00, the transfer between a $^6 3D_1$ and a $^6 1D_2$ sublevel is not zero, but noticeably weaker than inside a given $J$ multiplicity.

c) As $B$ increases, the Paschen-Back effect sets in, mixing together $^6 3D_1$ and $^6 1D_2$ wavefunctions. As a result, the distinction we made in § b above between $\Delta J = 0$ and $\Delta J \neq 0$ transfers disappears. Such is the physical origin of the phenomenon described in section 2.2 c).

d) The general decrease of all relaxation and transfer cross-sections for high enough values of $B$ arises from the increase of the energy difference in the imaginary exponential of (11, 5). When this exponential undergoes a sufficient number of oscillations during the collision time, the second member of (11, 5) becomes inefficient and the cross-sections tend toward zero. The magnetic field necessary for the full observation of such a behaviour is several times the critical field $B_a$ as already pointed out by reference [5] in a simpler case. For our present problem, we estimated $B_a$ to be 87 kG, in nice agreement with the observation of section 2.2 d) that most cross-sections are decreasing functions of the field in the vicinity of 100 kG and all of them for 500 kG.

3. Conclusion. — We have computed the effects of collisions against rare-gases of mercury atoms in either of two energetically very close levels $^6 1D_2$ and $^6 3D_1$ using in turn Van der Waals potential $V_{eff 1} = C_6 R^{-6}$ or potential $V_{eff 2} = C_6 R^{-6} + C_8 R^{-8}$ which includes the two first non-zero terms in the long range atom-atom interaction development. The latter calculation has been shown to be fairly successful in explaining zero field experimental results [7]. It has been extended to the case where a magnetic field up to 100 kG is present. Unfortunately, the problem of rare-gas collisional perturbation of the $(^6 3D_1, ^6 1D_2)$ multiplicity in a magnetic field suffers from having neither the angular simplicity encountered in the zero field problem, nor several simplifying features of the problem of reference [5]. (In [5], the absence of zero field splitting resulted in the independence of wavefunctions on the magnitude of $B$ and in a simple behaviour upon reversal of the sign of the interaction potential anisotropic part). Therefore, it seems dubious that an experimental test of the results of section 2 of the present paper could lead to really interesting physical conclusions in either of the two hypotheses of the experiment agreeing or disagreeing with the theory.

Acknowledgments. — We are deeply indebted to Dr J. C. Gay for very helpful discussions and suggestions.

References