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Excitation of $2\,^1S$, $2\,^1P$ and $3\,^1P$, $3\,^3P$ levels of helium in $He^+$ on $He$ collisions at a few hundreds eV

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Résumé. — On étudie expérimentalement l’excitation de l’hélium sur les niveaux $2\,^1S$, $2\,^1P$, $3\,^1P$ et $3\,^3P$, par impact d’ions $He^+$ d’une centaine d’eV. L’interprétation des résultats utilise une description moléculaire semi-diabatique du système $He^2$, et un traitement semi-classique de la collision elle-même. On a mesuré, par une technique de cohérence ion-photon, la section efficace différentielle pour l’excitation $2\,^1P$, à 100 et 150 eV (Lab), ainsi que la corrélation angulaire ion-photon à 100 eV et pour des angles de diffusion de 10,25 et 12,5°. Les résultats obtenus complètent des mesures effectuées précédemment sur le niveau $2\,^1S$ et montrent que les voies $2\,^1P$ et $2\,^1S$ sont couplées par un mécanisme secondaire de type rotationnel. L’effet d’un tel mécanisme sur les sections efficaces différentielle et totale est examiné dans le cas général où interviennent 2 états de symétrie $\Sigma^+$ et un état $\Pi^0$. La technique de cohérence ion-photon, appliquée aux photons $3\,^3P-2\,^3S$ ($\lambda = 3\,889$ Å) a permis de mesurer la section efficace différentielle pour l’excitation $3\,^3P$ à 120 et 150 eV (Lab). La polarisation des photons de cohérence à 150 eV et pour un angle de diffusion de 13,5° (Lab) montre que l’état moléculaire final conduisant au niveau $3\,^3P$ a la symétrie $\Pi^0$. Malgré le grand nombre d’états impliqués dans l’excitation $3\,^3P$ (et qui se manifestent par des effets Rosenthal dans la section efficace totale), on montre qu’un modèle extrêmement simplifié à 2 états reproduit grosso modo la section efficace différentielle, dont les caractéristiques générales sont déterminées surtout par le mécanisme primaire d’excitation. La même technique expérimentale, appliquée aux photons $3\,^1P-2\,^1S$ ($\lambda = 5\,016$ Å) a permis de mesurer la section efficace différentielle pour l’excitation $3\,^1P$ à 150 eV (Lab). L’application à l’excitation $3\,^1P$ du modèle à 3 états conduit à attribuer la symétrie $\Pi^0$ à l’état moléculaire final, ce que confirment les mesures de polarisation des photons de coincidence faires à 150 eV et aux angles de diffusion de 12, 13,5 et 15,5° (Lab).

Abstract. — The excitations of Helium on $2\,^1S$, $2\,^1P$ and $3\,^1P$, $3\,^3P$ levels in $He^+$ on $He$ collisions at low energy are investigated experimentally. The data are interpreted in the frame of a semi-diabatic description of $He^2$, using a semi-classical treatment of the collision. $2\,^1P$ differential cross sections at 100 and 150 eV (Lab) and angular ion-photon correlation functions at 100 eV (Lab) and laboratory scattering angles of 10.25 and 12.5 deg. have been measured using an ion-photon coincidence technique. These data, together with previous measurements on $2\,^3S$ excitation, show that channels $2\,^1P$ and $2\,^1S$ are coupled by a secondary rotational mechanism. The effects of such mechanisms on the differential and total cross sections of both excited channels are examined in the general case using a 3 state model including two $\Sigma^+$ states and one $\Pi^0$ state. $3\,^3P$ differential cross sections have been measured at 120 and 150 eV (Lab) by detecting in coincidence the scattered ion and the $3\,^3P$ photon ($\lambda = 3\,889$ Å). Coincidence polarization measurements at 150 eV, 13.5 deg. (Lab) show that the symmetry of the final molecular state leading to $3\,^3P$ is $\Sigma$. In spite of the large number of secondary mechanisms involved in the $3\,^3P$ excitation (which produce Rosenthal effects in the total cross section), it is shown that an extremely simplified two state calculation is able to give the general features of $3\,^3P$ differential cross section, which are mainly determined by the primary mechanism. A similar coincidence technique operating on the $3\,^1P$-$2\,^1S$ line ($\lambda = 5\,016$ Å) has been used to measure the $3\,^1P$ differential cross section at 150 eV (Lab). A calculation of the $3\,^1P$ excitation using a 3 state model is consistent with the polarization measurements at 150 eV, 12, 13.5 and 15.5 deg. (Lab) which show that the symmetry of the final molecular state is $\Pi^0$.

1. Introduction. — The theoretical treatment of the excitation of one specific level of Helium, in $He^+$ on $He$ collisions at relatively low energies (few hundreds eV), is generally made difficult, even for the lowest states, by the presence of interactions between different excited molecular states. These secondary mechanisms make impossible to treat separately each atomic level except, in the present
case, the lowest one ($2^3S$) which is well separated from the upper levels and for which a two state approximation [1, 2] gives a very satisfactory agreement with the experimental results. In the same time, the relative isolation of the $2^3S$ level simplifies also its experimental study since the excited level can be unambiguously characterized by an energy loss analysis of the scattered ions [3, 4]. As soon as the second excited level ($2^1S$) is considered, the excitation mechanisms become much more complex and it is no more possible to study this process independently from the $2p$ excitations. The $2^3P$ excitation differential cross sections have been measured at 150 eV (in the laboratory frame) by means of a scattered ion — recoil atom coincidence technique [5]. Stern et al. [6] attempted to interpret these results in a calculation where all excited $\Sigma_e$ states leading to He$^+ +$ He$^*$ ($n = 2$) were introduced. As expected, the calculated $2^3S$ differential cross section agrees well with the experiment while some discrepancy remains for the $2^1S$ excitation. Particularly, the calculated average value of the $2^1S$ cross section relatively to the $2^3S$ one is found smaller by a factor of about 4 than the experimental value. In order to get a better understanding of the $2^1S$ and more generally of the $n = 2$ excitations, the production of He($2^1P$) has been also investigated using an ion-photon coincidence method. Previous measurements of the ion-photon angular correlation at an impact energy of 150 eV (Lab) [7] have already shown that the molecular state leading to

$$\text{He}^+ + \text{He}(2^1P)$$

has the $\Pi$-symmetry. At this rather low energy the primary excitation mechanisms, i.e. the couplings between the incoming $\Sigma_e$ and $\Sigma_a$ channels and the excited molecular states, are essentially radial $\Sigma_e-\Sigma_a$ couplings; all $u$-states can be then excluded from the excitation processes. On another hand it is necessary to introduce a $\Sigma_e-\Sigma_g$ rotational coupling subsequent to the primary coupling, and leading to He($2^1P$) via a $\Pi$-state. It may be expected that this secondary mechanism will strongly modify the $\Sigma_e$-amplitude and finally the $2^1S$ population.

In the present paper, a 3 state model, involving a $\Sigma_e-\Sigma_a$ coupling at short internuclear distance and a rotational $\Sigma_e-\Pi_g$ coupling is studied. This simple model allows the correct interpretation of the $2^1S$ and $2^1P$ excitation differential cross sections as well as the angular correlation results. A similar mechanism has been proposed by Lefèbure [8] in order to explain the $3p$ excitations. This point of view is confirmed by our measurements of the coincident $3^1P-2^3S$ photon polarization which assign a $\Pi$ symmetry to the final molecular state. Thus it may be reasonably expected that a 3 state model similar to the previous one would be convenient for the $3^1P$ excitation treatment. Contrarily to the $3^1P$ level, polarization measurements [7] show that the $3^3P$ level is reached via a $\Sigma$ molecular state. In spite of the fact that many secondary mechanisms are present, in particular the $\Sigma_g-\Pi_g$ coupling which populates the $3^1P$ level, and $\Sigma_a-\Sigma_g$ couplings at large distance which produce Rosenthal effects in the total cross section [9, 10], the Stueckelberg oscillations of the $3^3P$ differential cross section are rather well reproduced in a very simple model involving the only primary $\Sigma_e-\Sigma_g$ coupling.

2. $2^1P$ and $2^3S$ excitations. — 2.1 Experimental results. — By detecting in coincidence the He$^+$ ions scattered in a given direction and the UV photons

![Experimental reduced differential cross section (DCS) $\rho_{ex}$ for $2^1P$ excitation at 100 eV-Lab, as a function of the Lab-scattering angle (upper scale) and of the reduced scattering angle : $\tau = E_{cm} \theta_{cm}$ (keV.deg).](image)

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3. $2^3P$ level is reached via a $\Sigma$ molecular state. In spite of the fact that many secondary mechanisms are present, in particular the $\Sigma_g-\Pi_g$ coupling which populates the $3^1P$ level, and $\Sigma_a-\Sigma_g$ couplings at large distance which produce Rosenthal effects in the total cross section [9, 10], the Stueckelberg oscillations of the $3^3P$ differential cross section are rather well reproduced in a very simple model involving the only primary $\Sigma_e-\Sigma_g$ coupling.

Fig. 1. — a) Experimental reduced differential cross section (DCS) $\rho_{ex}$ for $2^1P$ excitation at 100 eV-Lab, as a function of the Lab-scattering angle (upper scale) and of the reduced scattering angle : $\tau = E_{cm} \theta_{cm}$. Because of instrumental constraints, the angular range is restricted to 8-17 deg. (Lab). The reduced DCS is related to the usual DCS $\sigma$ by : $\rho = \sigma \cdot \theta_{cm} \sin \theta_{cm}$. In the present experiment $\rho_{ex}$ is simply equal, in relative value, to the ratio of the coincidence number to the total number of photons counted along the experimental run. The error bars correspond to the standard deviation of the statistical noise. The two broken lines indicate angles where polarization measurements are made (see Fig. 3). b) Calculated reduced DCS $\rho_{cal}$ for $2^1P$ excitation (i.e. for the $\Pi_g$ exit channel), in the 3 state model, without (broken line) and with (full line) the nuclear symmetry effect. c) Calculated reduced DCS $\rho_{cal}$ in the 2 state Landau-Zener model. d) Rotational coupling factors $f_{\Pi_g}$. The two branches starting from the angular threshold ($\tau_{th}$) correspond to factors $f_{\Pi_g}$ (upper branch) and $f_{\Pi_g}$ (lower branch) given in text. At the right side of point B these 2 factors have opposite signs and $\rho_{cal}$ oscillates out of phase with respect to $\rho_{cal}$. [image]
(2^1P-1^1S, λ = 584 Å) it is possible to measure:
(i) the ion-photon angular correlation, when the photon detector is moved in the collision plane,
(ii) the 2^1P excitation differential cross section, when the photons are detected perpendicularly to the collision plane. A description of the apparatus and typical angular correlation diagrams have been already given elsewhere [7, 11]. 2^1P excitation differential cross sections measured at 100 eV and 150 eV (Lab) are shown in figures 1a and 2a. Angular correlation curves obtained at 100 eV, for scattering angles of 10.25 and 12.5 degrees are given in figure 3. These correlation measurements clearly show that practically only m = ± 1 magnetic sub-levels (referred to the final direction of the molecular axis) are populated: this means that the symmetry of the molecular state which finally leads to the 2^1P levels is II. In the differential cross section, besides rapid oscillations due to the nuclear symmetry of the He^2 system, one can observe a very slight modulation, the frequency of which recalls a Stueckelberg type of oscillations. On the other hand, marked Stueckelberg oscillations are observed in the 2^1S differential cross section (see Fig. 4a). As noted above the frequency of these oscillations is in good agreement with a semi-quantal calculation taking into account only Σg states while the calculated 2^1S/2^3S ratio is about 4 times smaller than the experimental one.

2.2 Molecular Model. — At these low energies (100-150 eV) where all u-states can be ignored, the only states leading to the n = 2 excitations are four Σg states and two Πg states (Fig. 5). The Σg energies have been obtained by diagonalizing the electronic hamiltonian in the first seven excited Σg state subspace [6, 13]. The two Πg semi-diabatic states [8], represented by:

\( \text{core } \Sigma_g + 3d\pi_g \) \( ^2\Pi_g \) and \( \text{core } \Sigma_u + 2p\pi_u \) \( ^2\Pi_g \),

are correlated at infinite R to the 2^1P and 2^3P atomic levels respectively. The two cores as well as the external molecular orbitals having different symmetries
the crossing between the two \( \Pi_g \) states at about 2 atomic units (au) is quasi-diabatic. At small internuclear distance the \( ^1\Pi_g \) state (2) leading to He\(^+\) + He*(2\('P\)) is well described by the single configuration \((1s\sigma_g)^2\,3d\sigma_g\) and it is energetically very close to the \( ^3\Sigma_g \) state (1) leading adiabatically to He\(^+\) + He*(2\('S\)) and described in the same region by the configuration \((1s\sigma_g)^2\,3d\sigma_u\) (core \( ^1\Sigma_g + 3d\sigma_u \)).

Therefore in order to calculate the \( ^2\Sigma_g \) and \( ^2\Pi_g \) excitations of Helium, a simple 3 state model involving the incoming \( \Sigma_g \) state (0) and the two excited \( \Sigma_g \) (1) and \( \Pi_g \) (2) states will be used. In fact, another \( \Sigma_g \) state (3) is coupled to state (1) at the crossing point \( R_1 \approx 2.4 \) au; however this coupling occurs at a larger internuclear distance than the 0-1-2 interactions and its effect on the \( ^2\Sigma_g \) excitation is describable by a suitable branching ratio. State (0) is radially coupled to state (1) at the crossing point \( R_1 = 1.34 \) au. At the present energy, this coupling is rather weak since the \( 1s\sigma_g(2p\sigma_u)\) single configuration, which is a good description of state (0) at all distances, differs from the excited \( \Sigma_g \) configurations by two spin-orbitals [13]. The configurations corresponding to states (0) and (2) differ from each other by 2 spin-orbitals ; as the electronic angular momentum \( L_g \) is a mono-electronic operator, the rotational coupling between states (0) and (2) vanishes. On the other hand, in the region \( R < 3 \) au, where the potential energies are very close, states (1) and (2) are rotationally coupled.

2.3 SEMI-CLASSICAL THREE STATE MODEL. — More generally let us consider a 3 state problem where states (0) (incoming channel) and (1), of the same \( \Sigma_g \) symmetry, are coupled by a localized Landau-Zener interaction at their crossing point \( R_1 \). States (1) and (2) are nearly degenerated in the region \( R < R_3 \) where they are rotationally coupled (Fig. 6a). Following Ankudinov et al. [14], the time development of the collision is divided into intervals, as shown in figure 6b. As the particles approach each other \( (r < 0) \), state (0) crosses state (1) at time \( t_1 \); \( t = 0 \) corresponds to the turning point \( R_0 \); when the particles separate, the point \( R_1 \) is crossed again at time \( t_2 \). The distance \( R_3 \) is reached at time \( t_3 \), beyond which no interaction occurs between the different states. The range \( \Delta R \), where the 0-1 interaction takes place, can be estimated from [22]:

\[
\Delta R \approx \frac{\pi s \hat{R} |\Delta F|}{1/2}, \quad \text{at} \quad R = R_1
\]

where \( \hat{R} \) is the radial velocity, \( \Delta F \) is the slope of the energy difference and \( s \) is a dimensionless parameter close to unity. In the present case (\( E \geq 100 \) eV, \( |\Delta F| \approx 1.57 \) au), the value of \( \Delta R \) is approximately
Fig. 6. — a) Simplified potential energy diagram used in the 3 state model for $2^1S$ and $2^1P$ excitations: full lines: $^3S_2$ states; broken line: $^1P_1$ state. b) Same as (a), as a function of time, during a collision at given energy and impact parameter; $t = 0$ corresponds to the closest approach ($R = R_0$). c) Illustration of the different paths corresponding to partial amplitudes $A_1, A_2$ (in channel 1) and $B_1, B_2$ (in channel 2). $A_1, A_2$ are produced when the transition $0 \rightarrow 1$ takes place at time $t_1$, the rotational coupling acting then from $t_1$ to $t_2$. $A_1, B_1$ are produced when the transition $0 \rightarrow 1$ occurs at $t_3$, the rotational coupling acting from $t_3$ to $t_4$. d) The two partial amplitudes $A_1, A_2$ produced in channel 1 in the 2 state Landau-Zener model. The phase difference between $A_1$ and $A_2$ is proportional to the shaded area.

0.1 au. Then the region $\Delta R$ is crossed in a time sufficiently short to consider that the rotational coupling $1-2$ in this region has practically no effect. It is then justified to treat the crossing $R_1$ by a two state (0, 1) Landau-Zener model.

At time $t$, the wave function of the system can be expanded as:

$$\Psi = b_0(t) |0\rangle + b_1(t) |1\rangle + b_2(t) |2\rangle$$

$|0\rangle, |1\rangle, |2\rangle$ are the wave functions of states 0, 1, 2, for a nuclear separation $R(t)$; they describe single configurations, i.e., they are eigenfunctions of an approximate electronic hamiltonian:

$$H_0 = H_{e1} - V,$$

where $V$ contains electronic correlation terms.

From the time-dependent Schrödinger equation, one gets for the amplitudes $a_i$ defined as:

$$a_i = b_i \exp \left\{ \frac{i}{\hbar} \int_{t_i}^{t} E_j[R(t')] dt' \right\}, \quad i = 0, 1, 2$$

the set of coupled equations:

$$i\hbar \dot{a}_i = \sum_{j=0}^{2} a_j \left( |j\rangle \langle j| V - i\hbar \frac{\partial}{\partial t} \right) \langle j | \times$$

$$\quad \times \exp \left[ -\frac{i}{\hbar} \int_{t_i}^{t} (E_j - E_i) dt' \right].$$

As state vectors $|i\rangle$ depend on $t$ via $R$ only, the operator $\partial / \partial t$ can be replaced by:

$$\dot{R} \frac{\partial}{\partial R} + \dot{\theta} L_y$$

$\dot{R}$ is the radial nuclear velocity; $\dot{\theta}(t)$ is the polar angle of the internuclear axis $Z$ and $L_y$ the angular velocity in the collision plane. $L_y$ is the component of the electronic angular momentum on the nuclear rotation axis $y$. The radial nuclear motion as well as the electronic term $V$ couple only states of same symmetry, namely (0) and (1) in the vicinity of $R_1$. On the other hand the nuclear rotation only couples states (1)-(2) and (0)-(2), for which $\Delta A = \pm 1$, where $A$ is the component on the molecular axis $Z$ of the electronic angular momentum $^1L^1$. In the forthcoming applications the two configurations (0) and (2) will differ by two spin orbitals and the coupling 0-2 will be ignored in the present model.

Within the small time interval $(t_1, t_3)$ including

\(^1\) In the He$^-$-He collision, the electronic spin can be considered as completely decoupled and the so-called $A$-representation is valid; $L$ is here the orbital electronic momentum.
$t_1$, where the only 0-1 coupling takes place, the coupled equations for $a_0$ and $a_1$ are:

\[ i\hbar \dot{a}_{0,1} = a_{1,0} \left< 0, 1 \right| V - i\hbar \frac{\delta}{\delta R} \left| 0, 1 \right> \times \exp \left[ \pm \frac{i}{\hbar} \int_{t_1}^{t_1'} (E_1 - E_0) \, dt' \right]. \]

Then using the Landau-Zener approximation, one gets a relation between amplitudes $b_0$ and $b_1$ at times $t_1$ and $t_1'$:

\[ \begin{pmatrix} b_0(t_1') \\ b_1(t_1') \end{pmatrix} = \begin{pmatrix} g & s^* \\ -s & g \end{pmatrix} \begin{pmatrix} b_0(t_1) \\ b_1(t_1) \end{pmatrix}, \]

where $g = \exp(-\pi \nu)$, $\nu$ being the Landau-Zener parameter.

$V_{01}$ is the 0-1 interaction and $\Delta F = \left| \frac{dE_0}{dR} - \frac{dE_1}{dR} \right|$. The unitarity of the transformation implies that $\left| s \right|^2 = 1 - g^2$. In all practical cases considered further, $R_1$ is a short distance where all states are well described by single configurations. This means that the interaction $V_{01}$ is small and that the crossing $R_1$ behaves nearly diabatically ($\nu \ll 1$). In such conditions the probability $p$ that the system remains in a given state after the crossing is close to unity and:

\[ s \approx \sqrt{1 - p} \exp \left( \frac{i\pi}{4} \right), \text{ with } \left| s \right|^2 = 1 - p \ll 1. \]

As $b_2$ remains approximately constant within the interval $(t_1, t_1')$, the matrix $b$ of amplitudes $b_{0,1,2}$ transforms as:

\[ b(t_1') = G \cdot b(t_1) \]

where:

\[ G = \begin{pmatrix} g & s^* & 0 \\ -s & g & 0 \\ 0 & 0 & 1 \end{pmatrix}. \]

In the same way:

\[ b(t_2) = G \cdot b(t_2'). \]

During time intervals $[t_1, t_2]$ and $[t_2, t_3]$, only the rotational coupling between the quasi-degenerate states (1) and (2) is to be considered, then:

\[ i\hbar \dot{a}_0 = 0; \quad i\hbar \dot{a}_1 = a_s \left< 1 \right| \left. L_y \right| 2 \right> \hat{\theta}; \]

\[ i\hbar \dot{a}_2 = a_1 \left< 2 \right| \left. L_y \right| 1 \right> \hat{\theta}. \]

The two configurations 1, 2 are assumed to differ by their external molecular orbital only, respectively $n\ell\sigma_g$ and $n\ell\pi_g$, then:

\[ \frac{i}{\hbar} \left< 1 \right| \left. L_y \right| 2 \right> = \frac{i}{\hbar} \left< n\ell\sigma_g \right| \left. L_y \right| n\ell\pi_g \right>. \]

Generally a rotational coupling occurring at small distance can be considered as a constant, equal to its value at the united atom limit [15]. In all the region $R < R_3$ we shall take:

\[ \frac{i}{\hbar} \left< l \right| \left. L_y \right| l \right> \approx \frac{i}{\hbar} \sqrt{2} \left[ \left< l, 0 \right| \left. L_y \right| l, -1 \right> - \left< l, 0 \right| \left. L_y \right| l, +1 \right]. \]

Then the coupled equations are readily integrated between two times $t'$, $t''$:

\[ a_0(t'') = a_0(t') \]

\[ z(t'') = z(t'), \exp \left\{ \frac{i}{\hbar} [\theta(t'') - \theta(t')] \right\} \]

where $z = a_1 + ia_2$. Taking now into account the phase factors $\exp(iu_1)$, with:

\[ u_1 = \frac{1}{\hbar} \int_{t_1}^{t_2} E_1 \, dt \]

the amplitudes at the right side of $t_1$ are related to those at the left side of $t_2$ by:

\[ b(t_2) = J(t_2, t_1') \cdot b(t_1') \]

where:

\[ J(t_2, t_1') = \begin{pmatrix} \exp(-i u_0) & 0 & 0 \\ 0 & \exp(-i u_1) & 0 \\ 0 & 0 & \exp(-i u_2) \end{pmatrix} \cdot R(x) \]

with:

\[ R(x) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \alpha & -\sin \alpha \\ 0 & \sin \alpha & \cos \alpha \end{pmatrix} \]

and $x = \ell [\theta(t_2) - \theta(t_1)]$. 

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In the same way:

\[ b(t_3) = J(t_3^+, t_2^+).b(t_2^+) \]

\( J(t_3^+, t_2^+) \) is obtained from \( J(t_2^+, t_1^+) \) by replacing \( u_i \) by \( u_i \) and \( \alpha \) by \( \beta = \mathcal{E}[\theta(t_3) - \theta(t_2)] \).

As no coupling occurs beyond \( t_3^+ \), the final amplitudes \( b(+\infty) \) differ from \( b(t_3) \) only by phase factors \( \exp(-iK_i) \), where:

\[ K_i = \frac{1}{\hbar} \int_{t_i}^{t_{i+1}} E_i \, dt \]

and \( \alpha, \beta \) by \( \mathcal{E}[\theta(t_3) - \theta(t_2)] \).

The phase factor \( \exp(-iw_i) \) common to all amplitudes has been omitted.

In fact no interaction occurs before \( t_1^+ \), then the initial condition:

\[ b_i(-\infty) = \delta_{i0} \]

Well:

\[ b_1(t_1^+) = b_0i \]

Assuming as mentioned before that the crossing \( R_1 \) behaves nearly diabatically and neglecting \( \alpha^2 \) terms, one gets the final amplitudes into excited channels (1) and (2):

\[ b_1(+\infty) = A_1 + A_2; \quad b_2(+\infty) = B_1 + B_2 \]

Where (2):

\[ A_1 = s \cdot g \cdot \cos \beta \cdot \exp[-i(u_0 + K_1)]; \quad A_2 = -s \cdot g \cdot \cos(\alpha + \beta) \cdot \exp[-i(u_1 + K_1)]; \]

\[ B_1 = s \cdot g \cdot \sin \beta \cdot \exp[-i(u_0 + K_2)]; \quad B_2 = -s \cdot g \cdot \sin(\alpha + \beta) \cdot \exp[-i(u_1 + K_2)]. \]

The partial amplitudes \( A_{1,2} \) and \( B_{1,2} \) correspond to different possible paths starting from state (0) and leading to final states (1) and (2) (see Fig. 6c). The probability \( P_j \) for transition \( 0 \rightarrow j \) is then:

\[ P_j = |b_j(+\infty)|^2 = |f_1^j s_1 e^{-i\phi_1^j} + f_2^j s_2 e^{-i\phi_2^j}|^2 \]

\[ = (f_1^j s_1)^2 + (f_2^j s_2)^2 + 2f_1^j f_2^j s_1 s_2 \cos \chi \]

Where \( s_1, s_2 = \sqrt{p_{1,2}(1 - p_{1,2})}, \) \( p_{1,2} \) being the Landau-Zener probability \( p \) relative to paths \( A_1 \) and \( A_2 \), or \( B_1 \) and \( B_2 \), and

\[ f_j^i = \cos \left( \beta + \delta_1 \alpha - \delta_2 \frac{\pi}{2} \right) \]

\( \phi_{1,2} \) are the phases developed along paths \( A_1 \) and \( A_2 \), or \( B_1 \) and \( B_2 \) and

\[ \chi = \phi_1 - \phi_2 = \phi_1 - \phi_2 = \frac{1}{\hbar} \int_{t_i}^{t_{i+1}} (E_0 - E_1) \, dt. \]

In the special case where \( \mathcal{E} = 0 \), one gets the usual expression for the probability amplitude in a two state (0, 1) Landau-Zener-Stueckelberg model:

\[ b_1^LZ (+\infty) = A_1 + A_2 \]

Where the partial amplitudes (2):

\[ A_1 = s^* g \cdot \exp[-i(u_0 + K_1)]; \quad A_2 = -s \cdot g \cdot \exp[-i(u_1 + K_1)] \]

are related to different paths leading to state (1) (Fig. 6d), with the same phase difference \( \chi \) as before.

In all cases studied further, where \( \mathcal{E} \lesssim 3 \), the rotational coupling factors \( f_j^i \) are smoothly varying functions (compared to \( \cos \chi \)) of impact parameter \( b \). As a function of impact parameter, the probability \( P_j \) takes the following form:

\[ P_j(b) = p(b) [1 - p(b)].[(f_1(b))^2 + (f_2(b))^2 + \]

\[ + 2f_1(b)f_2(b) \cos \chi(b)] \]

Where \( p(b) = p_1(b) = p_2(b) \).

When \( \mathcal{E} = 0 \), it reduces to the usual Landau-Zener-Stueckelberg probability:

\[ P_LZ(b) = 2 p(b) [1 - p(b)].(1 + \cos \chi(b)). \]

The factor \( p(1 - p) \approx 1 - p \) slowly varies with \( b \), while the modulus of the phase difference \( \chi \) rapidly increases, and \( P_LZ \) exhibits regular Stueckelberg oscillations governed by \( \cos \chi(b) \) (Fig. 7a). As the factors \( f_j^i \) are smooth functions of \( b \), similar oscil-
Fig. 7. — a) Typical transition probability in the Landau-Zener model, as a function of the impact parameter $b$. b) Transition probabilities in channels 1 and 2, calculated in the 3 state model. The strong modulation seen on the Stueckelberg oscillations is governed by the rotational coupling factors.

Oscillations are expected in $P_j(b)$, but their relative amplitude is now modulated by the factor:

$$m_j(b) = 2 \cdot \frac{f_1 j_1}{(f_1 f_2)(f_1 f_2)}.$$

As a consequence, $P_j$ oscillates either in phase or out of phase with respect to $P_{LZ}$, according to the sign of $m_j$ (see Fig. 7b), and the oscillations are damped whenever $m_j \approx 0$. In conclusion the rapid oscillations in $P_j$ are of the Stueckelberg type and they are related to the primary excitation mechanism, whereas the slow modulation is connected to the secondary mechanism, i.e. to the rotational coupling between the two excited states (1, 2).

2.3.1 Differential cross sections. — Similar conclusions are easily derived for the differential cross sections calculated in the semi-classical approximation. The classical value of the angular momentum $l$ is related to the impact parameter by:

$$k_0 b \approx \hbar (l + \frac{1}{2}),$$

where $k_0$ is the initial wave number. The classical deflection function $\theta(l)$ for a two path configuration has two branches $\theta_{1,2}(l)$ which behave as shown in figure 8. Each specific angle, larger than the angular threshold $\theta_{th}$ is obtained for two values $l_{1,2}$ of $l$, each of them being related to one of the two different paths. The difference between the JWKB phases of the two corresponding amplitudes is :

$$\chi_{12}(\theta) = \int_{\theta_{th}}^{\theta} [l_1(\theta') - l_2(\theta')] d\theta'.$$

It is equal to the hatched area in figure 8. The scattering amplitude for excitation $0 \rightarrow j$ may then be written

$$F_j(\theta) = f_1(\theta) [S_1(\theta)]^{1/2} e^{-i\phi_1(\theta)} + f_2(\theta) [S_2(\theta)]^{1/2} e^{-i\phi_2(\theta)}$$

where:

$$S_1(\theta) = p_1(\theta) [1 - p_1(\theta)].S_1(\theta) ; p_1(\theta) = p[b_1(\theta)];$$

$$\sigma_{12}(\theta) = \frac{b_1(\theta) b_2(\theta)}{\sin \theta} d\theta$$

is the classical differential cross section calculated along path $i$. The differential cross section for $0 \rightarrow j$ excitation is :

$$\sigma_{12}(\theta) = |F_j|^2 = [f_1(\theta)]^2 S_1(\theta) + [f_2(\theta)]^2 S_2(\theta) + 2 f_1(\theta)f_2(\theta) \sqrt{S_1(\theta)S_2(\theta)} \cos \chi_{12}.\theta.$$
The difference between $S_1(\theta)$ and $S_2(\theta)$, due to the difference between $p_1(\theta)$ and $p_2(\theta)$, explains why the $\rho_{LZ}$ minima are not exactly zero. In addition, the indiscernibility of the two nuclei in the system $^4\text{He}_2$ produces a nuclear symmetry interference effect: the scattering amplitudes at center-of-mass angles $\theta$ and $\pi - \theta$ must be added and the differential cross section writes:

$$
\sigma(\theta) = |F(\theta) + F(\pi - \theta)|^2.
$$

It corresponds to a four term interference. At small angle, $|F(\theta)| \gg |F(\pi - \theta)|$ and the phase shift between $F_1(\theta)$ and $F_2(\pi - \theta)$ increases with $\theta$ more rapidly than $\chi_{12}(\theta)$; then the nuclear symmetry interference appears in $\sigma$ as an undulation of small amplitude and rather high frequency, superimposed on the modulated Stueckelberg oscillations.

The actual calculation of scattering amplitudes and differential cross sections has been carried out using the semi-quantal method [16] which is more precise than the semi-classical one, particularly in the angular threshold region. In this approximation the scattering amplitude is expressed as a sum of partial wave amplitudes, limited to even values of $l$ because of the nuclear symmetry:

$$
F_j(\theta) + F_j(\pi - \theta) = \frac{1}{2i \sqrt{k_0 k_j}} \times 
\sum_{l_{even} = 0}^{l_{max}} (2l + 1) G_j(l) P_l(\cos \theta)
$$

where $k_0, k_j$ are channel 0, j wave numbers and:

$$
G_j(l) = \sqrt{p(l)} [1 - p(l)] \times 
[ f_1(l) e^{-i\phi_1(l)} + f_2(l) e^{-i\phi_2(l)} ]
$$

$p(l)$ and $f_1(l), f_2(l)$ are simply obtained from the above semi-classical expressions by replacing $b$ by $(l + \frac{1}{2})/k_0$; $\phi(l)$ is the JWKB phase shift for partial wave $l$, evaluated along path $i$. It is assumed that the partial wave amplitude vanishes when $R_i$ lies in the classically forbidden region, i.e. when:

$$
l > l_{max} = R_i \left[ k_0^2 - \frac{2\mu}{R} E_0(R_i) \right]^{1/2}
$$

where $\mu$ is the reduced mass of the collision partners.

2.3.2 Total cross sections. — The total cross section for excitation $0 \to j$, at an impact energy $E$ is expressed as:

$$
Q_j(E) = 2\pi \int_0^{b_{max}} db.b.P_j(E, b)
$$

$$
= 2\pi \int_0^{b_{max}} db.b[p(1 - p)] \times 
[ (f_1)^2 + (f_2)^2 + 2f_1 f_2 \cos \chi ].
$$

The term containing $\cos \chi$ rapidly oscillates as a function of $b$ and its contribution to the total cross section vanishes. The squared rotational coupling factors $(f_i)^2$ represent the probability of transition $1 \to j$, due to the action of rotational coupling along path $i$; they may be also written:

$$
(f_i)^2 = \sin^2 \left( \frac{\Delta \theta_i + \delta_{1j} - \pi}{2} \right)
$$

where the quantities $\Delta \theta_1 = \theta(t_3) - \theta(t_1)$ and $\Delta \theta_2 = \theta(t_3) - \theta(t_2)$ are the rotation angles of the internuclear axis during the action of rotational coupling respectively along paths 1 and 2. The general behaviour of these functions of $E$ and $b$ is shown in figure 9a. The largest impact parameters ($b \approx b_{max}$) contribute predominantly to the total cross section. For energies largely above the threshold, these impact parameters can be considered as large in as much as
they correspond to small deflection angles (θ ≈ 10°). The trajectory is then practically a straight line. This corresponds to the following asymptotic forms:

\[ \Delta \theta_{1,2} \approx \arctg \left( \sqrt{\frac{R}{b}} \right)^2 - 1 \]

\[ \Delta \theta_{2} \approx \arctg \left( \sqrt{\frac{R}{b}} \right)^2 - 1 \]

On the other hand, when b tends to zero, \( \Delta \theta_{1,2} \to 0 \); \( \Delta \theta_{2} \) is a monotonic increasing function of b, whereas \( \Delta \theta_{0} \) has a maximum \( \Delta \theta_{0}(E) \), for a value \( b_{0}(E) \) of b. Then in a rather large interval \( \Delta b \) of impact parameter around \( b_{0} \), \( \Delta \theta_{2} \) keeps a stationary value, as well as the probabilities \((\ell \ell')_2^2\). As a consequence the total cross section \( Q \) will exhibit oscillations, around the half Landau-Zener total cross section, i.e.:

\[ \frac{1}{2} \cdot Q_{LZ} = 2 \pi \int_{0}^{b_{\text{max}}} p(1 - p) b \, db \]

(see Fig. 9b). This oscillating behaviour, entirely due to the secondary rotational coupling 1-2, has been confirmed by the calculation in several practical cases. Oscillations clearly appear in \( Q \) when the stationary phase method is applied to the integration over impact parameter:

\[ Q_{1,2}(E) \approx \frac{Q_{LZ}}{2} \pm b_{0}(E), p(b_{0}(E)) \cdot \left[ 1 - p(b_{0}, E) \right] \times \]

\[ \times \left[ \frac{2 \pi}{\ell} \left( \frac{\partial^2 \theta_{2}}{\partial b^2} \right)_{b_{0}} \right]^{1/2} \cos \left[ 2 \ell \cdot \Delta \theta_{0}(E) \right] \]

The extrema of \( Q \) are obtained for values of E such that:

\[ 2 \ell \cdot \Delta \theta_{0}(E) = k \pi \quad (k = 0, 1, 2, \ldots) \]

and the two cross sections are out of phase. As \( \Delta \theta_{0} < \pi \), the total number of oscillations is smaller than \( \ell \). Since \( b_{0} \) and \( \Delta b \) tend to zero as \( E \to \infty \), it may be expected that these oscillations be damped, and more and more spaced toward high energies.

### 2.4 APPLICATION TO 2 3S AND 2 1P EXCITATIONS.

The 3 state model has been applied to the special case of 2 3S and 2 1P excitations using, for \( E_{0} \), a diabatic potential obtained by fitting, out of the crossing region, an analytical form to the adiabatic potentials of Bardsley [17]:

\[ E_{0}(R) = 4.774 \cdot 10^{-0.8268} \exp(-0.949 \cdot R) \text{ au} \]

In the region of interest the potential for state (2) is taken identical to that of state (1) (first excited \( \Sigma^+ \) state). The same procedure as that used for \( E_{0}(R) \) has been applied to obtain \( E_{1}(R) \) from the adiabatic potentials of Stern et al. [18]:

\[ E_{1}(R) = E_{2}(R) = E_{0}(R) + 0.1(A^2 - 2A) + Q \]

where:

\[ A = (R/3.2)^{0.147} \exp[0.804(3.2 - R)] \text{ au} \]

\[ Q = E_{1}(\infty) - E_{0}(\infty) = 0.757 \text{ 4 au} \]

The constant interaction between states (0) and (1) has been evaluated from the energy splitting between the two corresponding adiabatic states, at \( R_{1} = 1.34 \text{ au} [17] \):

\[ V_{01} \approx 1.13 \times 10^{-2} \text{ au} \]

As said before the rotational coupling has been assumed to be a constant in the interval \( R \leq R_{3} \), and to vanish for \( R > R_{3} \). The value of the rotational coupling matrix element at the united atom limit is:

\[ \ell \cdot \frac{\langle \ell \cdot \ell | E_{0} \cdot E_{0} | \ell \cdot \ell \rangle}{R_{3}^2} \approx 0.02 \text{ au} \]

which gives the value \( R_{3} = 2.0 \text{ au at 100 eV (Lab)} \) and 1.48 au at 150 eV (Lab).

Differential cross sections for 2 3S excitation at 150 eV (Lab) (Fig. 4b) and for 2 1P excitation at 100 eV (Fig. 1b) and 150 eV (Fig. 2b) have been calculated using the semi-quantal approximation. Since the comparison to experimental values (Fig. 4a, 1a, 2a) is made only at relatively small angles, a straight line trajectory has been used in the calculation of the rotational coupling factors \( \ell \cdot \ell \text{ (Fig. 4d, 1d, 2d).} \)

It is seen that the 2 state calculation, corresponding to \( \ell = 0 \) (Fig. 4c) clearly disagrees with the measured 2 3S differential cross section. The agreement is greatly improved by the introduction of \( \Pi_{3} \) state (3) which gives rise to an inversion of Stueckelberg oscillations, at point A of figure 4 where the factor \( f_{1} \) vanishes. At the same time the calculated differential cross section for channel (2), i.e. for 2 1P excitation is seen to be as large as the 2 3S differential cross section, which shows the very important effect of the secondary rotational coupling; moreover it is in good agreement with the 2 1P experimental cross sections at 100 and 150 eV. It may be also noticed that the present 3 state model necessarily agrees with the polarization coincidence measurement on the 2 1P excitation since the 2 1P level is populated only via a \( \Pi \) state (Fig. 3).

In as much as rather large scattering angles (or
small impact parameters) may contribute significantly to the total cross sections, the rotational coupling factors have been re-evaluated by calculating the partial deflections $\Delta \theta_{1,2}$ on classical trajectories determined in the interval $(R_1, R_3)$ by potential $E_1(R)$. The calculated $2^3P$ total cross section is shown in figure 10a, as a function of energy (in the laboratory frame). As expected from the value $\ell = \sqrt{3}$ one observes only one and a half oscillation around half the value of the Landau-Zener total cross section $Q_{LZ}$, which gives rise to a peak at 70 eV, whereas the maximum of $Q_{LZ}$ lies at about 100 eV. The experimental values of the total cross section have been obtained by detecting on a channel electron multiplier all the UV photons emitted from the collision volume. In the low energy range ($E \leq 100$ eV), where the $n = 2$ levels are preferentially excited, it corresponds essentially to the $2^3P$ excitation, and it agrees rather well with the calculated cross section, better than it does with $Q_{LZ}$. On the other hand upper levels, specially $n = 3$, certainly contribute to the measured cross section at higher energy and this may explain why the experimental values decrease with energy slower than the calculated ones.

3. $3^3P$ and $3^1P$ excitations. — 3.1 Experimental results. — Reduced (1) differential cross sections observed at about 1200 eV.degrees, and in the range 1 200 eV.deg $< \tau < 1 800$ eV.deg. (where $\tau = E_{CM} \theta_{CM}$), the differential cross sections exhibit rapid undulations due to nuclear symmetry. At 200 eV, the $\tau$-range is wider (1 300-3 100 eV.deg.) and three Stueckelberg oscillations are clearly visible. Polarization measurements have been already made at 150 eV, 13.5 deg. [7] by detecting the coincident photons perpendicularly to a selected collision plane, through the interference filter and a linear polarizer. It was concluded that practically the only $m = 0$ magnetic sublevel of He($3^1P$), referred to the final direction of the molecular axis, was populated. This means that the symmetry of the molecular state which finally leads to He($3^1P$) is $\Sigma$. The total $3^1P$ excitation cross section has been obtained as a function of the collision energy from the total number of $3^1P-2^3S$ photons calibrated with respect to the incident ionic current.

![Fig. 10. — a) Total cross section for $2^1P$ excitation, as a function of impact energy. Full line : experiment (above 100 eV, upper levels are expected to contribute to the measured values). Broken line : 3 state model calculation. Dotted line : half Landau-Zener cross section. b) Same as (a), for $3^1P$ excitation.](image1)

![Fig. 11. — Reduced DCS for $3^3P$ excitation, at 120, 150 and 200 eV (Lab) Full line : experiment; the error bars are the standard deviation of the statistical noise. Broken line : 2 state calculation. (The experimental data are given in the same arbitrary unit for all energies.)](image2)
It is compared in figure 12 to the previous measurements of Dworetsky et al. [20]. The threshold located at 63 eV (Lab) is characteristic of the primary mechanism for \( n = 3 \) excitations, whereas the oscillating structure is generally interpreted as an interference due to long range secondary couplings [10].

Similar coincidence techniques, operating on the \( 3'P-2'S \) line (\( \lambda = 5016 \) Å) have been applied to study the \( 3'P \) excitation at 150 eV. Two Stueckelberg oscillations, accompanied by nuclear symmetry oscillations, are seen on the measured reduced differential cross section (Fig. 13a). Polarization measurements at scattering angles 12, 13.5 and 15.5 degrees (Lab) are shown in figure 14; here the coincidence number, calibrated with respect to the total number of scattered ions counted during the experimental run, is plotted as a function of the polarizer direction. A maximum value is obtained when the polarizer axis is perpendicular to the final direction of the molecular axis. If that direction is taken as a quantization axis, each particular magnetic sublevel corresponds to a definite polarization of the emitted light, and also to a definite \( A \)-symmetry of the final molecular state (\( A = 1 \) for \( m = \pm 1 \), \( A = 0 \) for \( m = 0 \)). Taking into account that the scattered ions are detected within an azimuthal angular range of \( \pm 30 \) deg., as well as the depolarization effect due to the mirror, the population of \( m = \pm 1 \) sublevels is estimated to be 7, 6 and 4 times larger than that of \( m = 0 \), respectively at scattering angles 12, 13.5 and 15.5 deg. This shows that \( 3'P \) excitation essentially proceeds via a final molecular state of

Fig. 12. — Total cross section for \( 3'P \) excitation. Broken line : ref. [20]. Full line : present measurements.

Fig. 13. — Same as figure 1, for \( 3'P \) excitation at 150 eV (Lab). 
(a) Experimental reduced DCS. The arrows correspond to polarization measurements (see Fig. 14). 
(b) Reduced DCS \( \rho_{\text{ex}} \) calculated in the 3 state model. 
(c) Reduced DCS \( \rho_{LZ} \) calculated in the 2 state model. 
(d) Rotational coupling factors \( f_\mu \), i.e. : \( f_1^2 \) (lower branch); \( f_2^2 \) (upper branch); between points B and B', \( \rho_{LZ} \) is out of phase with respect to \( \rho_{LZ} \).

Fig. 14. — Polarization diagrams for \( 3'P \) excitation at 150 eV (Lab). 
\( 3'P-2'S \) photons are detected through a linear polarizer, in coincidence with ions scattered at 12, 13.5 and 15 deg. (Lab). The coincidence number is plotted as a function of the angle between the incident direction and the polarizer axis. The error bars give the standard deviation of the counting statistics. The minimum of intensity observed in the final molecular axis direction corresponds to a preferential excitation of magnetic sublevels \( m = \pm 1 \).
II-symmetry. As it is for most of \( n = 3 \) excitations \[20\], the measured \( ^3 \Sigma \) total cross section (see Fig. 10b) shows marked oscillations, from a threshold of 63 eV up to 300 eV. The phase of these oscillations has a linear dependence with respect to the inverse relative velocity in the outcoming channel. This suggests the presence of a crossing located at large distance, between two excited states, with an associated area \([9, 10]\) \( \langle \Delta E, \Delta R \rangle \) of about 0.41 au.

3.2 DISCUSSION. — At low energy, only four \( \Sigma \) states are \textit{a priori} involved in the \( n = 3 \) primary excitation mechanism: the incoming state (0) and three excited \( \Sigma \) states, with a \( ^1 \Sigma_\text{g} \) core and external molecular orbitals \( 3s\sigma_\text{g}, 4d\sigma_\text{g} \) and \( 5g\sigma_\text{g} \), in the semi-diabatic description of Lefèbure. It may be noticed that the outer crossing of the two last states at \( R = 16 \) au (see Fig. 15), which also appears in adiabatic potential calculations \([10, 17]\), has been made responsible for the anticoincident oscillations of \( ^3 \Sigma \) and \( ^3 \Sigma \) total cross sections. Taking into account the II-symmetry of the final molecular state leading to \( \text{He}(^3 \Pi) \), one has to find some \( \Pi \) states coupled to the former excited \( \Sigma \) states. Only two \( \Pi \) states of core \( ^1 \Sigma_\text{g} \) are susceptible to be submitted to an efficient rotational coupling at short internuclear distance: those for which the external molecular orbitals are \( 4d\pi_\text{g} \) and \( 5g\pi_\text{g} \), coupled respectively to \( 4d\sigma_\text{g} \) and \( 5g\sigma_\text{g} \). (As all these excited states have the same \( ^1 \Sigma_\text{g} \) core, they will be noted further only by means of the external molecular orbital.) Finally 5 states are involved in the \( ^3 \Pi \) excitation which proceeds through the following mechanisms: \([8]\) (i) \( 4d\sigma_\text{g} \) and \( 5g\sigma_\text{g} \) states are populated by radial coupling with the incoming channel (0), at short distance \((R \approx 1.30 \) au\), (ii) then secondary rotational couplings feed \( 4d\pi_\text{g} \) and \( 5g\pi_\text{g} \) states, (iii) the amplitudes in channels \( 4d\pi_\text{g} \) and \( 5g\pi_\text{g} \) are mixed by a secondary radial coupling at large distance. The oscillations in the \( ^3 \Pi \) total cross section are clearly a consequence of the latter Rosenthal mechanism, since the calculated associated area between the two \( \Pi \) potential curves (from \( R = 1.30 \) au to the outer crossing point located at 18 au) is 0.38 au, in good agreement with the experimental value (0.41 au). As the \( 4d\sigma_\text{g}-4d\pi_\text{g} \) coupling \((\xi = \sqrt{3} \), \( R < 2 \) au\) is expected to be less efficient than the \( 5g\sigma_\text{g}-5g\pi_\text{g} \) coupling \((\xi = \sqrt{10} \), \( R < 5.2 \) au\), the \( ^3 \Pi \) cross sections may be reasonably calculated using the 3 state model formerly applied to \( ^3 \Pi \), \( ^3 \Sigma \) excitations, involving here the incoming state (0), plus states \( 5g\sigma_\text{g}(1) \) and \( 5g\pi_\text{g}(2) \). Potentials (1) and (2) are taken identical to those of the \( ^3 \Sigma \) calculation, except for the value of \( Q \) (0.85 au instead of 0.757 4 au), in order to get the correct \( ^3 \Pi \) dissociation limit. The reduced differential cross section has been calculated at 150 eV (Lab) using the semi-quantal method. It is compared to the experimental data and to the simple 2 state Landau-Zener calculation, in figure 13. It may be noticed that, within the angular range between points B and B', where the rotational coupling factors have opposite signs (see Fig. 13d), the 3 state differential cross section exhibits Stueckelberg oscillations which are out of phase with respect to those of the Landau-Zener cross section, in rather good agreement with the experiment. The calculated total cross section oscillates about three times (as expected from \( \xi \approx 3.16 \)) around half the Landau-Zener cross section (Fig. 10b). However it is seen that the present 3 state calculation is unable to reproduce the actual oscillatory structure of the experimental cross section, the frequency of which is rather a characteristic of the Rosenthal mechanism, as mentioned before. In fact a 5 state calculation, including all rotational and radial couplings would be necessary to correctly reproduce the total cross section, at least below 300 eV (Lab).

It is known from the polarization measurements that the final molecular state leading to \( ^3 \Pi \) excitation has the \( \Sigma \) symmetry. This makes the \( ^3 \Pi \) excitation mechanism much more complex than for the \( ^3 \Sigma \) excitation since a supplementary primary coupling, involving the \( 3s\sigma_\text{g} \) state and many other secondary \( ^1 \Sigma_\text{g}, \Sigma_\text{g} \) radial couplings at large distance need to be added to the former 5 state model. The great variety of these secondary mechanisms could explain the complex oscillatory structure seen in the \( ^3 \Pi \) total cross section, as well as some anomalies in the \( ^3 \Sigma \)

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![Fig. 15 — Potential curves for semi-diabatic states dissociating into : He\(^+\) + He\(^+\) \((n = 3)\). All these states have the configuration : core \(^1 \Sigma_\text{g}, \Sigma_\text{g} \), \(n\Sigma_\text{g}\) or \(n\Sigma_\text{g}\), respectively for \(^2 \Sigma_\text{g}\) states (full line) and \(^2 \Pi_\text{g}\) states (broken line). The incoming state \(3s\sigma_\text{g}(2p\sigma_\text{g})^2\) is also given. The open circles show the locations of the main secondary radial couplings. States labelled \(^0, 1, 2\) are those used in the 3 state model calculation. The energy splittings between \( n = 3 \) levels have been enlarged. A logarithmic scale is used for \( R < 10 \) au, a linear scale for \( R > 10 \) au.](image-url)
and $3^3S$ total cross section below 130 eV [10]. However the angular threshold, the Stueckelberg frequency and the nuclear symmetry frequency in the differential cross section are essentially determined by the primary excitation mechanism, i.e. radial couplings between the $2^2\Sigma_g^+$ incoming state and states $3\sigma_g$, $4d\sigma_g$, $5g\sigma_g$. This point is confirmed by the fact that an extremely simplified model, including only 2 states — (0) and $4d\sigma_g$ — is able to reproduce the general behaviour of the differential cross section (see Fig. 11). $\Sigma-\Pi$ couplings occurring at small distance and $\Sigma-\Sigma$ couplings at large distance modulate in a complex energy-dependent way (*) this simple Landau-Zener differential cross section.

4. Conclusion. — In the theoretical interpretation of the excitation of He on one specific level (or magnetic sublevel), in $He^+$ on He collisions at low energy, secondary mechanisms, which make interfere within each specific inelastic channel the amplitudes produced at small internuclear distance, need to be considered. From the experimental point of view the first evidence for such phenomena has been the observation of marked oscillations of the total cross sections, for most of the $n \geq 3$ levels. These interference effects (which appear in the total cross section, in spite of the integration over all impact parameters) are generally due, as shown by Rosenthal [10], to radial couplings at large internuclear distance between excited $\Sigma_g^+$ states.

However this type of secondary mechanism cannot explain our polarization (or angular correlation) measurements on $2^1P$ and $3^1P$ levels which clearly show that the symmetry of the final molecular state is $\Pi$. At low energy (few hundreds of eV) the incoming $2^2\Sigma_g^+$ state is only coupled to excited $2^2\Sigma_g^+$ states: therefore secondary rotational couplings $\Sigma-\Pi$ have to be introduced to explain the experimental results on $2^1P$ and $3^1P$ excitations. All $2^2\Sigma_g^+$ excited states, susceptible to interact with the incoming $2^2\Sigma_g^+$ state, have the semi-diabatic representation: core $^1\Sigma_g^+$, $nl\pi_g$. These molecular states are semi-diabatically correlated (i.e. in considering the outer molecular orbital as diabatic, as it is in $H_2^+$) at infinite $R$ to the $n_s$, $L_s$ level of He, with the rules: $l = 2$. $L_s$, $n = n_s + L_s$. It is seen that two different $\Pi_g$ states issued from the same $n$ level are correlated to excited levels of He with different $n_s$. Such states have a negligible mutual interaction since the numbers of nodes in their radial wavefunctions are different by 2 at least. As a consequence the excitation of He on a specific $n_s$ level implies only those semi-diabatic states which correlate at infinite $R$ with this $n_s$ level. For a given value of $n_s$, the possible values of $L_s$ are: $1$, $2$, ..., $n_s - 1$; each atomic state $(n_s$, $L_s)$ is correlated to $\Pi_g$ states $(nl\pi_g)$ with $l = 2, 4, \ldots, 2n_s - 2$ and $n = n_s + 1, n_s + 2, \ldots, 2n_s - 1$.

The corresponding rotational coupling term at the united atom limit: $\epsilon = \sqrt{[(l + 1)/2]}$ varies from $\sqrt{3}$ up to $[(n_s - 1)(2n_s - 1)]^{1/2}$. As $n_s$ increases the number of $\Pi_g$ states concerned with the rotational coupling becomes larger and the maximum value of $\epsilon$ increases (practically as $n_s$). Moreover the range of internuclear distance where states $\Sigma_g$ and $\Pi_g$ are quasi-degenerated becomes wider, because the size of the outer molecular orbital is enlarged and its energy becomes less sensible to $R$ as well as to the direction of the molecular axis. For $n_s = 2$ only one $\Pi_g$ state is involved; the effective range of the rotational coupling is rather short ($R_e \approx 2$ au) and $\epsilon$ gets its lowest possible value: $\sqrt{3}$. This is yet sufficient to change very substantially the phases and moduli of the inelastic amplitudes since half the amplitude primarily scattered into the $2^1S$ channel is brought into the $2^1P$ channel via the $\Pi_g$ state. For upper levels ($n_s \geq 3$) the rotational coupling is strong enough to make the total cross sections oscillate. In the same time a larger number of $\Sigma_g$ and $\Pi_g$ states has to be considered, which gives rise to other oscillations in the total cross sections, coming from radial couplings at large distance. Radial and rotational secondary mechanisms will also strongly modify the differential cross sections, in magnitude, angular threshold, phase of Stueckelberg or nuclear symmetry oscillations.

As we have seen, the excitation mechanisms become very complex as soon as $n \geq 3$ levels are considered.

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(*) The effect on the differential cross section of the long range couplings has been already studied for $4^1\Sigma_g^+$ excitations [21].
It would be useful to extend the coincidence-plus-polarization measurements to other excited levels (e.g. \(^3\)P\(_{1,3}\)), in order to somewhat clarify the situation by selecting the most important states and couplings. Then a more precise theoretical treatment would be possible. It should be finally pointed out that the greater problems are not concerned with potentials and primary couplings at short distance but rather with couplings between excited states which occur in a very wide range of internuclear distances and involve a number of states which fastly increases as higher and higher excited levels are considered.

References