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An adjustment of the Ne*2(3P0,2-1S0) potentials

to thermal-energy scattering data

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Résumé. — On présente ici une recherche semi-empirique des potentiels du dimère Ne*2, pour les états se dissociant en Ne(3P0,2) + Ne(1S0). Partant des potentiels ab initio calculés par Cohen et Schneider, on a déterminé une modification — aussi faible que possible et restreinte au seul domaine des distances intermédiaires (4-10 u.a.) — conduisant à un accord amélioré de la théorie et des expériences effectuées aux énergies thermiques. La modification proposée n’affecte que l’état 303A3+u. Il en résulte, après diagonalisation de l’interaction spin-orbite, des diminutions homogènes des potentiels 0-u , 1u(3P2) et 0-u(3P0). La bosse présente sur les deux premiers se trouve ainsi abaissée (de 108 à 21 meV), ce qui donne un accord satisfaisant avec les expériences effectuées sur la collision Ne(3P2)-Ne(1S0), particulièrement pour ce qui est de l’effet arc-en-ciel. L’élargissement imposé au puits 1u se trouve confirmé par le spectre d’émission de l’excimère. Aux énergies inférieures à 80 meV, la collision Ne(3P0)-Ne(1S0) est considérée comme purement élastique. Aux énergies supérieures, l’intervention de couplages dynamiques provoque une perturbation de la section efficace élastique, et l’apparition du processus superélastique: 3P0~1,2. On interprète ces deux effets en utilisant un modèle à deux états.

Abstract. — A semi-quantal interpretation of the Ne*2 potentials, for states dissociating into

Ne(2p5 3s, 3P0,2) + Ne(2p6, 1S0)

is presented. Starting from the ab initio potentials calculated by Cohen and Schneider, one determines a modification — as small as possible and confined to the intermediate distance range (4-10 a.u.) — yielding a better agreement between theory and experiment in the thermal energy range. The proposed modification affects only the 303A3+u state. After the diagonalization of the spin-orbit interaction, it results in consistent diminutions of the 0-u , 1u(3P2) and 0-u(3P0) potentials. The hump of the two former states is lowered (21 meV instead of 108 meV) which gives good agreement with experiments on the Ne(3P2)-Ne(1S0) collision, especially for the resulting rainbow effect. The widening imposed on the 1u-well is confirmed by the excimer emission spectra. At energies below 80 meV, the Ne(3P0) + Ne(1S0) collision is considered as purely elastic. Above this energy, dynamical couplings induce a perturbation of the elastic differential cross section and the 3P0~1,2 superelastic process. These latter effects are interpreted by using a simplified 2-state model.

1. Introduction. — It is well known that, by exciting a high-pressure rare gas, e.g. by means of fast electrons, it is possible to produce a significant amount of long-living excited dimers (excimers). Such relatively long lifetimes are related to the presence of deep wells (few 0.1 eV) in some of the potential curves of the excited molecular states. As the electronic ground state has a very shallow well (few meV), shifted toward larger internuclear distances, it is even possible to create a population inversion, inducing a laser effect in the ultra-violet range [1]. To get a complete understanding of the excimer population mechanisms, and the related relaxation processes, it is necessary to know the molecular properties of the diatomic system (potential energies, transition moments, etc.), as well as the characteristics of atom-atom collisions at low energy (direct and exchange elastic collisions, inelastic processes). From a theoretical point of view, the calculation of the potential energies — even for the lowest (e.g. metastable) states — is more difficult than for the alkali-rare gas systems, because an excited
rare gas dimer is not a one active electron system, but rather a one electron plus one hole system. Moreover, because of the u-g symmetry of the dimer, the number of molecular states dissociating into a given separated atom state, is increased, which makes more complex the interpretation of the experimental results.

Several experimental studies have been devoted to metastable neon on ground state neon collisions. The first one has been performed by Spiess et al. [2] at moderate energies (7-35 eV). In this energy range, where the collision energy can be well defined, a detailed investigation of the relatively small internuclear distance range (3-5 a.u.) can be achieved. In this region, avoided crossings begin to perturb strongly the potential curves and many inelastic processes, induced by radial or rotational couplings, become important. Up to now they have not been studied. At these rather large energies, particular effects (e.g. rainbow effects), which may be expected from the potential well and the hump of the 1_u and 1_g potentials (at about 3.5 a.u. and 5.8 a.u. respectively), cannot be studied in detail. More recently the Ne^2+ system has been investigated in the thermal energy range (typically 30-150 meV). The observation of UV absorption-emission spectra of dimers excited in a cooled discharge, is a very direct method for analysing the excited potential well [3-4], whilst the collision technique at thermal energies is much more sensitive to potential values comparable to the collision energy, i.e. in the present case, to the shape of the hump. The resonance absorption spectroscopy has been applied to study the reactions involving excited neon atoms, ground state atoms and electrons, in a pure afterglow plasma [5]. Quenching rate coefficients for the 3P^0,1,2 resonance absorption spectroscopy has been applied in a cell at room temperature (average energy : 25 meV). The transient response to a suddenly switched on (off) monochromatic laser beam, has shown the building up with time of the background contribution to the spectral profile, the shape and evolution of which give directly the so-called « collision-kernel » [7]. Moreover, in a recent experiment with 20Ne and 22Ne, two different « collision-kernels » have been observed, corresponding to direct and exchange elastic processes [8].

A differential analysis (in angle and energy) of the Ne^*-Ne collision at thermal energies can be performed by means of crossed beam methods. Actually the equality of the mass of the partners makes them rather difficult. Up to now, the method providing the highest angular and energetic resolutions, consists in crossing two supersonic beams of neon, metastable atoms being produced within one of them by a collinear electronic bombardment [9-10]. We have developed a simpler, but less performing technique, using two effusive beams of neon : by means of a synchronous chopping of these beams, combined with a time of flight measurement, it is possible to select the relative velocity [11]. Moreover, by detecting metastable atoms scattered in the direction perpendicular to the initial velocity plane, where neither elastic nor endothermic processes can be detected, we have observed the exothermic fine structure transition :

\[
\text{Ne}^3\text{P}_0 + \text{Ne}^4\text{S}_0 \rightarrow \text{Ne}^2\text{P}_2 + \text{Ne}^4\text{S}_0 + 98 \text{ meV} \quad [12].
\]

Few ab initio calculations have been performed on the Ne^2+ system. To our knowledge, none of them takes exactly into account the spin-orbit interaction. However such an exact treatment is not needed in the present case. The semi-empirical method suggested by Cohen and Schneider [13] gives a good enough estimation for this term : in a first step, ab initio electronic energies are calculated by a configuration interaction method, ignoring the spin-orbit hamiltonian H_so (A-basis); then, assuming the spin-orbit coupling constant independent of the internuclear distance R, adiabatic potentials (\(\Omega\)-basis) are calculated by diagonalizing the spin-orbit interaction matrix primarily written in the A-basis. Finally, to each magnetic sublevel \(M_J\) of a level \(1,3\Sigma^\pm\) are associated two \(\Omega\)-states (\(\Omega = |M_J|\) respectively of u- and g-symmetry. Other C.I. calculations of A-potentials performed by Iwata [14] are in rather good agreement with the previous ones, except a deeper well and a lower hump for the \(1,3\Sigma^\pm\) states. All these calculations using limited configuration interactions are expected to be correct only at rather small internuclear distances (\(< 5-6\) a.u.). At large distance, Cohen and Schneider fit their A-potentials to the standard asymptotic forms \(C_6/R^6\), or \(C_3/R^3 + C_6/R^6\), if the optical transition from the ground state is forbidden or allowed respectively). Such a fitting is easily made for repulsive potentials, but becomes more dubious for attractive potentials (e.g. \(1,3\Sigma^+\)). The shape of the potential humps which appear on some potentials at intermediate distances (\(R \sim 5-6\) a.u.) is still a matter of controversy. It may be noticed that the diagonalization of \(H_{so}\) makes \(1,3\Sigma^\pm\) participate only in the states 0_u and 1_u which dissociate into Ne^4S^0 + Ne^3P^0. Berman and Kaldor [15] have proposed another interesting approach in their A-potential calculation : as the ground state Ne^2+ molecule has a closed shell structure, the wavefunction of which is well known (and reasonably well represented by a HF function), these authors calculate directly the excitation energies by the random phase approximation, using a minimal MO-basis set which gives a good representation of the excited state in a large domain of distance. For all the states involved here and for \(R < 8\) a.u., their results are close to those of Cohen and Schneider. Another semi-empirical method for the calculation of rare gas dimer potentials, has been recently proposed by Vallée et al. [16]. The A-energies are considered as sums of three contributions :
(i) multipole interaction prevailing at large distance,  
(ii) e-Ne exchange term, (iii) Ne-Ne* core interaction. The last two terms contain some parameters, which are adjusted on the available spectroscopic data. In the intermediate distance range (which is here of the greatest interest), this simple method, when applied to Ne*, has not yet given very good results, but it is probably perfectible. The above decomposition of the potential energy recalls in some ways pseudo-potential and model-potential methods. Such methods have been successfully applied to Ar* [17]; they probably will be applied to Ne* in the near future.

Very few calculations have been devoted to the Ne*-Ne collision at thermal energies. The only complete ones have been performed by Cohen and Schneider [18] for the direct and exchange elastic scattering, and by Cohen et al. [19] for the inelastic processes. Some discrepancies appear between these calculations and experimental results: (i) the calculated $0_2^-$($3P_2$) and $1_1^1$($3P_2$) potentials exhibit at $R \approx 5$ a.u. a hump which is much higher (108 meV) than that given by experiment (20-30 meV); (ii) the behaviour of the calculated elastic differential cross section, particularly the location (and even the existence) of rainbow effects and the phase of u-g symmetry oscillations, is sometimes far from the experimental data; (iii) the effects of the calculated couplings between channels Ne($3P_o$) + Ne($1S_o$) and Ne($3P_{1,2}$) + Ne($1S_o$) are smaller at thermal energies than the observed ones. These discrepancies are certainly not imputable to the treatment of the collision itself, but rather to calculated potentials and couplings, or at least, to some of them.

The aim of the present paper is to determine the slightest possible modification (located within the largest uncertainty region : $4 \leq R \leq 8$ a.u.) of Cohen-Schneider's potentials, to account for the major part of the available experimental data at thermal energies: purely elastic scattering for the incoming channel Ne($3P_o$) + Ne($1S_o$) elastic scattering and fine structure transition for the incoming channel Ne($3P_o$) + Ne($1S_o$). As it will be seen later, such a small modification can actually be found. In fact it is primarily made on the $\Lambda$-states, which assures a consistent modification of the ${\Omega}$-states generated by the further diagonalization of the $R$-independent $H_{\omega}$ interaction matrix.

2. States dissociating into Ne*($2p^5 3s, 3P_2$) + Ne($2p^6, 1S_o$). — Six $\Omega$-states dissociate into this limit:

\[ 0_{6g}^1; 1_{1g}; 2_{2g} \, . \]

All $g$-states, generated by spin-orbit coupling of $3S_g^+$, $3P_g$ and $1P_g$ states, have purely repulsive potential curves, at least when energies smaller than 150 meV above the dissociation limit are considered. The $2_{2g}$ potential is also repulsive; it is identical to the $3P_a$ potential incremented by the fine structure constant: $\alpha = -0.00118$ a.u. The behaviour of $0_{6g}^1$ and $1_{1g}$ potentials is more complex: they exhibit a deep well at $R \approx 3.5$ a.u., and a hump at $R \approx 5$ a.u. For $R < 4.5$ a.u., they are close to the $3\Sigma_{g}^+$ potential. Cohen and Schneider have shown that the hump $1_{1g}$ is slightly higher than the hump $0_{6g}^1$ (respectively 108 meV and 106 meV). Nevertheless, in the further interpretation of the experimental data, these two potentials will be considered as identical, as well as the two potentials $0_{6g}^1$ and $1_{1g}$. The behaviour of all these potentials is shown in figure 1.

![Potential energy curves for $\Omega$-states dissociating into Ne($3P_2$) + Ne($1S_o$). Curves $0_{6g}^1$, $2_{2g}$, $2_{1g}$ are taken from reference [13]. The crosses correspond to the $0_{6g}^1$ potential of reference [13]. The full line is the $0_{6g}^1$ potential presently used.](image.png)
where $f_{u,g}$ are the scattering amplitudes for $\Omega_u,\Omega_g$ potentials. In the case of a $^{20}\text{Ne}^{20}\text{Ne}$ collisions, the nuclear symmetry of the system leads to the expression:

\[
\left(\frac{d\sigma}{d\omega}\right)_\alpha = \left(\frac{d\sigma}{d\omega}\right)_\alpha^d + \left(\frac{d\sigma}{d\omega}\right)_\alpha^e + 2\left[\left(\frac{d\sigma}{d\omega}\right)_\alpha^d \cdot \left(\frac{d\sigma}{d\omega}\right)_\alpha^e\right]^{1/2} \cdot \cos \Phi
\]

where

\[
\left(\frac{d\sigma}{d\omega}\right)_\alpha^d = \frac{1}{4} \left| f_u(\theta) + f_g(\theta) \right|^2
\]

is the direct elastic cross section, and

\[
\left(\frac{d\sigma}{d\omega}\right)_\alpha^e = \frac{1}{4} \left| f_u(\pi - \theta) - f_g(\pi - \theta) \right|^2
\]

is the exchange one.

$\Phi$, the phase-shift between the direct and exchange amplitudes, is a rapidly varying function of the scattering angle $\theta$. In most cases, the differential cross section $(d\sigma/d\omega)_\alpha$ presents rather slow oscillations, the frequency of which is related to the difference between $\Omega_u$ and $\Omega_g$ energies, and fast oscillations, due to the nuclear symmetry.

The $2_u, 2_g$ potentials, calculated by Cohen and Schneider, present very shallow wells at large distance ($R \approx 15$ a.u.), where the repulsive part of the interaction is dominated by the long range Van der Waals potential. These two potentials are very close to each other, so that the energy difference is not large enough to make the $u-g$ phase-shift vary by an amount of $\pi$, over the whole angular range (0-180°). As a consequence only nuclear symmetry oscillations appear in $(d\sigma/d\omega)_2$. The rainbow effects, which could be expected from the existence of the potential wells, are not visible, at least for energies equal to or larger than 60 meV.

The behaviour of the cross section $(d\sigma/d\omega)_2$ is drastically dependent on the location and the height of the $0^+_g$ potential hump. For instance, if the maximum lies above the collision energy, the scattering is mainly due to the repulsive branch of the potential and $(d\sigma/d\omega)_2$ looks like $(d\sigma/d\omega)_2$; on the contrary if the collision energy is larger than the height of the hump, a rainbow effect (plus eventually an orbiting) is expected. If such effects are present and observable, then the measured differential cross section will provide much information about the shape of the hump.

A first differential study of metastable neon-ground state Neon collisions in the energy range 30-150 meV, has been performed, by using two crossed effusive beams [11]. The ground state atom beam is chopped by a slotted disk. A pulsed electronic bombardment produces metastable atoms within the second beam. The synchronous chopping of the two beams allows selection of the relative velocity, by measuring the time of flight of the scattered metastable atoms. As the electron energy greatly exceeds the excitation threshold, the ratio of $^3\text{P}_2$ and $^3\text{P}_0$ populations is equal to the ratio of the statistical weights (5:1). In such conditions the measured differential cross section is close to the $\text{Ne}(^3\text{P}_2) - \text{Ne}(^1\text{S}_0)$ one. Figure 2 shows this cross section, measured in relative value, at 78 meV (in the CM frame). Because of the limited angular resolution ($\Delta \theta \approx 6^\circ$), fast oscillations are completely damped. The peak at 180° corresponds to the maximum of the exchange contribution. Another wider maximum is observed at about 160°. A second experimental study has been recently performed by Haberland et al. [9]. They use two crossed supersonic beams, which greatly improves the angle and energy resolutions. Metastable atoms are produced by a collinear electronic bombardment, and the $^3\text{P}_0$ population is destroyed by laser optical pumping. In figure 2 the measured differential cross section, for $E = 88$ meV, is shown. Now fast oscillations are seen in the range 50-140°. A well marked maximum is observed at 155°; it corresponds to the rainbow effect (seen in the exchange contribution) due to the $0^+_g, 1_g$ potential hump. Actually these experiments have been made at several energies, ranging from 68 meV up to 143 meV. The rainbow peak is present over the whole energy range. The behaviour of the exchange contribution at $\theta = 180^\circ$ as a function of the relative velocity is close to that previously observed in the effusive beam expe-

![Fig. 2](image-url)
Fig. 3. — Elastic differential cross section for Ne(3P2)\rightarrow Ne(' So) backward scattering as a function of $v_p/u$ ($v_p$ : relative velocity, $u$ : thermal velocity at 300 K). Squares : Ref. [9]; full circles : Ref. [11]. The two series of data are arbitrarily normalized at the most probable relative velocity ($v_p/u \approx 2.45$).

The presence of this rainbow effect implies that the $0^+_u$, $1_u$ potential hump is lower than the smallest collision energy considered here (68 meV). In our interpretation we have used the $2_u$, $2_g$, $0^+_u$ potentials calculated by Cohen and Schneider, fitted to the analytic forms:

$$C_6/R^6 + A/R^{-4} \exp(-\beta R), \quad \text{where } C_6 = -52.7 \text{ a.u.}$$

The constants $A$, $\alpha$, $\beta$ have been evaluated in order to get the numerical values given in reference [13] at $R = 5.6$ and 8 a.u. On the other hand, we have modified the $3\Sigma_u^+$ potential. After the diagonalization of $H_{so}$ this leads to a modification of the $0^+_u$, $1_u$ potential consisting in a marked diminution of the potential hump. It turns out that the height of this hump has a drastic influence on the location of the main rainbow peak (e.g., a variation of 0.25 meV may lead to a shift of $5^\circ$). Finally we have chosen the following potential (see Fig. 1) (all quantities are expressed in atomic units):

$$E_{0^+_u,1_u}(R) = C_M \left\{ \exp(-A(R-R_c)) - 1 \right\}^2 - 1 \right\} + 
\frac{C_6}{R^6 + B} + G \exp(-\alpha(R-R_0)^2)
+ D \cdot X^8 \cdot \exp(-\gamma(X^2 - 1))$$

where:

$$C_M = 0.01646 \quad C_6 = -52.7$$
$$A = 1.2048 \quad B = 16838$$
$$R_c = 3.5$$
$$G = 0.0062 \quad D = 0.001$$
$$\alpha = 0.4924 \quad X = 3.5/(R - 3.5)$$
$$R_G = 4.75.$$
of $v$, the locations of the peaks present in $\mathcal{F}(E)$ should coincide with those of the observed bands. Because of the overlapping of different factors $F(v, E)$, the number of maxima in the emission spectrum is generally smaller than the number of vibrational levels. In the present case, $\mathcal{F}(E)$ has been calculated, by using for $\text{I}_u(3\text{P}_2)$ the modified potential described before and for the electronic ground state a potential constructed with the spectroscopic data given by Tanaka and Yoshino [21] and at small distance, the repulsive potential given by Ford and Wheeler [22]. The radial wavefunctions $\Phi_0$ and $\Phi_1$ have been calculated by an algorithm [23], which gives at the same time the vibrational energies of the 11 existing levels. Figure 4 shows the calculated factor $\mathcal{F}(E)$. The positions of the 8 first bands observed by Tanaka and Walker are also indicated. Their energies agree fairly well with the maxima of $\mathcal{F}(E)$. This makes quite plausible the widening previously imposed to the $\text{I}_u$ potential well. The two supplementary observed bands correspond to transitions from (nuclearly) quasi-bound states of Ne*(3P2 + 3S0) to one or the other bound state of Ne2(1S0 + 1S0). As noticed by Tanaka and Walker, the shortest wavelength is 745 Å, which means that the energy of the highest quasi-bound state cannot exceed 20 meV, i.e. that the height of the potential hump is about 20-30 meV.

In another experiment of the same kind, Matsuura et al. [4] obtain similar results. However two supplementary bands, at larger wavelength, are observed. This leads to lower the minimum of the well ($-0.026$ 8 a.u. or $-0.023$ 0 a.u. according to the ground state potential used, instead of $-0.016$ 4 a.u.) keeping the same location ($R \approx 3.4$ a.u.). It may be noticed that such a change has practically no effect on the location of the rainbow maximum in the differential cross section. As a consequence, the corresponding change in the $3\Sigma_u^+$ potential at this short distance cannot be tested by a Ne*(3P2) + Ne or Ne*(3P2) + Ne collision experiment at thermal energy.

**3. States dissociating into Ne* (2p³ 3s, 3P0) + Ne (2p⁶, 1S0).** — The study of this couple seems to be a priori much easier than the previous one since only two molecular states ($0_u^-, 0_u^+$) have this dissociation limit. The $0_u^-$ (3P0) potential is obtained by the same way as the $0_u^-$ (3P2) potential, i.e. by diagonalizing the spin-orbit interaction matrix [13].

The $0_u^-$ (3P0) potential can be directly obtained from the $0_u^-$ (3P2) potential defined in § 1 and the $3\Pi_u$ potential given in reference [13] (1):

$$E[0_u^-(3\text{P}_0)] = \frac{[E(3\Pi_u)-\alpha].E(3\Pi_u)-[E(3\Pi_u)+\alpha].E[0_u^-(3\text{P}_2)]}{E(3\Pi_u)-E[0_u^-(3\text{P}_2)]-2\alpha}.$$  

The present $0_u^-(3\text{P}_0)$ potential is slightly lowered, with respect to that calculated by Cohen and Schneider, within the $R$-range 5.5-9 a.u. (see Fig. 5).

---

**Fig. 4.** — Sum $\mathcal{F}(E)$ of Franck-Condon factors, as a function of the photon energy $E$. The vertical arrows show the location of the band observed in the Ne2 emission spectrum (Ref. [3]); the horizontal bars show the widths of the observed peaks. The vertical broken line shows the dissociation limit.

**Fig. 5.** — Potential energy curves for $\Omega$-states dissociating into Ne*(2p³ 3s, 3P0) + Ne(1S0). Full line: present (the $0_u^-$ curve is identical to that given in Ref. [13]). Crosses: $0_u^-$ potential curve of reference [13]. Broken lines: potential curves of reference [10].

(1) All energies $E$ are such that $\lim_{R \to 0} E = 0$. 

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3.1 PURELY ELASTIC COLLISION. — The argument given before to justify the purely elastic character of the Ne\(^3\text{P}_2\) + Ne\(^1\text{S}_0\) collisions at thermal energies, partly fails in the present case, in as much as fine structure transitions \(^3\text{P}_o\) - \(^3\text{P}_2\), \(^2\text{P}_0\) are now exothermic (by 46 meV and 98 meV respectively). However these inelastic processes probably just begin to become significant in the present energy range. In a first step we shall consider a purely elastic collision and look further to the validity of this assumption, by a comparison of calculated and measured cross sections. In figure 6, the elastic differential cross section calculated by the semi-quantal method, at 68 meV is compared to the measurement of Beyer et al. \cite{10}. Here a laser \((\lambda = 5945 \, \text{Å})\) is used to destroy the \(^3\text{P}_2\) metastable atoms, before and after the collision; in such conditions the only \(^3\text{P}_o\) - \(^3\text{P}_o\) elastic process is measured. From the rather good agreement obtained, it may be stated that the set of potentials used here is adequate, at least in the internuclear distance range \(R > 6 \, \text{a.u.}\). In the present case, the fast oscillations are entirely due to the nuclear symmetry. The marked minimum at \(\theta \approx 65^\circ\) corresponds to a destructive \(u-g\) interference. It may be noticed that the \(0_u^+\) and \(0_g^+\) potentials of Cohen and Schneider are closer to each other than the present ones; if they were used, the calculated \(u-g\) phase-shift would have a slower dependence on \(\theta\) and this minimum would not exist. By using a fitting procedure at this energy, Beyer et al. \cite{10} obtain a couple of potentials which are very different from the present ones (see Fig. 5). This may be explained by the fact that the analytic form of these potentials has not the correct asymptotic behaviour at large distance \((R > 10 \, \text{a.u.})\).

3.2 INELASTIC SCATTERING. — In fact, several experimental data indicate that this good agreement between experiment and calculations based on purely elastic scattering is no longer preserved when the collision energy becomes larger than about 90 meV: (i) the elastic cross sections measured by Beyer et al. \cite{10} at 111 meV and 143 meV exhibit some anomalies in their \(u-g\) interference pattern; (ii) by detecting metastable atoms scattered in the direction perpendicular to the incident beam plane — which eliminates any elastic or endothermic collision process — \cite{12}, we have observed the superelastic fine structure transition:

\[
\text{Ne}^3\text{P}_o + \text{Ne}^1\text{S}_0 \rightarrow \text{Ne}^3\text{P}_2 + \text{Ne}^1\text{S}_0 + 98 \, \text{meV},
\]

with a differential cross section which is, at \(\theta \approx 90^\circ\) (CM), of the same order of magnitude as the elastic one; (iii) the quenching rate of the \(^3\text{P}_o\) level measured at low temperature (150 K) is larger than expected from theory \cite{6}. Therefore inelastic processes do participate in the scattering, at least for energies larger than 80-90 meV. Because of a larger energy threshold \((\approx 133 \, \text{meV})\), states dissociating into

\[
\text{Ne}^1\text{P}_r + \text{Ne}^1\text{S}_0
\]

generally correspond to closed channels. Moreover, as their couplings with states \(0_u^-(3\text{P}_o)\) occur at rather small internuclear distances \((< 4 \, \text{a.u.})\), all those states can be ignored. In the \(\Omega\)-basis set, all couplings are dynamical: the radial couplings \(0_u^-(3\text{P}_o)-0_u^-(3\text{P}_2)\) induce the fine structure transition \(^3\text{P}_{0-2}\), whereas the rotational couplings \(0_g^-(3\text{P}_o)-1_u^+(3\text{P}_{1.2})\) induce the \(^3\text{P}_{0-1.2}\) transition. Let us first examine the effect of the radial couplings. As previously noted by Cohen et al. \cite{19}, the \(0_u^+ - 0_g^+\) radial coupling occurs at rather short distance \((R \approx 4 \, \text{a.u.})\), which makes it negligible in the present energy range. Therefore only the \(u\)-scattering amplitudes (in \(^3\text{P}_o\) and \(^3\text{P}_2\) channels) need to be recalculated. Finally we are dealing with a two state problem involving only the \(0_u^- - 0_u^-\) radial coupling.

Since the states \(0_u^-(3\text{P}_{0,2})\) are completely decoupled from \(0_u^+\) states, they can be expanded separately, on two \(\Lambda\)-states only, namely:

\[
\begin{align*}
|0_u^+(3\text{P}_o)\rangle & = \cos \beta(R) |3\Sigma_u^+\rangle - \sin \beta(R) |3\Pi_u^+\rangle, \\
|0_g^+(3\text{P}_2)\rangle & = \sin \beta(R) |3\Pi_u^+\rangle + \cos \beta(R) |3\Sigma_u^+\rangle,
\end{align*}
\]

where:

\[
3\Pi_u^+ = \frac{1}{\sqrt{2}} [3\Pi_u(A = + 1) + 3\Pi_u(A = - 1)].
\]

(Orthonormalized real wavefunctions are used.) In as much as the radial coupling between \(\Lambda\)-states may
be regarded as giving a negligible effect in this low energy range, the radial coupling between $0_u^-$ states is simply related to the rotation angle $\beta(R)$, by:

$$\left\langle 0_u^- (3P_0) \left| \frac{\partial}{\partial R} \right| 0_u^- (3P_2) \right\rangle \simeq \frac{d\beta}{dR}.$$  

The rotation angle itself is readily obtained, by:

$$\sin 2\beta(R) = \frac{2 \langle 3P_0 | H_{0u} | 3\Sigma^+_u \rangle}{E[0_u^- (3P_0)] - E[0_u^- (3P_2)] - 3 \alpha}.$$  

$\beta(R)$ has been evaluated with the $0_u^-$ potentials given in reference [13], and with the present ones. $\beta(R)$ and its derivative are shown in figure 7. The present derivative (i.e. approximately the radial coupling) has a smaller maximum value than the other one, but the important point here is that it becomes significant at larger values of $R \sim 9$ a.u., i.e. typically in the range of the present distances of closest approach. As the transition probability is known to increase fast near its threshold, the present inelastic cross sections are expected to be larger than those calculated by Cohen et al. [19]. However it seems improbable that a factor as large as $10^3$ could be gained by this modification of the $u$-potentials. As a consequence it is necessary to examine in detail the role of the rotational couplings. In the $A$-basis, which is the most convenient for this discussion, the selection rules are very simple: $\Delta \Lambda = \pm 1$, $\Delta \Sigma = 0$, $\Delta S = 0$. Then 2 different rotational couplings appear:

$$3\Pi (\Sigma = 1) \leftrightarrow 3\Sigma^+ (\Sigma = 0); \quad 3\Pi (\Sigma = 0) \leftrightarrow 3\Sigma^+ (\Sigma = 0).$$

The second term becomes efficient at large distances, where $3\Pi_{u,u}$ and $3\Sigma^+_{e,e}$ states are degenerate. The effect of the first rotational coupling is very different for g- and u-symmetries: the energy gap between $3\Pi_u^g$ and $3\Sigma^+_u$ is too large at all distances to make efficient the coupling; on the contrary it turns out that, in the particular case of the Ne$^+_g$ system, the $3\Pi_u^g$ and $3\Sigma^+_g$ states become quasi degenerate at short distance ($4.7 \leq R \leq 7.5$ a.u.) (Fig. 8). The resulting couplings between the $\Omega = 0$ states are as follows:

$$\Omega = 0^- (3P_{0,2}) : 3\Pi' \leftrightarrow 3\Sigma_0$$
$$\Omega = 1^+ (3P_{1,2}; 1P) : 3\Pi \leftrightarrow 3\Sigma_1 1\Pi_0.$$  

Then a rigorous treatment of the problem involves 5 states (for each u, g symmetry), and for each value $l$ of the total angular momentum, the interaction matrix, in the $A$-basis, can be written:

$$[E(3\Pi') - \alpha \alpha \sqrt{2} E(3\Sigma^+) | 0 \quad L \quad 0 ]$$
$$\alpha \sqrt{2} \quad E(3\Sigma^+) | L \quad 0 \quad 0]$$

where

$$L(R) \simeq \frac{\sqrt{l(l+1)}}{2 \mu R^2} \langle 3\Pi | L_+ + L_- | 3\Sigma \rangle.$$  

Work is now in progress to treat this 5 state problem. The calculation is made difficult by the presence of long range coupling terms. Preliminary results have shown that the rotational couplings increase the transition probabilities by a factor of a few tens. In order to verify that the experimental results could be interpreted by introducing a sufficiently important rotational coupling, we tried to find a simple model involving fewer states and treatable by the semi-quantal method. As the radial couplings have a negligible effect, it is convenient to work in the $\Omega$-basis. As the most efficient rotational coupling is expected between the nearest states, a reasonable model consists in considering only the states $0_u^- (3P_0)$ and $1_u^- (3P_1)$ rotationally coupled via $L(R)$. It is assumed that the two potentials are degenerate for $R < R_S$ and that the rotational coupling acts only within that range. In this simplified model, only the $f_g$ scattering
amplitude is modified with respect to the purely elastic one:

\[ f_k(\theta) = \frac{1}{2ik} \sum_{l} (2l + 1) P_l(\cos \theta) \times \]
\[ \times \left[ e^{i(2\delta + s - 2S + s' + S')} \cos (S' - S) - 1 \right] \]

where \( \delta \) and \( S \) are respectively the JWKB phase-shift and the action calculated at \( R_\circ \) along the \( 0^+ \) potential, \( S' \) and \( S' \) are the actions at \( R_\circ \) calculated along the potentials \( E(0^+) \pm L(R) \).

The best results have been obtained by choosing: \( R_\circ = 7.5 \) a.u. and \( \langle L_\pm \rangle = 10 \). In such conditions, no inelastic effect is seen at energies below 80 meV. On the other hand at larger energy, e.g. 111 meV, the elastic cross section is perturbed (see Fig. 9). A marked decrease is seen around 110°. At the same time, since the perturbation affects the g-amplitude only, the destructive u-g interference at \( \theta = 50^\circ \) is partly cancelled. A good agreement with the experimental results of Beyer et al. [10] is seen. It could not be obtained without involving inelastic effects, at least with the present potential set. In the frame of this exceedingly simple treatment of the couplings, the calculated inelastic cross section is still a matter of doubt. Nevertheless its order of magnitude is directly related to that of the elastic perturbation, which has already revealed to be correct. In the present 2-state approximation only the \( ^3P_0 \rightarrow ^3P_1 \) transition occurs. In fact in a more rigorous 5 state treatment, transitions to states \( ^3P_1 \) and \( ^3P_2 \) would probably take place. It may be noticed that a good agreement with the experiment requires a surprisingly large value of the effective rotational coupling term. This effective value would probably be reduced in a more precise calculation. Nevertheless if a more realistic value \((\sim \sqrt{3})\) of \( \langle L_\pm \rangle \) could not give a sufficiently large inelastic cross section, the g-potential curves should also be revised.

4. Conclusion. — The purpose of this article is neither to give a new \textit{ab initio} calculation of the Ne\(^2\) potentials, nor to present a strict inversion of the scattering data yielding a unique set of experimental potentials. We have tried to use \textit{ab initio} potentials already calculated by Cohen and Schneider, which are probably close to reality, for most of them at all internuclear distances, for some of them at short \((R < 4 \) a.u.) and large \((R > 10 \) a.u.) distances. We have pointed out that the major part of the discrepancies between theory and experiment comes from the S-shaped branch (right side of the well and hump) of the \( ^3\Sigma^+ \) potential. Then it has been shown that a modification of only this part is sufficient to provide a reasonable agreement between theoretical predictions and a large variety of experimental data obtained in the thermal energy range. Some further developments are needed in order to confirm — or refute — our conclusions. From the experimental viewpoint, the inelastic processes occurring at low and moderate energies need to be studied in more detail (differential cross sections). On the other hand other \textit{ab initio} calculations (extended configuration interaction, pseudo- or model-potentials) are obviously necessary, especially in the region \( 4 \) a.u. < \( R < 10 \) a.u.

Scattering experiments have proven to be a powerful tool in the investigation of diatomic systems such as rare gas dimers, and a theoretical effort should be made also on the collision problem itself, particularly on the effects induced by the dynamical couplings.

Recently, extended CI calculations on the \( \text{Ar}_2 \) taking into account a \( R \)-dependent spin-orbit interaction, have been performed [24]. Crossed beam experiments are now in progress on elastic and — eventually — inelastic \( \text{Ar}^+ \)-Ar collisions at thermal energy. It will be interesting to compare this system to Ne\(^2\), concerning the shape of the potential curves (in particular the predicted absence of a hump in the \( 0^+_\circ \)) and also the effects of the dynamical couplings.

Fig. 9. — Elastic differential cross section for the Ne\(^2\)(\( ^3P_0 \)) - Ne\(^2\)(\( ^1S_0 \)) collision at 111 meV. (a) Calculated without coupling. (b) Full line : calculated with a \( 0^+_\circ \)-\( 1^+_\circ \) coupling (shifted by a factor \( \times 100 \)); points : experiment (Ref. [10]) in arbitrary unit.

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