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Relaxation of the sodium atom in the 4D level by collisions with noble gases. II. Theoretical aspects

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Résumé. — Dans des articles précédents [1-3], nous avons donné les résultats de mesures expérimentales sur les taux de relaxation des multipôles d'ordre k dans le niveau 4D du sodium et pour la cohérence 3S-4D. Ici, nous comparons ces valeurs expérimentales avec les valeurs théoriques que nous calculons à partir de différents types de potentiel. Nous montrons que l'interaction de Van der Waals en $C_6 R^{-6}$ n'est pas assez anisotrope pour décrire la relaxation des moments multipolaires d'ordre k . Pour l'argon, le krypton et le xénon, on obtient de bien meilleurs résultats en tenant compte du terme suivant en $C_8 R^{-8}$ dans le développement de l'interaction à longue distance. Les potentiels de Pascale et Vandeplanque [4] donnent de très bons résultats pour l'hélium. Les résultats sont également satisfaisants pour l'argon, le krypton et le xénon, mais l'accord pourrait encore être amélioré.

Abstract. — In previous papers [1-3] we have reported experimental measurements of the relaxation rates of the k -multipole moments in the 4D level of sodium and the 3S-4D optical coherence. In the present paper we compare the experimental values with those obtained theoretically for different types of potentials. We show that the Van der Waals $C_6 R^{-6}$ interaction is not sufficiently anisotropic to describe the relaxation of the k multipole moments. For Ar, Kr and Xe, much better results are obtained by taking into account the next term $C_8 R^{-8}$ in the expansion of the long-range interaction. The potentials of Pascale and Vandeplanque [4] give very good results for helium. The results are also satisfactory for Ar, Kr and Xe, but the agreement could still be improved.

In the preceding paper [1], we have presented the measurements of the relaxation cross-sections σ_k for the k multipoles ($k = 0, 1, 2, 3$) for the sodium atom in the 4D level by collision with noble gases atoms. In another paper [2], we reported the measurements of the broadening and shift cross-sections σ_b and σ_s for the 3S-4D two-photon transition induced by collisions with the same noble gas atoms. We discuss in this paper the theoretical information on the sodium-rare gas interaction potential which can be deduced from these measurements. This paper is divided into three parts. In the first part, we briefly recall the principle of the semi-classical calculation of the σ_k cross-sections. In a second part we discuss some general properties of the σ_k associated with the symmetry of the interaction potential. In the

last part we compare the experimental results with those obtained theoretically by assuming a particular form for the interaction potential (Van der Waals interaction, potentials of Pascale and Vandeplanque [4]).

1. Semi classical calculation of the collision cross-sections. — The principle of such a calculation is wellknown (see for instance [5]) and we just give the essential results in order to introduce the notation.

We consider a straight path trajectory model. The trajectory is defined by the relative velocity \mathbf{v} of the colliding atoms and the impact parameter b . If the interaction between the two atoms is described by an interaction potential $V(\mathbf{R})$, \mathbf{R} being the inter-nuclear distance, the problem of a single collision is reduced to the solution of the following Schrödinger equation :

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = [\mathcal{H}_0 + V(\mathbf{b} + \mathbf{v}t)] |\Psi(t)\rangle. \quad (1)$$

If we define $S(\mathbf{b}, \mathbf{v})$ as $U(+\infty, -\infty)$, where U is

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the time evolution operator, the variation ($d\rho/dt$) of the density matrix under the effects of collision is obtained by averaging over the probability of occurrence of the different collisions :

$$\frac{d\rho}{dt} = - \Phi \rho$$

$$\Phi = 2 \pi N \int_0^{+\infty} v f(v) dv \int_0^{+\infty} b db \times$$

$$\times [\langle S(\mathbf{b}, \mathbf{v}) \rho S(\mathbf{b}, \mathbf{v})^+ \rangle_{av} - \rho] \quad (2)$$

where N is the number of perturbers per unit of volume, $f(v)$ is the Maxwellian velocity distribution and the average is taken over the directions of \mathbf{b} and of the velocities.

As in previous works [5], we introduce an intermediate operator of the Liouville space $\Pi(b, v)$:

$$\Pi(b, v) \rho = - \langle S(\mathbf{b}, \mathbf{v}) \rho S(\mathbf{b}, \mathbf{v})^+ \rangle_{av} + \rho. \quad (3)$$

The elements of the matrix $\Pi(b, v)$ are the mean

rates of transfer or of decay induced by a collision of parameters b and v with all possible orientations of \mathbf{b} and \mathbf{v} . The symmetry properties of Π and Φ are obviously the same. They are rotationally invariant if the velocity distribution is isotropic. It is then of interest to use the basis of the Liouville space $|\alpha\beta L_\alpha L_\beta KQ\rangle$ defined by :

$$|\alpha\beta L_\alpha L_\beta KQ\rangle = \sum_{m_\alpha} (-1)^{L_\beta - m_\beta} \times$$

$$\times \langle L_\alpha L_\beta m_\alpha - m_\beta | KQ \rangle | \alpha L_\alpha m_\alpha \rangle \langle \beta L_\beta m_\beta |.$$

(The vectors $|\alpha\beta L_\alpha L_\beta KQ\rangle$ correspond to the irreducible tensors ${}^{L_\alpha L_\beta} T_Q^K$ of the ordinary space.) Because of the scalar character of Π in the Liouville space, the matrix elements of Π are equal to [5] :

$$\ll \alpha\beta L_\alpha L_\beta K' Q' | \Pi(b, v) | \gamma\delta L_\gamma L_\delta KQ \gg =$$

$$= \delta_{KK'} \delta_{QQ'} {}^{L_\alpha L_\beta}_{L_\gamma L_\delta} \Pi^k(b, v).$$

Using eq. (3) we express the matrix element ${}^{L_\alpha L_\beta}_{L_\gamma L_\delta} \Pi^k(b, v)$ as a function of the matrix elements of $S(\mathbf{b}, \mathbf{v})$:

$${}^{L_\alpha L_\beta}_{L_\gamma L_\delta} \Pi^k(b, v) = \delta_{L_\alpha L_\gamma} \delta_{L_\beta L_\delta} - \sum_{\chi\sigma} (-1)^{k+\chi+L_\beta+L_\gamma} \left\{ \begin{matrix} L_\alpha & L_\gamma & \chi \\ L_\delta & L_\beta & k \end{matrix} \right\} \times {}^{L_\alpha L_\beta}_{L_\gamma L_\delta} S_\sigma^\chi(b, v) {}^{L_\delta L_\beta}_{L_\gamma L_\delta} S_\sigma^{\chi*}(b, v) \quad (4)$$

where ${}^{L_\alpha L_\beta}_{L_\gamma L_\delta} S_\sigma^\chi$ is defined by :

$$S = \sum_{\substack{\chi\sigma \\ L_\alpha L_\beta}} {}^{L_\alpha L_\beta}_{L_\gamma L_\delta} S_\sigma^\chi(b, v) {}^{L_\alpha L_\beta}_{L_\gamma L_\delta} T_\sigma^\chi. \quad (5)$$

In the following we shall restrict the calculation of S to the five Zeeman sublevels of the 4D level ($L=2$). With such an approximation, we cannot find the quenching cross-section σ_0 , but the values calculated for the other σ_k can be compared with the experimental results. This comes from the fact that σ_0 is generally much smaller than the other σ_k (the only questionable case is helium). Moreover, in the special case of the potentials of Pascale and Vandeplanque [4], an exact calculation made by Pascale [6] for $\sigma(5/2 \rightarrow 3/2)$ gives cross-sections in agreement with ours with a precision of the order of 10 %.

We have also taken a mean relative velocity ($\bar{v} = \sqrt{8 kT/\pi M}$, M being the reduced mass) instead of averaging over the velocities. Under this assumption, the value of σ_k ($k = 1, \dots, 4$) is equal to :

$$\sigma_k = \int_0^{+\infty} {}^{LL}_{LL} \Pi^k(b, \bar{v}) 2 \pi b db. \quad (6)$$

For the case of the 3 S ($Lg = 0$) - 4 D ($L = 2$) two-photon transition, the two-photon excitation operator is purely quadrupolar [7], [8] and the broadening and shift cross-sections σ_b and σ_s are given by :

$$\sigma_b + i\sigma_s = \int_0^{+\infty} \frac{LQ}{LQ} \Pi^2(b, \bar{v}) 2 \pi b db. \quad (7)$$

In the following sections, we calculate these cross-sections. Before doing so, it would be interesting to know if there is any relation between σ_b and σ_k . For instance the experimental values obtained in the previous papers [1], [2] show that σ_k has the same order of magnitude as σ_b while in other experiments [9], [10] σ_k is much smaller than σ_b . Physically, it is obvious that σ_k cannot be much larger than σ_b because a collision which destroys the k -multipole of the excited state will also have a similar influence on the optical coherence. Mathematically, we demonstrate in Appendix I for a S-D transition that :

$$\bar{\sigma}_k \leq 2 \sigma_b \quad (8)$$

where $\bar{\sigma}_k$ is a mean value of the σ_k :

$$\bar{\sigma}_k = \sum_k \frac{2k+1}{(2L+1)^2} \sigma_k.$$

The inequality (8) gives an upper limit to the mean value of the relaxation rates of the multipole moments inside an excited level.

2. Results obtained in the asymptotic and adiabatic limits. — It is wellknown that some simple and interesting results can be obtained in the asymptotic

and adiabatic limits. In the present case, we show using these approximations that the hierarchy among the σ_k is sensitive to the tensorial order of the interaction potential.

2.1 ASYMPTOTIC APPROXIMATION. — This approximation is valid only in the case of a weak interaction, which allows a perturbation approach to be used. In practice, it is a very good approximation for large impact parameters. In order to know σ_k , we have to find the ${}^{LL}\Pi^k(b, v)$ values. Using formula (4) we obtain :

$${}^{LL}\Pi^k(b, v) = 1 - \sum_{\chi=0}^{2L} (-1)^{k+\chi} \left\{ \begin{matrix} L & L & \chi \\ L & L & k \end{matrix} \right\} \times \left(\sum_{\sigma} |{}^{LL}S_{\sigma}^{\chi}(b, v)|^2 \right). \quad (9)$$

Using the unitarity of the S matrix, this expression can be changed into :

$${}^{LL}\Pi^k(b, v) = \sum_{\chi=1}^{2L} \left(\frac{1}{2L+1} - (-1)^{k+\chi} \left\{ \begin{matrix} L & L & \chi \\ L & L & k \end{matrix} \right\} \right) \times \left(\sum_{\sigma} |{}^{LL}S_{\sigma}^{\chi}(b, v)|^2 \right). \quad (10)$$

Let us consider the interaction potential $V(\mathbf{R})$. Due to the rotational invariance about the internuclear axis and to the invariance by reflexion through a plane containing the internuclear axis, the expansion over the irreducible tensorial set only contains longitudinal ($q = 0$) and even rank ($k = 2p$) operators

$$V(\mathbf{R}) = V^0(R) T_0^0 + V^2(R) T_0^2 + V^4(R) T_0^4.$$

The T_0^0 operator corresponds to the isotropic part of the interaction Hamiltonian. Let us now assume that the anisotropic part has a definite rank K (K being equal to 2 or 4). In the perturbation approach, the S matrix is equal in first order to an operator of rank 0 plus an operator of rank K . It follows that at this degree of approximation, the various ${}^{LL}\Pi^k$ are proportional to the same quantity :

$${}^{LL}\Pi^k = g_{kK}^L \sum_{\sigma} |{}^{LL}S_{\sigma}^K(b, v)|^2 \quad (11)$$

with

$$g_{kK}^L = \frac{1}{2L+1} - (-1)^k \left\{ \begin{matrix} L & L & K \\ L & L & k \end{matrix} \right\}. \quad (12)$$

Table I.

	T_0^2 potential ($K = 2$)	T_0^4 potential ($K = 4$)
g_{1K}^2	7/70	14/42
g_{2K}^2	17/70	6/42
g_{3K}^2	22/70	9/42
g_{4K}^2	12/70	25/126

The values of g_{kK}^L are given in table I in the case of the 4D level ($L = 2$). It follows directly that the hierarchy of the ${}^{LL}\Pi^k$ (and here of the Π^k) depends on the rank of the interaction Hamiltonian. For a potential of rank 2, we obtain

$$\sigma_1 < \sigma_2 < \sigma_3$$

(we only consider the cross-sections which have been experimentally measured).

For a potential of rank 4, we find

$$\sigma_2 < \sigma_3 < \sigma_1.$$

2.2 THE ADIABATIC APPROXIMATION. — This approximation is valid when the interaction potential is large. In this case, the molecular levels (of the sodium-noble gas molecule) are well separated and the atom adiabatically follows each level. This approximation is valid if the energy separation between the molecular levels is larger than $1/\tau_c$, where τ_c is the duration of a collision. In practice, the condition is valid only for very small internuclear distances.

If the quantization axis Oz is taken parallel to the trajectory, we obtain in an elementary way the S matrix :

$$S |L, M\rangle = e^{i\alpha(|M|)} |L, -M\rangle. \quad (13)$$

The expansion of S over the irreducible tensorial basis set gives

$${}^{LL}S_{\sigma}^{\chi} = \text{Tr } {}^{LL}T_{\sigma}^{\chi} S = \sum_M (-1)^{L+M+\sigma} \sqrt{2\chi+1} \times \left(\begin{matrix} L & L & \chi \\ M & M & -\sigma \end{matrix} \right) \langle L-M | S | LM \rangle. \quad (14)$$

Using (9), (13) and (14), we find, after performing the summation over the 3j and 6j symbols :

$${}^{LL}\Pi^k = 1 - \frac{(-1)^k}{2k+1}. \quad (15)$$

We deduce from this that the adiabatic approximation gives the following hierarchy for the σ_k :

$$\sigma_2 < \sigma_3 < \sigma_1.$$

2.3 DISCUSSION OF THE RESULTS. — For the three heavier noble gases we have found experimentally the hierarchy (see preceding paper [1]) :

$$\sigma_1 < \sigma_2 < \sigma_3.$$

The comparison with the preceding analysis shows in that case that the relaxation in the 4D level is certainly related to a long-range anisotropic interaction which has the symmetry of a T_0^2 operator.

In the case of helium and neon, the experimental hierarchy is

$$\sigma_2 < \sigma_1, \sigma_3.$$

Theoretically, we have found this hierarchy both in the case of a long range T_0^4 interaction and in the case of the adiabatic approximation. It seems that the short and medium range interaction are dominant for these light elements : for instance, the value obtained for the ratio S/W (shift over broadening) is equal respectively to $+0.11$ and 0.10 for helium and neon [2], which is very different from the value expected for a long-range attractive interaction.

3. Numerical calculations for different types of potential. — We have performed a numerical calculation of eq. (1) for the three following potentials : a Van der Waals C_6/R^6 interaction ; a long-range $C_6/R^6 + C_8/R^8$ interaction ; and the potentials of Pascale and Vandeplanque [4].

3.1 THE LONG-RANGE INTERACTION. — As we shall see below, we first tried a simple Van der Waals interaction C_6/R^6 obtained from the dipole-dipole interaction at second order. The corresponding values of the σ_k coefficients being very different from the experimental results, we tried to improve the potential by taking into account the next term in the expansion of the long-range interaction. This term varies like R^{-8} and we now describe how it is calculated.

The interaction potential can be expressed using

the multipole moments of the sodium atom (labelled 1) and the noble gas atom (labelled 2) [11]. This can be written using symbolic notation :

$$H(\mathbf{R}) = \frac{1}{R^3} D_1 D_2 + \frac{1}{R^4} (D_1 Q_2 + D_2 Q_1) + \frac{1}{R^5} (D_1 O_2 + Q_1 Q_2 + D_2 O_1) + \dots \quad (16)$$

where D , Q and O are the dipole, quadrupole and octupole moments. In the present case, when the sodium atom is in the 4D excited state, we can neglect the terms involving the quadrupole and octupole moments of the noble gas because they are much smaller than those involving the dipole moment. The multipole moment of order k being proportional to the radius of the atom to the k th power, we have for instance :

$$\frac{D_1 Q_2}{Q_1 D_2} \simeq \frac{r_1 r_2^2}{r_1^2 r_2} \simeq \frac{r_2}{r_1}.$$

The radius of the noble gas in its ground state being about twenty times smaller than the radius of the sodium atom in its excited state, we are justified in neglecting $D_1 Q_2$ compared to $Q_1 D_2$.

The effective Hamiltonian $V(\mathbf{R})$, is obtained from

Table II.

	b_1 (a_0)	σ_1 ($100 a_0^2$)	σ_2 ($100 a_0^2$)	σ_3 ($100 a_0^2$)	σ_4 ($100 a_0^2$)	σ_b ($100 a_0^2$)	S/W
HELIUM							
Experiment		17.6 ± 2.5	13.6 ± 0.9	17.8 ± 3.3		14.6 ± 1.7	$+0.11$
C_6/R^6	6.25	3	5	5	4	9	-0.34
$C_6/R^6 + C_8/R^8$	15	11	13	14	12	13	-0.27
P. & V.	7	20	17	23	18	16	$+0.28$
NEON							
Experiment		16.4 ± 2.6	13.0 ± 1.9	16.0 ± 2.2		14.3 ± 1.2	-0.14
C_6/R^6	8	6	8	9	7	12	-0.34
$C_6/R^6 + C_8/R^8$	15	15	19	20	17	19	-0.29
P. & V.	12	34	32	41	35	24	$+0.12$
ARGON							
Experiment		20.8 ± 2.6	24.7 ± 3.9	26.9 ± 4.8		37.5 ± 3.8	-0.31
C_6/R^6	11	11	16	16	13	29	-0.34
$C_6/R^6 + C_8/R^8$	20	25	31	32	28	34	-0.29
P. & V.	12	31	30	30	31	30	-0.27
KRYPTON							
Experiment		31.4 ± 2.4	35.2 ± 5.3	39.6 ± 6.8		41.9 ± 4.4	-0.27
C_6/R^6	12	13	19	20	16	35	-0.34
$C_6/R^6 + C_8/R^8$	20	28	36	38	32	41	-0.29
P. & V.	15	36	36	38	35	37	-0.26
XENON							
Experiment		48.6 ± 8.5	49.3 ± 5.0	51.8 ± 6.5		43.8 ± 4.0	-0.31
C_6/R^6	13.5	16	24	25	20	43	-0.34
$C_6/R^6 + C_8/R^8$	21	33	42	45	38	50	-0.27
P. & V.	18	42	43	43	42	46	-0.26

a perturbation calculation up to the second order given in Appendix II. We find that

$$V(\mathbf{R}) = -\frac{\alpha e^2 \langle r_1^2 \rangle}{R^6} \left(\frac{1}{2} + \frac{3}{2} \cos^2 \theta \right) - \frac{\alpha e^2 \langle r_1^4 \rangle}{R^8} \times \\ \times \left(-\frac{3}{8} - \frac{21}{4} \cos^2 \theta + \frac{145}{8} \cos^4 \theta \right) \quad (17)$$

α being the polarizability of the noble gas, r_1 the distance between the electron and the nucleus in the sodium atom, θ the angle between the internuclear axis and \mathbf{r}_1 . The first term is the usual Van der Waals interaction for the alkali-noble gas interaction [12]. The second term is the first correction to the Van der Waals interaction; it is obtained by summing the dipole (2)-quadrupole (1) term to second order and the interference between the dipole (2)-octupole (1) and dipole (1)-dipole (2) terms.

3.2 NUMERICAL CALCULATION. — The numerical calculation has been performed using the method of Runge-Kutta. In order to reduce the calculation time, the time evolution operator is calculated over half a trajectory and the S matrix is obtained using symmetry relations. Knowing the S matrix, we can deduce the ${}^{LL}\Pi^k$ and ${}^{L0}\Pi^2$ coefficients. We obtain the σ_k by integrating over the impact parameter. The limits are taken as equal to $65 a_0$ (atomic unit) and b_1 . b_1 is chosen in order to obtain rapid oscillations of ${}^{LL}\Pi^k(b)$ and ${}^{L0}\Pi^2(b)$ in this region. For values of the impact parameter lower than b_1 , ${}^{LL}\Pi^k$ and ${}^{L0}\Pi^2$ are replaced by their mean values.

The numerical calculation has been performed using the simple Van der Waals interaction varying as $1/R^6$ (first term in formula (17)), the long-range interaction described by formula (17) and the potentials of Pascale and Vandeplanque. The corresponding results are reported in table II where they can be compared with the experimental results. For each noble gas and each potential we have reported the value of the relaxation cross-sections σ_k , the broadening cross-section σ_b , the ratio shift to broadening S/W and the lower impact parameter b_1 (the values are given in atomic units). We have also shown on figures 1, 2, 3 the variation of ${}^{LL}\Pi^2$, $\text{Re } {}^{L0}\Pi^2$ and $\text{Im } {}^{L0}\Pi^2$ respectively (which are related to the alignment, the broadening and shift) as a function of the impact parameter for the various potentials in the case of argon.

We now discuss in more detail the results obtained for each potential.

3.2.1 Van der Waals interaction. — In this case, we have made a single calculation for the five noble gases by using the reduced variable

$$q = \frac{\alpha \langle r^2 \rangle e^2}{\hbar v b^5}$$

which enables the system of differential equations

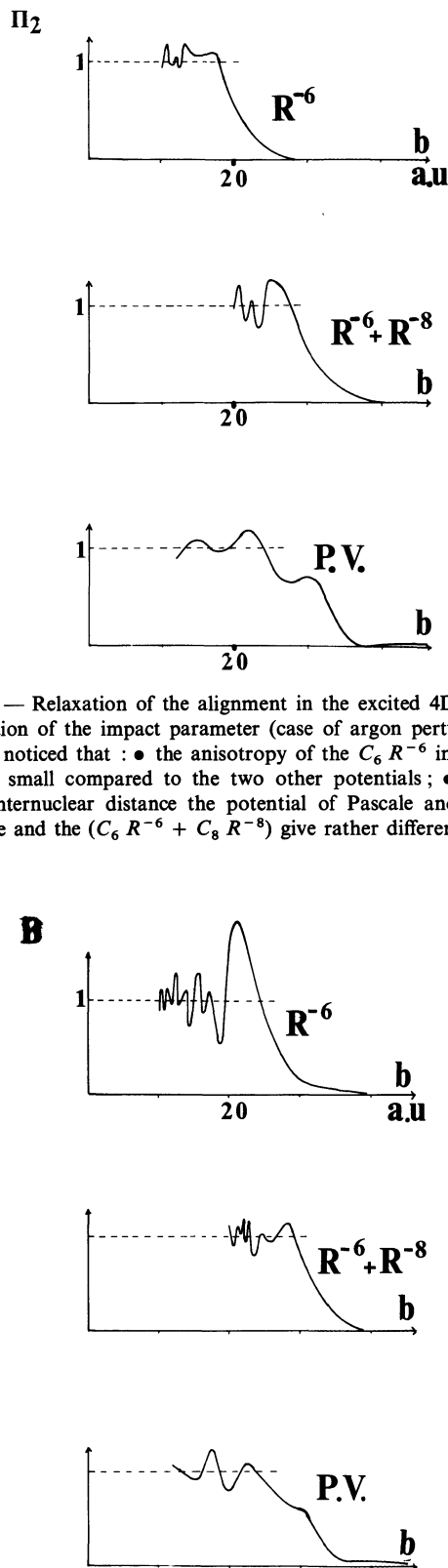


Fig. 1. — Relaxation of the alignment in the excited 4D level as a function of the impact parameter (case of argon perturber). It can be noticed that : • the anisotropy of the $C_6 R^{-6}$ interaction is very small compared to the two other potentials; • even at large internuclear distance the potential of Pascale and Vandeplanque and the $(C_6 R^{-6} + C_8 R^{-8})$ give rather different results.

to be solved independently of the particular noble gas. From this method of calculation it is evident that the ratio between the various cross-sections does not depend on the noble gas.

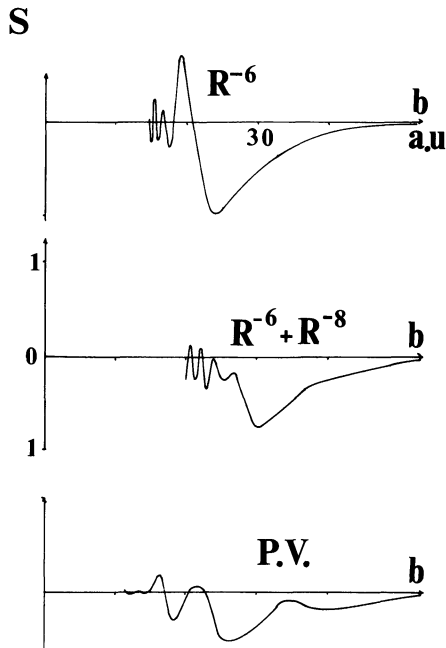


Fig. 3. — Relaxation of the 3S-4D optical coherence (shift) as a function of the impact parameter (case of argon perturber). For values of the impact parameter larger than $35 a_0$, the $C_6 R^{-6}$ and $C_8 R^{-8}$ interactions give practically the same value, but this value differs from that predicted by the potential of Pascale and Vandeplanque.

In the case of helium and neon, it is clear that such a potential cannot fit the experimental results. The value of the ratio S/W obviously indicates that even at large internuclear distances the Van der Waals interaction does not account for the experimental observations.

For the case of the heavier rare gases, the situation is more complex. The values obtained for the shift and the broadening are in good agreement with the experimental values, the difference being always less than 25 %. The agreement is worse for the σ_k cross-sections; they are too small by a factor of the order of 2. This comparison demonstrates that the anisotropic part of the Van der Waals interaction is certainly too small. On the other hand, the isotropic part is well described by the Van der Waals interaction.

3.2.2 The long-range $C_6 R^{-6} + C_8 R^{-8}$ interaction. — As in the case discussed above, this long-range interaction is not suitable for the case of helium and neon while clearly the short-range repulsive interaction is of essential importance. For the other noble gases, we obtain good agreement with the experimental results for all the quantities: broadening, shift and relaxation rates in the excited state. In particular, not only the order of magnitude is good, but the hierarchy of the σ_k : ($\sigma_1 < \sigma_2 < \sigma_3$) corresponds to the experimental case. This is a consequence of the tensorial nature of $V(\mathbf{R})$ (formula (17)). It can be shown, using formula (17), that the component of $V(\mathbf{R})$ associated with the T_0^2 tensorial operator is about three times larger than the T_0^4 component.

The hierarchy ($\sigma_1 < \sigma_2 < \sigma_3$) is thus a natural consequence of the discussion of § 2.1. Let us now discuss why the Van der Waals interaction is not a sufficiently good approximation here while, in most of the previous works on alkali-noble gas and Hg-noble gas collisions [9], [10], this interaction was sufficient to describe the experimental results for the heavier noble gases. This is due to the rather large extension of the wave function of the sodium atom in the 4D level. The influence of the Van der Waals interaction is important over a length λ_6 typically of the order of

$$\lambda_6 \sim \left(\frac{C_6}{\hbar v} \right)^{1/5}$$

while the C_8/R^8 term is important over a length of the order of:

$$\lambda_8 \sim \left(\frac{C_8}{\hbar v} \right)^{1/7}.$$

If we deduce C_6 and C_8 from eq. (17) and if we introduce $\langle r_1^4 \rangle \sim \langle r_1^2 \rangle^2$, we find:

$$\text{Log } \lambda_6 \sim \frac{1}{5} \text{Log } \frac{e^2 \alpha}{\hbar v} + \frac{1}{5} \text{Log } \langle r_1^2 \rangle$$

$$\text{Log } \lambda_8 \sim \frac{1}{7} \text{Log } \frac{e^2 \alpha}{\hbar v} + \frac{2}{7} \text{Log } \langle r_1^2 \rangle.$$

It is evident that, for small radii, λ_6 is larger than λ_8 , but when the radius increases, λ_8 may become of the order or larger than λ_6 . In the present case due to numerical coefficients, λ_6 and λ_8 have similar values for the isotropic part while λ_8 is larger than λ_6 for the anisotropic part. It follows that the broadening, and furthermore the shift which is sensitive to larger radius, are only slightly modified by the $C_8 R^{-8}$ term while the anisotropy depends essentially on the $C_8 R^{-8}$ term.

It is also evident from the previous analysis that the next term $C_{10} R^{-10} \dots$ may have some importance. In fact, it seems clear that even if, for the present case, the $C_6 R^{-6} + C_8 R^{-8}$ interaction potential gives good results, the expansion of the long-range interaction in powers of $1/R$ will be a progressively poorer approximation for higher energy levels. For these cases, one needs potentials calculated *ab initio*.

3.2.3 Potentials of Pascale and Vandeplanque. — Among the potentials which have been recently proposed for the alkali-noble gases interaction, those of Pascale and Vandeplanque have been the most commonly used. Their results give very good agreement with our experimental values in the case of helium. The order of magnitude obtained for σ_k and σ_b is good ⁽¹⁾, and the ratio S/W has the right

⁽¹⁾ Moreover, the slight disagreement between the experimental and theoretical values may be interpreted by the fact that we have neglected the 4F level in our calculations.

sign even if the shift is overestimated. Furthermore the hierarchy of the σ_k ($\sigma_2 < \sigma_1 < \sigma_3$) corresponds to the experimental results. For the neon case, the potentials are clearly inadequate for describing the experimental situation. For the heavier rare gases, the orders of magnitude of the quantities correspond to the experimental values, but the experimental hierarchy of the σ_k cross-sections is not reproduced by the calculations ⁽²⁾.

4. Conclusion. — We have compared in this paper previously obtained experimental results with theoretical predictions performed using different types of potentials. The usual Van der Waals interaction is clearly inadequate to describe most of the features of the experiment. The results have been considerably improved for the three heavier noble gases by taking into account the next term in the expansion of $V(R)$ in powers of $1/R$. Nevertheless we have discussed why this favorable situation cannot be extended to higher energy levels. This shows an important need for the calculation of *ab initio* potentials. We have performed the calculations with the potentials of Pascale and Vandeplanque. We have obtained an excellent agreement in the helium case, but for the other rare gases, and particularly in the case of neon, it appears that the potentials can still be improved in order to be closer to the physical reality.

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Appendix I. — We demonstrate in this Appendix an inequality between the relaxation rates of the optical coherence and of the multipole moments of the excited state.

Formula (4), applied to the case of $S(L=0) - L$ transition, gives the following results for $L_0^0 \Pi^2$ and $L_L^L \Pi^k$:

$$L_0^0 \Pi^2 = 1 - \frac{1}{\sqrt{2L+1}} {}^{LL}S_0^0(4D) {}^{00}S_0^0(3S)^* \quad (\text{AI.1})$$

$$L_L^L \Pi^k = 1 - \sum_{\chi\sigma} (-1)^{k+\chi} \left\{ \begin{matrix} L & L & \chi \\ L & L & k \end{matrix} \right\} | {}^{LL}S_{\sigma}^{\chi}(4D) |^2 \quad (\text{AI.2})$$

$$\begin{aligned} H(\mathbf{R}) &= \frac{e^2}{R^3} (x_1 x_2 + y_1 y_2 - 2 z_1 z_2) \\ &+ \frac{3e^2}{2R^4} [r_1^2 z_2 + (2x_1 x_2 + 2y_1 y_2 - 3z_1 z_2) z_1] \\ &+ \frac{e^2}{2R^5} [3r_1^2 (4z_1 z_2 - x_1 x_2 - y_1 y_2) + 5z_1^2 (3x_1 x_2 + 3y_1 y_2 - 4z_1 z_2)] \\ &+ \dots \end{aligned} \quad (\text{AII.1})$$

⁽²⁾ It is a little surprising (see Figs. 1, 2, 3) to observe that at even large internuclear distances, the values obtained for $\Pi(b)$ are different for the potential of Pascale and Vandeplanque and for

where ${}^{LL}S_0^0(4D)$ and ${}^{00}S_0^0(3S)$ are the component of rank 0 of the S matrix for collisions in the excited state and in the ground state. Because of the isotropic character of the interaction potential in a S level, ${}^{00}S_0^0(3S)^*$ is a simple phase factor (we assume, of course, that there is no quenching in this S level). It follows from (AI.1) that :

$$| {}^{LL}S_0^0(4D) | = \sqrt{2L+1} | L_0^0 \Pi^2 - 1 |. \quad (\text{AI.3})$$

Let us now consider the summation

$$\sum_k (2k+1) {}^{LL} \Pi^k.$$

By using the sum rules of the Wigner 6j coefficients and formula (AI.2) we find :

$$\sum_k (2k+1) {}^{LL} \Pi^k = (2L+1)^2 \left(1 - \frac{| {}^{LL}S_0^0(4D) |^2}{2L+1} \right). \quad (\text{AI.4})$$

It follows from (AI.3) and (AI.4) that

$$\sum_k \frac{2k+1}{(2L+1)^2} {}^{LL} \Pi^k = 2 \operatorname{Re} \frac{L_0^0 \Pi^2}{L_0^0 \Pi^2} - | \frac{L_0^0 \Pi^2}{L_0^0 \Pi^2} |^2. \quad (\text{AI.5})$$

From that, we deduce the inequality :

$$\sum_k \frac{2k+1}{(2L+1)^2} {}^{LL} \Pi^k < 2 \operatorname{Re} \frac{L_0^0 \Pi^2}{L_0^0 \Pi^2}. \quad (\text{AI.6})$$

Averaging over the velocities and over the impact parameters we obtain :

$$\sum_k \frac{2k+1}{(2L+1)^2} \sigma_k < 2 \sigma_b. \quad (\text{AI.7})$$

The first term of the inequality is a mean value of the relaxation rates of the k -multipole moments of the excited state. The inequality shows that this mean value is always smaller than twice the relaxation rate of the optical coherence.

Appendix II. — We describe here in more detail how we have derived the $(C_6 R^{-6} + C_8 R^{-8})$ interaction.

The Hamiltonian $H(\mathbf{R})$ (see formula (16)) has the following form, where we neglect the quadrupole and the octopole of the noble gas atom

the long-range $(C_6 R^{-6} + C_8 R^{-8})$ interaction. It may be suggested that the omitted $C_{10} R^{-10} \dots$ terms are of a great importance (see § 3.2.2).

where \mathbf{r}_1 and \mathbf{r}_2 are relative to the sodium and noble gas atoms. The effective potential $V(\mathbf{R})$ for a sodium atom in the n_1 level and a noble gas atom in the n_2 level (n_2 being the fundamental level) is

$$V(\mathbf{R}) = P(n_1, n_2) H(\mathbf{R}) \frac{1 - P(n_1, n_2)}{E_{n_1 n_2} - \mathcal{H}_0} H(\mathbf{R}) P(n_1, n_2) \quad (\text{AII.2})$$

where $P(n_1, n_2)$ is the projector over the $n_1 n_2$ sub-space and \mathcal{H}_0 is the Hamiltonian of the free sodium and noble gas atoms.

A classical procedure is to transform the formula (AII.2) by replacing $(E_{n_1 n_2} - \mathcal{H}_0)$ by a mean energy difference ΔE . This is justified for the alkali-noble gas pair because :

— the energy of the first excited state of the noble gas is much larger than the energy of the excited alkali atoms,

— the energy difference between the first excited state of the noble gas and its ionization limit is relatively small (compared to the ionization limit).

A further simplification results from the ground state of the noble gas having a zero angular momentum. It follows that all the crossed terms $\langle n_2 | x_2 y_2 | n_2 \rangle$ are equal to zero and that :

$$\begin{aligned} \langle n_2 | x_2^2 | n_2 \rangle &= \langle n_2 | y_2^2 | n_2 \rangle = \\ &= \langle n_2 | z_2^2 | n_2 \rangle = \frac{1}{3} \langle r_2^2 \rangle. \end{aligned}$$

The explicit expression of $V(\mathbf{R})$ is then equal to :

$$\begin{aligned} V(\mathbf{R}) = & - \frac{e^4}{3 R^6} \frac{\langle r_2^2 \rangle}{\Delta E} [\langle x_1^2 \rangle + \langle y_1^2 \rangle + 4 \langle z_1^2 \rangle] \\ & + \frac{3 e^4}{4 R^8} \frac{\langle r_2^2 \rangle}{\Delta E} [4 \langle x_1^2 z_1^2 \rangle + 4 \langle y_1^2 z_1^2 \rangle + \langle (r_1^2 - 3 z_1^2)^2 \rangle] \\ & + \frac{e^4}{3 R^8} \frac{\langle r_2^2 \rangle}{\Delta E} [25 \langle z_1^4 \rangle - 6 \langle r_1^2 z_1^2 \rangle - 3 \langle r_1^4 \rangle] + \dots \end{aligned} \quad (\text{AII.3})$$

The polarizability α of the noble gas is equal to :

$$\alpha = \frac{2 e^2}{3} \sum_{n'_2} \frac{|\langle n_2 | r_2 | n'_2 \rangle|^2}{E_{n_2} - E_{n'_2}}. \quad (\text{AII.4})$$

If we approximate the energy denominator by the same ΔE as before, we can replace

$$\frac{e^2 \langle r_2^2 \rangle}{\Delta E} \quad \text{by} \quad \frac{3}{2} \alpha$$

in formula (AII.3) and we obtain the formula (17) of the paper.

In order to perform the numerical calculation, we have replaced the mean values of r_1^2 and r_1^4 by their hydrogenic values, this being a very good approximation for the 4D level of sodium since the effective quantum number is very close to 4.

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