

Low-energy dissociative electron attachment to Cl₂ molecules

Ilya I Fabrikant[†], Thierry Leininger[‡] and Florent Xavier Gadéa[‡]

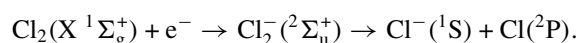
[†] Department of Physics and Astronomy, University of Nebraska, Lincoln, NB 68588-0111, USA

[‡] Laboratoire de Physique Quantique, UMR5626 du CNRS, IRSAMC, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 4, France

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Abstract. We calculate low-energy dissociative electron attachment to Cl₂ molecules using a semiempirical version of the resonance *R*-matrix theory. The theoretical cross section exhibits the $E^{1/2}$ threshold behaviour in a very narrow energy region and peaks at the energy $E = 0.05$ eV. This is explained by a very sharp variation of the Franck–Condon factor as a function of energy. The calculated cross sections and rate coefficients are in good agreement with experimental results.

The dissociative attachment (DA) of electrons to the Cl₂ molecule at energies below 1 eV occurs through formation of the $^2\Sigma_u^+$ negative-ion state according to the scheme [1, 2]



This process has been observed in several experimental studies [1, 3, 4]. All data exhibit a sharp zero-energy peak which is consistent with swarm studies [5]. This result is difficult to interpret theoretically, since the process is dominated by the p wave, and according to the Wigner threshold law the cross section should grow as a square root of the electron energy at low-enough energies. A similar situation occurs in low-energy attachment to F₂ [6].

Recent accurate calculations [7] of potential curves for Cl₂ and Cl₂[−] provide useful information regarding the dynamics of the process. The curve crossing between the Cl₂(X¹Σ_g⁺) and Cl₂[−](²Σ_u⁺) states occurs below the left classical turning point for the nuclear motion in Cl₂. For a qualitative discussion, the electron capture cross section can be written as [8]

$$\sigma_c = \frac{\pi^2}{E} \Gamma |\text{FC}|^2 \quad (1)$$

where E is the electron energy, Γ is the capture width and $|\text{FC}|^2$ is the Franck–Condon factor. Typically, the Franck–Condon factor changes relatively slowly in the near-threshold region, and the energy dependence of the cross section is mainly determined by Γ which gives an $E^{-1/2}$ law in the case of s-wave attachment and an $E^{1/2}$ law in the case of the p-wave attachment. However, in the case of attachment to Cl₂ the Franck–Condon factor drops very quickly with energy, therefore the DA cross section should exhibit a very sharp peak near threshold with the $E^{1/2}$ behaviour in the very narrow-energy region.

To confirm this conjecture, we have calculated DA cross sections using the resonance *R*-matrix theory [9, 10] in which the fixed-nuclei *R*-matrix as a function of internuclear distance ρ is given by one diagonal matrix element

$$R(\rho) = \frac{\gamma^2(\rho)}{W(\rho) - E} + R_b \quad (2)$$

where $W(\rho)$ is the lowest R -matrix pole and R_b is a background term weakly dependent on ρ . Outside the R -matrix sphere the electron is moving in the polarization potential of the Cl_2 molecule. Since the polarizability of Cl_2 is equal almost exactly to the polarizability of Cl multiplied by two, it can be assumed to be independent of ρ . If the Cl_2^- state is bound, the function $W(\rho)$ can be connected to the adiabatic energy curve by solving the matching equation

$$\psi = R \frac{d\psi}{dr} \Big|_{r=r_0} \quad (3)$$

for the energy E and adding it to the potential energy of the neutral $V(\rho)$. The function

$$U(\rho) = V(\rho) + W(\rho)$$

is an equivalent of the diabatic curve, although it is not identical to the diabatic curve of the projection-operator theory [11]. In the region where the negative-ion state is unbound the adiabatic curve cannot be determined unambiguously, but the common approach [11] is to determine the position of the electron scattering resonance as a function of ρ . In our case the known negative-ion curve can be used to restore the function $W(\rho)$. However, this procedure does not allow an unambiguous determination of the R -matrix parameter γ which is connected more with the resonance width rather than with the resonance position. Therefore, in the present calculations we used the recommended value of the DA cross section [2] at 0.1 eV which served as a normalization point for our calculations. Specifically, we parametrize γ as a function of ρ in the following form [9]:

$$\gamma(\rho) = \frac{\gamma_0}{1 + a \exp[\beta(\rho - \rho_0)]} \quad (4)$$

where ρ_0 is the equilibrium internuclear separation, and consider γ_0 , a and β as fit parameters. Our choice of the functional form of γ is connected with two requirements: first, γ should be a smooth function of ρ in the transition (Franck–Condon) region. Secondly, γ should be small at large internuclear separations in order to avoid complications related to the long-range behaviour of the non-local complex potential [9]. The reason why it is necessary to have more than one parameter to fit one experimental point is that the adiabatic energy curve also depends on γ , albeit to a lesser extent than on $U(\rho)$, therefore the fit for γ should be consistent with the *ab initio* results for the adiabatic curve.

The adiabatic resonance width is given by the expression

$$\Gamma(\rho) = -2\gamma^2 \text{Im } L^+ \quad (5)$$

where $L^+ = (u^+)' / \tilde{u}^+$, $\tilde{u}^+ = u^+ - R_b(u^+)'$, and u^+ and $(u^+)'$ are the radial electron wavefunction and its derivative calculated at the transition energy $W = U - V$ and corresponding to the outgoing-wave boundary conditions. The ρ dependence of the adiabatic width is mainly determined by the generalized logarithmic derivative L^+ rather than by $\gamma(\rho)$ which is a relatively slowly varying function. The absolute value of the DA cross section is determined by the value of γ in the narrow region of ρ between about 3.2 and 3.5 au. The obtained values of the parameters are $\gamma_0 = 0.0510$, $a = -0.876$, $\beta = -0.09536$ (all quantities are given in au). Note that with these parameters γ as a function of ρ has a pole, but its position lies far away from the Franck–Condon region, i.e. distances contributing to the DA process.

For calculation of the DA cross sections we include vibrational dynamics as described in [9, 12]. The S -matrix element for DA can be written in the following form [9, 12]:

$$S_{DA} = 2\pi i (\tilde{u}^+)^{-1} (1 + \gamma G^{(+)} \gamma L^+)^{-1} y \quad (6)$$

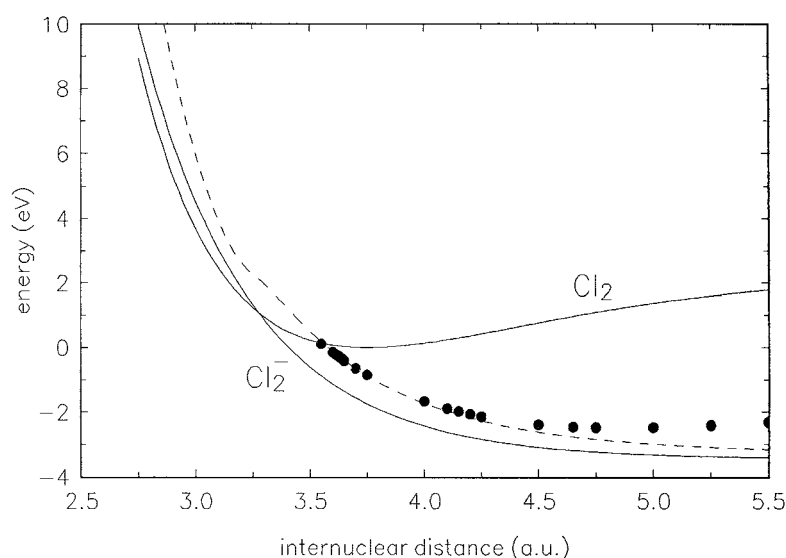


Figure 1. Potential curves of the problem. The curve for Cl_2 was fitted to reproduce the experimental vibrational energy for the $v = 0 \rightarrow v = 1$ transition and the dissociation energy. Full circles, computed energies [7] of the ground state of Cl_2^- . Broken curve, the adiabatic energy of Cl_2^- ; full Cl_2^- curve, the fit of the diabatic energy to the Morse function as described in text. All energies are counted relative to the Cl_2 energy at equilibrium.

where \tilde{u}^+ and L^+ have the same meaning as those in equation (5), except that they are now diagonal matrices with rows and columns corresponding to different vibrational channels ν , $G^{(+)}$ is the Green operator for the nuclear motion in the negative-ion state, and y is the vector of the first-order DA amplitudes

$$y_\nu = \langle \nu | \gamma | \psi^{(+)} \rangle \quad (7)$$

where $|\nu\rangle$ is the eigenstate of the vibrational Hamiltonian for the neutral molecule, and $\psi^{(+)}$ is the nuclear wavefunction describing the motion in the negative-ion state corresponding to the outgoing-wave boundary conditions. Because of the importance of the vibrational continuum for the calculation of the DA process [9, 11], equation (6) is actually an integral equation for S_{DA} . It is solved by the quasiclassical technique based on the quasiseparable representation of the Green operator [13].

In figure 1 we present the fitted potential curves of the problem. The neutral curve $V(\rho)$ and the ‘diabatic’ curve $U(\rho)$ were parametrized by Morse functions as follows:

$$V(\rho) = A(e^{-\alpha\rho} - 1)^2 \quad U(\rho) = B e^{-2\beta\rho} + D \quad (8)$$

where the numerical values of the parameters in au are $A = 0.09250$, $\alpha = 1.0593$, $B = 0.06275$, $D = -0.12693$, $\beta = 1.0300$. We did not try to fit the curves to the numerical data in the region above the equilibrium internuclear separation, since this region does not affect the DA dynamics.

In figure 2 we present the DA cross sections in the low-energy region and compare them with the recommended values of Christophorou and Olthoff [2]. The cross section exhibits p-wave behaviour in the energy range below 0.02 eV. Then its growth slows down, and the cross section passes the maximum at $E = 0.05$ eV. The sharp decrease above $E = 0.05$ eV is caused by two reasons: the very fast drop of the Franck–Condon factor discussed above and

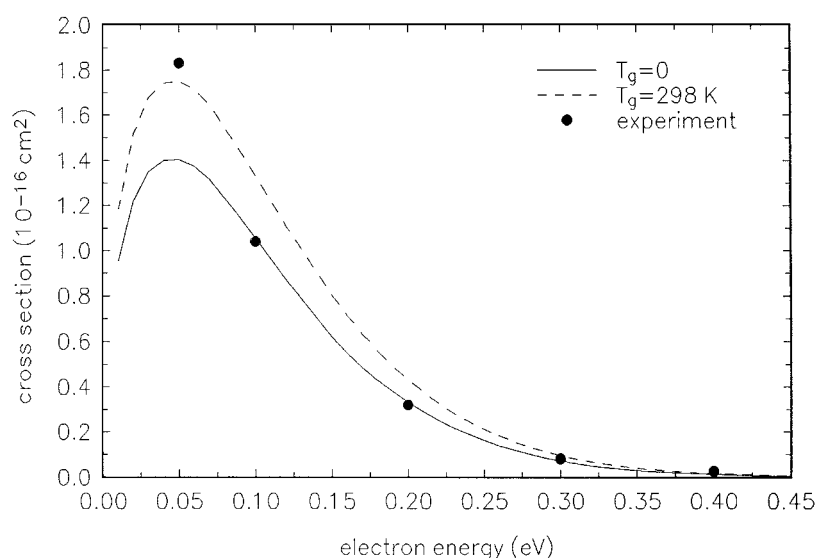


Figure 2. Cross section for dissociative attachment to Cl_2 for the target temperatures $T = 0$ and 298 K. Full circles, recommended values of Christophorou and Olthoff [2].

the decrease of the survival probability of the intermediate negative ion versus autodetachment. It is essential that this behaviour be independent of our normalization procedure. If we vary γ but keep the adiabatic anion curve fixed, the shape of the cross section does not change.

The cross section agrees very well with the experimental results of Kurepa and Belić [3], adjusted upwards by 30% by Christophorou and Olthoff [2]. (One should keep in mind, of course, the semiempirical character of our calculations due to the normalization procedure described above.) The value of our cross section at $E = 0.05$ eV, 1.4 \AA^2 , is below the recommended value 1.83 \AA^2 [2] and the zero-energy value of Kurepa and Belić, 2.02 \AA^2 . However, the zero-energy value is subject to substantial uncertainties due to the dependence on the tuning of the trochoidal electron monochromator [3]. Also, as we demonstrate in figure 2, the cross section in the low-energy region depends strongly on the gas temperature. The room-temperature cross section is substantially higher due to the contribution of higher vibrational states.

Because of this effect, and since the recommended value of Christophorou and Olthoff was extracted from the swarm measurements [5] of the attachment rate constant, we have calculated the attachment rate constant

$$k_{at} = \int v \sigma(v) f(v) dv \quad (9)$$

as a function of the mean electron energy $\langle E \rangle$ for different gas temperatures, assuming the Maxwell–Boltzmann distribution function $f(v)$ for electrons. In figure 3 we present the rate as a function of $\langle E \rangle$ for different gas temperatures. Theoretical k_{at} peaks at $\langle E \rangle = 0.075$ eV at all temperatures and exhibits good agreement with the experimental results of McCorkle *et al* [5]. Some disagreement between theoretical and experimental values might be attributed to the fact that the actual electron energy distribution in the swarm measurements is non-Maxwellian, especially for higher $\langle E \rangle$. Other experimental data for thermal rates compiled by Christophorou and Olthoff [2] also agree with our calculations. The most important fact is that all experiments yield k_{at} which peaks at about the same value of $\langle E \rangle$ close to our value

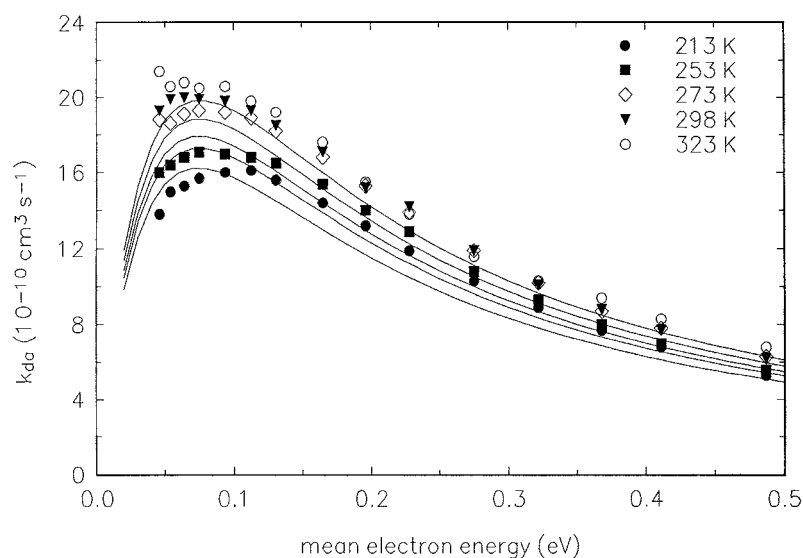


Figure 3. The electron attachment rate constant for Cl_2 for different gas temperatures. Theoretical curves correspond to $T = 213, 253, 273, 298$ and 323 K from bottom to top. Experimental data are taken from [5].

0.075 eV. This is the most convincing evidence of the validity of the Wigner p-wave behaviour in the low-energy region.

We conclude that the controversy regarding the p-wave type behaviour in DA to Cl_2 can be explained by the narrow region of validity of the Wigner law in this case caused by a very sharp drop of the Franck–Condon factor. Further refinement of this problem can be achieved by using electron sources with meV resolution. From the theoretical side, *ab initio* calculations of the resonance width should be performed as a further step. It is likely that the same situation occurs in DA to F_2 , and very accurate calculations of the anion $\text{F}_2^- (^2\Sigma_u^+)$ curve would help to resolve the existing controversy for this target as well.

Acknowledgments

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