

# Potential energy surface diabatisation: application to the study of excited atom deactivation by small molecules

A Sevin, A Papakondylis, C Giessner-Prettre, P Chaquin

Laboratoire de Chimie Organique Théorique (URA 506),  
Université Pierre-et-Marie-Curie, 4, place Jussieu, 75252 Paris Cedex 05, France

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**Résumé.** Des surfaces d'énergie potentielle quasi-diabatiques, calculées dans l'approximation à deux états selon un schéma proposé par Lorquet sont présentées pour les systèmes  $\text{Li}+\text{N}_2$  et  $\text{Mg}+\text{C}_2\text{H}_2$ , dans l'approche  $\text{C}_{2v}$ . On met ainsi en évidence les croisements entre un état de transfert de charge et les états excités de plus basse énergie, qui expliquent la formation d'exciplexes.

**Abstract.** Quasi-diabatic potential energy surfaces are calculated within the two-state approximation, according to a method developed by Lorquet, for  $\text{Li}+\text{N}_2$  and  $\text{Mg}+\text{C}_2\text{H}_2$   $\text{C}_{2v}$  systems. This way, the exciplex formation can be interpreted as resulting from crossings between charge transfer surfaces and low-lying excited states.

## Introduction.

The understanding of the physical quenching of excited metal atoms ( $\text{A}^*$ ) by small molecules  $\text{M}$ , i.e. electronic to vibrational, rotational and translational energy transfer, mainly depends on a couple of complementary limiting models.<sup>1</sup> The first one, originally proposed by Nikitin,<sup>2</sup> and further improved by Bauer, Fischer and Gilmore,<sup>3</sup> is based on the *diabatic* crossing of repulsive covalent potential energy surfaces (PESs),  $\text{A}^*\text{M}$ , with an attractive surface of ionic (charge-transfer, CT) character,  $\text{A}^+\text{M}^-$ . This model is well documented for systems in which the negative moiety  $\text{M}^-$  either is stable or, at least, is not of too high energy with respect to the asymptotic energy of the isolated neutral species. The second one, whose appellation "bond-stretch model" has been given by Hertel,<sup>4</sup> is of concern when an

\* Correspondence and reprints.

*adiabatic* weak stabilization of the covalent species arises via a small relaxation of the covalent molecule, so as to increase the overlap of the valence MOs of the metal and the  $\sigma^*$  MOs of the molecule. Examples of the first model are provided by the Na+HF,<sup>5</sup> Li+N<sub>2</sub>,<sup>6</sup> Mg+N<sub>2</sub>,<sup>7</sup> systems, while the second is illustrated by systems such as Na<sup>8</sup> or Mg<sup>9</sup> +H<sub>2</sub> and Mg+CH<sub>4</sub>.<sup>10</sup> In all the preceding cases, the physical quenching either competes, or is involved, in chemical quenching in which the electronic energy is transformed into chemical energy via bond breaking and/or making.

The preceding examples clearly illustrate the need for *complementary* analysis of adiabatic and diabatic surfaces, calculated at the same level of accuracy. Lorquet *et al.* have proposed several methods for calculating diabatic PESs starting from SCF-CI calculations.<sup>11</sup> We have adapted this formalism to the case of routine calculation of diabatic states, obtained from a limited CI space ( $\approx 100$  eigenstates), and we present here various results obtained with Li plus N<sub>2</sub> and Mg plus C<sub>2</sub>H<sub>2</sub>.

### Computation methods.

In a first step, the ab initio SCF-CI calculations have been achieved with the Monstergauss series of programs,<sup>12</sup> using the closed-shell Roothaan hamiltonian for the singlet species and the RHF Davidson hamiltonian for the doublet species.<sup>13</sup> We have used basis sets consisting of 6-31G functions<sup>14</sup>, augmented by diffuse s+p functions on Li, of exponent 0.008. The CI eigenfunctions, obtained through direct diagonalization, yielded the adiabatic surfaces. Then, in a second step, the coupling matrix  $\langle \Psi_i | \partial/\partial Q | \Psi_j \rangle$  was calculated between these states. These matrix elements can be exploited in two fashions. First, their magnitudes, as a function of the reaction coordinate, indicate the actual region of diabatic crossings that occur when they are maximum. Second, in the regions where avoided state crossings take place, the corresponding diabatic states can be obtained in the limiting approximation of a 2x2 problem, for which analytical solutions are available. In the latter case, the couple of adiabatic states  $\Psi_1$  and  $\Psi_2$  is transformed by an orthogonal transformation; via a  $\theta(Q)$  rotation, into quasi-diabatic states  $\chi_1$  and  $\chi_2$  for which the diabatic condition

$$\langle \chi_1 | \partial/\partial Q | \chi_2 \rangle = 0$$

is fulfilled. It has been shown that the rotation<sup>10</sup> angle is

$$\theta = \int \langle \Psi_1 | \partial/\partial Q | \Psi_2 \rangle dQ.$$

The  $\langle \Psi_1 | \partial/\partial Q | \Psi_2 \rangle$  matrix elements have been calculated by a finite difference method. For each calculated point, the molecule was kept fixed and the metal was

placed at  $R$  and  $R+dR$ , with a  $dR$  microdisplacement of  $0.01 \text{ \AA}$ . Within this approximation, the problem can be treated as a one-dimensional one. Obviously, the corresponding results are only of qualitative grade, so that this study only pretends to provide an insight on the actual ionic to covalent interplay. More accurate calculations would afford more precise data about the actual energetics, but would not significantly change the main features of the overall electronic mechanism. In what follows, we have selected two examples of model reaction coordinates that give simple information about the covalent and ionic surfaces in the vicinity of exciplexes energy minima that have been accurately defined in previous SCF-CI studies.

## Results

### $Li+N_2$

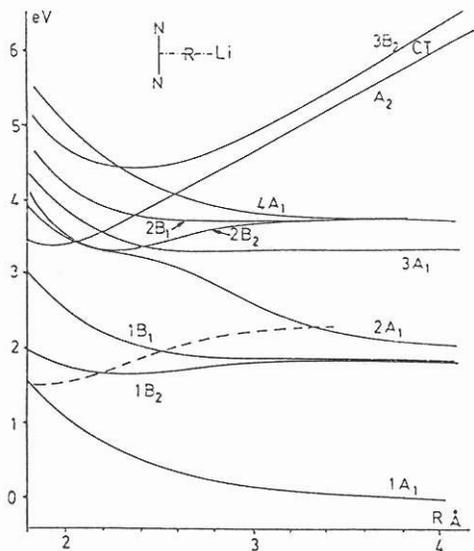


Fig. 1. Adiabatic PESs of  $Li+N_2$  ( $C_{2v}$ ) low-lying doublet states; dashed lines correspond to stretched  $N_2$  (see text).

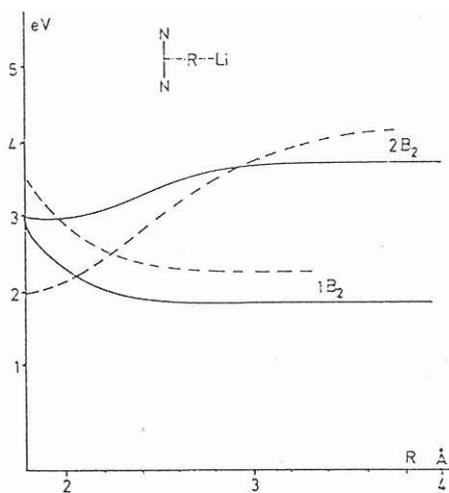


Fig. 2. Diabatic PESs of the lowest two  $B_2$  states of  $Li+N_2$ . The arrow recalls the abscissa of the CT- $2B_2$  maximum of the coupling constant. See also Fig. 1 caption.

The SCF-CI adiabatic PESs calculated for a  $C_{2v}$  geometry of approach, which has been shown to lead to the best exciplex stabilization, in the lowest excited states of

Li, are displayed in Fig. 1. Two types of reaction coordinate are reported. The first one (full lines), corresponds to  $N_2$  having the equilibrium distance of the isolated species (1.078 Å), and the second one (dashed lines) corresponds to  $N_2$  having the calculated equilibrium distance of isolated  $N_2^-$  (1.169 Å), limited to the lowest states of  $B_2$  symmetry. In these conditions, Q is identified with the distance between Li and the middle of  $N_2$ . It is worth focusing our attention on the lowest PES of  $B_2$  symmetry, that is asymptotically linked to the lowest  $2P$  excited state of Li. This state, which is purely of covalent character at large R, is pushed down by the descent of higher states when R decreases. The examination of the CI eigenfunctions clearly shows that at short R, the covalent character strongly mixes charge-transfer components corresponding to  $Li^+N_2^-$ , as previously corroborated by a VB analysis.<sup>6</sup> One sees that the PESs obtained when  $N_2$  is relaxed are of lower energy at sort R, thus indicating that the exciplex has a strong ionic character. On the other hand, a model of the charge transfer behavior is provided by the PES of  $A_2$  symmetry, since in the latter case, no valence or Rydberg state is present to interfere with it, so that it remains of purely ionic character at all R.

In Fig. 2 are reported two types of complementary informations, relative to the diabatic PESs obtained for the lowest states of  $B_2$  symmetry. Let us first discuss the behavior obtained when  $N_2$  has its equilibrium geometry (full lines). At large R, we have just recalled the abscissa of the maximum of the coupling constant between the descending charge-transfer and the Rydberg  $2^2P$  state of Li, corresponding to the  $2s \rightarrow 3p_y$  excitation with our axes convention, which occurs at  $R=2.3$  Å.<sup>15</sup> At short R, are displayed the calculated low energy diabatic PESs resulting from the charge-transfer, that has already crossed the Rydberg state, and the lowest valence state of Li, ( $2s \rightarrow 2p_y$ ), which takes place at  $R=1.8$  Å. (The behavior of the adiabatic states is recalled in dotted lines). When  $N_2$  is relaxed (dashed lines), we see that the behavior is similar, but that the diabatic crossing occurs at larger R. We clearly see that in the neighbourhood of the adiabatic exciplex an ionic/covalent diabatic crossing occurs, thus showing that the quenching mechanism is best described in terms of "harpooning", the switch from the covalent to the ionic surfaces taking place at short distance of interaction. Moreover, the possibility of relaxation of  $N_2$  will provide further stabilization to the exciplex. This finding is also in very good agreement with a parallel VB study of the same reaction coordinate.<sup>6</sup>

$Mg+C_2H_2$ .

A complete study of the adiabatic PESs of the system  $Mg+C_2H_2$ , including the possibilities of physical and chemical quenchings has been achieved.<sup>16</sup> In Fig. 3 we have restricted ourselves to displaying the behavior of the low-lying adiabatic singlet PESs, for the  $C_{2v}$  geometry of the system. Two types of curves are drawn : i) the first have been calculated with  $C_2H_2$  at its equilibrium geometry (C-C = 1.208 Å ; C-H = 1.058 Å) at infinite separation (in full lines), ii) the second with  $C_2H_2$  having the optimized geometry (see Fig.4) of the lowest energy exciplex (in dashed lines). As in the preceding paragraph, the reaction coordinate is assimilated to the distance between Mg and the middle of the triple bond.

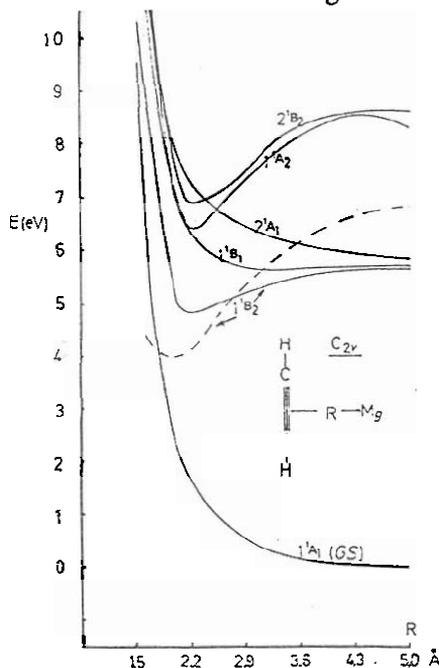


Fig. 3. Adiabatic PESs of  $Mg+C_2H_2$ . For the dashed lines, see Fig. 4 and text.

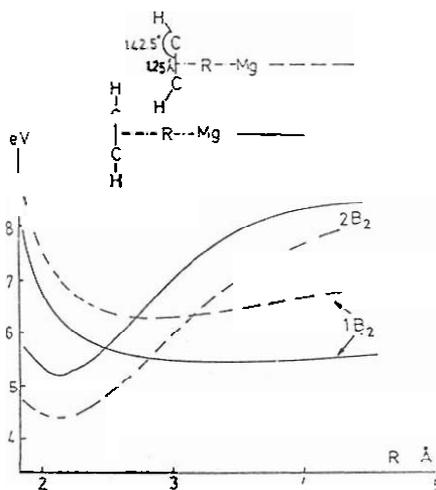


Fig. 4. Diabatic PESs of the lowest  $B_2$  states of  $Mg+C_2H_2$ . the arrows recall the abscissa of the maximum of the coupling constant for the other couples of states. See also text.

The asymptotic behavior of the couple of charge-transfer PESs, ( $A_2$  and  $B_2$  symmetry), lying at infinite separation about 10.5 eV above the ground state is not shown. At large distance, ( $R > 5\text{Å}$ ), they adiabatically avoid the acetylene excited states of same symmetry. Moreover, due to the limited size of our basis set, we have not included here the behavior of the states of asymptotic d symmetry, so that

several states, lying under the CT at large R, are missing. As an end result, at  $R \cong 5 \text{ \AA}$ , the highest PESs already have a strong charge-transfer character. The steep descent of this couple of states yields : i) the formation of deep exciplexes at high energy, along the  $1^1A_2$  and  $2^1B_2$  PESs, ii) the formation of an exciplex along the  $1^1B_2$  PES, that is asymptotically linked to the lowest  $1^1P$  excited state of Mg. Upon optimization of the exciplex geometry an energy gain superior to 1.5 eV is obtained (dashed lines).

The calculated diabatic behavior of the states of  $B_2$  symmetry is displayed in Fig. 4. At low energy, the charge-transfer diabatic state crosses the covalent  $1B_2$  state at  $R=2.5 \text{ \AA}$ , which is close to the position of the adiabatic energy minimum (in dotted lines). This seems to indicate that the ionic surface will be easy to reach. It is noteworthy that for the relaxed geometry of acetylene, the corresponding crossing takes place at a much larger distance, ( $R=3.18 \text{ \AA}$ ), far from the exciplex optimal geometry, thus indicating that the actual formation of an exciplex first occurs without relaxation of acetylene, the latter occurring only once a compact moiety is formed. This phenomenon is likely to provide the exciplex with an excess of vibrational energy mostly distributed along the C-C direction.

### Scopes and limitations of the method.

Although the value of the coupling constant is an index of the actual diabatic behavior, the two-state resolution remains a rather crude approximation, even when limited to a small region of a reaction coordinate. From a mathematical point of view, it requires that in the region where  $\langle \Psi_i | \partial / \partial Q | \Psi_j \rangle$  is noticeable, all other matrix elements involving  $\Psi_i$  or  $\Psi_j$  and other states be negligible. General discussions about the relevance of a reaction coordinate choice has been published.<sup>17</sup> All these considerations induce to conclude that this method only remains of qualitative grade, in the general framework of the Landau-Zener formalism. However, independent VB studies achieved on the same systems, with the same type of basis sets, yield quasi-diabatic crossings, between states of identical nature, at very similar R values. This agreement tends to show that our results are qualitatively satisfactory. The most important point remains that using the precedingly described method, very simple diabatic information can be obtained, thus allowing for simple descriptions of the actual electronic mechanism of quenching, for any type of state.

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