

**Non Adiabatic Effects and Radiationless Transitions**

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*Ab-initio* methods for computing stationary molecular states and radiationless transition probabilities between nonstationary states are discussed. The expansion methods, the molecular Hamiltonians, the adiabatic and diabatic representations, and the symmetry properties are briefly discussed. As an example, nonadiabatic effects in the V—N spectrum of C<sub>2</sub>H<sub>4</sub> and corresponding V—R<sub>y</sub> radiationless transitions in C<sub>2</sub>H<sub>4</sub> are investigated.

## 1. INTRODUCTION

Over the past few years, nonadiabatic effects in polyatomics and photochemical implications of the breakdown of the Born-Oppenheimer approximation have been investigated through *ab-initio* methods. Within this framework, some major theoretical problems are: (1) definitions of rotovibronic molecular Hamiltonians well suited for the investigation of nonadiabatic couplings and of large-amplitude vibrations; (2) expansions of the stationary molecular states on rotovibronic bases, taking into account the correct rotation, parity, and perturbation symmetries; (3) calculation of the electronic states and matrix elements in the adiabatic and diabatic representations; (4) calculation of the matrices of the molecular Hamiltonians and solution of the coupled or secular equations; (5) investigation of the radiative and nonradiative transition probabilities between stationary and nonstationary states. In this paper, I will briefly consider some of the previous problems and I will present some results of recent studies.

## 2. MOLECULAR SCHRÖDINGER EQUATION

In a body-fixed frame the time-independent molecular Schrödinger equation is

$$[\hat{H}(\omega, q, Q) - E_n] |n(\omega, q, Q)\rangle = 0, \quad (1)$$

where  $\omega$ ,  $q$ , and  $Q$  stand collectively for the rotational, electronic, and vibrational coordinates, respectively. The stationary molecular states  $|n\rangle$  can be expanded on a complete and orthonormal basis of known rotoelectronic states<sup>1</sup>  $|r_i e_K(\omega, q; Q)\rangle = |r_i(\omega)\rangle |e_K(q; Q)\rangle$ , where  $|r_i\rangle$  are rotational species and the electronic states  $|e_K\rangle$  depend parametrically on  $Q$ ,

$$|n\rangle = |\mathbf{re}\rangle \langle \mathbf{re} | n \rangle_{\omega q}, \quad (2)$$

where  $|\mathbf{re}\rangle$  is the row of the roto-electronic states and  $\langle \mathbf{re} | n \rangle_{\omega q}$  is a column of vibrational functions of  $Q$ . Alternatively, we can use a complete and orthonormal basis of known rotovibronic states<sup>2</sup>  $|r_i e_K v_j(\omega, q, Q)\rangle = |r_i e_K(\omega, q; Q)\rangle |v_j(Q)\rangle$ , where  $|v_j\rangle$  are vibrational species, and write

$$|n\rangle = |\mathbf{rev}\rangle \langle \mathbf{rev} | n \rangle_{\omega q Q} \quad (3)$$

From the Eqs. (1) and (2) we obtain the coupled equations

$$[\langle \mathbf{re} | \hat{H} | \mathbf{re} \rangle_{\omega q} - E_n \mathbf{1}] \langle \mathbf{re} | n \rangle_{\omega q} = 0, \quad (4)$$

where the matrix operator  $\hat{\mathbf{H}}^{re} = \langle \mathbf{re} | \hat{H} | \mathbf{re} \rangle_{\omega q}$  has elements  $\hat{H}_{i'K', iK}^{re}(Q) = \langle r_{i'K}, e_{K'} | \hat{H} | r_i e_K \rangle_{\omega q}$  which act on the vibrational functions  $\langle \mathbf{re} | n \rangle_{\omega q}$ , and  $\mathbf{1}$  is the unity matrix. By approximating  $\hat{H}_{i'K', iK}^{re} \approx \delta_{i'i} \delta_{K'K} \hat{H}_{iK, iK}^{re}$ , Eq. (4) gives the usual Born-Oppenheimer approximation. From the Eqs. (1) and (3) we obtain the secular equation

$$[\langle \mathbf{rev} | \hat{H} | \mathbf{rev} \rangle_{\omega q Q} - E_n \mathbf{1}] \langle \mathbf{rev} | n \rangle_{\omega q Q} = 0 \quad (5)$$

where the matrix  $\hat{\mathbf{H}}^{rev} = \langle \mathbf{rev} | \hat{H} | \mathbf{rev} \rangle_{\omega q Q}$  has elements  $\hat{H}_{i'K'j', iKj}^{rev} = \langle r_{i'K} e_{K'} v_{j'} | \hat{H} | r_i e_K v_j \rangle_{\omega q Q} = \langle v_{j'} | \hat{H}_{i'K', iK}^{re} | v_j \rangle_Q$ . Eq. (5) may be simplified by using for each roto-electronic species  $|r_i e_K\rangle$  the vibrational eigenstates  $|v_j^{iK}\rangle$  and eigenvalues  $\epsilon_j^{iK}$  of the diagonal operators  $\hat{H}_{iK, iK}^{re}$ . Thus,  $\hat{H}_{iKj', iKj}^{rev} = \delta_{j'j} \epsilon_j^{iK}$  and the comparison with the Born-Oppenheimer approximation is simpler. Of course, by using complete basis sets, Eqs. (1), (4), and (5) are fully equivalent.

Eqs. (4) and (5) show that the operators  $\hat{H}_{i'K', iK}^{re}(Q) = \langle r_{i'K} e_{K'} | \hat{H} | r_i e_K \rangle_{\omega q}$  play a central role in the theory. For their evaluation, we write the molecular Hamiltonian as

$$\hat{H}(\omega, q, Q) = \hat{T}^r(\omega, q, Q) + \hat{T}^v(Q) + \hat{H}^{el}(q; Q), \quad (6)$$

where  $\hat{T}^r$  and  $\hat{T}^v$  are the rotational and vibrational Hamiltonians, and  $\hat{H}^{el}$  is the usual electronic Hamiltonian, including possibly the mass polarization and spin-orbit corrections.  $\hat{H}^{el}$  is always written in terms of the cartesian coordinates in the body-fixed frame, whereas the form of  $\hat{T}^r + \hat{T}^v$  depends crucially on the choice of the body-fixed frame and of the vibrational coordinates (the rotational coordinates  $\omega$  are always the Euler angles relating the space-fixed and body-fixed frames). The usual choice of the Eckart conditions and of the normal coordinates yields the well-known Wilson-Decius-Cross roto-vibrational Hamiltonian<sup>3</sup>, which has been expressed in a final and elegant form by Watson for non-linear<sup>4</sup> and linear<sup>5</sup> molecules, and carefully discussed by Sutcliffe<sup>6</sup>. The Watson Hamiltonian is well suited for the study of the

roto-vibrational motion in the Born-Oppenheimer and small-vibration limits. When these approximations do not hold, as in photochemistry, the use of the Watson Hamiltonian leads to big difficulties<sup>7-9</sup>, and other definitions of the body-fixed frame and of the vibrational coordinates have been used<sup>9-17</sup>. For example, for a triatomic ABC molecule, by defining  $Q = (r, R, \Theta)$ , where  $r$  is the BC distance,  $R$  is the distance from A to the BC centre of mass and  $\Theta$  is the angle between  $\mathbf{r}$  and  $\mathbf{R}$ , we obtain<sup>11</sup> in atomic units

$$\hat{T}^v = -1/2 \left[ \mu_r^{-1} \frac{\partial^2}{\partial r^2} + \mu_R^{-1} \frac{\partial^2}{\partial R^2} + \mu_\Theta^{-1} \left( \frac{\partial^2}{\partial \Theta^2} + \cot \Theta \frac{\partial}{\partial \Theta} \right) \right], \quad (7)$$

where  $\mu_r^{-1} = m_B^{-1} + m_C^{-1}$ ,  $\mu_R^{-1} = m_A^{-1} + (m_B + m_C)^{-1}$ ,  $\mu_\Theta^{-1} = \mu_r^{-1} r^{-2} + \mu_R^{-1} R^{-2}$ , and the volume element is  $d\tau = dr dR \sin \Theta d\Theta$ . Alternatively, by defining  $Q = (R_1, R_2, \alpha)$ , where  $R_1$  and  $R_2$  are the AB and BC distances, respectively, and  $\alpha$  is the BAC angle, we have<sup>17</sup>

$$\begin{aligned} \hat{T}^v = 1/2 \left[ \mu_1^{-1} \frac{\partial^2}{\partial R_1^2} + \mu_2^{-1} \frac{\partial^2}{\partial R_2^2} + 1/2 \left( \mu_\alpha^{-1} - \frac{2 \cos \alpha}{m_A R_1 R_2} \right) \left( \frac{\partial^2}{\partial \alpha^2} + \cot \alpha \frac{\partial}{\partial \alpha} \right) + \right. \\ \left. + 1/2 \left( \frac{\partial^2}{\partial \alpha^2} + \cot \alpha \frac{\partial}{\partial \alpha} \right) \left( \mu_\alpha^{-1} - \frac{2 \cos \alpha}{m_A R_1 R_2} \right) \right] + \\ + m_A^{-1} \left( R_1^{-1} \frac{\partial}{\partial R_2} + R_2^{-1} \frac{\partial}{\partial R_1} \right) \left( \sin \alpha \frac{\partial}{\partial \alpha} + \cos \alpha \right), \end{aligned} \quad (8)$$

where  $\mu_1^{-1} = m_A^{-1} + m_B^{-1}$ ,  $\mu_2^{-1} = m_A^{-1} + m_C^{-1}$ ,  $\mu_\alpha^{-1} = \mu_1^{-1} R_1^{-2} + \mu_2^{-1} R_2^{-2}$ , and  $d\tau = dR_1 dR_2 \sin \alpha d\alpha$ . From Eqs. (7) and (8) it is clear that  $\hat{T}^v(r, R, \Theta)$  is simpler than  $\hat{T}^v(R_1, R_2, \alpha)$ .

In general, the vibrational Hamiltonian is given by<sup>4,5,18,19</sup>

$$\hat{T}^v = \sum_x \sum_y f_2^{xy}(Q) \frac{\partial^2}{\partial x \partial y} + \sum_x f_1^x(Q) \frac{\partial}{\partial x} + f_0(Q), \quad (9)$$

where  $x$  and  $y$  are two vibrational coordinates,  $f_i$  are functions of  $Q$  and  $f_0$  is a correction of the nuclear potential energy. The rotational Hamiltonian  $\hat{T}^r$  is, in general, more complicated since it contains rotovibronic coupling terms<sup>11,17</sup>; by assuming, however, a rotationless molecule, as it is usually done in photochemical processes,  $\hat{T}^r$  will be simply omitted later on. From  $\hat{H} = \hat{T}^v + \hat{H}^{\text{el}}$  and Eq. (9) we obtain<sup>20</sup>

$$\begin{aligned} \hat{H}_{K'K}^e(Q) = \langle e_{K'} | \hat{H} | e_K \rangle_q = \\ = \sum_x \sum_y f_2^{xy}(Q) \left[ \delta_{K'K} \frac{\partial^2}{\partial x \partial y} + g_{K'K}^x(Q) \frac{\partial}{\partial y} + g_{K'K}^y(Q) \frac{\partial}{\partial x} + h_{K'K}^{xy}(Q) \right] + \\ + \sum_x f_1^x(Q) \left[ \delta_{K'K} \frac{\partial}{\partial x} + g_{K'K}^x(Q) \right] + U_{K'K}(Q), \end{aligned} \quad (10)$$

with

$$g_{K'K}^x = \langle e_{K'} | \frac{\partial e_K}{\partial x} \rangle_q = -g_{KK'}^x, \quad (11)$$

by assuming a real electronic basis, and

$$h_{K'K}^{xy} = \langle e_{K'} | \frac{\partial^2 e_K}{\partial x \partial y} \rangle_q = \frac{\partial g_{K'K}^y}{\partial x} - \langle \frac{\partial e_{K'}}{\partial x} | \frac{\partial e_K}{\partial y} \rangle_{q'}, \quad (12)$$

$$U_{K'K} = \langle e_{K'} | \hat{H}^{\text{el}} + f_0 | e_K \rangle_{q'}. \quad (13)$$

The functions  $g_{K'K}^x$  and  $h_{K'K}^{xy}$  are the nonadiabatic vibronic coupling terms, and  $U_{K'K}$  are the nonadiabatic electronic coupling terms. Eq. (11) shows that  $g^x$  is a skew symmetric matrix with  $g_{KK}^x = 0$ .

The electronic states  $|e_K^A\rangle$ , which diagonalize the electronic Hamiltonian  $\hat{H}^{\text{el}}$ , define the adiabatic representation in which  $U_{K'K}^A = \delta_{K'K} U_{K'}^A$  are the usual adiabatic potential energies,

$$g_{K'K}^{Ax} = \langle e_{K'}^A | \frac{\partial \hat{V}^{\text{ne}}}{\partial x} | e_K^A \rangle_q (U_{K'}^A - U_{K'}^A)^{-1}, \quad (14)$$

where  $\hat{V}^{\text{ne}}$  is the potential energy between nuclei and electrons, and the diagonal terms  $\sum_{x,y} f_2^{xy} h_{KK}^{Axy}$  are the adiabatic corrections of the potential energies  $U_{K'}^A$  ( $g_{KK}^x = 0$ ). The nondiagonal terms  $g_{K'K}^{Ax}$ ,  $g_{K'K}^{Ay}$ , and  $h_{K'K}^{Axy}$  ( $K' \neq K$ ) couple the electronic states  $|e_{K'}^A\rangle$  and  $|e_K^A\rangle$  through the  $x$  and  $y$  vibrations and give rise to the breakdown of the Born-Oppenheimer approximation.

Since  $\partial/\partial x$  and  $\partial^2/\partial x \partial y$  commute with the electronic spin operator  $\hat{S}$ , the coupled states must have the same spin symmetry and the vibronic couplings give rise to the internal conversion between the adiabatic electronic states  $|e_{K'}^A\rangle$  and  $|e_K^A\rangle$ . In the (generalized) Born-Oppenheimer approximation  $g_{K'K}^{Ax} \approx h_{K'K}^{Axy} \approx 0$  for any  $K' \neq K$ ; Eqs. (14) and (12) show, however, that this approximation breaks down whenever crossings or avoided crossings occur between the potential energies  $U_{K'}^A$  and  $U_{K'}^A$ .

The electronic states  $|e_{K'}^D\rangle$ , which minimize the vibronic couplings  $|g_{K'K}^{Dx}|$  and  $|h_{K'K}^{Dxy}|$ , for  $K' \neq K$ , define the diabatic representations in which terms  $U_{K'K}^D$ . Since the adiabatic and diabatic bases are related by a unitary transformation, both being orthonormal, we have

$$|e^D(q; Q)\rangle = |e^A(q; Q)\rangle \mathbf{C}(Q),$$

$$\mathbf{U}^D = \mathbf{C}^\dagger \mathbf{U}^A \mathbf{C},$$

$$\mathbf{g}^{Dx} = \mathbf{C}^\dagger (\mathbf{g}^{Ax} \mathbf{C} + \frac{\partial \mathbf{C}}{\partial x}), \quad (15)$$

$$\mathbf{h}^{Dxy} = \mathbf{C}^\dagger (\mathbf{h}^{Axy} \mathbf{C} + \mathbf{g}^{Ax} \frac{\partial \mathbf{C}}{\partial y} + \mathbf{g}^{Ay} \frac{\partial \mathbf{C}}{\partial x} + \frac{\partial^2 \mathbf{C}}{\partial x \partial y}).$$

Eq. (15), and the conditions  $|\mathbf{g}^{Dx}|, |\mathbf{h}^{Dxy}| = \text{minima}$ , define in principle the diabatic states, although their actual calculation possess both conceptual and numerical difficulties. For example, Lichten<sup>21</sup> defined physical diabatic states dominated by simple electronic configurations (ionic, covalent, valence, Rydberg, etc.) and Smith<sup>22</sup> introduced strictly diabatic states which fulfill exactly the conditions  $\mathbf{g}^x = \mathbf{h}^{xy} = \mathbf{0}$ . Both definitions are incomplete: that of Lichten does not offer a firm method for the *ab-initio* calculation of diabatic species, and strictly diabatic states exist only for diatomics and do not exist for polyatomics<sup>23</sup>. Although the task of defining a general and useful diabatic representation is still an open problem, some authors<sup>24-26</sup> have recently presented new methods for overcoming the difficulties, one of which will be discussed later on.

### 3. APPLICATION TO C<sub>2</sub>H<sub>4</sub>

Since the usual point groups are not suitable for discussing the symmetry properties of molecular Hamiltonians and for classifying the rovovibronic states and operators, mainly for nonrigid molecules, Longuet-Higgins<sup>27</sup> defined the molecular symmetry group whose elements are, among others, the permutations of identical nuclei and the inversion of nuclei and electrons in the centre of mass. The Longuet-Higgins group is particularly suitable in solving the molecular Schrödinger equation, whenever nonadiabatic and large-vibrations effects are important, allowing an easy classification of states and operators. Indeed, if  $\hat{\alpha}(q, Q)$  is an operator depending on the electronic and vibrational coordinates ( $\hat{H}^{el}$ ,  $\partial/\partial x$ ,  $\partial^2/\partial x \partial y$ , dipole moment, etc.), the matrix element  $\alpha_{K'K}(Q) = \langle e_{K'}(q; Q) | \hat{\alpha} | e_K(q; Q) \rangle_q$  belongs to the vibrational representation contained in  $\Gamma = \Gamma_{K'} \times \Gamma_a \times \Gamma_K$  and it is zero if  $\Gamma$  does not contain any vibrational representation.

For example, Table I reports the symmetry species of some states and operators of C<sub>2</sub>H<sub>4</sub> undergoing a pure torsional motion around the CC bond.

TABLE I

*Symmetry Species of some States and Operators of C<sub>2</sub>H<sub>4</sub> Undergoing Pure Torsion<sup>a</sup>*

$G_{16}^{(2)}$	$D_{2h}$	$D_{2d}$	$ e_K\rangle$	$ b_m(\tau)\rangle^b$	Operators <sup>c</sup>
$A_{1g}^+$	$A_g$	$A_1$		$\cos 2m\tau$	$g_{12}^A, Z_{02}^A$
$A_{2u}^+$	$B_{1u}$	$A_2$	$ e_2^A\rangle$		
$B_{1g}^+$	$A_g$	$B_1$	$ e_0^A\rangle$	$\cos(2m+1)\tau$	$\cos\omega, Z_{02}^D$
$B_{2u}^+$	$B_{1u}$	$B_2$	$ e_2^D\rangle$		$Z$
$A_{1u}^-$	$A_u$	$A_1$		$\sin(2m+1)\tau$	$\sin\omega, Z_{01}^D$
$A_{2g}^-$	$B_{1g}$	$A_2$	$ e_1^D\rangle$		
$B_{1u}^-$	$A_u$	$B_1$		$\sin 2m\tau$	$\partial/\partial\tau, h_{12}^A, Z_{01}^A,$ $U_{12}^D, h_{12}^D$
$B_{2g}^-$	$B_{1g}$	$B_2$	$ e_1^A\rangle$		

<sup>a</sup> The diabatic representation is defined by  $l = 0$  and  $n = 1$ .

<sup>b</sup> Torsional basis.

<sup>c</sup>  $Z$  is the dipole-moment component along the CC bond.

Since the full Longuet-Higgins group is too large (96 elements), a simpler subgroup  $G_{16}^{(2)}$  has been considered<sup>26,28,29</sup> and it is suitable for  $T^v \approx -\frac{1}{2I_r} \partial^2/\partial \tau^2$ ,

where  $\tau$  is the torsional angle, and is isomorphous with the double group of  $D_{4h}$ . The correlations with the  $D_{2h}$  and  $D_{2d}$  point groups are also shown and the adiabatic electronic states are the  $|e_0^A\rangle$  ground species  $N(\tau^2)$  and the excited singlet states  $|e_1^A\rangle$  and  $|e_2^A\rangle$  which are linear combinations of the  $V(\pi\pi^*)$  and  $R_y(\pi 3p_y)$  configurations<sup>29</sup>. Note that  $\tau$  is not a symmetry coordinate and that the nonadiabatic couplings between the ground state and the excited species are symmetry forbidden for a pure torsional motion.

The diabatic representations of  $C_2H_4$  are defined<sup>26</sup> by  $|e_K^D\rangle$  states with constant and minimal nonadiabatic vibronic coupling  $g_{K'K}^D$  which has been obtained from the molecular symmetry properties. In a two-state problem the first of Eq. (15) reads

$$|e_1^D\rangle = |e_1^A\rangle \cos \omega + |e_2^A\rangle \sin \omega \quad (16)$$

$$|e_2^D\rangle = -|e_1^A\rangle \sin \omega + |e_2^A\rangle \cos \omega,$$

where the mixing angle  $\omega$  depends on  $\tau$  and defines the transformation matrix  $C$ , and the third of Eq. (15) gives

$$g_{12}^D = g_{12}^A - d\omega/dr. \quad (17)$$

Eq. (17) has been integrated with the condition that  $g_{12}^D$  is a constant, different from zero in general. Since  $g_{12}^A$  belongs to  $A_{1g}^+$  (Table I), we have

$$g_{12}^A(\tau) = a_0 + \sum_{m=1} a_{2m} \cos 2m\tau \quad (18)$$

and

$$\omega(\tau) = \omega(0) + (a_0 - g_{12}^D) + \sum_{m=1} (a_{2m}/2m) \sin 2m\tau. \quad (19)$$

A diabatic representation is defined by the constants  $\omega(0)$  and  $(a_0 - g_{12}^D)$  which were obtained by requiring that  $\cos \omega$  and  $\sin \omega$  of Eq. (16) belong to torsional representations of  $G_{16}^{(2)}$ . Straightforward application of the group theory then shows<sup>26</sup> that  $\cos \omega$  and  $\sin \omega$  belong to  $A_{1g}^+$ ,  $B_{1g}^+$ ,  $A_{1u}^-$ , or  $B_{1u}^-$  if, and only if,  $\omega(0) = l\pi/2$  and  $(a_0 - g_{12}^D) = n$ , where both  $l$  and  $n$  are integer numbers. The first condition defines the integration constant and the second one fixes the value of  $g_{12}^D$ , since  $a_0 = 0.778$  a. u. is known from the best fit<sup>29</sup> to the computed *ab-initio* values of  $g_{12}^A$ . This value of  $a_0$  and the condition  $(a_0 - g_{12}^D) = n$  imply that  $g_{12}^D$  must be different from zero and minimal (in absolute value) for  $n = 1$ . Therefore, by using  $l = 0$  and  $n = 1$ , the species of  $\cos \omega$  and  $\sin \omega$  and of the diabatic states and operators are immediately obtained and are reported in Table I.

The most relevant results of a nonadiabatic MRD-CI investigation of the V—N absorption spectrum of  $C_2H_4$  undergoing a pure torsional motion<sup>26,29</sup> are reported in Figures 1, 2, and 3. Figure 1 shows that the adiabatic potential curves of the excited states undergo a sharply avoided crossing upon twisting, with a minimal energy splitting of 0.05 eV at  $\tau = 22^\circ$ , while the diabatic curves cross near this point. Figure 2 shows that the nonadiabatic couplings in both representations are strongly peaked near the avoided crossing. In the diabatic representation  $U_{12}^D$  is by far the largest nonadiabatic term and the

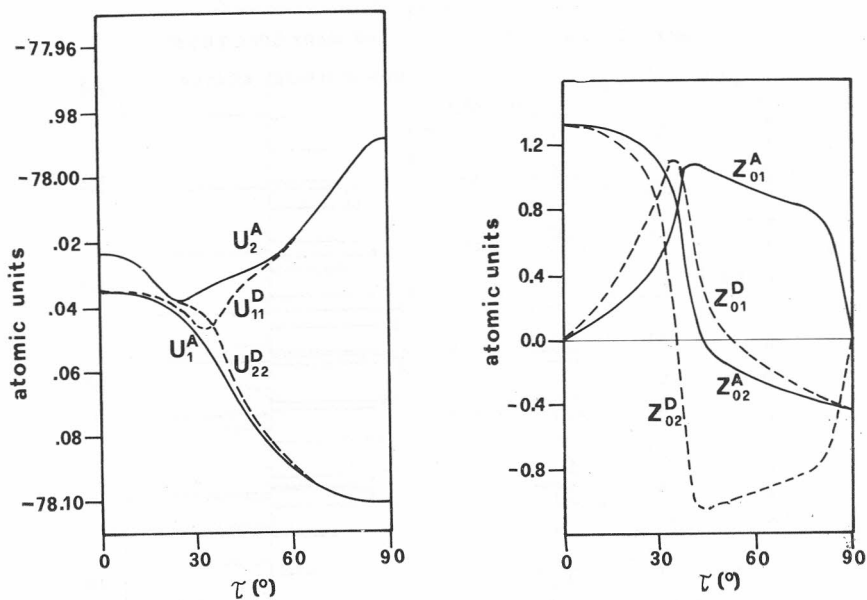


Figure 1.  $V$  and  $R_v$  states of  $C_2H_4$ . MRD-CI corrected potential curves  $U_{KK} = \langle e_K | H^{e1} | e_K \rangle_q - h_{KK}/qI_{\tau}$ , (left) and transition dipole moments from the  $N$  state  $Z_{0K} = \langle e_0 | \mu_2 | e_K \rangle_q$  (right) in the adiabatic (full lines) and diabatic (dashed lines,  $l = 0$  and  $n = 1$ ) representations. (from Ref. 26)

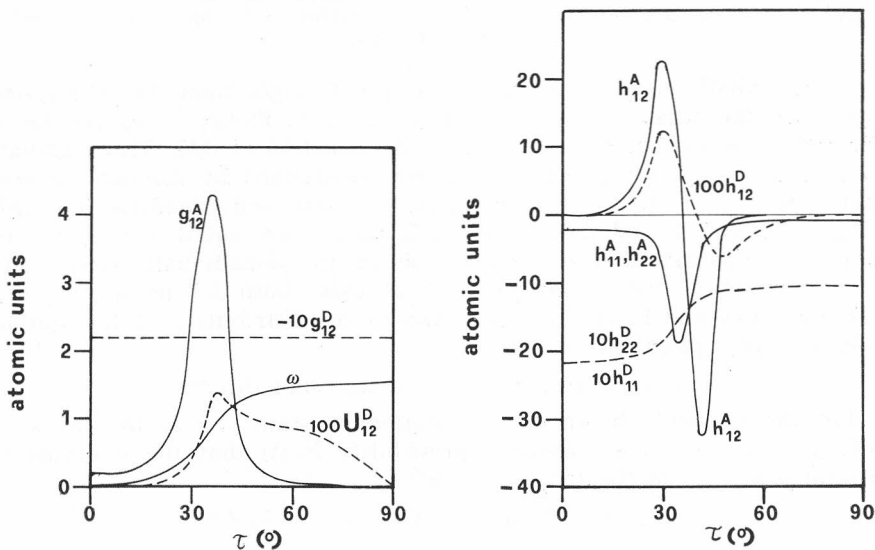


Figure 2.  $V$  and  $R_v$  states of  $C_2H_4$ . MRD-CI nonadiabatic couplings in the adiabatic (full lines) and diabatic (dashed lines,  $l = 0$  and  $n = 1$ ) representations. (from Ref. 26)

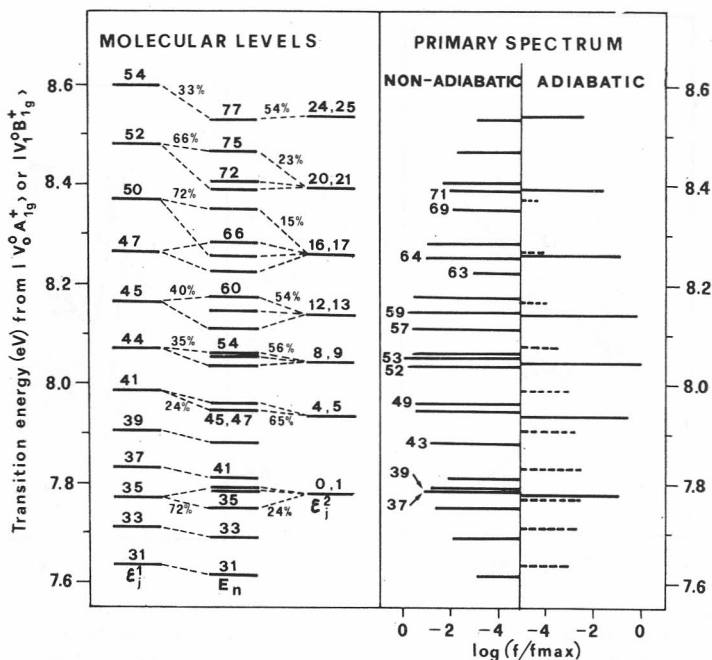


Figure 3. Central portion of the nonadiabatic and adiabatic absorption spectrum of  $C_2H_4$  from the degenerate ground states. Molecular levels (left): adiabatic  $\epsilon_j^1$  and  $\epsilon_j^2$  of the excited electronic states  $|e_1^A\rangle$  and  $|e_2^A\rangle$ , and nonadiabatic  $E_n$ ; the percentage of mixing of some adiabatic states is also shown. Primary spectrum (right): nonadiabatic and adiabatic dipolar intensities; the dashed and full lines in the adiabatic spectrum refer to the electronic states  $|e_1^A\rangle$  and  $|e_2^A\rangle$  respectively. (from Ref. 29)

total nonadiabatic coupling is about four times larger than the corresponding coupling in the adiabatic representation<sup>26</sup>. Finally, Figure 3 reports the adiabatic and nonadiabatic spectra of the V—N transition of  $C_2H_4$ . The nonadiabatic spectrum has been computed in both representations by solving the secular equation with the potential curves, dipole moments, and nonadiabatic couplings of Figures 1 and 2, and the nonadiabatic results are equal in both representations, as expected. Figure 3 clearly shows the nonadiabatic effects in the central portion of the V—N spectrum of  $C_2H_4$ , both in the mixing of the adiabatic states and in the irregular and broad distribution of the stationary levels and absorption intensities.

#### 4. RADIATIONLESS TRANSITION PROBABILITY

Let the molecule be in the nonstationary state  $|i\rangle$  at the initial time  $t = 0$ . The radiationless transition probability  $P_{fi}(t)$  that the molecule is in the final state  $|f\rangle$  at the time  $t > 0$  is<sup>30</sup>

$$\begin{aligned}
 P_{fi}(t) &= \left| \sum_n \exp(-i\omega_n t) \langle f|n\rangle \langle n|i\rangle \right|^2 = \\
 &= \sum_n |\langle f|n\rangle|^2 |\langle n|i\rangle|^2 + 2 \sum_{n < n'} \sum [\operatorname{Re}(\langle f|n\rangle \langle n|i\rangle \langle i|n'\rangle \langle n'|f\rangle) \cos \omega_{nn'} t + \\
 &\quad + \operatorname{Im}(\langle f|n\rangle \langle n|i\rangle \langle i|n'\rangle \langle n'|f\rangle) \sin \omega_{nn'} t], \quad (20)
 \end{aligned}$$



where  $|n\rangle$  are the stationary nonadiabatic states discussed previously,  $\omega_n = E_n/\hbar$ ,  $E_n$  being the nonadiabatic energies,  $\text{Re}(x)$  and  $\text{Im}(x)$  are the real and imaginary parts of  $x$ , and  $\omega_{nn'} = \omega_n - \omega_{n'}$ . The probability  $P_{fi}(t)$  defines the radiationless time-evolution of the initial state  $|i\rangle$  due to the transition to the final state  $|f\rangle$  and it is a function oscillating in time, sum of periodic functions each with period  $T_{nn'} = 2\pi/\omega_{nn'}$ .

For the discussion of the radiationless transitions between two excited adiabatic electronic states  $|e_K^A\rangle$  and  $|e_{K'}^A\rangle$ , let us consider the upper part of Figure 4 which shows the ground state  $|0\rangle$ , the adiabatic vibronic species  $|e_K^A v_j^K\rangle$  and  $|e_{K'}^A v_j^{K'}\rangle$ , and the stationary states  $|n\rangle$  which were excited at  $t=0$  through absorption from the ground state. In the dipolar approximation, the initial state is<sup>31</sup>

$$|i\rangle = \sum_n |n\rangle \langle n|i\rangle = \sum_n |n\rangle \langle n|\mu_a|0\rangle / [\sum_{n'} |\langle n'|\mu_a|0\rangle|^2]^{1/2}, \quad (21)$$

where  $\mu_a$  is the  $a$ -component of the dipole moment operator  $\mu$ . From Eqs. (20) and (21), the probability that the molecule is in any state  $|e_K^A v_j^K\rangle$  at  $t > 0$  is

$$P_{Ki}(t) = \sum_j P_{Kj,i}(t) = \sum_j \sum_n e^{-i\omega_n t} |\langle e_K^A v_j^K | n \rangle \langle n | \mu_a | 0 \rangle|^2 / \sum_{n'} |\langle n' | \mu_a | 0 \rangle|^2. \quad (22)$$

At  $t=0$ , Eq. (22) gives

$$P_{Ki}(0) = \sum_j |\langle e_K^A v_j^K | \mu_a | 0 \rangle|^2 / \sum_n |\langle n | \mu_a | 0 \rangle|^2 \leq 1, \quad (23)$$

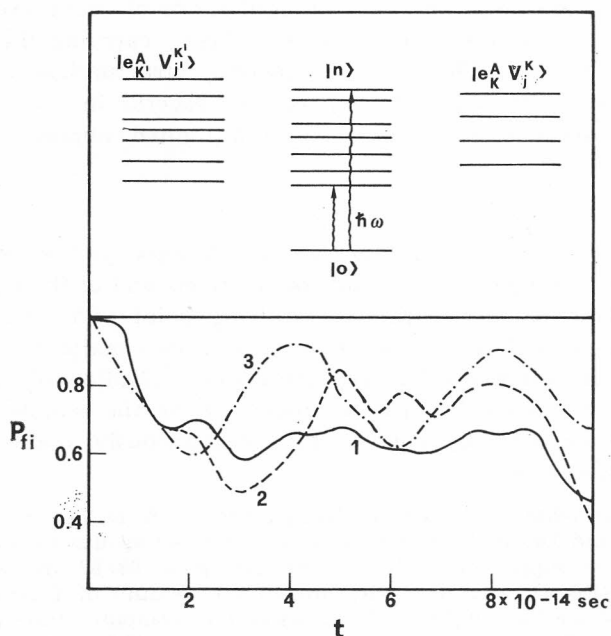


Figure 4. Upper part: simplified energy-level scheme for radiationless transitions. Lower part: curves (1), (2), and (3) show  $P_{2i}$ ,  $P_{2i'}$ , and  $P_{i''i''}$  for the V—R<sub>y</sub> system of C<sub>2</sub>H<sub>4</sub>, where  $|i\rangle$ ,  $|i'\rangle$ , and  $|i''\rangle$  are different initial state.

*i. e.* the molecule is in both electronic states, but mainly in that with greater transition dipole moments to the ground state. In the theory of radiationless transitions, one generally assumes<sup>32</sup> that absorption from the ground state is allowed for the  $|e_K^A v_j^K\rangle$  states and forbidden for  $|e_{K'} v_j^{K'}\rangle$ ; in this case  $P_{Ki}(0) = 1$ . This assumption is, however, not necessary when the stationary Schrödinger equation has been solved. Whenever the nonadiabatic couplings are zero, *i. e.* when the adiabatic states are also stationary, it is easy to check from Eqs. (22) and (23) that  $P_{Ki}(t) = P_{Ki}(0)$ , *i. e.* no time-evolution of the initial state occurs, as expected.

The lower part of Figure 4 shows the radiationless transition probabilities  $P_{fi}(t)$  between some states of the V—R<sub>y</sub> system of C<sub>2</sub>H<sub>4</sub>. Curves (1) and (2) show  $P_{2i}(t)$ , of Eq. (22), to the second electronic state from two different initial states: the first  $|i\rangle$  has been excited from both degenerate ground species  $A_{1g}^+$  and  $B_{1g}^+$ , and the second  $|i'\rangle$  has been excited only from the  $A_{1g}^+$  ground state. In both cases  $P_{2i}(0) = 0.994$ , *i. e.* the system is by far in the second electronic state at  $t = 0$ , according to its larger transition moments to the ground species (see Figure 3), but the following time-evolutions are considerably different. In fact, curve (1) shows that  $P_{2i}$  first decays quickly and then has some broad oscillations around 0.65, and finally, at larger times, undergoes a second decay. Since the oscillations of  $P_{2i'}$  (curve (2)) are more evident, we note that interference effects between the two ground states quench the  $P_{2i'}$  oscillations and give the rather flat  $P_{2i}$  curve (1). This result is confirmed by the large and regular oscillations of curve (3) which shows  $P_{i''i''}(t)$ , where  $|i''\rangle$  is the vibronic state of  $|e_2^A\rangle$  carrying the largest transition moment to  $|0\rangle$ . Therefore, in general, structureless time-evolutions may be due to interference effects between several involved states, while well-resolved curves may be ascribed to a limited number of interacting species.

## 5. CONCLUSION

We have reported in this paper on an example of the use of *ab-initio* methods in the investigation of nonadiabatic effects and of their photochemical implications. This is only a possible starting point and much more work is needed in this field. I summarize here only two major points: (i) use of exact spinless Hamiltonians for triatomics and derivation of similar Hamiltonians for large molecules; (ii) improvement of the simple treatment of radiationless transitions by considering simultaneously both radiative and nonradiative processes.

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## SAŽETAK

## Neadijabatski efekti i prijelazi bez zračenja

Carlo Petrongolo

Razmatrane su *ab initio* metode za proračune stacionarnih molekulskih stanja kao i za određivanje vjerojatnosti prijelaza bez zračenja između nestacionarnih stanja. Određeni su neadijabatski efekti u V—N spektru C<sub>2</sub>H<sub>4</sub> i odgovarajući V—Ry prijelazi bez zračenja.