

3P076

Electronic spectra and photodissociation of vinyl chloride and its derivatives

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Vinyl chloride (C_2H_3Cl), VC, is an atmospheric pollutant. Evidence showed that VC causes cancer in human beings. Because of this, understanding of photochemistry and spectroscopy of VC is important. There were a few studies in this direction in the past however there are many questions yet to be answered. For example, very recently, $\pi,3s$ state has been assigned as the optically bright state.^{1,2} It is contradictory to the earlier assumption that $\pi \rightarrow \pi^*$ (transition from C=C bonding to its anti-bonding orbital. For orbital character see Table 1) excitation is the main electronic transition in VC. Another thing is that though the optically bright state has generally been thought to be predissociated by the repulsive $n\sigma^*$ (transition from Cl non-bonding to C-Cl anti-bonding orbital), recently it has been proposed that dissociation in VC happens through $\pi\sigma^*$ state and not through $n\sigma^*$ state.³ These foregoing facts reveal that a thorough study to clarify the doubts and assumptions is necessary. Hence we studied VC to (1) obtain its absorption spectrum by using SAC-CI and to assign the excitations including $\pi \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$, and $n \rightarrow \pi^*$ and (2) understand the C-Cl bond breaking mechanism by studying the potential energy surfaces (PES) of its excited states.

The vertical absorption spectra were obtained by using SAC-CI. Various basis sets up to Aug-cc-pVTZ with necessary Rydberg functions on carbon and chlorine atoms were utilized for this purpose. PES were obtained mainly using D95(d,p) basis set.

We show the character of n , π , π^* , and σ^* in Table 1. A few vertical excitation energies with oscillator strengths along with available experimental and theoretical results are tabulated in Table 2. Our results agree well with the experimental results. Particularly, the energy (6.96 eV) obtained for the $\pi \rightarrow \pi^*$ excitation agrees well with the experimental values (6.7–6.9 eV). These results and the oscillator strengths obtained here clarify that the main excitation in VC is the $\pi\pi^*$ excitation [with a small contribution of out of plane $n(Cl \text{ lone pair})$ in the $\pi\pi^*$ excitation]. The basis sets used in the previous studies were insufficient to describe the $\pi \rightarrow \pi^*$ excitation properly. Other valence excitation ($\pi \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, and $n \rightarrow \pi^*$) energies and Rydberg excitation ($\pi \rightarrow 3s$, $\pi \rightarrow 3p\sigma$, and $\pi \rightarrow 3p\pi$) energies were also obtained.

PES (see figure 1 and 2) obtained along the C-Cl bond length clearly shows the formation of avoided crossing between bright $\pi\pi^*$ and $n\sigma^*$ states at around 1.85 Å. This reveals that the excited VC transfers from the bound $\pi\pi^*$ state to the dissociative $n\sigma^*$ state through level crossing. Meanwhile, PES obtained along C=C torsion provides interesting results that the low lying two states, $\pi\sigma^*$ and $\pi\pi^*$, mix from the very beginning of torsion. As the twisting angle increases, the mixing becomes stronger and stronger. Hence, C-Cl dissociation can also

takes place through $\pi\sigma^*$ state after mixing. The study on 2-D PES incorporating both C–Cl bond length and C=C twisting is underway.

Table 1. Nature of π , π^* , σ^* , and n orbitals.

Nature	C=C	C–Cl
π	bonding	anti-bonding
π^*	anti-bonding	anti-bonding
σ^*	anti-bonding	anti-bonding
n	-	bonding

Table 2. Vertical excitation energy (ΔE) and oscillator strength (f) of VC.

Nature	SAC-CI		Past studies	
	ΔE (eV)	f	Theory	Expt.
$\pi, 3s/\sigma^*$	6.81	0.0111	6.68 ²	
π, π^*	6.96	0.3274	7.46, ² 7.40 ³	6.7-6.9⁴
$\pi, \sigma^*/3s$	6.99	0.0035	7.27, ² 7.26 ³	
$\pi, 3p\sigma_x$	7.48	0.0006	7.48 ²	
$\pi, 3p\sigma_y$	7.70	0.0102	7.56 ²	
n, π^*	7.82	0.0005	7.90 ³	
$\pi, 3p\pi$	7.89	0.0098		7.82 ⁵
n, σ^*	8.20	0.0012	8.50 ³	

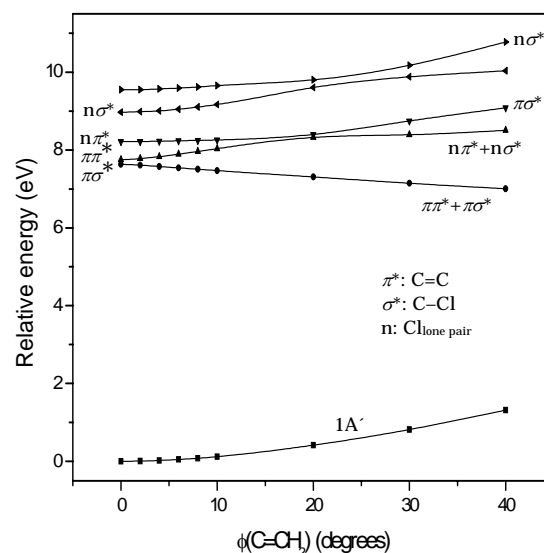


Fig. 1. PES along C=C twisting

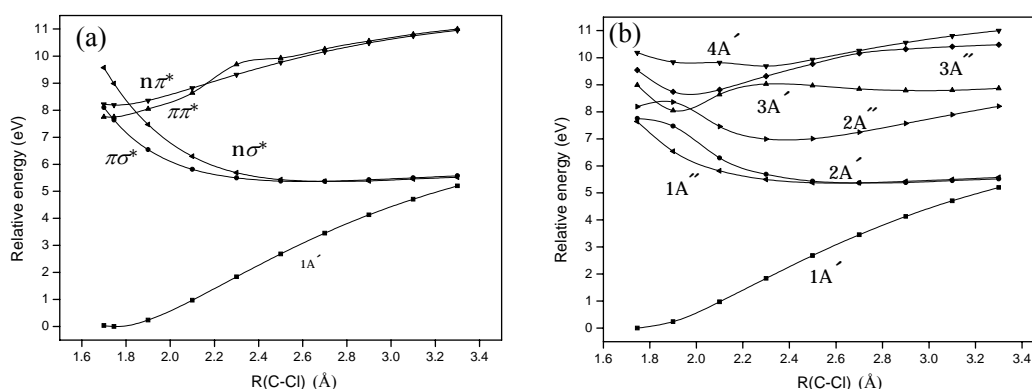


Fig. 2. PES along C–Cl bond (a) diabatic PES of $\pi\sigma^*$, $\pi\pi^*$, $n\pi^*$, and $n\sigma^*$ states (b) adiabatic PES of a few low-lying states

References:

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