

## Chapter 2 Problems

1. (To answer this question fully requires knowledge of some of the material covered in Chapters 1, and Chapters 5 to 7, including Study Box 7.1.)
- (a) Briefly outline experimental strategies currently available for measuring the partitioning of energy between vibration, rotation, and translation in the products of an exothermic atom transfer reaction



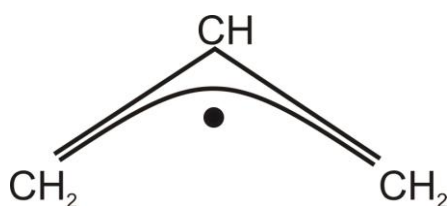
- (b) How may the properties for vibrational and translational energy disposal be influenced by the topography of the potential energy surface over which the reaction proceeds, and by the masses of atoms involved? Illustrate your answer by reference to the data, determined at 300 K, for the following reactions

	$\langle f_{\text{vib}} \rangle$	$\langle f_{\text{trans}} \rangle$	Product scattering
$\text{H} + \text{Cl}_2 \rightarrow \text{HCl}(v', j') + \text{Cl}$	0.39	0.54	backward
$\text{Cl} + \text{HI} \rightarrow \text{HCl}(v', j') + \text{I}$	0.71	0.16	forward

[  $\langle f_{\text{vib}} \rangle$  and  $\langle f_{\text{trans}} \rangle$  are the mean fractions of the total energy disposed into vibration and translation, respectively.]

2. In this question we use a very simple theory of bonding, known as Hückel theory, which ignores the effects of electron repulsion and electron correlation, to obtain information about the relative barrier heights of two reactions. (If you are unfamiliar with Hückel theory, you will need to read about this first in one of the recommended standard texts, for example, refs. [1, 70].)

Use Hückel theory and the variation principle to construct the secular equations for the  $\pi$  orbitals of the allyl radical shown below.



Determine the molecular orbital energies and the linear combinations of atomic orbitals associated with them. Show that the charge density arising from the  $\pi$  electrons is uniform at each carbon atom in the allyl radical. Using Hückel theory to estimate the appropriate barrier heights, suggest the most likely point of attack on the allyl cation,  $C_3H_3^+$ , by a nucleophilic reagent. You may assume that the  $\sigma$ -bonding framework is unaffected by the attack of the nucleophile.

3. (a) How is a *stationary point* on a PES defined? What differentiates a *saddle point* from an energy minimum?

(b) What information do we commonly calculate from the Hessian of the PES (a generalization of the second derivative of the energy for a diatomic molecule) at an energy minimum? Can you relate this information to Newton's law for motion close to the energy minimum? What corresponding information could we calculate from the Hessian at a saddle point?

(c) Saddle points are viewed as 'separating' and 'connecting' the reactant and product valleys on a PES. For many chemical reactions, there are many stationary points on a PES (Figure 2.4 is a simple example). Quantum chemistry programs can determine stationary points on a PES. Given that a saddle point geometry has been found, how would you determine which 'reactants' and 'products' are connected by this saddle point?