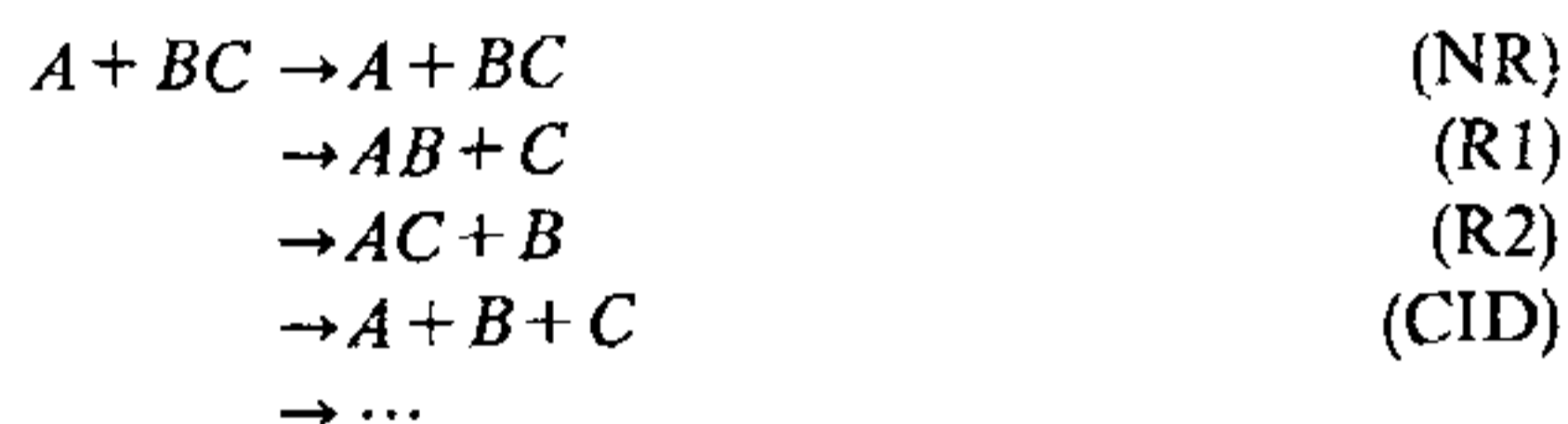# Channel control in chemical reactions

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Recent developments towards channel control in chemical reactions are reviewed briefly. Vibrationally mediated photodissociation is discussed in detail using HI photodissociation as an example.

SEVERAL strategies have been proposed over the years to control the outcome of a collision event, to effect one channel preferentially over the other. Considering one of the simplest collisions, that between an atom (A) and a diatom (BC) as an example, several outcomes are possible depending upon energy and other factors:

$$A + BC \rightarrow A + BC \qquad \text{(NR)}$$
$$\rightarrow AB + C \qquad \text{(R1)}$$
$$\rightarrow AC + B \qquad \text{(R2)}$$
$$\rightarrow A + B + C \qquad \text{(CID)}$$
$$\rightarrow \cdots$$

The simplest means of channel control known to chemists for a long time has been to increase the relative translational energy (E_{trans}) of reactants by supplying heat. For $E_{trans} < E_{th}$ where E_{th} is the threshold energy for the exchange reaction, the only channel available is NR. For $E_{trans} > E_{th}$ the exchange channel R1 opens up. Similar constraints hold for R2 and CID channels. Depending upon the system, charge transfer and other channels open up at different E_{trans}. In the last 2–3 decades it has been realized that for many reactions the reagent vibrational excitation enhances the reaction cross-section more selectively than E_{trans}^1. The reagent rotation plays a subtler role[2]. For many reactions, rotational excitation of a reactant molecule leads initially to a decrease in the reaction cross-section. Invariably this trend is followed by rotational enhancement, becoming comparable to vibrational enhancement.

While such strategies rely upon initial state preparation of reactants, substantial effort has gone into examining the possibility of controlling the collisional outcome by intervening at the transition state[3]. We must add that the success via this route has been rather limited so far.

Unimolecular reactions and intramolecular vibrational relaxation

In the case of unimolecular reactions, one is always concerned about the possibility of energy randomiza-

tion. A large number of experimental investigations[4] of state- and bond-selected unimolecular reactions through vibrational overtone excitation, internal conversion or stimulated emission pumping have shown that energy placed in one particular vibrational mode gets distributed into others. Alternatively, there does not seem to be clear cut evidence for mode selectivity in unimolecular reactions. Attempts have been made to understand the factors responsible for intramolecular vibrational relaxation (IVR) and to look for means of attaining mode selectivity[5]. One way to circumvent the IVR is to use a laser excitation pulse, short enough in time scale that the reaction is over before energy is randomized as has been demonstrated by Zewail and coworkers[6]. Theoretically, it has been pointed out that there could be local modes, excitation of which can lead to mode-selective chemistry[7]. Experimental evidence has come recently[8]. For example, excitation of the OH mode in HOD favours the $H_2 + OD$ formation in

$$H + HOD \rightarrow H_2 + OD$$
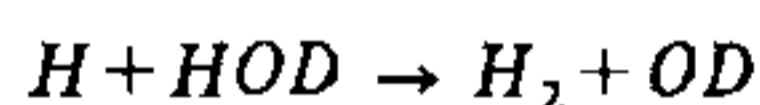
while OD excitation in HOD leads to HD + OH formation:

$$H + HOD \rightarrow HD + OH.$$

Coherence control scheme

Brumer and Shapiro[9] pointed out how it might be possible to utilize the coherence property of a laser to obtain preferentially one set of products over another. For example, the excitation of a molecule in state $|E_1\rangle$ to some energy E could be accomplished by single photon excitation using a laser frequency of ω_3 or by a 3-photon process using a laser of frequency $\omega_1 (3\omega_1 = \omega_3)$ as illustrated in Figure 1 a. When both paths are 'on' at the same time the probability of excitation consists of terms P_3 and P_1 corresponding to the two laser excitations and also an interference term P_{13}. Since the product obtained is dependent on the prepared state, it is possible to control the channel outcome by controlling the relative intensity and relative phase of the two lasers. Experimental evidence for the viability of such a scheme has become available recently[10].

Some of the alternative schemes that have been proposed are given in Figure 1 b-d. In the scheme in Figure 1 b, a superposition state $|\chi(t)\rangle = C_1 |E_1\rangle$
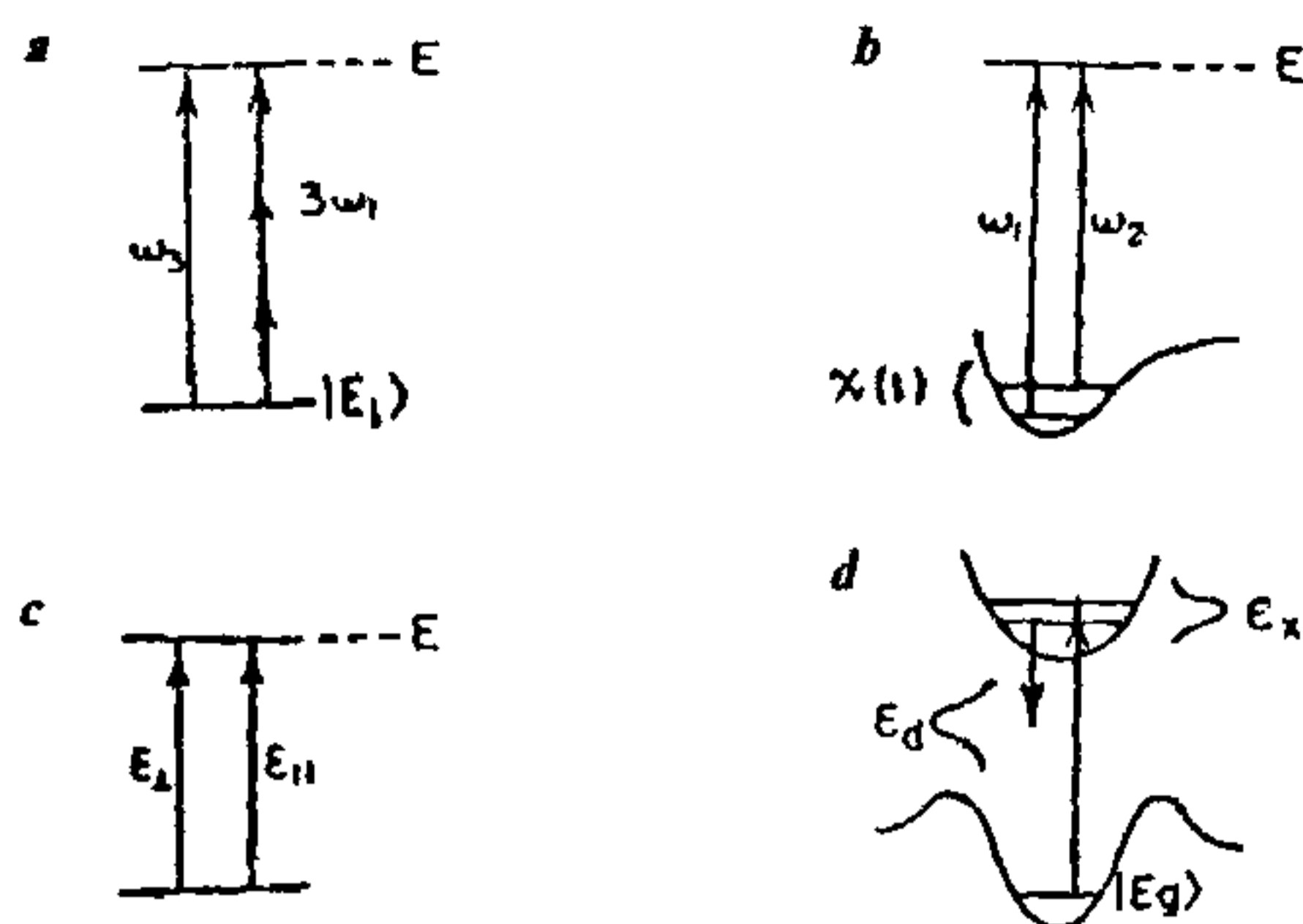
Figure 1. Different coherence control schemes proposed. (Adapted from ref. 11).

$+ C_2 | E_2 \rangle$ is prepared initially and then it is photodissociated with different fields

$$\bar{\varepsilon}(t) = \bar{\varepsilon}_1 \cos[(\omega_1 + \theta_1)t] + \bar{\varepsilon}_2 \cos[(\omega_2 + \theta_2)t] \quad (1)$$

which raise the levels to energy E. The field parameters as well as the coefficients C_1 and C_2 are experimentally controllable quantitites. The scheme in Figure 1c envisages using two independent optical routes involving parallel and perpendicular components of a single electric field to excite to the continuum. The channel control in this case can be accomplished by varying the degree of polarization.

In contrast to the schemes in Figure 1a–c which rely on the use of CW laser(s), the one in Figure 1d makes use of two laser pulses. The first excitation pulse would produce a superposition state while the second pulse would take it to a continuum. The control parameters here are the time delay between the two pulses and the coefficients of the superposition state. For a more detailed discussion of the coherence control approach and its variations, the reader is referred to a recent review by the proponents[11].

Bimolecular collisions

It has been known for long that the collisional outcome is strongly dependent on the vibrational phase of the diatomic molecule under attack[12]. Plots of final action of the reagent/product versus initial vibrational phase of the reactant reveal reactive and non-reactive bands and 'fractal zones' in the switch-over region. For example, see ref. 13. With the advent of femtosecond pulses, excitation of molecules with a particular bond distance (or vibrational phase) has become a reality[14]. Therefore it is not unrealistic to expect this route to yield tangible results in the near future.

The non-adiabatic route

Several schemes have been proposed in the last few years to achieve channel control through a non-adiabatic route. Rice and coworkers[15] proposed a *pump and dump* scheme which envisages exciting a molecule electronically (using a pump laser), letting the system time-evolve on the excited state and stimulating de-excitation (dump) onto the lower channel as illustrated in Figure 2. Using a model system they showed (numerically) that channel control could be achieved by adjusting the time delay between the pump and the dump pulses. Gadzuk[16] pointed out how the same could be accomplished in an adsorbate molecule by altering the workfunction of a metal surface by depositing alkali metal atoms, for example, without using laser pulses. Schematics of the proposal are given in Figure 3. The scheme has been used to explain the observed[17] unusually large vibrational excitation of NO after it has suffered collision with Pt metal. Several workers (for example, see ref. 18) have examined the possibility of using differently shaped pulses to achieve channel control. Rabitz and coworkers[19] and Manz and coworkers[20] have examined the possibility of inverse quantum mechanical control. That is, depending upon the choice of products, work out (inversely) the requirement of the shape of the field and then put it to practice.

Vibrationally mediated photodissociation

Attempts have also been made to obtain one set of products preferentially over another by combining initial state preparation with photodissociation. For example, using model calculations, Imre and co-workers[21] pointed out the predominance of one isotopic channel over the other in the photodissociation of HOD, arising from initial vibrational excitation.
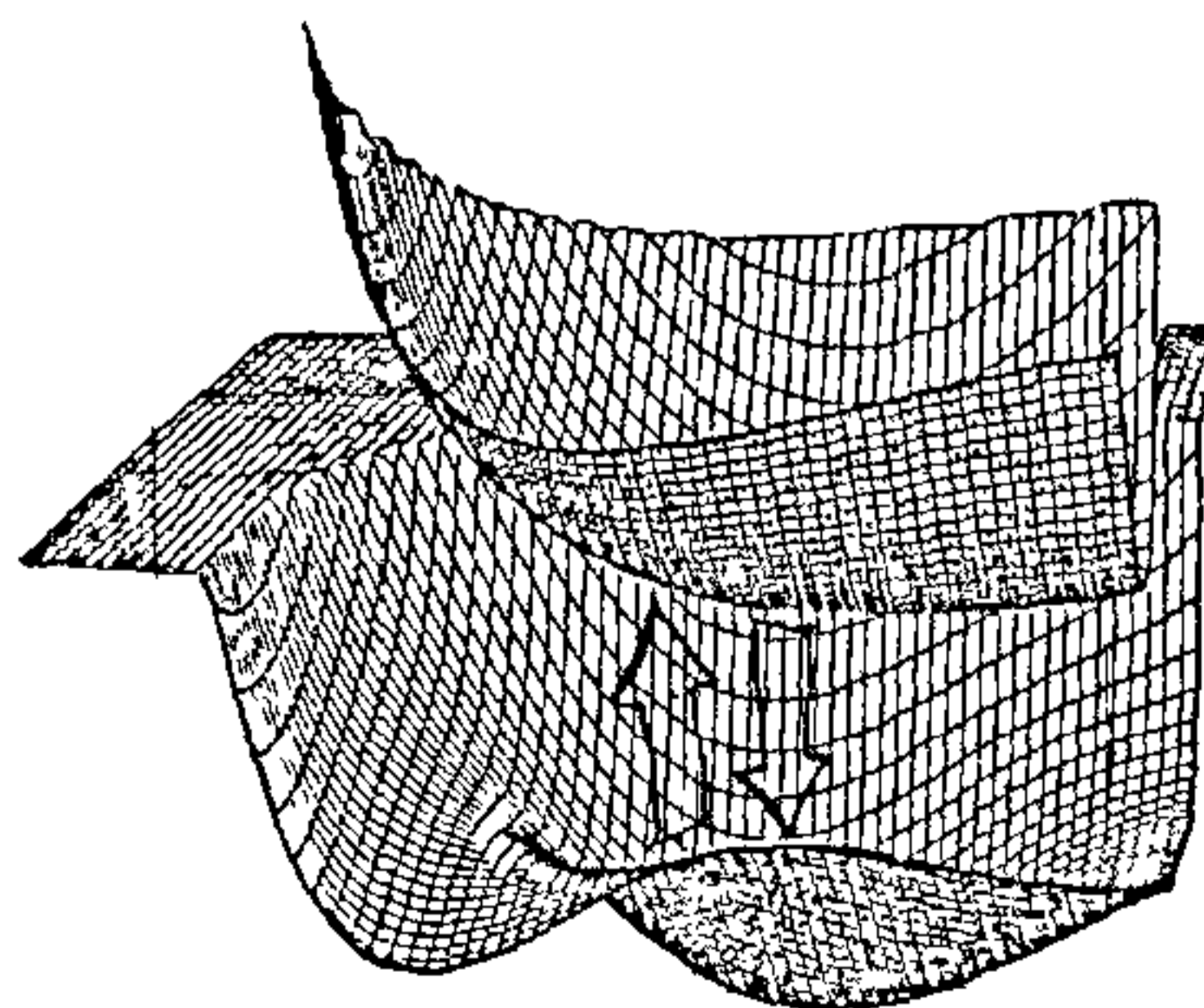

Figure 2. Illustration of the pump and dump scheme involving two electronic states[15].
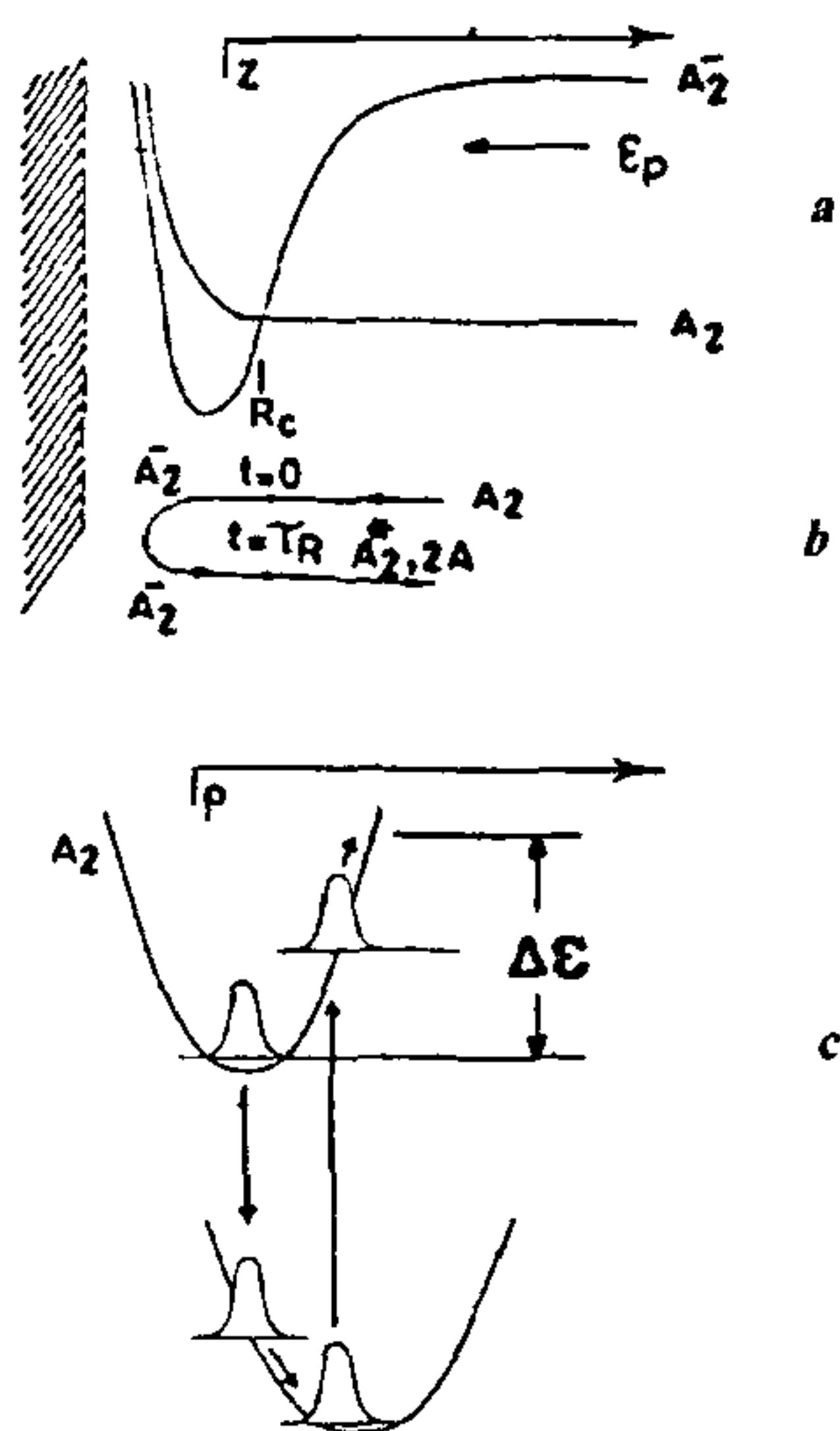
Figure 3. a, Diabatic potential energy curves for the molecule (A_2)-surface and negative ion (A_2^-)-surface interactions. The charge transfer takes place at the crossing point, represented as R_c. b, Time line showing the state of the adsorbate at various times along its scattering trajectory. c, Intramolecular potential energy curves as a function of internal vibrational coordinate for A_2 and A_2^-. The wavepacket dynamics on both the surfaces as dictated by the time line in the middle is also shown[16].

Crim and coworkers[22] have demonstrated experimentally vibrationally mediated photodissociation in HOD leading to a higher OD/OH branching ratio.

Several studies have shown that the preference of one product channel over another is dependent on the vibrational state of the molecule undergoing photodissociation. For instance, experimental[23] and theoretical[24] studies on CH_3I photodissociation have shown that the vibrational excitation in the CH_3 umbrella mode(ν_2) results in a lower I*/I branching ratio Γ. Similarly, Kash and Butler[25] found that I* formation in the photodissociation of ICN decreased with vibrational excitation of the parent molecule. Theoretical studies of Hartke et al.[26] have shown that the Br*/Br population ratio increases initially and then decreases with increase in vibrational excitation in the case of Br_2 photodissociation. Recently we have found[27] that the branching ratio for I* and I formation in the photodissociation of HI is strongly dependent on the initial vibrational state of HI. These results can be understood in terms of non-adiabatic coupling between photoexcited states of the molecule and as a matter of fact vibrationally mediated photodissociation can be used as a sensitive probe of

non-adiabatic coupling between states as illustrated below for HI.

In the near UV region, HI photodissociates into $H + I(^2P_{3/2})$ and $H + I^*(^2P_{1/2})$. The following potential energy curves are accessible in this energy range: $^3\Pi_1$, $^1\Pi_1$, $^3\Sigma_1$ and $^3\Pi_0$ as illustrated in Figure 4a. Among these the former two correlate with the $H + I$ channel while the latter two correlate with the $H + I^*$ channel. All the four states are radiatively coupled to the ground state ($^1\Sigma_0$). Except for the $^3\Pi_0$ state, all other states are non-adiabatically coupled to each other.

The ground electronic state of HI is represented by a Morse curve and the ground vibrational state ($v'' = 0$) wave function is transposed on the excited state potential energy curves given by Levy and Shapiro[28] and time-evolved using the corresponding excited state Hamiltonian. We have made use of the transition dipole moments reported by the same authors. The non-adiabatic effects are fully taken into account by solving the multi-electronic state time-dependent Schrödinger
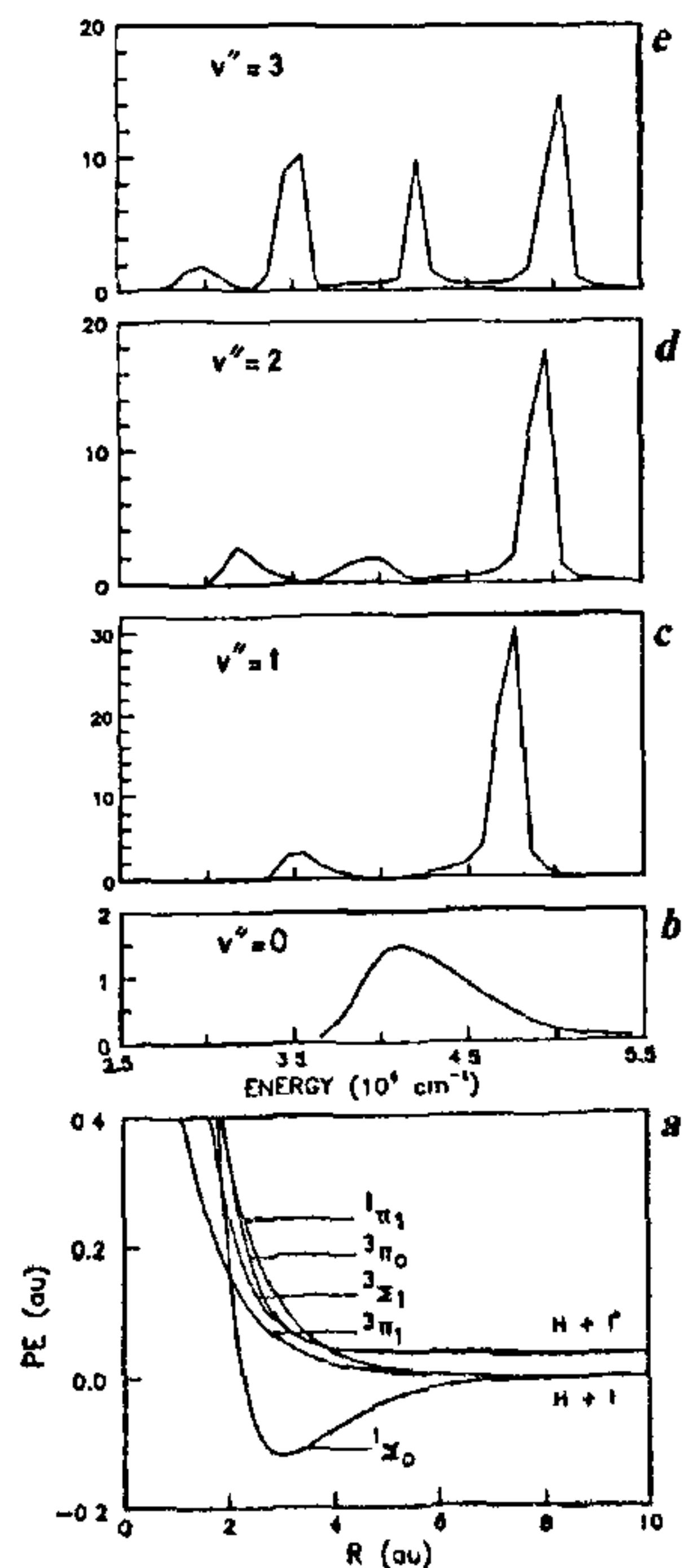

Figure 4. a, Plots of potential energy curves for HI b-e, represent the dependence of I*/I branching ratio, Γ, on the excitation energy of light for $v'' = 0, 1, 2$ and 3 respectively.

equation:

$$i\hbar \frac{\delta}{\delta t} \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} = \begin{pmatrix} H_{11} & V_{12} & V_{13} & 0 \\ V_{21} & H_{22} & V_{23} & 0 \\ V_{31} & V_{32} & H_{33} & 0 \\ 0 & 0 & 0 & H_{44} \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix}$$

(2)

where the subscripts $1, 2, 3$ and 4 represent $^3\Pi_1$, $^1\Pi_1$, $^3\Sigma_1$ and $^3\Pi_0$ states respectively.

Details of the computational methodology are given elsewhere[27]. Results shown in Figure 4 b–c demonstrate clearly that the shape of $\Gamma(E)$ is strongly dependent on the initial choice of v'': these are $v'' + 1$ peaks. Much of it can be explained on the basis of the 'reflection principle' and the non-adiabatic coupling between the excited states. The implication is that vibrational phase (or equivalently the bond distance) at the time of photoexcitation plays a crucial role in deciding the channel outcome.

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