

CHAPTER 1

Introduction

1.1 What is VMP and How Does it Work?

Vibrationally mediated photodissociation (VMP) is a special case of photodissociation where *vibrational* excitation of (in most cases) the ground electronic state of a molecule precedes its *electronic* excitation to a higher, dissociative electronic state.^{1–6} In a sense, all photodissociation processes conducted in a sample of molecules could be considered as VMP due to thermal vibrational population, unless $kT \ll$ lowest vibrational frequency of the molecules. However, although we will occasionally refer to examples of thermal vibrational population, our main interest will be state-selected VMP, where a specific rovibrational state is prepared. State-selected VMP utilizes, mostly, pulsed lasers in a double-resonance scheme where both the vibrational pre-excitation and the electronic excitation are resonant. As noted in the preface, we will deal with “isolated” neutral molecules in the gas phase; VMP in complexes, clusters or the condensed phase will not be discussed. VMP studies aim to unravel the influence of the vibrational pre-excitation on the photodissociation cross section, the quantum states of the photofragments and the branching ratio between them as well as their angular distribution. This influence is discussed in detail in the following chapters. Here, we introduce the concept of VMP *via* simple examples. The methodology of state-selected VMP is exemplified in Figure 1.1 for a bound–free transition (excitation to a purely repulsive electronic state) in a molecule that contains at least one hydrogen atom, RH, where R represents one or more atoms. RH is chosen as an example since this class of molecules has been the most popular VMP species due to the R–H vibrational modes that are readily excited (at higher frequencies than other modes). Further details on the experimental techniques utilized in the three steps described in the figure, vibrational pre-excitation, excitation to a dissociative electronic state and detection of the ensuing photofragments, as well as on other techniques, are given in Chapter 3.

Vibrationally Mediated Photodissociation

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Published by the Royal Society of Chemistry, www.rsc.org

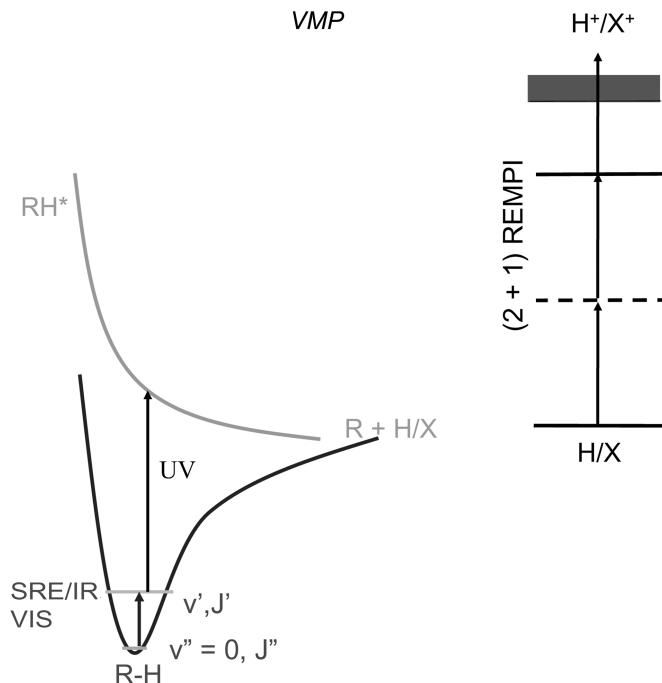


Figure 1.1 An artist's concept of the methodology of state-selected VMP in an RH molecule. It consists of three steps: (1) An R-H vibrational mode is initially excited to a specific (v' , J') state; an infrared (IR) photon or stimulated Raman excitation (SRE) is utilized for preparing fundamental vibrations or low overtones, near-IR (NIR) or visible (VIS) photon for exciting high overtones. (2) An ultraviolet, UV, (or sometimes VIS) photon is utilized for electronic excitation and UV photons for (3) monitoring the ensuing photofragments (H or X, which is, in many VMP studies, a halogen atom). In the present example resonantly enhanced multiphoton ionization (REMPI) is shown as the means for monitoring an atomic photofragment; the solid line denotes the resonant state reached by two-photon excitation and the dashed line an intermediate, virtual state. Molecular fragments are commonly monitored *via* laser-induced fluorescence (LIF).

A schematic description of the potential-energy curves and absorption spectra in “non-VMP” and VMP is depicted in Figures 1.2 (a) and (b), respectively, for a bound-free transition in a diatomic molecule – photodissociation from the vibrationless ground state (a) and from a vibrationally excited state (b) are compared. The former is characterized by a broad structureless absorption spectrum of the parent molecule, due to the reflection of the vibrationless ground-state wavefunction on the upper potential-energy curve. The latter is characterized by a spectrum that reflects extended regions on the ground-state potential onto the dissociative upper state.² Figure 1.2 indicates that when the dissociation

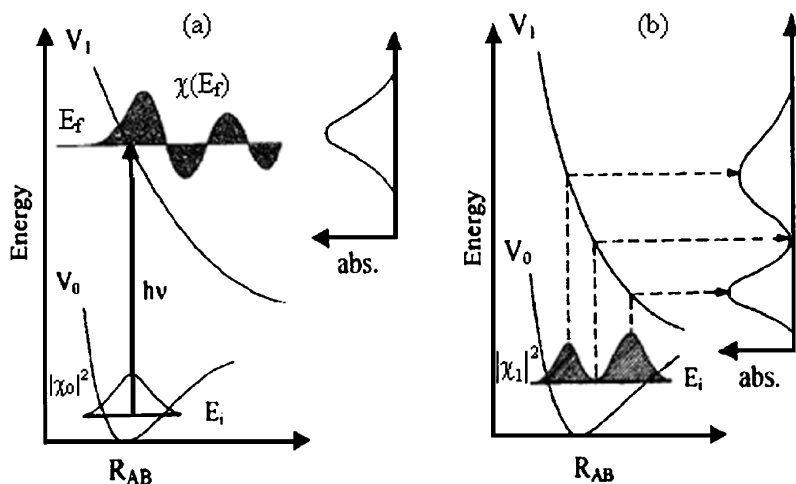


Figure 1.2 Schematic illustration of photodissociation of a diatomic molecule AB *via* excitation to a purely repulsive electronic state. V_0 and V_1 are the potential-energy curves for the ground (bound) and excited (repulsive) electronic states, respectively, as a function of the internuclear distance R_{AB} . E_i and $E_f = E_i + E_{\text{photon}} (= h\nu)$ are the initial and final energies of these states. (a) Absorption from the vibrationless ground state χ_0 to $\chi(E_f)$, the continuum wavefunction. (b) Absorption from the $v=1$ vibrationally excited state of the ground electronic state, χ_1 ; transitions from the midpoint and from locations close to the turning points of the classical vibration are shown (the shapes of the different $\chi(E_f)$ functions are omitted here). Promotion of extended regions on the ground electronic state onto the dissociative potential-energy curve is reflected in the absorption spectrum in both (a) and (b). Adapted from Ref. 4 with permission.

is promoted from a vibrationally excited state, different regions of the repulsive excited state are accessed compared to those from the vibrationless ground state.

It is very important to note here that the transitions shown in Figures 1.1 and 1.2 are vertical, namely, the coordinates of the nuclei in the molecule remain unchanged during the electronic transition. This is not fortuitous, it exemplifies the Franck–Condon (FC) principle that plays a major role in VMP and is discussed and referred to throughout the monograph. Indeed, as we will see, VMP is effective when there is a favorable FC overlap between the vibrationally excited states of the ground electronic state and those of the electronically excited dissociative or predissociative states. If, in addition, the initially prepared vibrational states survive intramolecular vibrational redistribution (IVR) until the subsequent electronic excitation takes place, dissociation of the electronically excited molecule could be controlled by preparing specific vibrational states.

The direct, bound–free photodissociation of a diatomic molecule presented in Figure 1.2(b) is the simplest example of VMP. However, the major part of the monograph deals with larger molecules and, in many cases, with indirect photodissociation, where a potential barrier in the dissociation exit channel

precludes direct dissociation. In molecules larger than diatomic, multi-dimensional potential-energy surfaces (PES) determine the motion of the atoms. The potential-energy curves of a diatomic molecule (Figure 1.2) also represent one-dimensional cuts through a multidimensional PES and often serve as a simple description of VMP in larger molecules.

In most cases VMP has been carried out in the first absorption band of the molecule at hand. This is since in the studied molecules absorption from vibrationally excited states of this band is usually in the mid- and near-ultraviolet (UV) or visible (VIS) wavelength regions readily accessed by existing high-power lasers. $\lambda \sim 193$ nm was popular in the early days of VMP due to the availability of the ArF excimer laser; longer wavelengths have been mostly applied in later studies. Also, almost all state-selected VMP studies have been performed with pulsed lasers with a temporal pulsewidth of at least a few nanoseconds (ns). This was partly due to the fact that these lasers provided the required energy for VMP – typically millijoules and microjoules for vibrational and electronic excitation, respectively; ns pulses also enabled selective rovibrational excitation with higher resolution than that possible with shorter pulses.

Numerous methods have been devised for studying a variety of VMP aspects and they are described when individual molecules are discussed in the following chapters. To conclude this introduction on how VMP works, we mention two noteworthy points: (1) VMP is often compared to isoenergetic one-photon excitation from the vibrationless ground electronic state. For this comparison the wavelength for electronic excitation in the former has to be redshifted with respect to that in the latter (see Figure 1.2). (2) Many recent VMP studies have been conducted in samples cooled *via* supersonic expansion. This results in reducing the Doppler linewidths of the monitored transitions and the rotational temperature as well as the population of low-lying vibrational states (and thus minimizes the contribution of hot bands to the spectrum). All this leads to less congestion and extra narrowing and simplification of the spectrum.

1.2 Why VMP?

VMP has been of both theoretical and applied interest. From a theoretical perspective, exploring how vibrational pre-excitation affects the course of photodissociation and correlating the findings with the topology of PES have long been important parts of molecular processes studies.^{2,5,6} As we will see in many examples, one-photon dissociation and VMP, conducted at the same total energy, often result in different quantum states and branching ratios of the photofragments. This means that vibrational pre-excitation may have a dynamic role rather than an energetic role. The role of the FC factors in the efficacy of the electronic excitation step and of the exit-channel interactions in the dissociation process have been extensively studied and referred to in the examples presented in the monograph. The most prominent conclusion inferred from these studies is that due to the FC principle, starting the electronic

excitation from a specific vibrationally excited state rather than another, enables access to a different region of the upper PES and may affect the dissociation.

The theoretical investigations have been accompanied by experimental studies aimed at applications of VMP for several purposes. Most notable is the application of VMP to the so-called “mode-selective” or “bond-selective” dissociation, namely, to control the dissociation products (the terms mode-selective and bond-selective are usually used as synonyms although, strictly speaking, the former should refer to selective pre-excitation of a vibrational mode and the latter to the resulting selective bond cleavage). This aspect of VMP will be extensively presented in many examples.

A related but somewhat different application of VMP is for isotope separation. Isotope separation that is based on the different frequencies of electronic excitation of different isotopes of atoms or molecules depends on the small difference in the electron reduced mass when the atoms are light and on nuclear volume effects (*e.g.*, core polarization) when the atoms are heavy.⁷ However, this isotopic shift is much smaller than the shift in the vibrational frequencies in molecules due to the large difference in the reduced mass of the vibrating oscillator.⁸ It is thus easier to selectively excite a specific rovibration of a specific molecular isotope (so-called isotopologue) and then photodissociate it rather than other isotopologues by using appropriate redshifted wavelengths. Moreover, by preparing different vibrational states in a molecule that contains different atomic isotopes, different isotopic photoproducts can be preferentially produced from the same molecule (this is a special case of the above-mentioned control of dissociation products). The pre-eminent example of preferential production of different isotopes from the same molecule is the VMP of HOD (see Section 6.4).

An additional application of VMP is in vibrational spectroscopy. Monitoring high-overtone and combination transitions encounters the problem that their intensities are exponentially decreasing functions of the total change of vibrational quantum number, Δv . A crude rule of thumb is that the magnitude of this decrease is $\sim 10^{-\Delta v}$ for hydride stretches.⁹ Also, when spectroscopy studies are conducted in molecular beams, the low density of the target molecules adds to the difficulty of measurement.

These difficulties can be largely alleviated by applying VMP for the following reasons. (1) The action spectrum, *i.e.* the photoproduct yield as a function of the wavelength of the vibrational pre-excitation, is monitored rather than directly measuring the intensity of vibrational bands. The appearance of the bands in the action spectrum is often enhanced due to a better FC overlap of the initially prepared vibrational state in the ground electronic state with that in the excited state. (2) Even if the FC overlap is not favorable, the detection of the photoproduct by resonantly enhanced multiphoton ionization (REMPI) adds several orders of magnitude to the signal as compared to direct detection of vibrational bands, since ions can be monitored with very high sensitivity. Signal enhancement is also achieved, although to a lesser extent, for detection by laser-induced fluorescence (LIF).

The role of VMP in other molecular spectroscopy and molecular dynamics scenarios will be recognized from the examples given in the text. A notable example, with important implications to atmospheric chemistry, is production of the atmospherically important species $O(^1D)$ from vibrationally excited ozone in the longer-wavelength “tail” ($\lambda > 310$ nm) of its solar photolysis. Indeed, VMP may play a role in any environment where molecules are electronically excited.

1.3 Organization of the Monograph

The methodology is that VMP is presented in this monograph *via* specific examples, starting with diatomic molecules (Chapter 4), continuing with tri- and tetratomic molecules (Chapters 5–7) and ending with larger molecules (Chapter 8). Original studies are quoted, wherever appropriate, and many original drawings are adapted. Due to the limited length of the monograph, a choice has to be made. Some examples, which were considered heuristic, are presented in detail, others are only briefly described or just cited. Once again, we apologize for any possible oversight. To become acquainted with the technical language used in these examples, two short overviews precede Chapters 4–8, one on theoretical aspects and one on experimental methods.

Chapter 2 lists the key questions that have to be addressed for understanding VMP, which include, but go beyond, those addressed in photodissociation in general. It then explains the main approaches for calculating PESs and in this context presents the Born–Oppenheimer approximation, which is also the basis for the FC principle. Approaches for computing photodissociation cross sections are then presented, namely, classical trajectories, and quantum-mechanical time-independent and time-dependent approaches; this is followed by an explanation of the concept of conical intersections, which is utilized to account for radiationless transitions between nonadiabatic PESs. The next part of this chapter briefly discusses vector correlations in VMP, *i.e.* the relation between the directions of the vectors inherent in the initiation and dynamics of the photodissociation process, when the photons applied for both vibrational pre-excitation and electronic excitation are polarized. In the final part of the chapter intramolecular vibrational dynamics, in particular IVR, is discussed.

In Chapter 3 we present the major experimental methods for VMP studies. The experimental realization of VMP involves three major steps: Preparation of a vibrational state, promotion of this state to a higher PES(s) followed by dissociation of the molecule, and finally interrogation of the ensuing photo-fragments. The main experimental approaches usually utilized for each step are presented. It is noteworthy that for vibrational preparation we present methods that have been widely used as well as some that have been hardly (or not yet) applied in VMP but have a potential for exciting vibrational levels that are otherwise difficult to reach.

In Chapter 4 VMP of diatomic molecules is discussed, only briefly, since mode- or bond-selective dissociation, which has been the main reason for the

recent interest in VMP, is not relevant for these molecules. However, the presentation of VMP studies of diatomic molecules serves to demonstrate, for the simplest cases, the effect of rovibrational parent excitation on the photodissociation dynamics, *e.g.*, enhancement of the dissociation cross section, polarization dependence of product angular distribution, and branching ratios between electronic states of the products.

Chapters 5 and 6 discuss the VMP of triatomic molecules, the simplest polyatomics where mode- or bond-selective dissociation can be demonstrated. Also, triatomics are small enough to allow *ab initio* calculations of PESs and photodynamics, although they possess several vibrational degrees of freedom, like stretches and bends, which play a principal role also in larger molecules. VMP of several triatomic molecules, excluding water, is described in Chapter 5. Chapter 6 presents, in some detail, the VMP studies of water isotopologues. It was the extensive theoretical and experimental investigations of H₂O and HOD that opened a new era of detailed studies of state-to-state photodissociation out of specific rovibrationally excited states of polyatomic molecules.

In Chapter 7 we move on to tetratomic molecules and dwell, in particular, on acetylene isotopologues, ammonia isotopologues and isocyanic acid, for which extensive state-to-state VMP studies have been carried out. The VMP theories and experiments for tetratomic molecules are obviously more complex than those for triatomics. The additional atom adds additional degrees of freedom that complicate both theory and experiment. Moreover, due to the additional degrees of freedom, IVR is expected to obscure mode selectivity. Also, in contrast to the triatomic molecules, in particular the water molecule where detailed calculations predicted selectivity, similar predictions were not available prior to VMP experiments. Nevertheless, mode selectivity has been observed in several tetratomic molecules.

In Chapter 8 we deal with VMP of even larger molecules, where a much higher complexity is expected. Moreover, it is anticipated that IVR in these molecules would preclude mode- or bond-selective dissociation on the ns timescale. Indeed, at present mode-dependent enhancement in photodissociation has been observed for only one “larger than tetratomic” molecule, methylamine. We start this chapter with a presentation of the VMP of methylamine isotopologues and then move on to haloalkanes, where, in some instances, vibrational pre-excitation changes the electronically excited states accessed in photodissociation and the branching ratio between the atomic photofragments. We then deal with phenol, where the dynamics of conical intersections in this large molecule is exemplified, and finally report on VMP of other “larger than tetratomic” molecules.

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