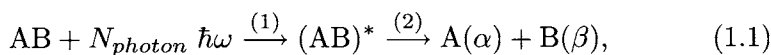


1

Introduction

The fragmentation of a bound molecule through absorption of one or more photons is called photodissociation. The electromagnetic energy of the light beam is converted into internal energy of the molecule and if the transferred energy exceeds the binding energy of the weakest bond, the molecule will irreversibly break apart. Let us, as an example, consider the dissociation of a parent molecule AB into products A and B, where A and B represent either structureless atoms or molecules with internal degrees of freedom of their own. Formally we write a photodissociation process as



where $\hbar\omega$ is the energy of one photon with frequency ω and N_{photon} is the number of absorbed photons. $(AB)^*$ represents the excited complex before it breaks apart and the labels α and β specify the particular internal quantum states of the newborn products. The first step indicates absorption of the photons by the parent molecule and the second step represents the fragmentation of the excited complex.

In the center of our discussion of photodissociation dynamics are questions like the following:

- 1) How does the photon cleave the molecular bond?
- 2) What is the lifetime of the intermediate complex?
- 3) What are the primary fragments?
- 4) How does the absorbed energy partition among the various degrees of freedom of the products?
- 5) What is the internal quantum state distribution of the fragments?
- 6) How does the dissociation depend on the initial state or the temperature of the parent molecule?

In this monograph we shall attempt to answer these questions in the light of experimental and theoretical advances achieved in the last decade or so.

1.1 Types of photodissociation

Dissociation energies vary from a few thousandths of an eV for physically bound van der Waals molecules to several eV for chemically bound molecules. Van der Waals molecules are bound by the weak long-range forces and exist only at very low temperatures, either in a supersonic beam or in the interstellar space (Buckingham, Fowler, and Hutson 1988). Typical examples are:[†]

He...HF ($D_0 = 0.88$ meV; Lovejoy and Nesbitt 1990)

Ar...HCl ($D_0 = 14.2$ meV; Howard and Pine 1985)

HF...HF ($D_0 = 131.7$ meV; Dayton, Jucks, and Miller 1989).

Representative examples of chemically bound molecules which will play vital roles in this monograph are:

ClNO ($D_0 = 1.62$ eV; Bruno, Brühlmann, and Huber 1988)

H₂O₂ ($D_0 = 2.12$ eV; Giguère 1959)

H₂O ($D_0 = 5.11$ eV; Herzberg 1967).

The extremely wide range of possible dissociation energies necessitates the use of different kinds of light source to break molecular bonds. Van der Waals molecules can be fragmented with single infrared (IR) photons whereas the fission of a chemical bond requires either a single ultraviolet (UV) or many IR photons. The photofragmentation of van der Waals molecules has become a very active field in the last decade and deserves a book in itself (Beswick and Halberstadt 1993). It is a special case of UV photodissociation and can be described by the same theoretical means. In Chapter 12 we will briefly discuss some simple aspects of IR photodissociation in order to elucidate the similarities and the differences to UV photodissociation.

Figure 1.1 illustrates the two basic types of photodissociation of a chemically bound molecule. In Figure 1.1(a) the photon excites the molecule from the ground to a higher electronic state. If the potential of the upper electronic state is repulsive along the intermolecular coordinate R_{AB} , the

[†] The dissociation energy D_0 is measured from the zero-point level of the parent molecule to the zero-point level(s) of the products.

1.1 Types of photodissociation

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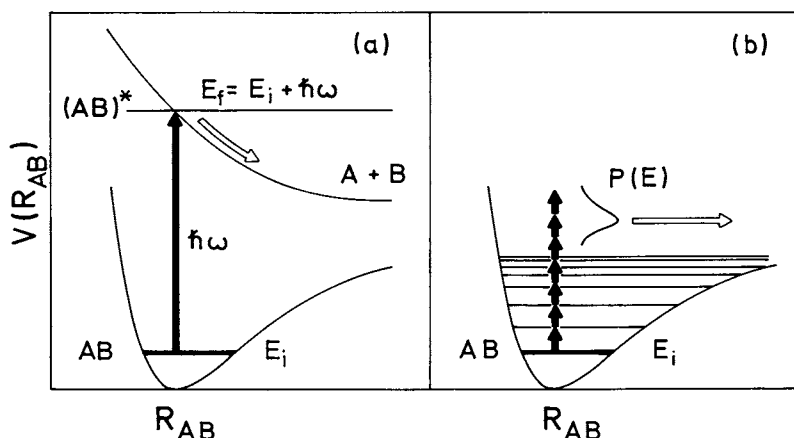


Fig. 1.1. Schematic illustration of photodissociation with a single UV photon (a) and with many IR photons (b). R_{AB} is the intermolecular separation of the two fragments A and B. In (a) the photon creates a single quantum state in the upper electronic state while in (b) the photons produce a comparably broad ensemble of states with energy distribution $P(E)$.

excited complex $(AB)^*$ ultimately dissociates. Part of the photon energy $E_{\text{photon}} = \hbar\omega$ is consumed to break the A-B bond and the *excess energy*

$$E_{\text{excess}} = E_{\text{photon}} - D_0 = E_{\text{trans}} + E_{\text{int}}$$

partitions between the translational energy E_{trans} and the internal energy E_{int} of the product atoms or molecules (including vibrational, rotational, and electronic energy).

UV photodissociation is usually carried out with long light pulses of low intensity and narrow bandwidth. These conditions guarantee — at least in principle — that the photon creates a single quantum state in the upper electronic manifold with corresponding energy $E_f = E_i + E_{\text{photon}}$, where E_i is the energy of the parent molecule. We shall demonstrate below that under such well defined conditions the main observables, i.e., the absorption spectrum and the product state distributions, uniquely “reflect” the molecular wavefunction of the particular quantum state of the parent molecule before the excitation. How the dynamics in the upper electronic state mediates this type of “reflection” is one of the central issues of this monograph.

Multiphoton dissociation takes place in the electronic ground state as illustrated in Figure 1.1(b) (Grunwald, Dever, and Keehn 1978; Schulz et al. 1979; Golden, Rossi, Baldwin, and Barker 1981; Letokhov 1983; Reisler and Wittig 1985; Lupo and Quack 1987). Since the exact number of absorbed photons cannot be controlled, the laser creates an ensemble of quantum states above the dissociation threshold with a distribution of

energies $P(E_f)$. As a consequence, multiphoton dissociation is subject to unavoidable averaging over many quantum states. It requires basically different theoretical tools and models than dissociation with a single photon. Therefore, we shall not further discuss it in this monograph.

Figure 1.1(a) illustrates the simplest type of UV photodissociation. Upon excitation the two fragments immediately repel each other and the excited complex $(AB)^*$ fragments directly on a very short time scale. We will demonstrate below that this kind of photodissociation can be satisfactorily treated in the framework of classical mechanics. The photodissociation of H_2O in the first absorption band is a prototype of direct photodissociation (see Section 1.5 and the review of Engel et al. 1992). In contrast, Figure 1.2 schematically illustrates two examples of indirect photodissociation. In (a) the photon excites first a binding electronic state which by itself cannot break apart. However, if the molecule undergoes a transition from the binding state to another electronic state whose potential is repulsive, the complex will ultimately decay with a rate that depends on the coupling between the two electronic states. The final fragmentation takes place in a different electronic state than the one originally excited by the photon. This process is called *electronic predissociation* or Herzberg's type I predissociation (Herzberg 1967:ch.IV).[†]

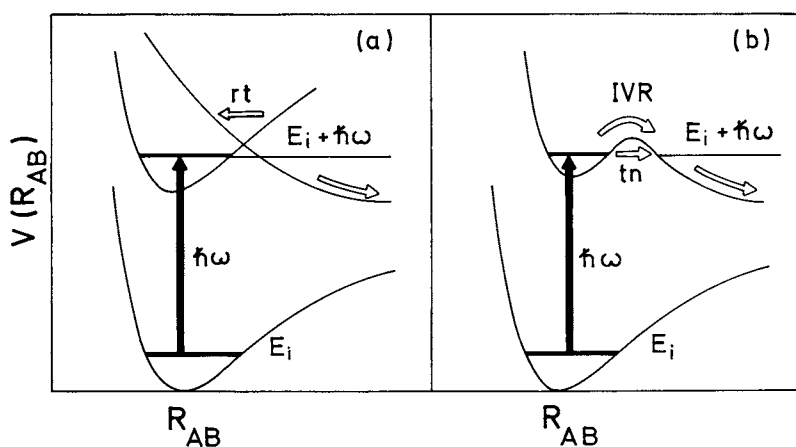


Fig. 1.2. Schematic illustration of electronic (a) and vibrational (b) predissociation. In the first case, the molecule undergoes a radiationless transition (rt) from the binding to the repulsive state and subsequently decays. In the second case, the photon creates a quasi-bound state in the potential well which decays either by tunneling (tn) or by internal energy redistribution (IVR).

[†] The word “predissociation” means that the molecule dissociates before it can decay to the electronic ground state by emission of a photon.

1.2 Why photodissociation dynamics?

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An example is the photodissociation of H_2S which will be discussed in Chapter 15.

Figure 1.2(b) elucidates a different type of predissociation. The potential has a well at close distances and a barrier that blocks the dissociation channel. The barrier might be considered to be the result of an avoided crossing with a higher electronic state. In this case the photon excites quasi-stable (so-called “resonance”) states inside the well which are prevented from immediate dissociation by the potential barrier. They can decay either by tunneling through the barrier or by *internal vibrational energy redistribution* between the various nuclear degrees of freedom if more than two atoms are involved. The lifetime of the compound depends on the tunneling rate and/or the efficiency of internal energy transfer. Figure 1.2(b) illustrates *vibrational predissociation* or Herzberg’s type II predissociation (Herzberg 1967:ch.IV). The photodissociation of CH_3ONO in the first excited singlet state, which we will discuss in detail in Chapter 7, is an illuminating example.

Figure 1.3 shows two additional types of photodissociation. In (a) the photon excites first a binding electronic state which subsequently decays following a transition to the lower electronic state. This produces a highly excited vibrational-rotational quantum level above the dissociation threshold of the electronic ground state which eventually breaks apart. Alternatively, in (b) a highly excited quantum state above the dissociation threshold is created directly by pumping a large amount of energy into the molecule by single-photon excitation of overtone vibrations. Both processes are known as *unimolecular reactions* (Forst 1973; Hase 1976; Quack and Troe 1977; Crim 1984; Pritchard 1985; Reisler and Wittig 1986; Crim 1987; Pilling and Smith 1987; Gilbert and Smith 1990). Representative examples are the photodissociation of H_2CO (Moore and Weisshaar 1983) and H_2O_2 (Crim 1987), respectively.

The distinction between the various dissociation schemes (with the exception of multiphoton dissociation) is rather artificial from the formal point of view. Common to direct dissociation, predissociation, and unimolecular decay is the possibility of state-specificity, i.e., the dependence of the dissociation on the quantum state of the parent molecule (Manz and Parmenter 1989). The absorption of a single photon uniquely defines the energy in the dissociative state. As we will demonstrate in subsequent chapters, one can treat all three classes of fragmentation with the same basic theoretical tools. However, the underlying molecular dynamics is quite different demanding different interpretation models.

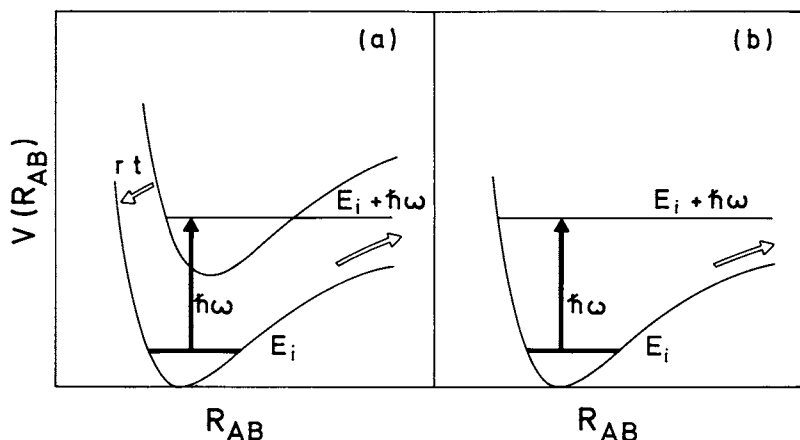
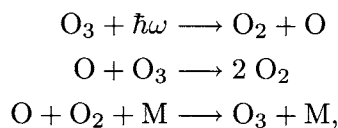


Fig. 1.3. Schematic illustration of unimolecular decay induced by electronic excitation. In (a) the photon creates a bound level in the upper electronic state which subsequently decays as a result of a radiationless transition (rt) to the electronic ground state. In (b) overtone pumping directly creates a quantum state above the threshold of the electronic ground state. In both cases the dissociation occurs in the electronic ground state.

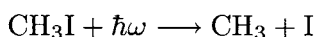
1.2 Why photodissociation dynamics?

Photodissociation is at the heart of *photochemistry* (Turro 1965, 1978; Calvert and Pitts 1966; Ben-Shaul, Haas, Kompa, and Levine 1981; von Büнау and Wolff 1987; Wayne 1988; Klessinger and Michl 1989). In many cases, the photofragments are radicals which rapidly undergo secondary and tertiary reactions. Photodissociation is the motor for many important chain reactions determining the complex chemistry in the atmosphere. The sun supplies sufficient UV radiation to keep the motor going (Okabe 1978). The ozone cycle,



for example, is vital for all life on earth. It controls the global abundance of O_3 in the upper atmosphere which is essential for the absorption of harmful UV radiation.

Photodissociation is the starting point for many *chemical lasers* such as the iodine laser discovered by Kasper and Pimentel (1964). The reaction



1.2 Why photodissociation dynamics?

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yields an inverted population of the two electronic states of iodine, $^2P_{1/2}$ and $^2P_{3/2}$, which allows a laser to be built on the subsequent $^2P_{1/2} \rightarrow ^2P_{3/2}$ electronic transition. The final state distributions of photofragments are often inverted, which is a necessary prerequisite for the operation of lasers (Ben-Shaul et al. 1981:ch.4). Detailed understanding of the above reaction and similar processes is undoubtedly desirable in order to develop and control new laser sources systematically. Understanding of photodissociation is also very important in astrophysics (Kirby and van Dishoeck 1988).

Besides its practical importance, photodissociation — especially of small polyatomic molecules — provides an ideal opportunity for the study of molecular dynamics on a detailed state-to-state level. We associate with molecular dynamics processes such as energy transfer between the various molecular modes, the breaking of chemical bonds and the creation of new ones, transitions between different electronic states etc. One goal of modern physical chemistry is the microscopical understanding of molecular reactivity beyond purely kinetic descriptions (Levine and Bernstein 1987). Because the “initial conditions” can be well defined (absorption of a single monochromatic photon, preparation of the parent molecule in selected quantum states), photodissociation is ideally suited to address questions which are unprecedented in chemistry. The last decade has witnessed an explosion of new experimental techniques which nowadays makes it possible to tackle questions which before were beyond any practical realization (Ashfold and Baggett 1987).

Photodissociation combines aspects of both molecular spectroscopy and molecular scattering. The spectroscopist is essentially interested in the first step of Equation (1.1), i.e., the absorption spectrum. In the past six decades or so methods of ever increasing sophistication have been developed in order to infer molecular geometries from structures in the absorption or emission spectrum (Herzberg 1967), whereas the fate of the fragments, i.e., the final state distribution is of less relevance in spectroscopy. The decay of the excited complex is considered only insofar as the widths of the individual absorption lines reflect the finite lifetime in the excited state and therefore the decay rate of the excited molecule.

The second step in (1.1), i.e., the fragmentation of the excited complex belongs to the field of molecular collisions. The actual decay mechanism, the partitioning of the excess energy, and the population of the possible quantum states of the products are the central themes. However, we must emphasize from the outset of this monograph that the distinction between absorption and fragmentation is — in principle at least — artificial. The two steps in (1.1) belong together and must be considered as an entity.

1.3 Full and half collisions

Photodissociation can be viewed as the second half of a full collision. Let us consider an atom A colliding with a diatom BC as illustrated schematically in Figure 1.4. In a full collision, the reactants are prepared separately at infinite distances where the interaction between them is zero. During the collision they form an intermediate complex $(ABC)^*$ which in the end decays to the four possible product channels with the diatomic fragments being created in particular internal quantum states. In photodissociation, on the other hand, the excited complex is generated by electronic excitation of the initially bound parent molecule ABC. The photon promotes ABC to a higher electronic state where it dissociates, either immediately if the potential is repulsive or after a delay if a barrier hinders the fragmentation. In any case, the second step of photodissociation is equivalent to the second step of a full collision which explains the terminology “half collision”.

The decay of the complex is described by exactly the same equations of motion independent of its creation, namely Hamilton’s equations in classical mechanics and Schrödinger’s equations in quantum mechanics. Only the initial conditions for the ultimate fragmentation step are different because they reflect how the intermediate complex was formed. However, these differences lead to several important implications!

Let us denote by j the rotational angular momentum of the diatomic entity BC and by l the orbital angular momentum of atom A with respect to BC. The total angular momentum of the entire system is then defined by $\mathbf{J} = \mathbf{j} + \mathbf{l}$ and the corresponding quantum number will be denoted by J . It is, of course, conserved during the collision. The definition of scattering or photodissociation cross sections unavoidably involves an average over total angular momentum states from $J = 0$ to some maximum value J_{max} with each term being weighted by $(2J + 1)$ (Child 1974:ch.3; Levine and Bernstein 1987:ch.2; Hirst 1990:ch.7; Child 1991:ch.8; Chapter 11 of

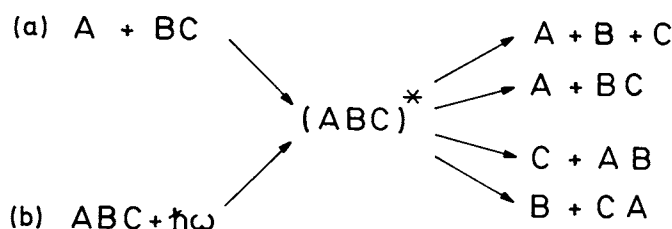


Fig. 1.4 Schematic illustration of a full collision (a) and a half collision (b).

1.3 Full and half collisions

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this monograph).[†] This holds equally for full as well as half collisions. However, the consequences are quite different in the two cases.

Under normal conditions for an atom-molecule collision the summation over J extends over many (of the order of one hundred or even more) so-called partial waves which makes the practical calculation rather cumbersome. An even more serious problem is the substantial blurring of distinct dynamical structures such as quantum mechanical interferences or resonances. Since these structures depend parametrically on J , the summation over all possible J values rapidly washes out finer details.

Excitation with a photon, on the other hand, is subject to the dipole selection rule (see Chapter 11)

$$\Delta J = J_i - J_f = 0 \quad \text{or} \quad \pm 1,$$

where J_i and J_f are the total angular momentum quantum numbers before and after the absorption of the photon, respectively. As a consequence of this selection rule the number of angular momentum states, which must be taken into account in the calculation of photodissociation cross sections, is comparatively limited. For a given temperature T the distribution of initial states is determined by the Boltzmann distribution

$$P_T(J_i) \propto (2J_i + 1) e^{-B_{rot} J_i(J_i+1)/k_B T},$$

where B_{rot} and k_B are the rotational constant of the molecule and Boltzmann's constant, respectively. The Boltzmann distribution is under normal experimental conditions confined to a relatively small range of J_i values and because of the selection rule the same holds also for J_f .

Thus, even at room temperature ($T = 300$ K) only very few states, in comparison to full collisions, contribute to the dissociation cross sections which significantly reduces the numerical efforts and suppresses incoherent averaging. The result is a clearer picture of the fragmentation dynamics and the possibility of resolving resonance structures which are very difficult to observe in full collisions. Cooling the gas in a molecular beam down to temperatures of the order of 50 K or below leads to a further reduction of the possible angular momentum states. Therefore, many experiments can be modelled with the restriction that $J = 0$ in both electronic states and almost all theoretical investigations take advantage of this limitation.

Furthermore, the total energy E_f in half collisions can be relatively easily controlled by variation of the photolysis wavelength. This is essential for the detection of resonances and other structures which require high

[†] In classical mechanics, the summation over the total angular momentum quantum number, $\sum_J (2J + 1) \dots$, corresponds to an integral over the impact parameter b according to $\int db b \dots$

energy resolution. On the other hand, controlling the scattering energy in full collisions is undoubtedly more problematic.

1.4 From the spectrum to state-selected photodissociation

In this section we summarize briefly the various cross sections which can be measured in a photodissociation experiment, starting with the least resolved quantity, the absorption spectrum, up to the most detailed ones, final state resolved cross sections following the dissociation of a particular vibrational-rotational state of the parent molecule. We illustrate the hierarchy of possible measurements by an important example, the photodissociation of H_2O sketched in Figure 1.5.[†] For reviews of modern experimental methods see Leone (1982) and Ashfold and Baggott (1987), for example.

1.4.1 The absorption spectrum

The most averaged quantity is the absorption spectrum or total absorption cross section $\sigma_{tot}(\omega)$ which, loosely speaking, measures the capability of a molecule to absorb radiation with frequency ω (for a rigorous definition see Chapter 2). As the name suggests, the total cross section is defined irrespective of the fate of the excited complex and the population of the possible fragmentation channels.

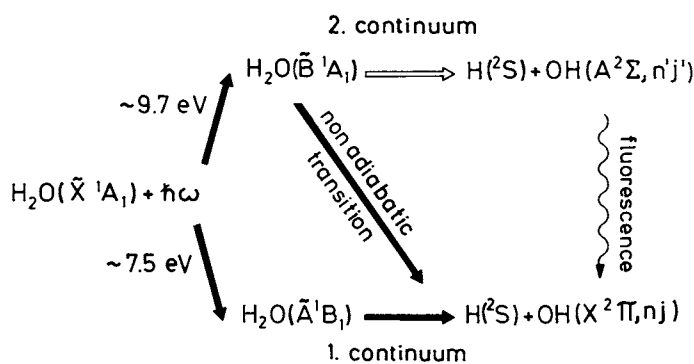


Fig. 1.5. Schematic representation of the photodissociation of H_2O in the first two absorption bands. The corresponding potentials are illustrated in Figures 1.12 and 1.13. Further explanation is given in the text.

[†] The photodissociation of H_2O in the first two absorption bands will be amply discussed in this monograph. For reviews see Andresen and Schinke (1987), Docker, Hodgson, and Simons (1987), and Engel et al. (1992). H_2O can be considered as a prototype for the photodissociation of triatomic molecules.