

# Chapter 1

## Infrared Photodissociation

Vibrational spectroscopy paired with quantum chemistry offers a direct and generally applicable experimental approach to structural investigation of neutral and charged clusters in the gas phase [31,32]. There are several experimental methods to measure a vibrational spectrum and the choice depends on the specific nature of the system of interest. In this experimental work, the vibrational spectra of small, mass-selected, cluster ions in the gas phase are measured by infrared (IR) photodissociation (PD). The aim of this chapter is to answer three questions: (*i*) What kind of information does vibrational spectroscopy provide? (*ii*) What is infrared photodissociation (IR-PD) and why is it a good method to investigate small cluster ions? (*iii*) How does IR-PD work?

### 1.1 Vibrational Spectroscopy

A system with  $N$  atoms bound in a potential  $V$  has  $3N-6$  internal degrees of freedom.<sup>1</sup> Given the masses of the  $N$  atoms, the dynamics of the system is completely described by the potential  $V$ , which includes information about the interactions between atoms and their equilibrium configuration (Section 1.1.1). The dynamics of the system can be probed by observing how the system interacts with light (Section 1.1.2). However, structural determination of the system is not straightforward from the bare knowledge of its dynamics. Therefore, a comparison of the experimental results with quantum chemical calculations is necessary for a unique structural assignments.

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<sup>1</sup>For a linear arrangement of the atoms the internal degrees of freedom are  $3N-5$ , but in the following only the more general case will be considered.

### 1.1.1 Normal Modes of Vibration

A system is in equilibrium when the potential energy  $V$  has an extremum. Thus, at equilibrium,

$$\left(\frac{\partial V}{\partial q_i}\right)_0 = 0 \quad (1.1)$$

for every  $q_i$  ( $i = 1, \dots, 3N - 6$ ), where the  $q_i$  are the  $3N - 6$  coordinates necessary to describe the vibrations of the system. For every small displacement in the neighborhood of a stable equilibrium configuration, the time independent potential  $V$  can be developed in Taylor series:

$$V = V_0 + \sum_{i=1}^{3N-6} \left(\frac{\partial V}{\partial q_i}\right)_0 q_i + \frac{1}{2} \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 q_i q_j + \text{higher order terms.} \quad (1.2)$$

The zero of the potential energy may be conveniently chosen at equilibrium, and thus  $V_0 = 0$ . At equilibrium, the first derivatives are zero according to (1.1). Therefore, by neglecting all higher order terms ( $>2$ ), which corresponds to the harmonic approximation, only the second order term in the potential energy  $V$  remains. Thus, from Newton's second law, one obtains:

$$\frac{d^2 q_i}{dt^2} = - \left(\frac{\partial V}{\partial q_i}\right) = - \sum_{j=1}^{3N-6} \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 q_j. \quad (1.3)$$

Solving these equations of motion leads to a determinant whose eigenvalues yield the vibrational frequencies, known as *normal frequencies*. The eigenvectors describe the atomic displacements involved in each of the vibrations characterized by one of the eigenvalues. The eigenvectors corresponding to the different eigenvalues are called *normal modes of vibration*. One may transform the  $q_i$  into a set of orthogonal coordinates  $\xi_i$  consisting of eigenvectors. Such coordinates are called *normal coordinates*.

This simple harmonic approximation proves to be satisfactory in many cases but fails, for example, in the case of strong hydrogen bonds (see Chapter 6). In such cases, anharmonicity needs to be taken into account, higher order terms in (1.2) have to be considered, and the vibration of the molecule cannot be described by a set of independent equations anymore. This leads to shifts of the eigenvalues and to couplings of the originally uncoupled normal modes.

### 1.1.2 Infrared Active Modes

According to classical electrodynamics, any motion that is connected with a change of its dipole moment leads to the emission or absorption of radiation. During the

vibrational motion of a molecule, the charge distribution undergoes a periodic change and therefore, in general (but not always), the dipole moment changes periodically. In the harmonic oscillator approximation, any vibrational motion of the molecule may be resolved into a sum of normal vibrations and the normal frequencies are the frequencies that are emitted or absorbed by the molecule. These frequencies lie in the IR region of the electromagnetic spectrum.

Normal vibrations that are associated with a change of dipole moment are called *infrared active*, while vibrations for which the change of charge distribution is such that no change of dipole moment arises are called *infrared inactive*. In the classic harmonic oscillator approximation only the fundamental frequencies can be active: the overtones and combination tones are inactive since the (harmonic) vibrational motion does not contain these frequencies.

If  $M_x$ ,  $M_y$ , and  $M_z$  are the three components of the dipole moment vector  $\mathbf{M}$  of the molecule in the direction of the coordinate axes in a displaced position of the nuclei, and if  $M_x^0$ ,  $M_y^0$ , and  $M_z^0$  are the three components of the dipole moment  $\mathbf{M}^0$  in the equilibrium position, then, for sufficiently small displacements, one can expand  $M_x$ . Using the normal coordinates  $\xi_i$ , one has

$$M_x = M_x^0 + \sum_i \left( \frac{\partial M_x}{\partial \xi_i} \right)_0 \xi_i + \dots \quad (1.4)$$

and similarly for  $M_y$  and  $M_z$ . By definition, normal coordinates are the eigenvectors of an oscillation and therefore,

$$\xi_i = \xi_i^0 \cos(2\pi\nu_i t + \phi_i). \quad (1.5)$$

According to (1.4), the dipole moment  $\mathbf{M}$  of the molecule will change with the frequency  $\nu_i$  of the normal vibration  $i$  if, and only if, at least one of the derivatives  $\left(\frac{\partial M_x}{\partial \xi_i}\right)_0$ ,  $\left(\frac{\partial M_y}{\partial \xi_i}\right)_0$ ,  $\left(\frac{\partial M_z}{\partial \xi_i}\right)_0$  differs from zero. The intensity of this infrared fundamental band is proportional to the square of the vector representing the change of the dipole moment for the corresponding normal vibration near the equilibrium position, that is, it is proportional to

$$\left( \frac{\partial M_x}{\partial \xi_i} \right)_0^2 + \left( \frac{\partial M_y}{\partial \xi_i} \right)_0^2 + \left( \frac{\partial M_z}{\partial \xi_i} \right)_0^2. \quad (1.6)$$

A change of the quadrupole moment or of the magnetic dipole moment may also lead to emission or absorption of radiation. In the infrared, the intensity of this emission or absorption is in most cases negligible [33].

If the anharmonicity of the vibrations is taken into account, the classical vibrational motion also contains the frequencies  $2\nu_i$ ,  $3\nu_i$ ,  $\dots$ , and furthermore  $\nu_i + \nu_k$ ,  $\nu_i - \nu_k$ ,  $2\nu_i + \nu_k$ ,  $\dots$ . Therefore, in the infrared spectrum, overtone and combination vibrations may also occur in addition to the fundamentals, if they are connected with a

change of dipole moment. However, they will be much weaker than the fundamentals, since the anharmonicity is small in general, except for large amplitude motion of the nuclei.

## 1.2 Introduction to Infrared Photodissociation (IR-PD)

An IR-PD spectrum is measured by irradiating gas phase particles with tunable, monochromatic IR light and monitoring the yield of parents and/or fragments as a function of the irradiation wavelength. In order to induce fragmentation, the parent AB (possibly an ion) is required to absorb sufficient energy to overcome the (lowest) dissociation threshold. Once a metastable ro-vibrational state is reached, intramolecular energy distribution will eventually lead to dissociation:



This process can take place only if the photon frequency  $\nu$  corresponds to the frequency of an IR active mode of the particle. Thus, the observed dissociation is directly related to the vibrational spectrum of the species under investigation. Typical dissociation energies of covalent bonds are at least 1 eV or higher, while their fundamental vibrational transitions are found well below this limit<sup>2</sup>. It is therefore clear that absorption of multiple IR photons is required.

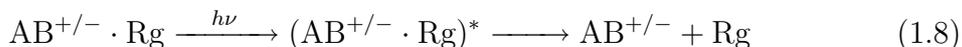
In practice, gas phase cluster sources produce distributions of particles with different sizes. An IR spectrum of such a particle distribution is difficult to interpret, because it is difficult to distinguish between different absorbing species. However, experiments on cluster ions do not present such difficulty, because ions can be mass-selected prior to photodissociation. Since one of the fragments generally remains charged, also the particle detection can easily be accomplished mass-selectively. In IR-PD, photon absorption is, thus, indirectly detected by monitoring fragment ion production and parent ion depletion. This can be done background free and with nearly 100% detection efficiency. On the contrary, a direct IR absorption measurement is very difficult with cluster ions because of the very low number densities, in the order of one million ions per cubic centimeter, or  $\sim 3 \cdot 10^{-12}$  mbar partial pressure at 20 K, due to space charge effects.

Until the middle of the 1990's, vibrational spectroscopy of mass-selected cluster ions was restricted to the region below 5  $\mu\text{m}$ , namely the region of O–H stretches, overtones and combination bands, as well as narrow parts of the spectrum around 6 and 10  $\mu\text{m}$ , accessible using CO and CO<sub>2</sub> laser radiation, given the high number of

<sup>2</sup>The V=O stretch mode, for example, is found at  $\sim 120$  meV.

IR photons that have to be absorbed to induce dissociation [34]. This dramatically changed with the introduction of free electron lasers (FELs) operating in the IR to molecular spectroscopy by Meijer, von Helden and coworkers in 1996 [35]. The FEL used in these experiments generates intense (up to 100 mJ per 5  $\mu$ s macro pulse) and continuously tunable IR radiation from 5 to 250  $\mu$ m (2000 to 40  $\text{cm}^{-1}$ ) [36, 37]. The experiment described in this work were done using FEL radiation in a narrower region, concentrating on the fingerprint region of the electromagnetic spectrum where most of the characteristic IR fundamental transitions lie (500–2000  $\text{cm}^{-1}$ ).

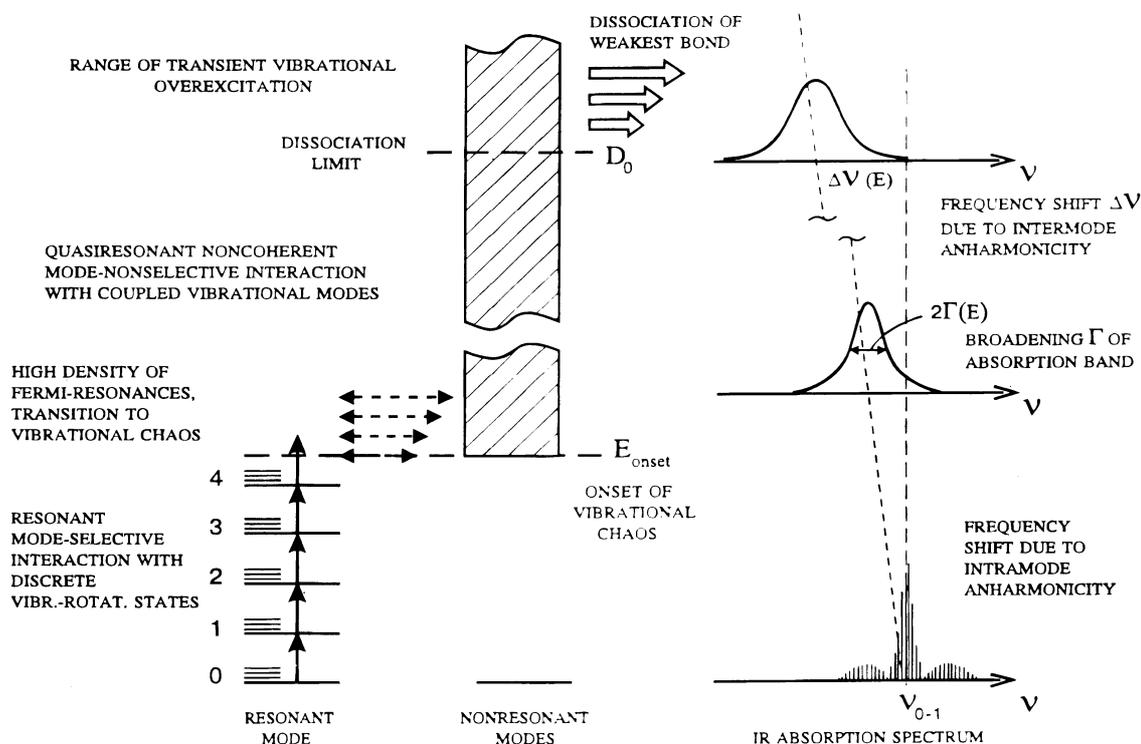
A useful variant of IR-PD, which allows to lower the number of photons needed is the messenger atom technique [38]:



By forming ion–rare gas atom (Rg) complexes the dissociation threshold of the system is lowered, generally below the photon energy, so that the absorption of a single photon can be detected. This approach is attractive for those systems where the perturbation induced by the messenger atom can be neglected and the formation of such complexes is feasible.

### 1.3 Multiple Photon Infrared Photodissociation

Figure 1.1 schematically shows the three basic stages of multiple photon excitation and subsequent dissociation of polyatomic molecules in a resonant IR field. (i) In the lower vibrational transitions, the molecule in an IR field of moderate intensity is subject to resonant multi-step excitation. This is accomplished due to compensation of the anharmonic frequency detuning of successive vibrational transitions by changes in the molecular rotational energy, anharmonic splitting of excited degenerate vibrational states, etc. In cases when at any of the lower transitions there is no true anharmonicity compensation, two- and three-photon vibrational transitions with near-to-resonance intermediate levels can occur. This stage determines the selectivity of the multiple photon excitation. (ii) As a polyatomic molecule is excited to upper vibrational levels, the number of possible vibrational transitions from a given vibrational-rotational state increases sharply. This is due to a high density of vibrational molecular levels with a great number of interacting degrees of freedom. Anharmonicities also introduce a coupling mechanism between different modes, which allows internal vibrational redistribution (IVR). This nearly continuous density of states is termed the *vibrational quasicontinuum*. If the fluence of an IR pulse is rather high, a polyatomic molecule is able to climb up the levels of the vibrational quasicontinuum, even though the absorption cross-section of transitions between them is small. (iii) In the field of a rather high-fluence (see Section 1.3.4) IR pulse a polyatomic molecule can accumulate an energy comparable to the dissociation energy through transitions in the vibrational



**Figure 1.1:** Main features of Infrared Multiple Photon Photodissociation [39].

quasicontinuum. This energy is distributed over many vibrational degrees of freedom since there are numerous combinational overtones that can participate in the absorption. Furthermore, the coupling between states increases with increasing density of states and dissociation of the weakest bond(s) is observed. These three stages are discussed in detail in the following three sections.

### 1.3.1 Lower Vibrational Levels

In the region of lower discrete vibrational levels, a molecule interacting with an IR field undergoes successive stimulated resonant transitions on the ladder of vibrational levels. Of particular importance here is that each vibrational level splits into a great number of rotational and vibrational-rotational sublevels due to vibration-rotation coupling. Due to this the molecules are initially distributed over a large number of sublevels, even if they are concentrated in the ground vibrational state. This, of course, impedes simultaneous excitation of the molecules from all the sublevels under a monochromatic IR field. On the other hand, such splitting opens up many potential pathways for multi-step and multiphoton excitation of molecules in rather intense IR fields despite of anharmonic frequency shifts in successive vibrational upward transi-

tions.

The IR radiation intensity essential for a molecule to pass through the entire region of lower vibrational levels up to the region of vibrational quasicontinuum depends substantially on the intrinsic attributes of the molecular species. Indeed, the type of molecule governs the value of anharmonicity, the character of splitting of each vibrational level and the position of the vibrational quasicontinuum limit. In a three-atom molecule for instance, the anharmonic shift is large, the number of split sublevels for each vibrational level is small and the vibrational quasicontinuum limit is almost lifted to the dissociation limit. In this case, extremely intense IR fields are required for multiphoton excitation of such molecules, which could overcome the anharmonic bottleneck by power broadening (dynamic Stark effect). Therefore, multiple photon dissociation of two- and three-atomic molecules has been observed only for a limited number of systems [40, 41].

For complex polyatomic molecules, on the other hand, the anharmonic shift is moderate, the number of split sublevels is very large and the vibrational quasicontinuum limit drops very low, down to the first vibrational level. In this case, it is possible to excite the molecules from the ground states directly to the vibrational quasicontinuum by absorption of a single photon. The situation is typical for isolated molecular ions with the number of atoms higher than  $\sim 9$ , ( $> 20$  vibrational modes) [42].

For a considerable fraction of molecules, initially distributed over lower sublevels, to be involved in effective multiple photon excitation and reach the vibrational quasicontinuum, it is necessary that the IR laser radiation should comply with at least two conditions: (i) the radiation frequency must lie within the band of vibrational absorption; (ii) the radiation intensity must exceed a certain value. That depends greatly on the type of molecule and the accuracy of tuning the IR field frequency. Understandably, the threshold value varies over a very wide range; from  $10^3$  W/cm<sup>2</sup> for heavy and complex molecules to  $10^9$  W/cm<sup>2</sup> for smaller ones. These values only refer to the intensity needed to pass from the region of lower vibrational transitions to the region of the vibrational quasicontinuum.

In general, for intensities below  $10^9$  W/cm<sup>2</sup>, the power broadening is small in comparison with the typical values of anharmonicity [43, 44]. One mechanism of compensation of anharmonic shift at lower transitions is *rotational compensation*. The different resonant frequency of excited states due to anharmonicity can be compensated by transitions in which  $\Delta J \neq 0$ . Another mechanism is *anharmonic splitting*. Inclusion of anharmonicity in the terms of the Hamiltonian corresponding to degenerated modes not only brings shifts of levels, but also partial removal of degeneracy (and breakdown of the selection rules). Typical values for anharmonic splitting are comparable with anharmonic shift values [44, and references therein].

### 1.3.2 Vibrational Quasicontinuum

With increasing internal energy, both the density of states and coupling between modes (and thus IVR) increase. The density of states is determined by the size of the molecule or cluster and the values of the vibrational frequencies of the fundamental modes and scales roughly with  $E^{(3n-7)}$  (where  $n$  is the number of atoms,  $n \geq 3$ , and  $E$  is the internal energy) [45]. This density of states quickly reaches values of many states per  $\text{cm}^{-1}$  for systems containing only a few atoms at internal energies of  $>1000 \text{ cm}^{-1}$  and can reach extremely high values for larger systems at higher internal energies.

An important parameter for the value of the IVR rate is the internal energy at which the line broadening caused by IVR is approximately equal to the average mode spacing, given by the density of states. Under this condition, IVR is fast and rapid absorption of photons can take place. Typical time scales for intramolecular relaxation of highly excited polyatomic molecules in this quasi-continuum regime are  $10^{-12}$  to  $10^{-11}$  s [45].

In the quasicontinuum, instead of narrow resonances of multiple photon absorption, a wide smooth absorption resonance appears around every vibrational mode which is IR active. First, the integral absorption cross-section gradually increases as the vibrational energy is increased. This is explained by an increase in the vibrational amplitude of a highly excited molecule. Second, the absorption maximum frequency gradually shifts to the long-wavelength region with increasing vibrational energy. The value of such a shift depends linearly on the value of the vibrational energy, and the coefficient of such a shift is determined by the anharmonicity constants. Third, the absorption band width grows with an increase of vibrational energy since the anharmonic interaction for highly excited states increases.

### 1.3.3 Dissociation of Molecules Excited by IR Laser Radiation

The strong excitation of molecules under IR laser radiation can lead to dissociation, emission of electrons, or emission of photons, the microscopic equivalent of evaporation, thermionic emission, and radiative cooling, respectively. The branching ratio between these processes depends on the internal energy and the properties of the species. Photon emission can be approximately described by the Stefan-Boltzmann law. The emission intensity then scales as  $T^4$  and is dominant at lower excitation energies. The rate constants for dissociation or electron emission grow exponentially with internal energy and will thus dominate at higher energies. For most molecules or clusters, dissociation will be much faster than the emission of electrons, as typical bond dissociation energies are lower than typical values for ionization potentials.

The possibility of strong molecular over-excitation relative to the dissociation limit remains restricted, because the dissociation rate is highly dependent on the excess

molecular energy (above the dissociation limit) and grows rather fast. At high internal energies, IVR is very efficient and statistical theories often give a good description of the observed kinetics. Those theories are built on assumptions such that each energetically allowed quantum state has the same *a priori* probability to be occupied and that there is a free flow of energy in the system. Then, the rate constant for dissociation is given by:

$$k(E) = \frac{\sigma N(E - E_0)}{h\rho(E)} \quad (1.9)$$

where  $\sigma$  is a reaction symmetry factor,  $N(E - E_0)$  is the sum of the available states above the transition state (at energy  $E_0$ ) leading to products,  $h$  is Planck's constant and  $\rho(E)$  is the density of states at energy  $E$  [46].

### 1.3.4 Fluence and Intensity Dependence

In order to reach the dissociation energy of a molecule, a minimal intensity is necessary to climb the ladder of the lower vibrational levels *and* also a minimal fluence to pump energy through the quasicontinuum. In other words, for a minimal necessary fluence, there is a maximal laser pulse length, which will give the necessary intensity.

Kolodner et al. [47] compared the multiphoton absorption of SF<sub>6</sub> using 500 ps, 10 ns, and 100 ns CO<sub>2</sub> laser pulses of  $\sim 1.5$  J/cm<sup>2</sup>. For the same fluence, the dissociation yield changes only 20% even though the peak power changes by over a factor of 200. This implies that at such high laser powers there is little “bottleneck” effect in multiphoton excitation over the initial discrete levels due to frequency mismatch. The same conclusion was reached by Gower et al. [48] who varied the pulse duration by a factor of 5 and showed that the multiple photon dissociation of many polyatomic molecules have energy thresholds, but not power thresholds.

However, at low laser intensities, multiple photon absorption data show significant dependence on the laser peak power. Kwok [49] measured the average number of IR photons absorbed by SF<sub>6</sub>,  $\langle n \rangle$ , versus the laser pulse fluence for CO<sub>2</sub> laser pulses of several different pulse widths. He shows that there is significant difference in  $\langle n \rangle$  for pulses with the same fluence but different pulse widths of 30, 50, and 150 ps respectively. Together with the measurements of Black et al. [50] and Bagratashvili et al. [51], Kwok's results show that for fluences less than 1 J/cm<sup>2</sup> there is a factor of 30 difference in  $\langle n \rangle$  between pulses of 150 ps and 120 ns. For higher laser fluence  $J$  ( $>1$  J/cm<sup>2</sup>), the difference in  $\langle n \rangle$  becomes smaller as  $J$  is increased. These results support the picture that the bottleneck effect of the discrete levels is significant only at low intensities.

As discussed by Bloembergen and Yablonovitch [52], the absorption in the quasicontinuum is fluence dependent rather than intensity dependent as in the lower vibrational level transitions. One way of looking at the absorption properties of the

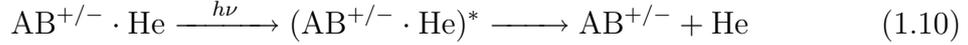
quasicontinuum is to obtain the change of absorption cross section  $\sigma$  as a function of the laser energy absorbed by the molecule. This can be deduced from the  $\langle n \rangle$  versus  $J$  curve through  $\sigma = d\langle n \rangle/dJ$ . The same value can be measured directly using two laser beams, one acting as a pump and the other acting as a weak probe. Comparison of  $\sigma$  at a certain internal energy deposited into the molecule by a laser pulse with a cross section  $\sigma_{\text{th}}$  measured with the same internal energy deposited as thermal excitation shows an interesting fact [49]: Initially, at low internal energies,  $\sigma$  is much smaller than the corresponding  $\sigma_{\text{th}}$ . However, at very high internal energies near the dissociation threshold,  $\sigma$  becomes the same as  $\sigma_{\text{th}}$ , within experimental error. This leads to the conclusion that the energy distribution among various modes near the dissociation threshold is close to random. The same conclusion has been obtained by Grant et al. [53] who observed the angular and velocity distribution of the reaction products. If the molecules are pre-heated to the quasicontinuum,  $\sigma$  measured with laser excitation then agrees qualitatively with  $\sigma_{\text{th}}$ . This is consistent with the argument that the absorbed energy is more or less randomized in the quasicontinuum [43].

A further requirement that has to be met by laser pulses for successful IR-PD experiments is posed by practical experimental conditions. For gas phase experiments, molecules or clusters are not fixed in space but move with typical velocities of hundreds of micrometers per microsecond. Thus, a typical interaction time between a molecule and a collimated or focused IR beam with a diameter of hundreds of micrometers to millimeters is on the order of microseconds. For multiphoton excitation experiments, a *high fluence per microsecond* is thus essential. Furthermore, at pressure in the range of a few Pascal (see Section 2.2), the mean free path is in the range of hundreds of micrometers and the mean time between collisions is of the order of some microseconds. Therefore, again, a high fluence per microsecond allows for multiphoton excitation under collision-less conditions.

## 1.4 Messenger Atom: Single Photon Infrared Photodissociation

IR multiple photon dissociation can be difficult to apply in the case of small and/or very strongly bound systems (see Section 1.3.1), where many photons are required to reach the quasicontinuum. This difficulty can be circumvented by attaching a weakly bound rare gas atom to the species of interest, forming a cluster–messenger atom complex [38]. If one assumes that the bond between the species under investigation, a cluster ion for the experiments presented in this work, and a rare gas atom, e.g. helium, is weak, only a minor perturbation of the electron distribution is to be expected. Furthermore, ion–rare gas atom binding energies are typically lower than a few hundred wavenumbers and therefore a single IR photon supplies enough energy

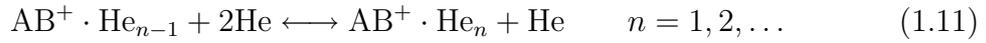
for dissociation (if one is interested in the 500 to 2000  $\text{cm}^{-1}$  spectral region). The absorption of a single IR photon by the cluster ion–rare gas complex, e.g.,  $\text{AB}^{+/-} \cdot \text{He}$ , is then signaled via vibrational predissociation,



if the photon energy exceeds the binding energy of the complex.

While this method has been successfully applied to studies on many atomic and molecular ions, its extension to polyatomic cluster ions formed by association reactions, for example, in standard laser ablation sources, remains nontrivial. Such cluster ions are formed in the (pulsed) expansion following the generation of an electrical neutral plasma and often remain too hot to bind a rare gas atom, in particular a helium atom, because the internal degrees of freedom are not sufficiently cooled.

For the experiments in this work, such messenger atom complexes of positive ions are formed in the cold radio frequency ion trap by collisions with helium buffer gas [54]. The formation of such complexes under very similar conditions has been previously observed in drift tube experiments reported by Kobayashi and coworkers [55,56]. The complexes are formed by the three-body association reaction,



and they can break apart by the reverse reaction, namely collision induced dissociation. The equilibrium ion concentrations are determined by the rates for the forward and backward reaction. Resonant absorption of IR radiation by the ion complex leads to vibrational predissociation and consequently to a temporary change in ion concentrations until the bare ion is able to dissipate the excess energy, reform a complex and return to equilibrium. Therefore, IR spectroscopy of the parent ions  $\text{AB}^+$  can be studied by mass-selectively monitoring changes in the  $\text{AB}^+ \cdot \text{He}_n$  ion yield as a function of photon wavelength directly after irradiation with a tunable IR source.

The bond between the cluster ion and the rare gas atom is described by an ion–induced dipole interaction. In first approximation, the induced dipole moment,  $\mathbf{M}$ , is equal to  $\alpha \mathbf{E}$ , where  $\alpha$  is the polarizability and  $\mathbf{E}$  the electric field. In the case of a helium atom with a spherical symmetry in the field of a point charge,  $\mathbf{M}$  will be aligned with the segment connecting the helium atom to the charge. Therefore the electrical potential  $\phi(r)$  at distance  $r$  due to the induced dipole  $\mathbf{M}$  is  $\phi(r) = M/(4\pi\epsilon_0 r^2)$ . Assuming that the induced dipole moment is due to the electric field generated by a point charge at distance  $r$  so that  $E \propto 1/r^2$ , one obtains that  $\phi(r) \propto \alpha/r^4$ , i.e., the potential falls with the fourth power of the distance from the point charge. As a consequence, creation of messenger atom complexes is in general possible for small cluster ions and for those cluster ions where the charge remains localized on some terminating atom [54].

### 1.4.1 Single and Multiple Photon IR-PD: A Brief Practical Comparison

The multiple and the single photon IR-PD methods present some complementary features.

**Size:** In general multiple photon IR-PD can only be applied on larger clusters, where the quasi continuum can be reached within the absorption of few photons; single-photon IR-PD can only be applied to those cluster ions which have a charge sufficiently localized to bind a rare gas atom at finite temperature and this is usually the case for smaller species, where the multiple photon IR-PD is not feasible.

**Interpretation:** Multiple photon IR-PD can be applied on bare clusters without the necessity to consider any possible perturbation induced by the rare gas atom. However, overtones and combination bands can be excited due to the high laser power needed by the process complicating the interpretation of the spectra. Furthermore, the intensities of the absorption bands do not depend only on the excited dipole strengths but are rather given by the convolution of dipole strengths with internal energy redistribution efficiency. In principle, in single photon IR-PD one cannot exclude a perturbation of the species under investigation by the presence of the messenger atom, although these perturbations are often of minor extent. However, the process involves the absorption of a single photon and the measured spectra represent directly the dipole strengths of the excited transitions. Furthermore, the comparatively lower laser power required by the process makes the excitation of overtones and combination bands unlikely.

**Sensitivity:** When measuring a multiple photon IR-PD spectrum one can usually monitor the formation of a fragment ion in dependence on the laser wavelength: this is in principle a background free measurement. However, determining the necessary laser power can be non-trivial. For low laser power, some absorption bands would not be detectable, whereas with too high laser power, overtones and combination bands can be excited. Therefore, careful observation of band intensities versus laser power is necessary. In single photon IR-PD experiments, the abundance of cluster ion–rare gas complexes is generally much lower than the abundance of bare cluster ions. Therefore, monitoring of cluster ion–rare gas depletion offers a better signal contrast than monitoring bare cluster ion yield. However, the cluster ion–rare gas yield mirrors every instability of the cluster source, although an averaging occurs due to the accumulation in the ion trap. Anyway, if the cluster ion–messenger atom bond strength is lower than the photon energy, every single photon absorbed will induce depletion in the ion yield.