Infrared spectroscopy of mass-selected aromatic and diamondoid molecular ions: a laboratory quest for the organic inventory in space

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Evidence of the observable Universe, its vastness and constituents, is provided by the light that reaches Earth. Laboratory infrared (IR) spectroscopy is essential to the study of the interstellar and circumstellar media since many space environments are populated with organic gas molecules and solid dust species absorbing and emitting at infrared wavelengths. While direct IR photon-absorption techniques are a common practice to record spectra of gas-phase neutral molecules, they do not work for isolated, mass-selected ionized molecules due to their mutual electrostatic interaction that inevitably lead to low densities. An important technique to circumvent this problem is infrared multiple-photon dissociation (IRMPD) action spectroscopy. The IRMPD technique used in this Thesis relies on ion trapping technology and mass spectrometry methods and is introduced in this chapter. An overview of some foundations in molecular spectroscopy is also given, as well as an introduction to the quantum chemistry computations used to predict electronic molecular structures and to model the infrared activity of the molecular species studied.
2 Laboratory Methods

2.1 Introduction

Laboratory spectroscopy investigates the fundamentals of matter through its interactions with light. The basic principle consists of measuring the amount of light absorbed or emitted from a source by the medium under study. The electric forces holding the nuclei together in a molecule determine the type of chemical bonds, and keep the nuclei vibrating around an equilibrium position at frequencies that fall in the infrared region. Therefore, infrared-based spectroscopic methods are essential in the determination of molecular geometries and intramolecular dynamics, as well as in the identification of structural isomers and conformational dynamics.

In space, about 30% of the light produced by stars is converted to infrared cosmic radiation through absorption-emission and/or scattering processes. Dust is an important component of the interstellar medium and the main source of infrared light after being heated by energetic photons. For regions characterized by large-scale dynamics and turbulence, or under strong gravitational pulling (e.g., as in protoplanetary disks), dust and gas is kinetically heated and subsequently cools down by emitting at millimeter and IR wavelengths.

The UIR emission bands (see Sec. 1.2.3) are the result of an absorption-emission process in which UV photons are absorbed by poly-aromatic species, raising their internal energies (∼1000 K) and subsequently cooling by IR fluorescence in the mid-IR spectral range. In this Thesis, laboratory infrared characterization of PAH-derivative and diamondoid- molecular species is undertaken in the mid-IR range. Ideally, laboratory infrared spectra in emission offer the best approach to study the UIR phenomenon (see Sec. 1.2). While most modern spectroscopic techniques yield absorption spectra, these still provide essential information (such as anharmonicity of vibrational modes, or optical properties) that is required to understand interstellar emission mechanisms, as well as the infrared signatures needed for detection of possible interstellar constituents.

Absorption spectra of available neutral PAHs obtained using conventional spectroscopic methods, e.g., KBr pellets with grating or fourier transform (FT-) IR spectrometers, have been catalogued ever since these species came on the market. Some gas-phase spectra of neutral PAHs have also been recorded using thermal vaporization of the PAHs combined with IR direct absorption (Joblin et al. 1995) or emission spectroscopy (Shan et al. 1991, Cook et al. 1996), and jet-expansion molecular beam methods (Piest et al. 2001). Obtaining IR spectra for the cationic PAHs constituted a larger challenge, that was first tackled by the group of Vala. Thermally vaporized PAHs were ionized using electron impact (EI) ionization and deposited into a cryogenic matrix at ∼12 K — quenching the rotational motion of the molecules — which was then analyzed using an FTIR spectrometer (Szczechanski et al. 1992, Szczechanski & Vala 1993). Alternatively, neutral PAHs were deposited into the cryogenic matrix and ionization was induced in-situ using an UV source. Using this method, Hudgins, Allamandola and coworkers at the NASA Ames group recorded the spectra of a large number of PAH cations (Hudgins & Allamandola 1995) and created a database of spectral properties. Matrix-based methods provide high-resolution IR spectra with band profiles as narrow as 1 cm$^{-1}$ FWHM$^1$ that

\[1\text{Full Width at Half Maximum of a spectral band.}\]
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can provide links to processes of interstellar dark, dense clouds where absolute temperatures are around 10 K. Possible matrix effects on IR band positions and relative intensities have been investigated (Joblin et al. 1994), and such influences can be important when studying spectral properties of PAH species embedded in interstellar ices (Bernstein et al. 2005).

Measuring gas-phase spectra of isolated ionized PAHs is challenging as the ion densities typically obtained in mass spectrometers are extremely low, so that no direct absorption spectra can be recorded. Emission spectra of cationic PAHs had been recorded in the 3 µm region of the spectrum (Williams & Leone 1995), however, extension to the astrophysically important range between 6 and 16 µm required the use of a cryogenic IR spectrometer. Saykally and coworkers had developed such an instrument to study the emission spectra of various neutral PAH species (Cook et al. 1996) and successfully coupled this spectrometer to a high-current ion source to record the emission spectrum of the pyrene cation (C_{16}H_{10}^+) (Kim et al. 2001). Other gas-phase methods developed since the 1990’s make use of laser-based photo-dissociation spectroscopy and rely on mass-spectrometric ion detection, rather than on photon detection. One implementation of these methods produces weakly bound clusters of rare gas atoms (or small molecules such as H_2) and the ion under study; upon IR absorption by the ion, the rare gas atom is detached, which is signalled in the mass analyzer. This method, often referred to as messenger-atom spectroscopy was pioneered by Lee and coworkers (Okumura et al. 1990) and was applied to several small PAHs using the radiation produced by an IR free electron laser (FEL) in the group of Meijer (Piest et al. 1999). Alternatively, using a mJ-energy optical parametric oscillator (OPO), the group of Duncan applied the messenger technique to record IR spectra of the protonated forms of benzene (Doublerly et al. 2008) and naphthalene (Ricks et al. 2009) by producing Ar van der Waals complexes in the expanding beam of a pulsed discharge nozzle, and recording the IR-induced Ar detachment with a TOF mass spectrometer. This yielded the IR spectra of the protonated species at a resolution of a few wavenumbers.

In 2000, Meijer’s group showed that the IR pulse energies of the FEL were sufficient to dissociate not only weakly bound clusters, but also the PAH ion itself, which grounded the way for IR multiple-photon dissociation (IRMPD) spectroscopy of mass-selected PAH ions (Oomens et al. 2000, 2006b). The combination of tandem mass spectrometry with laser spectroscopy has developed into an experimental approach that is able to address the spectroscopy of a large variety of ionized species that are not easily studied with conventional spectroscopic methods (Bréchignac & Pino 1999, Ricks et al. 2009, Knorke et al. 2009, Useli-Bacchitta et al. 2010). It is this method that is applied in this Thesis to obtain IR spectra for a series of cationic PAH derivatives and related species.

Along with the experimental spectroscopy of PAH species, quantum-chemical computed spectra have played a major role in the development of the PAH hypothesis (Pauzat et al. 1992, Langhoff 1996, Bauschlicher et al. 2010, Malloci et al. 2011). The rapid development in density functional theory (DFT) boosted by the ever-increasing speed of modern processors now makes it possible to reliably compute IR spectra for PAHs in the size up to hundreds of atoms. Not only are the computed spectra used to support experimental data, they have especially also been applied to predict IR spectra for species
that are not easily accessible experimentally. Extensive databases containing theoretical spectra of PAHs and many of their derivatives in different charge states are now freely available (Bauschlicher et al. 2010, Cami et al. 2010). Similar DFT-based computational methods are applied in this Thesis to investigate the electronic structures and IR activity of the species investigated experimentally.

In the subsequent sections the problem arising when attempting to measure gas-phase spectra of molecular ions using direct absorption techniques is discussed. Then, an expression relating the integrated absorption intensity of an IR band with molecular structural properties (e.g. dipole derivatives) is deduced. It will become clear that even though this expression is derived within the harmonic approximation and linear absorption techniques, it is yet useful to understand the IR activity of the molecular ions studied using non-linear absorption methods such as IRMPD spectroscopy. Furthermore, when combined with quantum chemistry calculations it is possible to differentiate species in terms of electron dynamic correlation. Next, the IRMPD spectroscopic technique is explained and the ion trap setup and associated instrumentation is described. Finally, an introduction is given to the quantum-chemistry computational methods used in this Thesis.

2.2 The Absorption–Density Spectroscopic Paradigm

The amount of light removed from a source beam by an absorbing medium composed of \(N\) non- (or weakly-) interacting molecules per unit volume (\(\text{cm}^{-3}\)) in a differential optical path \(d\ell\) (cm) is

\[ -dI = \sigma_{\tilde{\nu}} N I d\ell \]  

(2.1)

where \(I\) (W cm\(^{-2}\)) is the instantaneous beam intensity and \(\sigma_{\tilde{\nu}}\) (cm\(^2\)) is the molecular absorption cross-section. The subindex \(\tilde{\nu}\) shows the frequency dependence (in wavenumbers, cm\(^{-1}\)). The solution of eq. 2.1 is \(I = I_0 \exp(-\sigma_{\tilde{\nu}} N \ell)\), where \(I_0\) is the incident beam intensity. Thus, the absorbance, \(A_{\tilde{\nu}} = \ln\left(I_0/I\right)\), exhibits a logarithmic dependence between the ratio of incident and transmitted light, in relation with the absorption coefficient, \(\alpha_{\tilde{\nu}} \equiv \sigma_{\tilde{\nu}} N\) (cm\(^{-1}\)). This implies that \(A_{\tilde{\nu}}\) varies linearly with the number density of absorbing molecules and optical length:

\[ A_{\tilde{\nu}} = \alpha_{\tilde{\nu}} \ell = \sigma_{\tilde{\nu}} N \ell \]  

(2.2)

This is Beer-Lambert’s law for direct-absorption IR spectroscopy. The integrated absorption cross-section \(A\) (cm\(^2\) cm\(^{-1}\)), is obtained by integration of the absorbance over the absorption band, divided by the number density and optical path length:

\[ A = \int_{\text{band}} \sigma_{\tilde{\nu}} d\tilde{\nu} = \frac{1}{N \ell} \int_{\text{band}} \ln\left(\frac{I_0}{I}\right) d\tilde{\nu} \]  

(2.3)

which holds for infrared spectra of trapped, isolated absorbing molecules contained in an optical gas cell. The quantity \(A\) is the true theoretical strength of a transition, or simply, intensity. In quantum-chemical calculations, computed IR intensities are customary reported in units of length per amount of molecular gas (km mol\(^{-1}\) = 10\(^5\) cm mol\(^{-1}\) = 10\(^5\) cm\(^2\) mol\(^{-1}\) cm\(^{-1}\)).
2.2 The Absorption–Density Spectroscopic Paradigm

It is clear from eq. 2.2 that the effectivity of a direct IR photon-absorption technique is strongly determined by the number of molecular absorbers per unit volume (the number density, \( N \)). Now, suppose the absorbance centered over an IR band of a given molecular species with characteristic cross-section \( \sigma^a_\nu \) will be measured in its neutral and ionized forms employing an optical gas cell and a linear ion trap, respectively. The absorbance in both cases is \( A^o_\nu = \sigma^a_\nu N^o \ell^o \) and \( A^i_\nu = \sigma^a_\nu N^i \ell^i \), where \( \ell^o \) and \( \ell^i \) are the optical path lengths for the gas cell and ion trap. The cross-section \( \sigma^a_\nu \) is assumed not to change upon ionization at such band transition. By exploring the densities \( N^o \) and \( N^i \) attained respectively inside the gas cell and the ion trap, the problem arising in the direct-absorption ion trap experiment can be clearly recognized.

First, in gas-cell experiments, typical neutral pressure values \( P \) range within a few Torr, for instance, such as in CW laser mid-IR spectroscopy (Tittel et al. 2003). Therefore, for the neutral molecular gas in a cell at, say, \( P = 1 \) Torr, the number density of molecules \( N^o \) can be computed in a straightforward manner using the ideal gas law, \( PV = nRT \), where \( n \) is the amount of gas in moles, \( R \) the universal gas constant (82.0574 cm\(^3\) atm K\(^{-1}\) mol\(^{-1}\)), and \( T \) is the temperature in Kelvin. Solving for the amount of gas per volume (mol cm\(^{-3}\)) at room temperature \((\sim 300 \) Kelvin\) gives

\[
n \frac{V}{V} = \frac{P}{RT} = \frac{1.3158 \times 10^{-3} \text{ atm}}{(82.0574 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})(300 \text{ K})} = 5.345 \times 10^{-8} \text{ mol cm}^{-3}
\] 

(2.4)

where 1 Torr = 1.3158 \times 10^{-3} \text{ atm}. Therefore, the number density of neutral molecules \( N^o \) is \( N_A(n/V) \), where \( N_A \) is Avogadro’s number (6.022 \times 10^{23} \text{ mol}^{-1}). This gives \( N^o = 3.218 \times 10^{16} \text{ cm}^{-3} \).

On the other hand, the number density of molecular ions \( N^i \) is governed by the electric forces keeping the ions in confinement. Then, the maximum amount of ions stored is achieved when the electric field due to the effective potential generated by the ion trap is balanced to the total electric field due to the space charge generated by the ion cloud. Assuming that the ion cloud confined in a linear ion trap has a cylindrical geometry, Gauss law \( \oint_S \mathbf{E} \cdot \mathbf{dA} = Q/\varepsilon_o \) can be readily applied. The Gauss surface \( S \) enclosing a cylindrical ion cloud volume is \( 2\pi bL \) (where \( b \) is the radius and \( L \) the length of the cylindrical ion cloud), whereas the net charge \( Q \) due to the total number of enclosed ions (each having an elementary charge \( e \)) is found by integrating the charge density over the cylindrical volume \( \tau = \pi b^2 L \). Thus, assuming a constant space charge density \( (eN^i) \), application of Gauss law to our physical situation leads to

\[
E(2\pi bL) = \frac{eN^i}{\varepsilon_o} \int_\tau d\tau = \frac{eN^i}{\varepsilon_o} (\pi b^2 L)
\]

(2.5)

where \( E \) is the electric field (V/m) due to the enclosed charge density, and \( \varepsilon_o \) is the electrical permittivity in vacuum \((8.85 \times 10^{-12} \text{ C / V m})\). Solving for \( E \) results in

\[
E = \frac{eN^i b}{2\varepsilon_o}
\]

(2.6)
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For a linear quadrupole ion trap, the effective potential is \( V_e(r) = V_{RF}(q/4)(r/r_o)^2 \) (March & Hughes 1989), where \( V_{RF} \) is the RF amplitude of the time-dependent part of the applied ion trap voltage, and \( q \) is a stability parameter that arises when solving the equations of motion (Mathieu equations) that describe the trajectories of the ions. The generated electric field is \( |E| = \frac{\partial V_e}{\partial r} = \frac{q V_{RF}}{2b} \) at \( r = r_o = b \). By balancing this equation with eq. 2.6, a solution for the number of ions per volume \( N^i \) can be found such that

\[
N^i = \frac{q V_{RF} e_o}{e b^2} \tag{2.7}
\]

Using some typical values for \( q = 0.7 \) and \( V_{RF} = 100 \) V, and assuming a cylindrical ion cloud with radius \( b = 3 \) mm, numerical substitution in eq. 2.7 gives

\[
N^i = \frac{(0.7)(100 \text{ V})(8.85 \times 10^{-12} \text{ C} / \text{ V m})}{(1.602 \times 10^{-19} \text{ C})(3 \times 10^{-3} \text{ m})^2} = 4.296 \times 10^{14} \text{ m}^{-3} = 4.296 \times 10^{5} \text{ cm}^{-3} \tag{2.8}
\]

Now, assuming a desired outcome such that \( A_o \tilde{\nu} = A_i \tilde{\nu} \), implies that \( N_o \ell_o = N_i \ell_i \). Solving for \( \ell_i \) yields \( \ell_i = (N_o/N^i)\ell_o \). Therefore, by recalling the number densities \( N^o \) and \( N^i \) calculated above, in order to satisfy the \( A_o^c = A_i^c \) condition, the length of the linear ion trap must be \( N_o/N^i = 7.5 \times 10^{10} \) times longer than the length of the gas cell. Action spectroscopy encompass techniques that circumvent this engineering ‘inconvenience’ by measuring the induced effects of the absorbing light instead of the light itself. Infrared multiple-photon dissociation (IRMPD) spectroscopy is one of such techniques, which is used to conduct the research presented in this Thesis.

2.3 Spectroscopic Transitions and Observables

Consider a sample of gas phase molecules in a cell at temperature \( T \) subject to laser irradiation. A molecule with internal degrees of freedom (electronic, vibrational, rotational) represented by a quantum state \( n (\epsilon, \nu, J) \) makes a transition to an upper state \( n' (\epsilon', \nu', J') \) when it absorbs a photon of energy

\[
E = h f_{\epsilon'\epsilon n}, \tag{2.9}
\]

where \( f_{\epsilon'\epsilon n} \) is the frequency (s\(^{-1}\)) of the photon and the relative populations of the two states are governed by the Boltzmann distribution

\[
\frac{N_{n'}}{N_n} = \exp (-h f_{\epsilon'\epsilon n}/kT) \tag{2.10}
\]

where \( k \) is the Boltzmann constant. The number of photon absorption events (transition probability) per unit time in the presence of the radiation laser field with energy density \( u(f_{\epsilon'\epsilon n}) \) is written as (Hilborn 2002)

\[
R_{n'n} = (8\pi^3 / 3h^2) \mu_{n'n}^2 u(f_{n'n}) \tag{2.11}
\]
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where the transition dipole moment $\mu_{n' n}$ describing the coupling of the field and an absorbing molecule—having an electric dipole moment $\mu = (\mu_x, \mu_y, \mu_z)$ defined in a molecule-fixed Cartesian system—that undergoes the $n' \leftarrow n$ quantum transition is (Demtröder 2005)

$$\mu_{n' n} = \langle n' | \mu | n \rangle = \int \Psi_{n'}^* \mu \Psi_n \, d^3 r$$

(2.12)

where the term on the right is the transition moment integral involving the two quantum state wavefunctions $\Psi_{n'}$ and $\Psi_n$. This integral determines the selection rules of a spectroscopic transition.

For photons with infrared energies there is usually no change in electronic quanta but only a change in vibrational and rotational quantum numbers. Thus, for a given electronic state, a vibrational transition is accompanied by a series of rotational transitions. The two states involved in the dipole transition matrix $\langle n' | \mu | n \rangle$ are then associated with the vibrational-rotational wavefunction $\Psi_{vJ}$. An approximation based on Eckart conditions minimize the coupling between vibration and rotation states by defining a fixed frame on a semi-rigid molecule, and the wavefunction can be written as a product of vibrational and rotational wavefunctions, $\Psi_{vJ} = \Psi_v \Psi_J$ (Wilson Jr. et al. 1955). The matrix elements $\langle n' | \mu | n \rangle$ in integral form are

$$\langle n' | \mu | n \rangle = \langle v' J' | \mu | vJ \rangle = \int \Psi_{v' J'}^* \mu \Psi_{vJ} \, d^3 r$$

(2.13a)

$$= \int \Psi_{v}^* \Psi_{J'}^* \mu \Psi_v \Psi_J \, d^3 r.$$  

(2.13b)

Evaluation of the matrix elements for a vibrational transition requires summation over all associated rotational quantum numbers $J$ and $J'$. Experimentally, the intensity of a gas-phase infrared band represents a convolution over the fine structure of rotational line intensities.

The quantity $(8\pi^3/3h^2)\mu_{n' n}^2$ in eq. 2.11 is the Einstein coefficient $B_{n' n}$ of the radiative absorption process (Hilborn 2002) and its nature is governed by the molecular structure. Therefore a link between spectroscopic observables (i.e. experimental infrared intensities and frequencies) and the molecule–field interaction can be drawn and provides the information to characterize molecule physical properties. In order to fully describe the molecule–field interaction, the spontaneous and stimulated radiative emission processes need to be considered via the $A_{nn'}$ and $B_{nn'}$ Einstein coefficients, respectively. Then, the rate of absorption of energy $dE/dt$ is simply given by the difference between the rate of absorption and the rate of emission multiplied by the energy absorbed during the transition (Atkins & Friedman 2011):

$$\frac{dE}{dt} = [N_n R_{n' n} - N_{n'} R_{nn'}] h f_{n' n}$$

(2.14)

where $N_n$ and $N_{n'}$ are the populations for the lower and upper states, and $R_{n' n} = B_{n' n} u(f_{n' n})$ and $R_{nn'} = B_{nn'} u(f_{nn'}) + A_{nn'}$. In terms of radiative lifetimes, $A_{nn'}^{-1}$ is large in comparison

\(^2\)For some molecular systems (for instance, long polyenes) the spacing between electronic $\pi \pi^*$ energy levels lie in the IR range and a photon in that range could induce transitions between electronic quantum levels.
with our experimental time sequence and \( R_{n'n'} \approx B_{n'n'}u(f_{n'n'}) \). Thus the net absorbed energy per unit volume (\( d\tau = ad\ell \), where \( a \) is the beam area) is

\[
\frac{dE}{d\tau} = (N_n - N_{n'})\hbar f_{n'n'}B_{n'n'}u(f_{n'n'})
\]

(2.15)

where \( B_{n'n'} = B_{n'n'} \) because \( \mu_{n'n'}\mu_{n'n'}^{\ast} = \mu_{n'n'}\mu_{n'n'} \). Then, the decrease in intensity or the energy absorbed in a unity cross-section (\( a = 1 \)) along a differential optical path length \( d\ell \) is

\[
-dI = \frac{I}{c}h f_{n'n'}(N_n - N_{n'})B_{n'n'}d\ell
\]

(2.16)

where the field is expressed in terms of the beam intensity \( I = cu \). In view of eq. 2.13 and using the explicit form of \( B_{n'n'} \), eq. 2.16 can be re-written as

\[
-d \ln I = \frac{8\pi^3f}{3hc}(N_v - N_{v'})\left| \langle v' | \mu | v \rangle \right|^2 d\ell
\]

(2.17)

where the quantization of the rotational motion is omitted in the transition matrix and can be included later as a rotational factor. Similarly, the rotational contribution to the population difference is implicit in \( (N_v - N_{v'}) \). The frequency \( f \) refers to an infrared photon frequency and its subscript is dropped. Integration of eq. 2.17 yields

\[
\ln \left( \frac{I_o}{I} \right) = \frac{8\pi^3f}{3hc}(N_v - N_{v'})\left| \langle v' | \mu | v \rangle \right|^2 \ell
\]

(2.18)

where \( I_o \) is the incident laser beam intensity. By comparing eqs. 2.18 and 2.3, it is seen that this expression relates the integrated absorption intensity directly to the difference in vibrational state populations, and the square of the vibrational transition matrix, that is,

\[
A = \frac{1}{N\ell} \int_{\text{band}} \ln \left( \frac{I_o}{I} \right) df = \frac{8\pi^3f}{3hc}(N_v - N_{v'})\left| \langle v' | \mu | v \rangle \right|^2
\]

(2.19)

In order to relate infrared band intensities to physical quantities such as dipole derivatives —which are closely connected to the electronic structure of a molecule — the matrix elements \( \langle v' | \mu | v \rangle \) need to be investigated:

\[
\langle v' | \mu | v \rangle = \int \Psi_{v'}^\ast \mu \Psi_v d^3r
\]

(2.20)

Firstly, the vibrational wavefunctions involved in the transition \( v' \leftarrow v \) (eq. 2.20) are each a product of wavefunctions \( \psi_{v_i} \) defined with respect to vibrational normal coordinates \( Q_i \)

\[
\Psi_v = \psi_{v_1}(Q_1)\psi_{v_2}(Q_2) \ldots = \prod_{i=1}^{3N-6} \psi_{v_i}(Q_i),
\]

(2.21)

where the number of factors is equal to the number of vibrational degrees of freedom of the (non-linear) molecule. Each function \( \psi_{v_i} \) satisfies the Schrödinger equation \( H_i \psi_{v_i}(Q_i) = E_i \psi_{v_i}(Q_i) \) such that

\[
\frac{-\hbar^2}{2} \frac{\partial^2 \psi_{v_i}(Q_i)}{\partial Q_i^2} + \frac{1}{2}k_iQ_i^2 \psi_{v_i}(Q_i) = E_i \psi_{v_i}(Q_i)
\]

(2.22)
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This is the equation of the harmonic oscillator of unity effective mass and force constant \( k_i = \omega_i^2 \). Therefore, the vibrational eigen-functions and eigen-energies are (Atkins & Friedman 2011)

\[
E_{\nu_i} = (\nu_i + \frac{1}{2})\hbar \omega_i, \quad \psi_{\nu_i} = D_{\nu_i} H_{\nu_i}(\alpha Q_i) \exp(-\alpha^2 Q_i/2)
\]  

with \( \alpha = (k_i/\hbar^2)^{1/4} \), \( D_{\nu_i} = (\alpha/2^{\nu_i+1/2})^{1/2} \) as normalization constant, and \( H_{\nu_i} \) are Hermite polynomials. The \( Q_i \) coordinates describe the vibrations of the molecule as a linear combination of \( 3N - 6 \) separate harmonic oscillators at a frequency \( f_i = \omega_i/2\pi \).

Secondly, consider the dipole moment \( \mu \) which is expanded in a Taylor series with respect to the normal coordinates around the equilibrium position

\[
\mu = \mu_o + \sum_i \left( \frac{\partial \mu}{\partial Q_i} \right)_o Q_i + \frac{1}{2} \sum_{i,j} \left( \frac{\partial^2 \mu}{\partial Q_i \partial Q_j} \right)_o Q_i Q_j + \frac{1}{6} \sum_{i,j,k} \left( \frac{\partial^3 \mu}{\partial Q_i \partial Q_j \partial Q_k} \right)_o Q_i Q_j Q_k + \ldots
\]  

where \( \mu_o \) is the (permanent) dipole moment when the nuclear displacements are zero. In view of the solutions represented by eq. 2.23, in the harmonic regime, the nuclei in the molecule exhibit small oscillatory displacements around the equilibrium, and higher-order terms can be neglected. Thus, the vibrational transition matrix or transition integral (eq. 2.20) is

\[
\langle v' | \mu | v \rangle = \mu_o \langle v' | v \rangle + \left( \frac{\partial \mu}{\partial Q_i} \right)_o \langle v' | Q_i | v \rangle
\]  

where the first term is zero (as determined by the orthogonality of vibrational eigenstates). Eq. 2.25 determines the coupling between the dipole moment and the electromagnetic field, and hence, the allowed IR active transitions. This is the gross selection rule which defines the occurrence of a vibrational transition \( \nu' \leftarrow \nu \) whenever the change in dipole moment along \( Q_i \) is non-zero.

An explicit form of the transition matrix is obtained by operating the \( i \)-th normal coordinate expressed in terms of the annihilation and creation operators \( Q_i = \sqrt{\hbar/2\omega_i}(a_i^\dagger + a_i) \):

\[
\langle v' | Q_i | v \rangle = \sqrt{\hbar/2\omega_i} \left( \sqrt{v+1} \langle v' | v+1 \rangle + \sqrt{v} \langle v' | v-1 \rangle \right)
\]  

Accordingly, the transition integral is non-zero for transitions that occur only by a change of one vibrational quantum number, +1 or -1. This condition defines the electric-dipole harmonic selection rules \( \Delta \nu = \pm 1 \). At high internal energies, the integral is also non-zero for transitions involving higher vibrational states as long as \( \Delta \nu = \pm 1 \). These transitions produce vibrational hot bands. For fundamental absorption transitions \( \nu' = 1 \leftarrow \nu = 0 \), the transition matrix element becomes

\[
\langle v' | \mu | v \rangle = \sqrt{\frac{\hbar}{8\pi^2 f_i}} (v+1) \left( \frac{\partial \mu}{\partial Q_i} \right)_o
\]
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where \( f = \omega / 2\pi \) and \( h = 2\pi h \). Therefore, substituting eq. 2.27 back into eq. 2.19 and noting that for infrared energies \( h f \gg kT \), the Boltzmann vibrational populations satisfy

\[
N_v \gg N'_v,
\]

the absorption band intensity due to the \( i \)-th fundamental vibrational mode is

\[
A_i = \frac{\pi}{3c} \left( \frac{\partial \mu}{\partial Q_i} \right)^2
\]

(2.28)

where \( \left( \partial \mu / \partial Q_i \right)^2 = \left( \partial \mu_x / \partial Q_i \right)^2 + \left( \partial \mu_y / \partial Q_i \right)^2 + \left( \partial \mu_z / \partial Q_i \right)^2 \). Thus, the observed intensities \( A_i \) in an IR spectrum are those due to transitions involving a change of one vibrational quantum number (e.g., fundamentals or hot bands) and are associated with a change in the molecular dipole moment along the normal coordinates (\( \partial \mu / \partial Q_i \neq 0 \)), for which magnitudes are given by \( \left( \partial \mu / \partial Q_i \right)^2 \).

Relating the intramolecular charge distribution and its fluctuations along vibrational distortions to IR intensities requires a proper transformation of \( Q_i \) normal coordinates into internal vibrational coordinates \( R_k \), or into Cartesian atomic displacements \( x_k \), of the molecule (Wilson 1941, Thorndike et al. 1947, Gussoni 1990). For instance, the transformation in terms of \( R_k \) coordinates is

\[
R_k = \sum_i L_{ki} Q_i
\]

\[
\frac{\partial \mu}{\partial R_k} = \sum_k (L^{-1})_{ik} \frac{\partial \mu}{\partial Q_i}
\]

(2.29)

where \( L_{ki} \) is the transformation matrix. The \( R_k \) coordinates represent bond lengths and bond angles (e.g., out-of-plane, torsional) as vibrational degrees of freedom of the molecule. Ambiguity in the signs of the dipole derivatives and \( R_k \) coordinates is a major problem that becomes harder to solve for large polyatomic molecules. A transformation into atomic displacements yields the definition of the so-called atomic polar tensor (APT) of the molecule. The interpretation of IR intensities via the APT provides a localized character for the behavior of the charge distribution along vibrations.

Introducing mass-weighted coordinates \( q_i \) in terms of the \( 3N_a \) Cartesian displacements (where \( N_a \) is the total number of atoms), such as \( q_i = m_i^{1/2} x_i \) (where \( m_i \) is the atomic mass displaced along \( x_i \)), allows us to search for ways in which normal coordinates are written directly as linear combinations of \( q_i \). Furthermore, if a set of mass-weighted coordinates \( \{q_i\} \) is used as a basis to span the irreducible representations of the point group of the molecule, the symmetry for each normal coordinate \( Q_i \), or vibrational mode, can be found via their mutual transformations under the operations of that group. The symmetry species of normal modes are used to predict when fundamental transitions \( \langle \{1\} | \mu | \{0\} \rangle \) are allowed. If the symmetry of \( Q_i \) is the same as the one of \( \mu_x, \mu_y \), or \( \mu_z \), then \( \langle \{1\} | \mu | \{0\} \rangle \neq 0 \) and the corresponding fundamental transition is IR active (since the vibrational ground state is totally symmetric under all operations of the group and the first excited vibrational state has the same symmetry as its corresponding normal coordinate mode). This is the basic procedure of group theory to study the IR activity of molecules and is used throughout this Thesis. Further details can be found in the relevant chapters.
2.4 Ion Trap Infrared Multiple Photon Dissociation Spectroscopy

The IRMPD spectroscopic technique used to conduct the research presented in this Thesis consists in applying a combination of four technological resources: (1) an ion trapping scheme, (2) high-sensitivity mass spectrometry, (3) an ionization source, and (4) a tunable high-fluence IR laser source. Points (1)–(3) comprise the ion trap machine described in Sec. 2.4.2, and (4) is the free electron laser (FEL) for infrared experiments—FELIX—described in Sec. 2.4.1.

In FEL-based IRMPD spectroscopy, a sample of gas-phase trapped molecular ions is heated up through incoherent multiple photon excitation using a high-fluence IR FEL-source. The excitation is always initiated by a resonant absorption event that provides the vibrational mode selectivity; thus, electronic structure information is, in principle, yet encoded in the IRMPD spectrum as shown in e.q 2.28. The generation of a subpopulation of ions with very high internal energies is achieved that eventually relaxes via unimolecular statistical dissociation (Bagratashvili et al. 1985); resulting in one or more fragments. This excitation mechanism is mediated by a fast diffusion of the absorbed photon energy — originally pumped into the \( \nu_i \) vibrational mode of the ion species — to a number of coupled vibrational dark states (quasi-continuum). The photon-energy diffusion or \textit{intramolecular vibrational energy redistribution} (IVR) defines the lifetime (\( \tau \)) of the excited, bright (non-stationary) state (|\( \nu \rangle \)) as \( \tau = \frac{1}{2\pi\Gamma} \), where \( \Gamma \) is the IVR transition rate \( (s^{-1}) \) given by Fermi’s golden rule

\[
\Gamma = \frac{2\pi}{\hbar} \left| \langle \nu' | \mu | \nu \rangle \right|^2 \rho_{\nu}(E)
\]  

(2.30)

where |\( \nu' \rangle \) is the set of coupling final states and \( \rho_{\nu} \) is the density of vibraional states (number of states per unit energy) at the internal energy \( E \) of the molecular ion. Thus, the IVR rate depends on the strength of the coupling (squared transition matrix) and the available density of states, and is essential to the success of the technique since it allows the excited mode to decay in time for the arrival of the next FEL micropulse (see next section for details on the FEL pulse structure).

The integrated dissociation yield \( D \) is the ratio of total number of fragment ions over the total number of ions (fragments and parent)

\[
D(\lambda_{\text{FEL}}) = \frac{\sum_m S^m_{f}}{\sum_m S^m_{f} + S_p},
\]  

(2.31)

where \( m \) runs over the ionic fragments produced under IRMPD, and \( S^m_{f} \) and \( S_p \) are the intensity signals for the \( m \)-fragment ion and parent target ion, respectively. These ion signals are recorded as the FEL wavelength \( \lambda_{\text{FEL}} \) is continuously tuned. The function \( D(\lambda_{\text{FEL}}) \) is the \textit{IRMPD absorption cross-section} and provides the gas-phase IR spectrum. Taking as an example PAH species, the dissociation thresholds are typically in the 3.5–8 eV range. This requires the absorption of tens to hundreds of IR photons. Clearly, due to the true anharmonic shape of the \( \nu_i \) potential, excitation does not occur climbing the vibrational ladder (\( \nu_i = 0 \rightarrow \nu_i = 1 \rightarrow \nu_i = 2 \ldots \)) but via anharmonic couplings (IVR mechanism) with other modes in the ion.
Table 2.1 – Specifications of the Free-Electron Laser for Infrared Experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>wavelength (λ_{FEL}) range</td>
<td>3–250 µm</td>
</tr>
<tr>
<td>macropulse repetition rate</td>
<td>≤10 Hz</td>
</tr>
<tr>
<td>macropulse duration</td>
<td>&lt; 10 µs</td>
</tr>
<tr>
<td>micropulse duration</td>
<td>6–100 optical cycles</td>
</tr>
<tr>
<td>micropulse repetition rate</td>
<td>1 GHz or 25 MHz</td>
</tr>
<tr>
<td>micropulse energy</td>
<td>1–50 µJ</td>
</tr>
<tr>
<td>micropulse power</td>
<td>0.5–100 MW</td>
</tr>
<tr>
<td>spectral bandwidth</td>
<td>~0.2–7 %</td>
</tr>
<tr>
<td>polarization</td>
<td>linear (&gt; 99 %)</td>
</tr>
</tbody>
</table>

2.4.1 Free Electron Laser for Infrared Experiments

A free-electron laser (FEL) uses relativistic electrons to generate tunable laser radiation. The principle of operation consists of first generating electron bunches which are accelerated by a linear particle accelerator (linac) to a speed close to \( c \) and then guided through an undulator. The undulator consists of an array of magnets with alternating polarity that induces a wiggle motion on the electrons and hence, a change in the direction of their velocity vectors, generating in this way synchrotron radiation. Two high-reflectivity mirrors are placed on either side of the undulator as illustrated in Fig. 2.1, and function as an optical resonator. The undulator’s magnetic field is varied in order to tune the wavelength (\( \lambda_{FEL} \)) of the IR photons. Table 2.1 lists the specifications of the FEL source (Oepts et al. 1995) employed in this Thesis. The structure of the FEL pulse consists of a macropulse composed of about 5000 micropulses (at a 1 GHz micropulse rate), at a rate of 10 Hz. A typical value of the macropulse power is 420 mW at 13 µm, which at 10 Hz yields a pulse energy of 42 mJ. In particular, these values corresponded to experiments in which the pulse duration and RMS bandwidth were 7 µs and 0.22 %, respectively.

![Figure 2.1 – Core components of a Free Electron Laser. Taken from Pellegrini & Reiche (2007).](image)

2.4.2 Ion Trap Machine

The ion trap machine is the primary experimental setup used to apply the IRMPD action-spectroscopy technique, and is coupled to a beamline of the IR free-electron laser FELIX.
2.4 Ion Trap Infrared Multiple Photon Dissociation Spectroscopy

It consists of a Paul-type quadrupole ion trap (Paul 1990) attached to a time-of-flight (TOF) mass spectrometer. An illustration of the complete instrumental arrangement is presented in Figure 2.2. FELIX is located in a radiation-shielded basement where it spans more than 20 m in length, whereas the Paul-ion-trap plus TOF-mass-spectrometer are situated on an optical table.

The Paul ion trap (Jordan TOF Products, Inc.) is used to store and mass select molecular ions. It is composed of three main parts (see Fig. 2.2): two endcap electrodes with hyperbolic geometry, and a 2-cm inner diameter electrode ring to which a 1 MHz RF-voltage is applied. The amplitude of the RF-voltage determines the mass-dependent stability of the ion trajectories. The entire trap is biased at a high voltage that is varied depending on the experiment from +1000 to +1400 VDC. This bias sets the potential difference with respect to the 0 V reference of the TOF mass spectrometer.

The TOF mass-spectrometer employs a TOF field-free tube of ca. 60 cm for mass analysis. The endcap closer to the TOF tube has a 3-mm hole through which ions are extracted. Ejection of ions is achieved employing a delay generator (Stanford Research Systems DG535) that sends a trigger pulse to the Jordan electronics supply, which switches off the RF at the next zero crossing. After a few RF cycles the bias at the 3-mm hole endcap is pulsed down by ca. –250 VDC. A dual microchannel plate (MCP) detector is placed at the other end of the TOF tube and registers the ion currents. The MCP amplifier is connected to a 16-bit analog-to-digital converter (Acqiris digitizer, Agilent Tech.) that is card-plugged to a PC. The digital signal is processed by a PC LabView routine, which also commands the delay generator and the basic operational functions of FELIX (e.g., beam attenuation, changing of wavelength).

Preparation of the target molecular ion is achieved employing one of the following methods depending on the molecular species under investigation: UV photoionization, UV dissociative ionization or charge/proton transfer (chemical ionization). All molecular species fall in five broad molecular subfamilies and Fig. 2.3 shows representative hydrocarbon structures for each subfamily.

For aromatic species, a cloud of precursor gas-phase molecules is first ionized with a
focused 193-nm (ArF) excimer laser (PSX-501, Neweks Ltd). The ionization potentials (IPs) of aromatic molecules fall in between 6–9 eV. Therefore the non-resonant absorption of two photons ($2 \times 6.4 \text{ eV}$) provides sufficient energy to remove an electron from the π highest occupied molecular orbital (HOMO). If the resulting radical cation is the target, then it is mass selected and isolated. Table 2.2 lists all molecular species investigated with their corresponding ionization methods. For instance, for aryl$^+$ targets (Chapters 3 and 4), UV dissociative ionization is applied to aromatic halide (Br) precursors, where photo-ionization of the bromo-precursor is accompanied by C–Br bond cleavage. Gas-phase protonation of nitrogenated PAHs is achieved by self-protonation, that is, proton transfer from the neutral to the radical cation (Chapter 6). Diamondoid cations are produced by charge transfer from a UV photo-ionized aromatic ion species brought into the trap simultaneously (Chapter 5). A detailed explanation of the preparation of each target ionic species is found in the experimental section of the corresponding chapter.

The excimer laser is triggered and synchronized to the experimental sequence through the delay generator, which is commanded by the PC. All neutral species are heated and the vapors guided towards the center of the trap by a built-in graphite oven placed closeby, or if the investigated species has a high vapor pressure, via a needle leak valve. The UV laser beam is guided vertically to the center of the trap through two ca. 2.5 mm holes drilled in the central ring electrode as shown in Fig. 2.2.
2.4 Ion Trap Infrared Multiple Photon Dissociation Spectroscopy

Table 2.2 – Molecular hydrocarbon species<sup>a</sup> studied in this Thesis.

<table>
<thead>
<tr>
<th>Target ion</th>
<th>Molecular precursor</th>
<th>Ionization method</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aryl cations</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>naphthyl&lt;sup&gt;+&lt;/sup&gt;</td>
<td>1-(2-)bromonaphthalene</td>
<td>UV dissociative ioniz.</td>
<td>3,4</td>
</tr>
<tr>
<td>phenanthryl&lt;sup&gt;+&lt;/sup&gt;</td>
<td>9-bromophenanthrene</td>
<td>UV dissociative ioniz.</td>
<td>4</td>
</tr>
<tr>
<td>pyrenyl&lt;sup&gt;+&lt;/sup&gt;</td>
<td>1-bromopyrene</td>
<td>UV dissociative ioniz.</td>
<td>4</td>
</tr>
<tr>
<td><strong>Nitrogenated PAH cations</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>quinoline&lt;sup&gt;•&lt;/sup&gt;</td>
<td>quinoline</td>
<td>UV photo-ionization</td>
<td>6</td>
</tr>
<tr>
<td>isoquinoline&lt;sup&gt;•&lt;/sup&gt;</td>
<td>isoquinoline</td>
<td>UV photo-ionization</td>
<td>6</td>
</tr>
<tr>
<td>benzo-h-quinoline&lt;sup&gt;•&lt;/sup&gt;</td>
<td>benzo-h-quinoline</td>
<td>UV photo-ionization</td>
<td>6</td>
</tr>
<tr>
<td>acridine&lt;sup&gt;•&lt;/sup&gt;</td>
<td>acridine</td>
<td>UV photo-ionization</td>
<td>6</td>
</tr>
<tr>
<td>phenanthridine&lt;sup&gt;•&lt;/sup&gt;</td>
<td>phenanthridine</td>
<td>UV photo-ionization</td>
<td>6</td>
</tr>
<tr>
<td>dibenzo-f,h-quinoline&lt;sup&gt;•&lt;/sup&gt;</td>
<td>dibenzo-f,h-quinoline</td>
<td>UV photo-ionization</td>
<td>6</td>
</tr>
<tr>
<td>H&lt;sup&gt;+&lt;/sup&gt; quinoline</td>
<td>quinoline</td>
<td>chemical ionization</td>
<td>6</td>
</tr>
<tr>
<td>H&lt;sup&gt;+&lt;/sup&gt; isoquinoline</td>
<td>isoquinoline</td>
<td>chemical ionization</td>
<td>6</td>
</tr>
<tr>
<td>H&lt;sup&gt;+&lt;/sup&gt; benzo-h-quinoline</td>
<td>benzo-h-quinoline</td>
<td>electrospray ioniz./FTICR</td>
<td>6</td>
</tr>
<tr>
<td>H&lt;sup&gt;+&lt;/sup&gt; acridine</td>
<td>acridine</td>
<td>chemical ionization</td>
<td>6</td>
</tr>
<tr>
<td>H&lt;sup&gt;+&lt;/sup&gt; phenanthridine</td>
<td>phenanthridine</td>
<td>chemical ionization</td>
<td>6</td>
</tr>
<tr>
<td><strong>Diamondoid molecules</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>diamantyl&lt;sup&gt;+&lt;/sup&gt;</td>
<td>diamantane</td>
<td>chemical ionization</td>
<td>5</td>
</tr>
<tr>
<td>triamantyl&lt;sup&gt;+&lt;/sup&gt;</td>
<td>triamantane</td>
<td>chemical ionization</td>
<td>5</td>
</tr>
<tr>
<td><strong>Buckybowl Corannulenes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>corannulene (neutral)</td>
<td>corannulene</td>
<td>solid KBr pellet/FTIR</td>
<td>7</td>
</tr>
<tr>
<td>corannulene&lt;sup&gt;•&lt;/sup&gt;</td>
<td>corannulene</td>
<td>UV photo-ionization</td>
<td>7</td>
</tr>
<tr>
<td>H&lt;sup&gt;+&lt;/sup&gt; corannulene</td>
<td>corannulene</td>
<td>electrospray ioniz./FTICR</td>
<td>7</td>
</tr>
<tr>
<td><strong>Five-ring PAH cations</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pentacene&lt;sup&gt;•&lt;/sup&gt;</td>
<td>pentacene</td>
<td>UV photo-ionization</td>
<td>8</td>
</tr>
<tr>
<td>picene&lt;sup&gt;•&lt;/sup&gt;</td>
<td>picene</td>
<td>UV photo-ionization</td>
<td>8</td>
</tr>
</tbody>
</table>

<sup>a</sup> The ionization state of all species is singly positively charged (•) and they could have closed-shell or open-shell (+) electronic configurations. In Chapters 7 and 8 the * is dropped for simplicity.
2 Laboratory Methods

During UV photo-ionization of the neutral precursors, UV-induced fragments are normally produced parallel to the parent target ion. Therefore, before FEL IR irradiation, the UV-induced fragments are ejected by briefly (2–3 ms) raising the RF-amplitude voltage, which is controlled by a DC signal sent with the delay generator to the remote control input of the power supply of the ion trap. Depending on the DC pulse height (0–9 V), the low-mass cut-off of the ion trap can be set just below the mass of the parent ion. Thus, the trajectories of the UV-induced fragments become unstable resulting in an isolated parent target ion.

![Mass spectra during an experimental cycle](image)

**Figure 2.4** – Mass spectra during an experimental cycle (a,b) and IRMPD signal (c). Note that at $\lambda_{\text{FEL}} = 8.2 \, \mu\text{m}$, the ion signal of the fragment $m/z$ 153 has its largest value, and hence, corresponds to the most intense absorption feature in the IRMPD spectrum.

After mass-isolation, FEL IR irradiation of the target ion cloud is carried out at a wavelength ($\lambda_{\text{FEL}}$) that is continuously varied. For those wavelengths corresponding to the IR active vibrational transitions of the ionic species, many photons are absorbed inducing a population of hot ions that relaxes via dissociation. This mechanism is described by the unimolecular dissociation reaction

$$C_{13}H_{9}N^{\bullet\bullet} \rightarrow IR (C_{13}H_{9}N^{\bullet\bullet})^* \rightarrow C_{11}H_{7}N^{\bullet\bullet} + C_{2}H_{2}$$

where benzo-h-quinoline ($C_{13}H_{9}N$) is used as an example. Figure 2.4 shows the mass
spectra before and after FEL IR irradiation. First, the fully isolated C$_{13}$H$_9$N$^+$ ion (m/z 179) is shown in Fig. 2.4a. Then, FEL IR photodissociation yields the C$_{11}$H$_7$N$^+$ product ion (m/z 153) via C$_2$H$_2$-loss (26 amu). Fig. 2.4b shows the mass spectrum recorded an instant after irradiation at $\lambda_{\text{FEL}} = 8.22 \, \mu m$. At this wavelength, the number of m/z 153 photo-product ions has its largest value, as clearly corroborated by the resulting IRMPD spectrum in Fig. 2.4c.

A secondary experimental setup used is the in-house Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer coupled also to the FEL beamline (Valle et al. 2005). This was employed to record the IR spectrum of protonated benzo-h-quinoline, presented in Fig. 6.5, and the IR spectrum of protonated corannulene, presented in Fig. 7.3. Although the same IRMPD principle is used, this technique differs from the ion-trap machine in a number of essential ways. For instance, instead of detecting directly the ion current with a TOF mass-spectrometer for mass analysis of the molecular species, the angular frequencies $\omega_i$ of the ions in cyclotron motion are registered as a multi-component sinusoidal signal that is Fourier-transformed to obtain their masses. This is the principle behind the Penning trap which consists of a strong, spatially homogeneous static magnetic field (radial confinement via a Lorentz force) and an axial electric field (axial confinement) to induce the cyclotron motion (Guan & Marshall 1995). FTICR mass spectrometers are comprehensively reviewed, see e.g., Marshall et al. (1998).

2.5 Computational Quantum Chemistry

A primary goal in computational quantum chemistry is the calculation of the adiabatic potential energy surface—PES, the electronic energy plus the repulsive energy of the nuclei as a function of spatial coordinates—of a N-body system ($N_e$ electrons and $N_n$ nuclei) in the ground state by finding solutions to the time-independent, non-relativistic electronic Schrödinger equation:

$$\hat{H}\psi_e(r; R) = E(R)\psi_e(r; R)$$  \hspace{2cm} (2.32)

where the electronic Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i}^{N_e} \nabla_i^2 - \frac{e^2}{4\pi\varepsilon_0} \sum_{i}^{N_e} \left( \sum_{A}^{N_n} \frac{Z_A}{r_{iA}} - \sum_{i \neq j}^{N_e} \frac{1}{r_{ij}} \right)$$ \hspace{1.5cm} (2.33)

and $r$ and $R$ are the electronic and nuclear position vectors such that ($r_1, r_2, \ldots, r_{N_e}$) and ($R_1, R_2, \ldots, R_{N_n}$). The energy terms on the right-hand side are due to the total kinetic energy of the electrons ($\hat{T}$), the electron–nuclei electrostatic interactions ($\hat{V}_{Ne}$), and the electron–electron repulsions ($\hat{V}_{ee}$). The electronic energy $E(R)$ is calculated for a fixed set of nuclei positions $R$. Thus, the eigenfunction $\psi_e(r; R)$ does not depend dynamically on $R$ but only parametrically. It follows the adiabatic adjustment concept on the passage to new equilibrium positions: a fast oscillating system (e.g. the electronic motion) adjusts
to a slowly oscillating system (e.g. nuclear motion), thus to a new equilibrium position. This is the Born-Oppenheimer approximation that permits to split the total wavefunction of the N-body system into an electronic and a nuclear part (vibrational and rotational motion), i.e., \( \Psi = \psi_e \times \psi_n \). This allows to compute the total energy of system, \( E_{\text{tot}} \), by adding up at the end the nuclei energy to the electronic energy such that \( E_{\text{tot}} = E + E_n \).

Finding the lowest stationary point of the PES constitutes a theoretical characterization of the equilibrium electronic structure of a molecular (N-body) system. Second derivatives of the PES with respect to generalized molecule-fixed nuclei coordinates yield the force constant matrix, which is diagonalized in order to find the vibrational mode frequencies.

### 2.5.1 Many-Electron Wavefunction

The ground-state wavefunction, \( \Psi^o \), of an \( N_e \)-electron system moving in a \( N_n \)-nuclei field is formulated by simplifying the \( r_{ij} \) dependence of the electron–electron repulsion term in the Hamiltonian (eq. 2.33). If each electron moves in an \( N_e - 1 \) averaged field, the total \( N_e \)-electron wavefunction \( \Psi^o \) can be written as a product of one-electron wavefunctions:

\[
\Psi^o(r_1, r_2, \ldots, r_{N_e}) \approx \prod_{m=1}^{N_e} \psi^o_m(r) = \psi^o_1(r_1)\psi^o_2(r_2)\psi^o_3(r_3) \ldots \psi^o_{N_e}(r_{N_e}) \tag{2.34}
\]

where each electron occupies a molecular orbital \( m \). Since electrons are fermions, the wavefunction must obey Pauli’s principle, that is, \( \Psi^o \) must be antisymmetric whenever two electrons exchange positions. To ensure this, \( \Psi^o \) is written as a Slater determinant of spinorbitals \( \phi_m(i) \), which are products of spatial wavefunctions and spin-space functions, \( \alpha(m_s = +1/2) \) or \( \beta(m_s = -1/2) \):

\[
\Psi^o(1, 2, \ldots, N_e) = \left( \frac{1}{N_e!} \right)^{1/2} \begin{vmatrix}
\varphi_1(1) & \varphi_2(1) & \ldots & \varphi_{N_e}(1) \\
\varphi_1(2) & \varphi_2(2) & \ldots & \varphi_{N_e}(2) \\
\vdots & \vdots & \ddots & \vdots \\
\varphi_1(N_e) & \varphi_2(N_e) & \ldots & \varphi_{N_e}(N_e)
\end{vmatrix} \tag{2.35}
\]

where the spinorbital functions \( \varphi_m(i) \) are orthonormal. A molecular orbital, \( \varphi_m(i) \), is expanded using a set of basis functions, which are defined as linear combinations of atomic orbitals (LCAO). The product of \( \varphi_m \) with its complex conjugate provides a physical observable: the electron density distribution. A closed shell molecular system has an even number of electrons, all paired in \( N_e/2 \) MOs. The highest occupied molecular orbital (HOMO) most influences the physical properties of a molecule such as its geometry, infrared activity, or chemical reactivity. An open shell system, on the other hand, has an odd number of electrons and the HOMO is singly occupied, which then becomes a singly occupied molecular orbital (SOMO). This has important consequences to the binding between nuclei, and therefore to the molecular geometry, and is reflected in its infrared activity. For instance, upon ionization of neutral closed-shell PAH systems an electron is removed from the \( \pi \) HOMO forming an open-shell PAH radical cation. IR spectroscopy
provides evidence for the difference in electronic properties of the PAH system in these two charge states.

The ground-state many-electron wavefunction in the form given in eq. 2.35 can be found via the \textit{ab initio} Hartree-Fock formalism, in which electron-electron interactions are inherently treated in average. Then, the LCAO molecular orbital solutions (and corresponding energies) are found by solving the Schrödinger non-linear equations in an iterative manner using a starting approximated total wavefunction until self-consistency is achieved, hence, an (averaged) self consistent field (SCF) is obtained. In restricted Hartree Fock (RHF) theory, the molecule has all LCAO orbitals doubly occupied (closed shell system). To find solutions to open-shell systems, there are the restricted open-shell Hartree Fock (ROHF) and unrestricted Hartree Fock (UHF) methods. These are extensions of RHF theory having an additional treatment to deal with the singly occupied LCAO molecular orbital.

2.5.2 Density Functional Theory

Instead of calculating the exact wavefunction of the molecule, density functional theory (DFT) attempts to calculate its exact electron density. The main body of calculations in this Thesis is based on DFT. DFT finds its origin in the statistical model developed by Thomas and Fermi in 1927 to describe the electronic structure of atoms. The model relies on the \textit{uniform electron gas approximation} and an important corollary is the total kinetic energy of the electrons in an atom expressed as a functional, which takes the electron density function $\rho(r)$ over a given region in space (Atkins & Friedman 2011):

$$T[\rho] = C \int \rho(r)^{5/3} \, d^3r$$  \hspace{1cm} (2.36)

where $C$ is $3^{5/3} \hbar^2 / 10m_e (8\pi)^{2/3}$. The Thomas–Fermi (TF) energy functional incorporates the attraction of the electrons and nuclei ($V_{Ne}$), and the electron–electron repulsion ($V_{ee}$), all as functionals of the electron density:

$$E_{TF}[\rho] = T[\rho] + V_{Ne}[\rho] + V_{ee}[\rho]$$  \hspace{1cm} (2.37)

Application of a variational principle, in which the evolution of $\rho(r)$ under a fixed number of electrons (via the Lagrange multiplier $\mu$) is such that it minimizes $E_{TF}$, yields the total bound energy of the atom. That is,

$$\frac{\delta E_{TF}[\rho]}{\delta \rho} = \mu.$$  \hspace{1cm} (2.38)

However, an important drawback in the TF model is the omission of electron exchange in $V_{ee}$. This term has a classical Coulombic part depending on a singly spatially-valued density function, $J[\rho(r)]$, but also, a non-classical part that depends on two locations, $K[\rho(r, r')]$. Paul Dirac revised the uniform gas approximation and proved that the exchange functional $K[\rho(r, r')]$ can be written as if it depends on a single location
\[ K[\rho(r, r')] \rightarrow K[\rho(r)] = C_{exc} \int \rho(r)^{4/3} \, d^3 r \quad (2.39) \]

This is the expression for the exchange contribution under a local density approximation (LDA). In 1964 Hohenberg and Kohn proved that there cannot exist two N-body systems (each with \( N_e \) electrons and \( N_n \) nuclei) with Hamiltonians \( H_1 \) and \( H_2 \), and respective external nuclear potentials \( v_1(r_1) \) and \( v_2(r_2) \) (in which the electrons move), possessing the same \( \rho(r) \). Therefore, the existence of a ground-state electron density function uniquely corresponds to one external potential \( v(r) \), and it determines all the properties of the molecule, including its wavefunction. Thus, this theorem proves that the ground state energy \( E \) of a molecule is a functional of one unique \( \rho(r) \) function:

\[ E[\rho] = T[\rho] + \int \rho(r)v(r)d^3r + V_{ee}[\rho] \quad (2.40) \]

In comparison with eq. 2.37, the first term on the right is the kinetic energy of the \( N_e \) electrons in the molecule, the second is the potential energy \( (V_{Ne}[\rho]) \) of \( N_e \) electrons due to the \( N_n \) nuclei, and the third term is the self-interaction electron energy. As in the TF model, \( V_{ee}[\rho] \) has a classical, \( J[\rho] \), contribution and a quantum-mechanical, \( K[\rho] \), contribution.

A second theorem provides the means by which a lower bound energy of the molecule is determined through a trial density function \( \rho_t(r) \). That is, for \( N_e \) electrons moving in an external potential \( v_t(r) \), the ground state energy \( E[\rho_t] \) is a stationary minimum if and only if \( \rho_t(r) \) is the ground-state electron density function: \( E[\rho_t] = \langle \Psi | H_t | \Psi \rangle \geq E_0 \). This establishes a variational criterion and is essential to DFT. This variational principle was applied in the TF model without justification.

Kohn & Sham (KS) proved in 1965 a third essential theorem which permits to find \( \rho(r) \) from a set of one-electron \( N_e \) equations, in analogy to HF theory. They defined a reference system of non-interacting \( N_e \) electrons moving in an effective reference KS potential \( v_{KS}(r) \) that yields an electron density identical to the one of the real interacting system. This implies that the wavefunction describing the motion of the non-interacting electrons upon \( v_{KS}(r) \) can be formulated as a Slater determinant (eq. 2.35) of LCAO one-electron spinorbitals \( \varphi_i \). These are the eigenfunctions of the Kohn-Sham equations

\[ \left( -\frac{\hbar^2}{2m_e} \nabla^2 + v_{KS}(r) \right) \varphi_i(r) = \epsilon_i \varphi_i(r) \quad (2.41) \]

where \( \epsilon_i \) are the corresponding orbital energy eigenvalues. The total density of the \( N_e \)-electron system is

\[ \rho(r) = \sum_{i=1}^{N_e} |\varphi_i(r)|^2 \quad (2.42) \]

The KS equations are found by minimising the total energy functional (eq. 2.40) with respect to a set of spinorbitals \( \varphi_i \) to yield the KS potential

\[ v_{KS} = v(r) + \frac{\delta J[\rho]}{\delta \rho(r)} + \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \quad (2.43) \]
where the second term is the classical Coulomb potential energy defined as the functional derivative of \( J[\rho] \)

\[
\frac{\delta J[\rho]}{\delta \rho(r)} = \frac{e^2}{4\pi \varepsilon_0} \int \frac{\rho(r')}{|r-r'|} d^3r'
\]

(2.44)

and the third term defines the exchange-correlation local potential \( v_{xc}(r) \)

\[
v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}
\]

(2.45)

The functional \( E_{xc}[\rho] \) is the error in the total energy that arises as the outcome of using the non-interacting KS electron system plus the classical treatment of the electron-electron interaction.

Modern DFT developments focus on obtaining the proper exchange interaction function \( v_{xc}(r) \) from the functional \( E_{xc}[\rho] \). Conventionally, the exchange-correlation functional \( E_{xc}[\rho] \) is approximated in an exchange and correlation terms

\[
E_{xc}[\rho] = E_X[\rho] + E_C[\rho]
\]

(2.46)

A simple approximation is the Slater X\( \alpha \) method in which \( E_{XC}[\rho] \approx E_X[\rho] \) and Dirac’s LDA formulation for an inhomogeneous many-electron system is used. Thus, \( E_X[\rho] = -1/2K[\rho] \) and

\[
E_{xc}[\rho] = \int \rho^{4/3}(r) d^3r
\]

(2.47)

This LDA form performs very well for slow-varying electron density systems. However, most molecular systems are characterized by density fluctuations and the LDA fails to reproduce them. Fluctuations can be accounted for by density gradients, which led to the emergence of generalized gradient approximation (GGA) functionals of the form

\[
E_{xc}[\rho] = \int f(\rho(r), \nabla \rho(r)) d^3r
\]

(2.48)

A highly successful gradient-correction to the LDA exchange functional (B88X) was done by Becke in 1988. Becke88X functional attempts to reproduce the \( 1/r \) asymptotic behaviour of the exchange energy density:

\[
E_{xc}[\rho] = b \int \rho^{4/3}(r) \frac{x^2}{(1 + 6b x \sinh^{-1} x)} d^3r
\]

(2.49a)

with

\[
x = \frac{|
\nabla \rho|}{\rho^{4/3}}
\]

(2.49b)

where \( x \) is a dimensionless non-uniformity parameter. The parameter \( b = 0.0042 \) a.u. is found by adjusting the LDA and Becke exchange terms to the exact HF exchange energies of He to Rn noble gas atoms. A GGA functional for the correlation energy \( E_C \) was derived also in 1988 by Lee, Yang, & Parr (LYP) using the Colle–Salvetti formalism for the He
atom. By combining the B88X and LYP functionals, the BLYP method is obtained in which the exchange-correlation functional energy depends on both $\rho$ and $\nabla \rho$.

An important source of error still remains due to the lack of adiabatic coupling between the non-interactive KS system and the real molecule. The adiabatic connection approximation attempts to correlate both systems by including a degree of exact HF exchange energy. This leads to the formulation of hybrid HF/DFT methods.

The B3LYP hybrid functional (Becke 1993) is a state-of-the-art method (includes as well other functionals such as the LDA functional of Dirac, the B88X and LYP) and is extensively employed in chemical physics. Therefore, in order to evaluate and compare our computational results to available literature, the B3LYP functional is adopted here as the base DFT method. Complementary ab initio and DFT methods are, nonetheless, used as detailed in the relevant chapters.