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IR spectroscopy on gas-phase molecules with a free electron laser

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Abstract

Mass selective gas-phase infrared spectroscopy using pulsed, high power InfraRed (IR) radiation produced by the Free Electron Laser (FEL) 'Free Electron Laser for Infrared eXperiments' (FELIX) is demonstrated. Two complementary excitation schemes are used. In the first experiment, para amino benzoic acid (PABA) is infrared excited using FELIX and then ionized using a vacuum ultraviolet (VUV) F_2 laser. In the second experiment, C_{60} is multiphoton excited by FELIX to energies high enough that the molecule can undergo autoionization. In both experiments, spectra are obtained by monitoring the ion of interest as a function of IR wavelength in the 100–2000 cm^{-1} range. It is demonstrated that these spectra contain the same information as direct IR absorption spectra. The sensitivity of these methods, however, is many orders of magnitude higher than that of conventional IR absorption spectroscopy. Details of the two different ionization mechanisms are discussed.

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1. Introduction

A large amount of the understanding of molecular structure stems from the study of the interaction of molecules with light. Light in the infrared (IR) spectral region is of particular interest since this is the energy range of molecular vibrations and it thereby probes the forces holding the atoms in molecules together. Traditionally, this interaction is studied by analyzing the amount of light absorbed as a function of IR frequency after passing through either a solid, liquid or gas-phase sample. A serious limitation of this approach is its inherent low sensitivity and its lack of selectivity; in a mixture of compounds or in an impure sample, it is not clear which constituent is responsible for the observed absorption.

The sensitivity of direct absorption measurements can be greatly enhanced when use is made of the Cavity Ring Down (CRD) method, which combines efficient multi-passing with tolerance to light source intensity fluctuations [1]. The first use of an FEL for CRD experiments was reported at the 1996 FEL Users Workshop in Rome, Italy, [2], and more recently such measurements have been applied in a study of the absorption of ethylene in the 10–11 μm region [3]. A resolution higher than determined by the bandwidth of the FEL was

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achieved by spectrally analyzing the light prior to detection with a FT-spectrometer, and a significant increase in sensitivity relative to 'conventional' IR absorption measurements was demonstrated.

In the UV or visible region of the spectrum, techniques such as Resonance Enhanced Multi-Photon Ionization (REMPI) and Laser Induced Fluorescence (LIF) combine a high sensitivity with species selectivity, and are well established. Some multi-photon ionization and fluorescence studies where one photon is in the IR do exist [4–9]. In addition, Esherick et al. showed greatly improved sensitivity in stimulated Raman spectroscopy by combining this technique with resonant laser ionization [10,11]. To obtain information similar to that obtained in direct absorption spectroscopy, a widely tunable IR excitation source as well as a detection method for IR excited molecules, that is preferably not vibrational mode specific, is needed. Over the last years Free Electron Lasers (FEL) have become available to users [12–15]. Their performance characteristics make them the ideal light sources for studies of this kind.

Here we present results from two complementary experiments. In the first experiment, para amino benzoic acid (PABA) is first excited by the FEL and then ionized by a vacuum ultraviolet (VUV) excimer laser operating on F_2 at 158 nm. PABA is chosen because its Ionization Potential (IP) is located about 1000 cm^{-1} above the photon energy of an F_2 laser, thereby enabling selective ionization of IR excited levels [9]. In the second experiment, gas-phase C_{60} molecules are resonantly excited by FELIX to very high internal energies [16]. At sufficiently high internal energies, C_{60} is seen to undergo autoionization [17–19]. No additional VUV photons are used in the latter experiment and the ionization of C_{60} solely results from the absorption of several hundred IR photons per molecule. In both experiments, scanning the IR laser and recording the (mass-selected) ion yield as a function of IR frequency, results in an 'action spectrum' that closely resembles the gas-phase IR absorption spectrum of the sample. In both experiments, the density of neutral molecules is very low and spectra can be recorded with sensitivities that are many orders of magnitude higher than in conventional absorption spectroscopy.

2. Experimental

The experiments have been performed at the 'Free Electron Laser for Infrared eXperiments' (FELIX) user-facility in Nieuwegein, The Netherlands [15,20]. This laser produces pulsed IR radiation that is continuously tunable over the 100–2000 cm^{-1} range with a bandwidth that can be varied from 0.5% to 5% of the central frequency. The light output consists of macropulses of about 5 μs duration containing typically 50 mJ of energy. Each macropulse consists of a train of micropulses which are 1 ns apart. In the present experiment, the micropulses have a full width at half maximum of approximately 10 optical cycles, i.e. a pulse duration of 0.3 ps at 10 μm, and FELIX runs at a 10 Hz repetition rate.

The experimental apparatus consists of a turbo-pumped vacuum chamber containing a Time-of-Flight (TOF) mass spectrometer. The compact TOF unit is designed to fulfill second order space focussing conditions [21]. A schematic is shown in Fig. 1. The electrodes are gridless to achieve maximum transmission. There is a 30 mm distance between the electrodes of the extraction region, a 37 mm distance between the electrodes of the acceleration region and a 200 mm drift path between the last electrode and the micro channel plate (MCP) detector. Typical voltages used are 3000, 1950 V and ground at the first second and third electrode, respectively. The mass resolution under these conditions is about 200. Ions are detected on a micro-channel plate (MCP) detector. The ion signal is amplified and recorded on a digital oscilloscope (LeCroy 9430). The data are then transferred to a PC for further analysis.

In the IR/VUV double resonance experiment on PABA, a small amount of solid PABA is placed in the vacuum chamber, close to the extraction region of the TOF. The vapor pressure of PABA is estimated to be 1×10^{-7} Torr. The IR light enters the experimental apparatus through a ZnSe window. The IR beam is not focussed and has a diameter of about 3 mm. About 1 μs after the end of

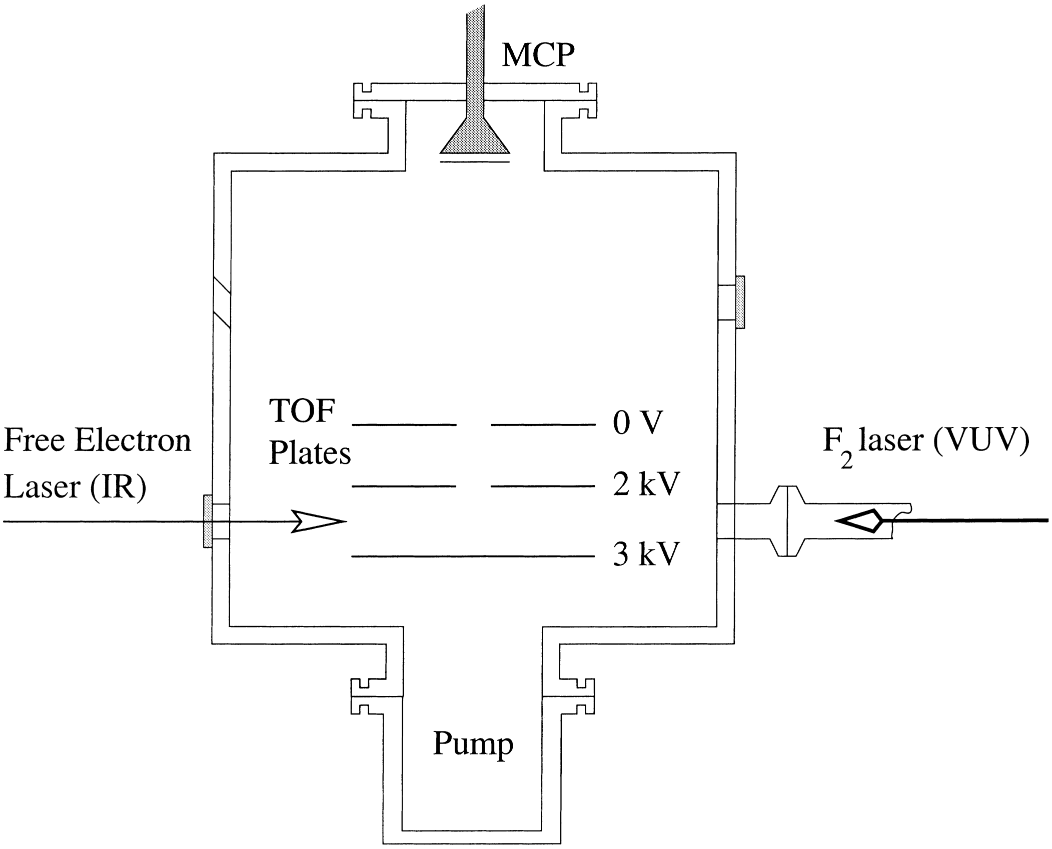

Fig. 1. Schematic of the experimental apparatus. Molecules are ionized between the lower two TOF plates. In the case of the IR/VUV double resonance experiment on PABA, an unfocussed IR and an unfocussed VUV laser are used. In the case of the IR–REMPI experiment on C_{60}, only IR light is used which is then focussed by a lens.

the FELIX macropulse, an F_2 laser (158 nm, Lambda Physik EMG 102) is fired. The VUV light travels through an evacuated tube into the vacuum chamber, counterpropagating the FELIX beam. A circular, 5 mm diameter, aperture limits the VUV beam diameter and no focussing is applied. The energy in the 10 ns duration VUV pulse is approximately 0.1–1.0 mJ in the ionization region. Both beams overlap in the extraction region of the linear TOF setup.

In the IR–REMPI experiment on C_{60}, an effusive molecular beam of C_{60} is generated by evaporating pure C_{60} (Hoechst, 'Super Gold Grade' C_{60}, purity $\geqslant$ 99.9%) from a quartz oven. A 2 mm hole in a stainless steel plate placed 1 cm away from the oven between the extraction electrodes, serves to better define the molecular beam geometry. With an oven temperature of 875 K, the density of C_{60} in the interaction region is estimated to be around 10^{10} molecules/cm^3. The effusive molecular beam crosses the FELIX laser beam perpendicularly. C_{60} molecules with a most probable velocity of 190 m/s will interact with a train of 300–1000 micro-pulses, depending on the size of the laser focus, i.e. depending on the wavelength. The FELIX beam enters the vacuum chamber and is focussed with a KRS5 lens with a focal length of 7.5 cm in the region between the extraction plates of the TOF mass spectrometer. The beam waist varies from approximately 60 to 200 μm in scanning FELIX from 6 to 20 μm, yielding maximum power densities of 1×10^{12} to 3×10^{10} W/cm^2 per micropulse, respectively.

3. Results

3.1. *IR/VUV double resonance experiments on PABA*

In Fig. 2(a), the PABA parent ion signal is shown as a function of the FELIX frequency. Clearly, several peaks can be identified. The width of the peaks is wider than the bandwidth of the FELIX radiation by about a factor three. It should be noted that a weak ion signal, on the order of a few ions/pulse, is recorded even with no IR laser present. This signal results from the one photon VUV ionization of thermally populated levels and gives rise to a nonzero baseline. In Fig. 2(b) the experimental 444 K gas-phase IR absorption spectrum [22] is shown. The peaks in this spectrum coincide well in position, width and relative intensity with the double resonance spectrum shown in Fig. 2(a). Only minor differences are seen. The peaks in Fig. 2(b) all show a small shift to lower frequency of, on average, 11 cm^{-1}. Also, the peaks in Fig. 2(b) are somewhat broader than the peaks shown in Fig. 2(a). Both observations can be attributed to the higher sample temperature used in the direct IR absorption measurements. An elevated temperature will give a wider rotational envelope and therefore broader lines, whereas the frequency shift can be explained by anharmonic cross coupling of the IR active modes to thermally excited modes. In Fig. 2(c) the calculated IR absorption spectrum of PABA is shown. The calculations are performed with the Becke3LYP [23] method as implemented in *Gaussian 94* and Dunning's D95(d,p) [24] basis set is used. The calculated stick spectrum is convoluted with a Gaussian lineshape with a full width at half maximum of 20 cm^{-1} and the calculated frequencies are not scaled. The agreement between the calculations and the experiment is very good. The disagreement in line positions is less than 1%, a surprisingly small number, especially when considering that Hartree Fock frequencies are usually calculated too high by more than 10%.

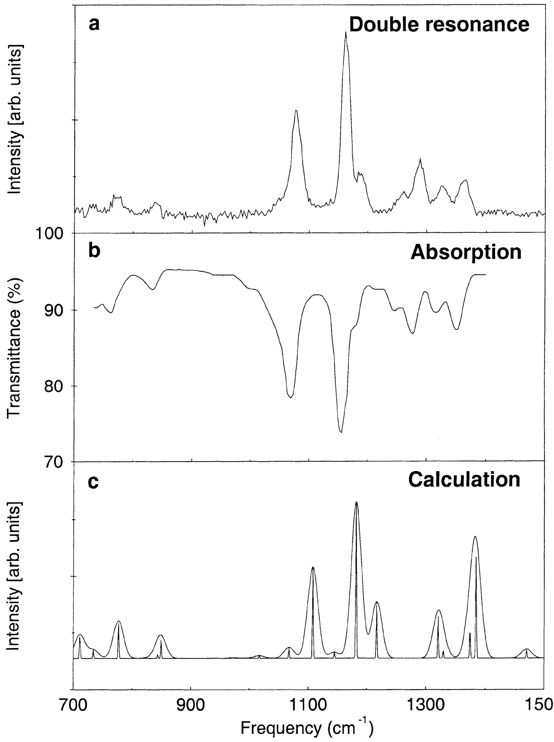

Fig. 2. Shown is (a) the measured IR/VUV double resonance spectrum of PABA, (b) the gas-phase IR absorption spectrum of PABA taken at 444 K [22], and (c) the calculated IR absorption spectrum of PABA.

3.2. *IR–REMPI experiments on C_{60}*

Fig. 3 shows the TOF mass spectrum obtained when C_{60} is being ionized with the focussed FELIX beam at 19.2 μm. A strong peak at $m/z = 720$ amu and a much weaker peak at $m/z = 696$ amu are observed, resulting from C_{60}^+ and C_{58}^+. The small amount of C_{58}^+ (resulting from fragmentation of C_{60}) is rather surprising, since, in multiphoton ionization studies of C_{60} using UV or VIS lasers, large amounts of fragments are observed [19]. In fact, even more surprising is the observation of C_{60}^+, since for C_{60} to thermally ionize, an internal energy of 35–40 eV is required, which, at 19.2 μm, corresponds to the absorption of about 600 photons by a single molecule.

The C_{60}^+ ion yield can be measured as a function of FELIX frequency and the resulting spectrum is shown in the upper part of Fig. 4. Four peaks can readily be identified. In the lower part of Fig. 4, the IR absorption spectrum of a thin film of solid C_{60} is shown. Again four lines can be seen and they

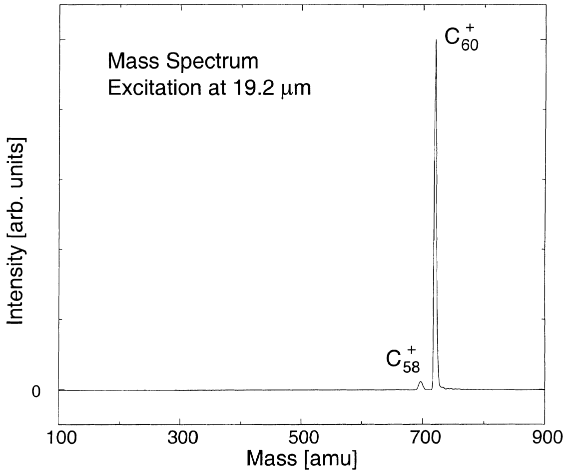

Fig. 3. TOF mass-spectrum, recorded with FELIX on the C_{60} resonance at 19.2 μm, i.e. following resonant absorption of about 600 IR photons. The only fragment observed is due to C_2 loss.

correspond to the four well known IR allowed F_{1u} fundamental modes of icosahedral C_{60} [26]. The two spectra show a clear correspondence in both their line positions as well as in the relative intensities of the lines. Nonetheless, it can be seen that the resonances in the IR–REMPI spectrum are systematically shifted to slightly lower frequencies than in the thin film absorption spectrum and the lines in the IR–REMPI spectrum are slightly asymmetric. Further, it can be noted that the strongest lines in the IR–REMPI spectrum are those that show the smallest frequency shift with respect to the corresponding lines in the thin film absorption spectrum.

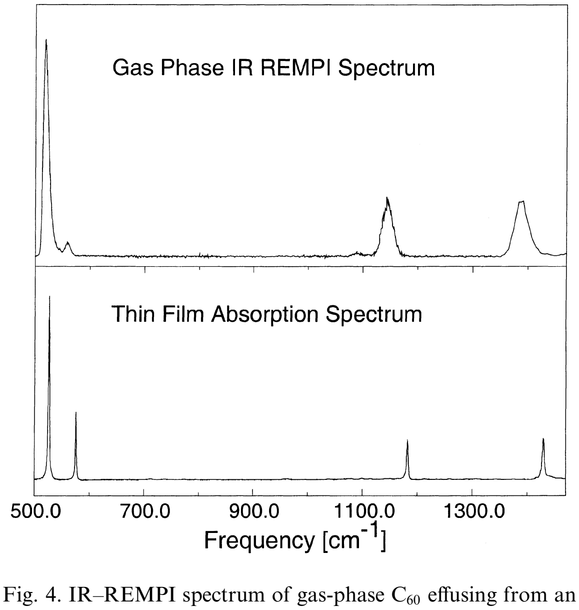

Fig. 4. IR–REMPI spectrum of gas-phase C_{60} effusing from an oven at 875 K (upper part) and IR absorption spectrum of a thin film of solid C_{60} at room-temperature (lower part), both showing the four IR allowed absorption lines.

4. Discussion

In both measurement schemes presented above, scanning the IR laser yields spectra that closely resemble the IR absorption spectra of the molecules. The sensitivities, however, are many orders of magnitude higher than those of conventional absorption spectroscopy. Although the initial and resonant absorption of one or more IR photons yield the spectral information and is similar in both schemes, the subsequent steps that lead to ionization are rather different.

At first sight, the excitation and ionization mechanism for PABA might look straightforward: the molecule first absorbs an IR photon and is then ionized by the VUV photon, as together they contain more energy than required for ionization. However, the observation that the IR/VUV double resonance spectrum is so similar to the IR absorption spectrum is not a priori expected. The PABA spectrum shown is determined by both the IR absorption as well as the VUV ionization cross sections. As the VUV ionization cross section will depend on the vibrational level in the ground electronic state, one could expect the double resonance spectrum to be different from the absorption spectrum. The similarity of the two spectra can be rationalized by the influence of Intramolecular Vibrational energy Redistribution (IVR). It is well known that for molecules containing more than a few atoms, IVR is usually very fast, taking place on a sub-nanosecond timescale. The energy of the absorbed IR photon will therefore be quickly randomized in the molecule and the system will have lost all memory of its initial vibrational state by the time the VUV photons arrive.

Ionization will thus take place from many different quantum states, even though a single, well defined state is initially prepared by the IR photon. For the ionization cross section, the total amount of energy in the system is therefore a more important parameter than which quantum state is initially prepared by the IR laser.

The observation that C_{60} can be resonantly ionized by only IR photons seems astonishing. At least several hundred IR photons need to be absorbed by a single C_{60} molecule before it will ionize in the experimental time window and this might therefore appear to be a rather unlikely process. One also might expect that, after absorption of a few IR photons, the molecule runs out of resonance with the IR laser due to the intrinsic anharmonicities of the vibrational modes. The observation that so many IR photons can be absorbed by the molecule can again be explained by IVR, in combination with the size of the molecule, i.e. the vastness of its phase–space, and the pulse structure of FELIX. As in the case of PABA, IVR is expected to be very fast, occurring on a subnanosecond timescale. The molecule can therefore absorb one IR photon in a FELIX micropulse and, by the time the next micropulse arrives (1 ns later), the energy of the previous photon is completely randomized in the molecule. With 174 internal degrees of freedom and an average vibrational frequency of 950 cm^{-1} [25], on average less than two quanta need to be put in each vibrational mode of C_{60} to reach the required energy of 35–40 eV. By the sequential pumping of IR photons into the molecule, accompanied by thermalization via IVR, the C_{60} molecule can then be resonantly heated up to energies at which ionization becomes efficient.

In both the FELIX induced C_{60} and the FELIX induced PABA spectrum, the line positions are shifted with respect to the absorption lines of solid C_{60} and heated gas-phase PABA, respectively. These frequency shifts as well as the asymmetric lineshapes can be explained by anharmonic cross coupling of the IR active modes to all other excited modes, as a result of which lines will gradually shift to lower frequency with increasing internal excitation [27]. Apart from sequential single photon absorption per micropulse, it cannot be excluded that multi photon transitions occur during a micropulse. The most intense multi photon transitions will be those that are in near-resonance with IR allowed single photon transitions, which will therefore also lead to resonance lines that are shifted to lower frequencies due to the anharmonicity of the ladder to be climbed.

The excitation and ionization schemes presented here both yield IR spectra of gas-phase samples and it is interesting to see how general these schemes are and how readily they can be applied to other molecules. In the UV/VUV excitation scheme, the photon energy of the VUV laser can be chosen such that it lies just below the IP of the species of interest. Modern methods of tunable VUV generation make this method applicable to a variety of molecules as well as to interesting species such as radicals or transient species where IR spectroscopic information could not be obtained so far. Furthermore, only moderate IR laser powers are required in this experiment, since only one photon per molecule needs to be absorbed. The IR–REMPI method is less general, although we consider the process from a fundamental viewpoint to be more interesting. For autoionization to be efficient, a prerequisite is that the IP is close to – or lower than – the energy required for the molecule to dissociate. For fullerenes this is the case, since they are very strongly bound and possess low IP's. Most other molecules, however, will dissociate rather then ionize when being resonant to the strong IR laser field, an interesting research-area by itself. The IR–REMPI process as such is 'highly exciting' and measuring properties as, for example, the power and fluence dependence of the autoionization yield can give valuable information on the energetics and dynamics of hot molecules.

5. Conclusions

Pulsed, high power free electron lasers can be used for sensitive and mass selective gas-phase IR spectroscopy. Two complementary experiments are presented. In the first experiment, PABA is excited using the FEL and then ionized using an F_2 VUV laser. In the second experiment, C_{60} is multiphoton excited by the FEL to energies high enough for the molecule to undergo autoionization. In both experiments, fast Intramolecular Vibrational energy Redistribution is important in the excitation and ionization mechanism. Spectra are obtained by monitoring the ion of interest as a function of IR wavelength. These spectra can give the same information as direct IR absorption spectra, but with orders of magnitude higher sensitivities.

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