



IR-REMPI spectroscopy for thermometry of C₆₀

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Abstract

Gas-phase C₆₀ molecules are excited with a 30 ps 266 nm Nd:YAG laser, followed by a train of high-power infrared (IR) sub-picosecond pulses from a free electron laser (FEL), which resonantly heats the molecules up to internal energies at which they efficiently undergo delayed ionization. By tuning the IR laser wavelength, IR-REMPI spectra are obtained. These are compared to simulations, giving detailed insight into the influence of UV pre-excitation on the IR laser ionization process of C₆₀ molecules. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Fullerenes are uniquely suited to study the microscopic equivalent of the thermal electron emission from heated surfaces, the thermionic emission of electrons from gas-phase molecules and clusters. This phenomena is unique to strongly bound species and now observed to occur for metal clusters [1,2], metal-carbide, oxide and nitride clusters [3–5] as well as for fullerenes [6–8]. Among these species, C₆₀ is the molecule for which the most information on structure and energetics is available.

Understanding the thermionic emission from small isolated systems will yield new insights and a better understanding of intramolecular energy transfer and relaxation processes. In order for thermionic emission to occur, large amounts of vibrational energy have to be exchanged with electronic energy and the

timescales and mechanisms are presently not well understood.

Traditionally, the energy needed for thermionic emission to occur is deposited in the molecule by absorption of UV or visible light. In this case, excited electronic states are populated initially, which are assumed to relax rapidly to the electronic ground state surface. A more direct approach is to resonantly excite the IR active vibrational modes of a molecule or cluster itself, using IR radiation. In this case, there is no ambiguity about whether the process of thermionic emission starts from the ground state or an excited state surface.

Initiating thermionic emission of gas-phase species using IR light requires a bright and tunable IR source. With the advent of free electron lasers, such light sources are now available. We have recently demonstrated IR laser-induced thermionic emission to be efficient for C₆₀ [8–10], larger fullerenes [11] as well as for metal-carbide clusters [4]. In the experiment and calculations presented here, the in-

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fluence of ultraviolet (UV) pre-excitation on the efficiency of IR multi-photon ionization of C_{60} is studied. It is expected that the efficiency of multi-photon ionization is highly dependent on the initial energy distribution of C_{60} molecules. UV pre-excitation can lead to an energy distribution quite different from thermal, but still well defined.

2. Experimental

The experiments are performed at the ‘free electron laser for infrared experiments’ (FELIX) user facility in Nieuwegein, The Netherlands [12]. FELIX produces IR radiation, continuously tunable over the 40–2000 cm^{-1} range. The light output consists of macropulses at 10 Hz repetition rate of about 5 μs duration containing up to 100 mJ of energy. Details on the experimental setup have been described previously [9,11] and only a brief outline is given here. The IR radiation of FELIX is focused onto an effusive beam of C_{60} molecules. If on a vibrational resonance, these molecules are excited to high internal energies such that they efficiently undergo thermionic emission [8]. The ions produced are detected using a linear time-of-flight (TOF) mass spectrometer. Infrared resonance enhanced multi-photon ionization (IR-REMPI) spectra are recorded by measuring the C_{60}^+ ion current as a function of IR laser wavelength.

To monitor the effect of different internal energy distributions on the multi-photon ionization process, UV quanta are used to create well-defined internal energy distributions. In these UV pre-excitation experiments, the C_{60} molecules are first exposed to 30 ps pulses of UV light followed by FELIX. The UV pulses originate from a Nd:YAG laser, quadrupled to 266 nm. The last mirror, coupling the UV light into the vacuum chamber, is mounted on a translation stage, giving the opportunity to vary the UV sheet position relative to the FELIX focus. Within several μs , this light is followed by the macropulse of FELIX. The ions produced are detected in the same way as described before.

To achieve well-defined internal energy distributions, the absorption of UV photons has to be carried out in a controlled manner. The energy of an UV photon (4.7 eV) is initially absorbed as electronic

energy, which does not cause immediate ionization (IP of $C_{60} = 7.6$ eV [13]). The lifetime of most electronic states is very short (sub-nanosecond) and fast energy transfer into the vibrational modes of the electronic ground state (S_0) occurs (internal conversion). By using very short UV pulses, redistribution of energy in the molecules has not fully taken place, and absorption of a second photon will lead to a substantial amount of direct C_{60}^+ ions. Maintaining the intensity of the UV beam at a level just below the threshold for this direct ionization of C_{60} , the average number of UV photons absorbed cannot exceed one by much. Likewise, the intensity of the FELIX radiation is reduced to a level such, that ionization by FELIX alone is minimized. In this way, the contribution to the ion yield from the separate light sources is negligible. With these settings and with both lasers running, the ions created are a direct result from the absorption of a combination of photons coming from the UV and the IR laser. This ‘double-resonance’ signal is monitored as a function of the IR laser wavelength to give the IR-REMPI spectra of the UV pre-excited molecules.

3. Results and discussion

In Fig. 1A, the IR-REMPI spectrum of C_{60} is shown, measured without UV pre-excitation. Below,

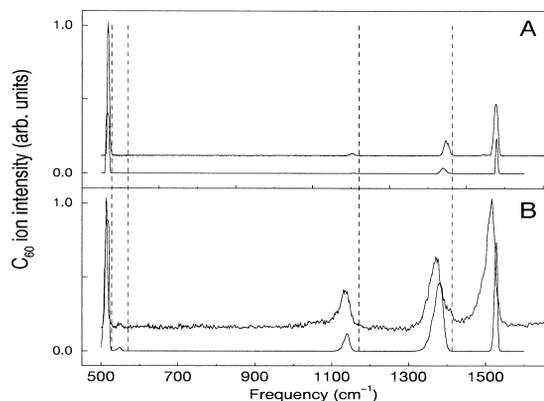


Fig. 1. (A) IR-REMPI spectrum of ground state C_{60} with the theoretical simulation just below. (B) IR-REMPI spectrum of UV pre-excited C_{60} molecules, again with the theoretical simulation just below. The dashed lines are the positions of the C_{60} emission lines at 950 K [15].

a theoretical simulation is depicted, of which details will be given later. The first three bands of the experimental spectrum at 518, 1150 and 1397 cm^{-1} , correspond to three of the four IR active fundamental F_{1u} modes of C_{60} [14]. The fourth IR active fundamental (545 cm^{-1}) is very weak and not visible in this spectrum. In addition, C_{60} has one weak and one strong combination band around 1500 cm^{-1} , which is visible here. These four peaks are also observed in the theoretical spectrum, although the peak at 1150 cm^{-1} is not visible on this scale, due to its weakness. The dashed lines are the central positions of the emission lines of C_{60} in the gas phase at 950 K [15], located at 528, 570, 1171, and 1411 cm^{-1} . The observed red-shift of the IR-REMPI peaks, with respect to the emission lines, is solely due to the anharmonicity of the vibrational modes. This can be quite substantial since many hundreds of IR photons are absorbed before thermionic emission occurs.

In Fig. 1B, the experimental IR-REMPI spectrum is shown with UV pre-excitation, together with its theoretical analogue. In these spectra all fundamental modes are visible. All peaks, except for the lowest frequency one, are broadened significantly. Furthermore, an additional substantial red-shift of up to 25 cm^{-1} is observed for these peaks. The relative intensities of the peaks in both experimental spectra are very similar, however it can be noted that the lowest frequency peak in Fig. 1B has become smaller, relative to the others.

The first excited electronic state of C_{60} , the triplet state T_1 , is the only electronically excited state that has a lifetime as large as microseconds. The reported lifetimes for this state range from 2 to 41 μs [16,17], strongly depending on internal energy. Since FELIX follows the UV light after several microseconds, it cannot be excluded that the vibrational frequencies of the excited triplet state, instead of the singlet ground state are measured in the IR-REMPI spectrum. However, several arguments contradict this hypothesis.

As seen in Fig. 1 the number of resonances are the same in both A and B. This is strong evidence that both spectra A and B originate from the same electronic state. From an electronically excited state one would expect more IR active bands due to a lowering of symmetry. A second argument concerns the lifetime of the pre-excited state. This is examined

by varying the time delay between UV pre-excitation and IR ionization. In those experiments, the UV excitation occurs spatially before the IR excitation (by using the translation stage) to compensate for the velocity of the C_{60} beam. By doing so, these molecules can be pre-excited tens of microseconds before FELIX probes the molecules, and only a small loss of the ion intensity is observed. Substantial more loss of this double resonance signal would be expected if this were due to the triplet state.

The most convincing argument, however, is the theoretical simulation. To confirm that the observed peaks in the pre-excited IR-REMPI spectrum belong to C_{60} in its electronic ground state, a simulation of the IR excitation process of C_{60} is carried out. The results of the simulation, as will be presented in the following, show that the additional red-shift of the prominent peaks in the pre-excited IR-REMPI spectrum can well be explained by the anharmonicity of the vibrations, taking into account the set of different vibrational energy level distributions, reached by absorption of respectively 0,1,2,3, . . . UV photons. The red-shift values can be used to measure the average energy of pre-excitation, and IR-REMPI spectroscopy can thus be used for thermometry of C_{60} .

4. Simulations of the spectra

The IR-REMPI spectra of C_{60} with and without UV pre-excitation are simulated using a model which assumes that UV pre-excitation creates an ensemble of electronically excited molecules with a Poisson distribution of absorbed UV quanta. The molecules then relax rapidly to vibrationally excited levels in their electronic ground states. After relaxation, the molecules interact with the IR light of FELIX.

The dynamics of a population distribution among vibrational levels can be described by the kinetic equations

$$dn_i/dt = F_{i+1,i} + F_{i-1,i} - F_{i,i+1} - F_{i,i-1} \quad (1)$$

where n_i is the population of the i th level in a vibrational manifold, and $F_{i,j}$ is the rate of the

Table 1

Parameters used in the simulations. The integral absorption cross-sections are given by A_m , the anharmonicity parameters by a_m , and the broadening parameters by b_m [10]

ω_0 (cm^{-1})	A_m (cm)	a_m ($\text{cm}^{-1}/\text{quant}$)	b_m ($\text{cm}^{-1}/\text{quant}$)
526.5	0.277×10^{-16}	0.387×10^{-1}	0.825×10^{-2}
575.8	0.777×10^{-17}	0.640×10^{-1}	0.825×10^{-2}
1182.9	0.772×10^{-17}	0.257	0.370×10^{-1}
1435.2	0.108×10^{-16}	0.419	0.370×10^{-1}
1539.0	0.200×10^{-17}	0.102	0.100×10^{-1}

population flow from level i into level j , induced by FELIX. $F_{i,j}$ can be written as

$$F_{i,j} = \frac{I}{\hbar \omega} \sigma_{i,j} \cdot n_i \quad (2)$$

where I is the laser intensity, $\hbar \omega$ is the photon energy, and $\sigma_{i,j}$ is the vibrational absorption cross-section of the $i \rightarrow j$ transition.

In this way, one obtains the following rate equations for the IR-REMPI excitation of the energy ladder via successive absorption of IR quanta [10]

$$\frac{1}{I} \cdot \frac{dn_i}{dt} = \frac{dn_i}{d\Phi} = \frac{1}{\hbar \omega} (\sigma_{i+1,i} \cdot n_{i+1} + \sigma_{i-1,i} \cdot n_{i-1} - \sigma_{i,i+1} \cdot n_i - \sigma_{i,i-1} \cdot n_i) \quad (3)$$

where Φ is the fluence of the infrared laser pulse. The modeling of absorption cross-sections was based on the experimental data on anharmonicity and broadening parameters, and on integral absorption cross-sections of vibrational bands of C_{60} [15]. We assume that both the width of the peaks and the resonant frequency depend linearly on the internal energy E_i as $\Gamma(E_i) = a_m \cdot i$ and $\omega_{res} = \omega_0 + b_m \cdot i$. Table 1 gives an overview of the parameters used. A more detailed description is available elsewhere [10]. The ionization rate of an excited molecule is calculated by using the thermionic model [18,19]. In this model dissociation is neglected, since the ionization potential is substantially smaller than the dissociation limit.

The rate equations (3) are solved numerically. The initial population distribution over the vibrational manifold is taken to be a Boltzmann distribution at a temperature equal to the oven temperature.

The additional ultraviolet photons shift the whole energy distribution by discrete amounts

$$n_m(E) = n_B(E - m \cdot \hbar \omega) \quad (4)$$

where m is the number of absorbed UV quanta and $\hbar \omega$ is the energy of an UV quantum. The distribution of absorbed UV quanta is assumed to be a Poisson distribution

$$P_m = \langle q \rangle^m \cdot e^{-\langle q \rangle} / m! \quad (5)$$

where P_m is the probability that a molecule absorbs m UV quanta, $\langle q \rangle$ is the average number of absorbed quanta.

The simulated spectra are shown in Fig. 1 in comparison to the experimental spectra. The broadening parameter of the 1183 cm^{-1} band is not known from literature but was taken to be equal to the corresponding parameter of the 1435 cm^{-1} band. These two bands are stretch modes, so it is natural to suppose that the magnitude of the spectroscopic parameters is about the same. This appears justified by the good agreement between the simulated and measured spectra.

The anharmonicity parameter of the combination band at 1539 cm^{-1} is initially taken to be equal to the parameter of the 526 cm^{-1} band. Here, we supposed that this band is a combination of two bending modes like the 526 cm^{-1} mode. After comparison with experiment this value is adjusted such that good agreement with the measured intensity of this peak is achieved. The discrepancy in the width of the peak can be due to the interference with the

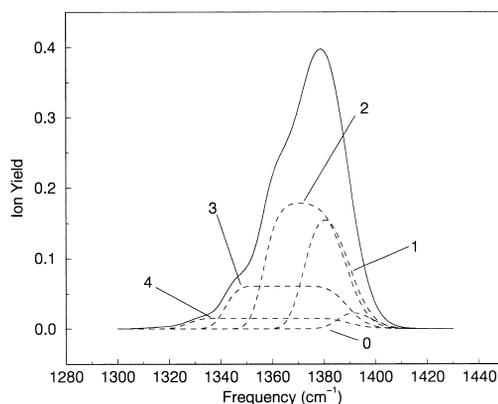


Fig. 2. Fragment of the simulated spectrum with the decomposition of the peak around 1380 cm^{-1} .

neighboring combination bands, which are not yet taken into account.

In the course of the calculation, the average number of UV quanta was varied and the best agreement with the experimental spectra was achieved at $\langle q \rangle \approx 1$. It is, however, important to note that, when the distribution of C_{60} molecules absorbs one quantum on average, a significant amount of the molecules absorb two or more quanta. The calculations show that the position of the peaks in the IR-REMPI spectrum of pre-excited C_{60} molecules is mostly determined by the molecules which absorb two UV quanta. Although the number of these molecules is smaller, the probability to ionize them by IR radiation is much higher than for molecules with one UV photon absorption. This is illustrated in Fig. 2 where the peak at 1380 cm^{-1} is shown with the spectral contributions from molecules which absorbed 0,1,2,3,4 UV quanta, indicated separately. It is clear from this figure that contributions from C_{60} molecules that have absorbed more than one UV quantum, can not be neglected. Experimental evidence for this is the large width of the observed peaks which is explained by the large width of the Poisson distribution and can not be explained if we assume that only one UV quantum is absorbed by C_{60} .

The vibrational excitation energy spectra (total energy; thermal + UV + IR photons) are simulated for the cases of pre-excitation by 1 and 2 UV quanta

as well as without UV pre-excitation. These spectra are shown in Fig. 3. It is seen from these calculations that the excitation energy can reach the value of 40–50 eV. This fact is interesting not only because it explains the high ionization yield but it opens the opportunity to reach very highly excited states of C_{60} via IR excitation.

5. Conclusion

Absorption of UV quanta prior to infrared laser ionization results in broadening and shifting to lower frequencies of the vibrational resonances of C_{60} in the IR-REMPI spectra. Experimental conditions are maintained such, that an average absorption of one UV quantum is assured. The obtained IR-REMPI spectra of these pre-excited molecules indicate that these originate from the vibrationally hot ground state, and not from the meta-stable triplet state. The initial UV (electronic) excitation is converted to vibrational energy in the electronic ground state. A theoretical simulation of the spectra is carried out with a Poisson distribution of absorbed UV quanta. The best agreement with experiment is indeed obtained with the Poisson distribution centered around 1 UV quantum.

Absorption of more UV photons leads to higher vibrationally excited C_{60} molecules, which have an increased IR laser ionization efficiency. The actual ionization yield depends on the product of the number of molecules in the selected pre-excited states and the ionization efficiency from these states. It is observed that the dominant contribution to the ionization yield in our experiment is actually from molecules that absorbed 2 UV quanta. The red-shift values of the peaks in the IR-REMPI spectra can be used to measure the average energy of pre-excitation, and IR-REMPI spectroscopy can thus be used for thermometry of C_{60} .

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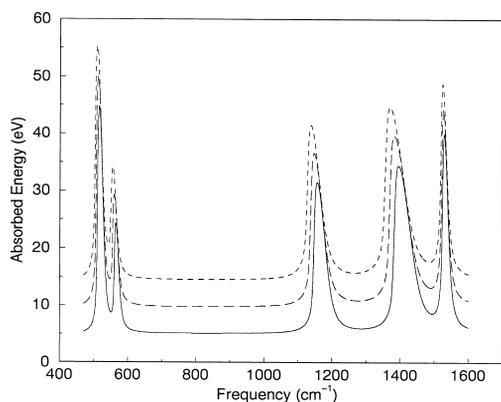


Fig. 3. Three simulations of vibrational excitation energy spectra with 0, 1, or 2 UV quanta, respectively, in bottom to top order.

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