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Infrared laser excitation of gas phase molecules prior to field ionization[☆]

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Abstract

Infrared multiphoton absorption is introduced as a method of direct heating of gas phase molecules prior to field ionization. This approach appears to be a very effective way to increase fragmentation following field ionization of the vibrationally excited molecules. Comparison is made with the method of electrical heating of the emitter which results in an indirect heating of the molecules prior to field ionization.

Keywords: Diethyl ether; Emitter heating; Field ionization; Infrared laser excitation

1. Introduction

Field ionization (FI) is known to be a soft ionization method for the mass spectrometric analysis of volatile molecules [1,2] and has been applied frequently in kinetic studies of unimolecular ion decompositions [3–6]. A major problem in field ionization kinetic (FIK) studies is that often the small amount of energy (0.2–0.4 eV) deposited [7] in excess of the ionization energy of the molecules during ionization results in limited or even no fragmentation of the generated molecular ions. This limited or absent fragmentation makes it experimentally either difficult or impossible to perform FIK studies.

Various techniques have been used to overcome this problem by increasing the internal energy of the molecules prior to FI. For example, indirect heating of the molecules has been achieved by electrically heating the emitter [8,9]. However, it has been shown [10] that heating of the emitter to temperatures in excess of 1000 K does not increase further the internal energy of the molecules. Other attempted ways to indirectly heat the molecules concern the operation of the sample inlet system and ion source at elevated temperatures [10] or the heating of the emitter in field desorption studies using near infrared [11] or visible radiation [12].

In this paper the application of infrared (IR) multiphoton absorption to increase directly the internal energy of the molecules prior to FI is presented.

IR multiphoton absorption by polyatomic

[☆] Dedicated to the late Professor A.O. Nier for his enthusiasm and contributions to mass spectrometry.

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molecules can be explained with a simple model [13]. The rovibrational energy levels of a molecule are divided into three regions. The region of lowest energy is the discrete state region where the bandwidth of the laser is much less than the separation between the energy levels. IR photon absorption in this region is highly wavelength dependent. The discrete energy level region is followed by the quasi-continuum where energy levels mix and the laser excites many levels at once. Wavelength selectivity strongly decreases in this region. The final region is the dissociative continuum where a complete mixing of energy levels exists resulting in a continuum. Strong excitation by any wavelength in this region leads to dissociation.

In the case of large molecules, such as diethyl ether, it is assumed that a substantial part of the molecules can be excited to the quasicontinuum at room temperature after absorption of only a few photons [14]. This fraction can possibly be increased by a slight thermal heating of the molecules or by resonant absorption of one (or two) IR photons. Diethyl ether is used to illustrate the effect of IR multiphoton absorption upon its FI mass spectrum. The effect of direct heating of the molecules with the laser is compared to that of indirect heating using the emitter. Therefore, the inlet system and the ion source were kept at a constant temperature and diethyl ether was chosen as it has an absorption band around $10.6\ \mu\text{m}$ corresponding to the wavelength of the laser used.

2. Experimental

The FI mass spectrometric experiments were performed on a double-focusing quadrupole hybrid mass spectrometer with BEqQ configuration (ZAB-HFqQ Fisons, Manchester, UK). Samples were introduced into the ion source (420 K) through a heated septum inlet

(420 K). The ionization gauge indicated that the pressure in the source was about 5×10^{-3} Pa. The $10\ \mu\text{m}$ activated tungsten emitter was heated by passing through it a well-defined current between 0 and 60 mA. The laser used to heat up the molecules was an 80 W CW CO_2 laser (Electrolux PB 1500) operating at a fixed wavelength of $10.6\ \mu\text{m}$ and was fired via windows through the ion source perpendicular to the ion beam axis. A cylindrical lens ($f = 30\ \text{cm}$) was used to focus the laser beam between the emitter and the counter electrode which were separated by $\pm 1.5\ \text{mm}$. The dimensions of the laser focus were $9\ (\text{height}) \times 0.9\ (\text{width})\ \text{mm}$ measured for both at $(1/e^2)$ of the maximum intensity.

3. Results and discussion

Fig. 1 shows the FI mass spectrum of diethyl ether obtained at different heating conditions, all other experimental settings and conditions being kept constant. No peaks due to fragmentation of the molecular ions are detected in the spectrum of the unheated diethyl ether (Fig. 1(a)). Indirect heating of the diethyl ether molecules through emitter heating shown in Figs. 1(b) and 1(c) clearly promotes fragmentation. However, the effect of direct heating of the diethyl ether molecules with the laser has a much more significant effect as shown in Fig. 1(d). Large fragmentation peaks at m/z 59 and 29 are observed together with some smaller fragment ion peaks at m/z 15, 30, 31, 43, 44 and 45. These peaks are also present in the electron impact mass spectrum of diethyl ether although their relative intensities are quite different from those of Fig. 1(d). It is therefore very unlikely that the corresponding fragment ions would originate from FI of laser induced neutral dissociation products of diethyl ether. The formation of such neutral dissociation products would require the absorption of at least 30 IR photons, consider-

Fig. 1. Field ionization spectra of diethyl ether recorded at the double-focus point behind the electric sector of the double-focusing hybrid mass spectrometer used (see Experimental) with (a) unheated emitter, laser off (b) heated emitter (40 mA), laser off, (c) heated emitter (60 mA), laser off, and (d) unheated emitter, laser on 11 W. The recorded intensities of the peaks in the mass range m/z 10–50 have been multiplied by a factor of 25 in all spectra.

ing the IR laser wavelength of $10.6 \mu\text{m}$ used which corresponds to 11.3 kJ mol^{-1} and the homolytic bond dissociation energies of C–O and C–C bonds which are between 335 and 375 kJ mol^{-1} .

The following experiments have been performed to further support experimentally the conclusion that the laser induced and increased fragmentation is a result of direct vibrational excitation and not indirect heating of the molecules, for example through heating of the emitter or counter electrode by the laser. For that reason a number of parameters has been monitored as a function of the laser focus position which has been moved from beyond the counter electrode to beyond the emitter in the FI source. The effect of the laser position

Fig. 2. Different parameters monitored as a function of the position of the laser focus with respect to the emitter and counter electrode in the field ionization (FI) ion source: $\square$, laser power measured behind and outside the FI source; $+$, temperature of counter electrode; Δ , resistance of emitter. The intensity of the FI fragment ion peak at m/z 59 in arbitrary units (a.u.) and as a function of the position of the laser focus is depicted by the solid line. The positions of the emitter and counter electrode (1 mm thick) are indicated by the broken vertical lines.

on these parameters is shown in Fig. 2, where the positions of the emitter and counter electrode are also indicated. The parameters monitored are the temperature of the counter electrode measured with a thermocouple, the emitter resistance which is a measure of its temperature, the laser power measured after transmission of the laser beam through the FI source and the intensity of the fragment ion peak at m/z 59.

Laser impact on the counter electrode is clearly seen from Fig. 2 which shows that the laser beam is completely blocked by the counter electrode, that is at $\pm 9.8 \text{ mm}$ laser focus position no laser power is measured behind and outside the FI source. A drop in laser power is also detected when the laser beam is partially blocked by the emitter "holder" from 11.8 mm and onwards (see Fig. 2). Impact of the laser beam on the counter electrode is also evident from the temperature rise of the counter electrode. All corresponding temperature

readings were taken 30 s after switching on the laser beam. Some of the temperature readings have been taken before thermal equilibrium was reached. These are indicated by the arrows in Fig. 2, where an upwards arrow means a still rising temperature and a downwards arrow the opposite.

Heating of the emitter with the laser results in an increase of the emitter resistance corresponding to an increase in temperature. The absolute increase in temperature can not be given as the temperature coefficient of the activated tungsten emitter is not known. The small increase in emitter resistance observed when the laser hits the counter electrode (at 10 mm) is due to reflection of the laser light from the counter electrode onto the emitter.

From these measurements it is clear that it is possible to position the laser focus between the emitter and the counter electrode thereby avoiding any significant heating of either of them. The FI mass spectra presented in Fig. 1 have all been recorded with the laser focus positioned at the maximum laser power transmission through the FI source, corresponding to minimal heating of the counter electrode and emitter. Moreover, no correlation is observed between laser heating of the counter electrode or the emitter and the generation of the fragment at m/z 59. Therefore it can be safely concluded that the heating of the gas phase diethyl ether molecules, as reflected by their enhanced fragmentation upon FI, is due to IR multiphoton absorption and not due to indirect laser heating via parts of the FI source.

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