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# Intermolecular proton transfer from visible laser light-excited indene radical cations to reference bases in the gas phase

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## Abstract

It is shown by the use of Fourier transform ion cyclotron resonance mass spectrometry that indene radical cations excited by laser light of 514.5 nm are more reactive toward reference bases than ground state indene radical cations. Such excitation effects proton transfer from the indene radical cation to reference bases where a reaction in the ground state of the reaction partners is endothermic up to a maximum of 48 kJ/mol. (Int J Mass Spectrom 197 (2000) 211–217) © 2000 Elsevier Science B.V.

**Keywords:** Light-induced proton transfer; Indene radical cation; Ion/molecule reaction; Bracketing; Fourier transform ion cyclotron resonance; Two-photon dissociation

## 1. Introduction

Flowing afterglow (FA) [1–3] and Fourier transform ion cyclotron resonance (FTICR) [4–6] mass spectrometry have been applied extensively over the past decades to study gas phase ion/molecule reactions. These studies have provided a wealth of information and detailed knowledge on reaction mechanisms and kinetics [7–13], ion structures [14,15], and thermodynamic properties [16,17] where the species involved are in their ground states. For example, proton affinities have been obtained for hundreds of molecules using the bracketing [18–20] (usually by FTICR), equilibrium, and kinetic methods [21–25] [mostly by use of triple stage quadrupole (TSQ), mass

analyzed ion kinetic energy (MIKE), ion trap (IT), FA, and FTICR instruments]. Much less is known, however, about the change of such properties when the molecules or corresponding protonated species are internally excited. By using, among others, FTICR and the monitor ion technique/differential reactivity method [26,27] which are based on chemically monitoring charge or proton transfers from excited ions to suitable monitor molecules in the ground state, the gas-phase reactivity of a number of small excited ions has been investigated [26–28]. Recently there is a growing interest in the gas-phase chemical reactivity of larger excited ions. FTICR is a suitable method studying such chemical reactivity because it allows an extensive manipulation of stored ion populations at low pressures ( $\sim 10^{-9}$  Torr) and investigation of bimolecular ionic reactions over a time scale from milliseconds to several hours.

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In a previous article the visible laser light-induced intermolecular proton transfer from gas-phase protonated naphthalene to neutral molecules has been reported [29].

In this article the difference in the proton transfer capability of the non-excited and visible laser light-excited odd electron indene radical cation has been probed by use of the bracketing method. The monitoring of such differences in reactivity induced by the laser light may partially shed some further light on not yet fully understood mechanisms of matrix assisted laser desorption ionisation (MALDI) [30–36] where pulsed laser light and a chromophore as matrix are used to evaporate and protonate analyte molecules. This protonation of analyte molecules has been proposed to occur in the gas phase by reaction of the electronically excited matrix molecules with the ground state analyte molecules [32]. Afterwards the ejection of species into the gas phase and possible ionisation processes in MALDI mass spectrometry have been described [33]. Recent studies propose multicenter excitation of matrix molecules and charge transfer from neutral excited matrix molecules to other neutral matrix molecules, whereby the generated charged matrix species subsequently protonate the analyte [35–37].

The probing of differences in reactivity of visible light-excited and nonexcited polycyclic aromatic hydrocarbon (PAH) ions is further of astrophysical interest where recent FA studies have focused on the role possibly played by PAHs, PAH radical cations and protonated PAHs in the diffuse interstellar bands [38,39].

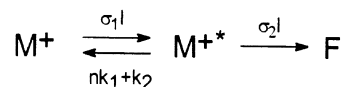
Sec. 2 will successively and briefly describe the necessary conditions for the photochemical experimental setup, the performed photochemical experiments, and the applied pulse sequences for obtaining (by the bracketing method) the data presented. Finally, the results will be presented and discussed.

## 2. Conditions for the photochemical setup

A brief discussion of the experimental conditions to be fulfilled for studying a bimolecular photochem-

ical reaction of ions is given here (for more details see [29]). First, the indene radical cation, to be studied and generated by electron ionisation of indene, should absorb photons at the wavelength of 514.5 nm of the argon ion laser used. Second, to be certain that the proton transfer occurs from the excited indene radical cation, it must be shown that the indene radical cation obeys the rules of two-photon dissociation. In that way there is evidence for the existence of an electronically excited state between the ground state and the dissociation limit. Third, the excited indene radical cation should have a lifetime of several hundreds of milliseconds, which is the time scale of the FTICR experiment during which the proton transfer from the excited ion to the reference base occurs.

Scheme 1 presents the case for a pure two-photon dissociation of ion  $M^+$  where the symbols  $\sigma_1$  and  $\sigma_2$  are the photon absorption cross sections,  $I$  the laser light intensity,  $k_1$  the rate constant for collisional deactivation,  $k_2$  the rate constant for radiative deactivation,  $n$  the density of neutral molecules,  $M^{+*}$  the excited ion, and  $F$  the generated fragments.



Scheme 1. Reaction scheme for a pure two-photon dissociation process of  $M^+$  (see the text).

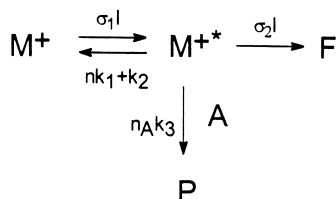
On the basis of Scheme 1 it has been shown [40,41] that the decay of the ion abundance is singly exponential

$$M(t, I)/M(t, 0) = \exp[-I^2 \sigma_1 \sigma_2 t / \{nk_1 + k_2 + I(\sigma_1 + \sigma_2)\}] \quad (1)$$

Here  $M(t, I)$  and  $M(t, 0)$  are the ion abundances after  $t$  seconds with and without irradiation. Eq. (1) implies that  $-I/\ln\{M(t, I)/M(t, 0)\}$  should be linear with  $1/I$ .

Scheme 2 is an extension of Scheme 1 to include photochemical reactions of  $M^{+*}$  with substrate molecules  $A$  to give the bimolecular reaction products  $P$ , in which  $n_A$  is the density of molecules  $A$  and  $k_3$  the

bimolecular rate constant for reaction of  $M^{+*}$  with A.



Scheme 2. Reaction scheme for a pure two-photon dissociation process of  $M^+$ , in which the singly photon excited  $M^{+*}$  reacts with molecule A to give  $P$  in competition with absorption of the second photon to give  $F$  (see the text).

From Scheme 2 it follows that the ratio of product  $P$  and fragment  $F$  ion abundances is given by

$$P/F = n_A k_3 / \sigma_2 I \quad (2)$$

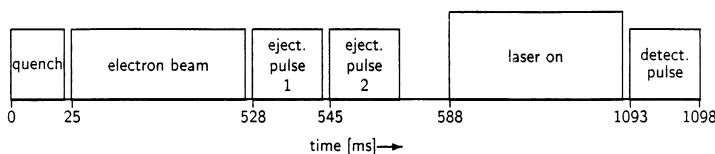
### 3. Experimental

The experiments were performed with a laboratory-built Fourier transform ion cyclotron resonance (FTICR) mass spectrometer equipped with three inlet systems, a 1.4 T 12-inch Varian magnet used at 1.25 T, and a home-built stored waveform inverse Fourier

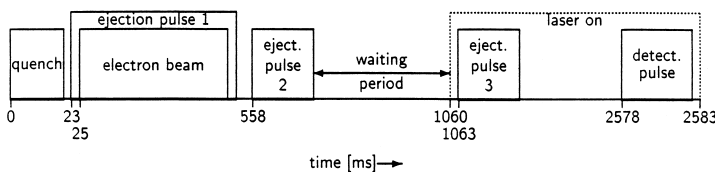
transform [42] (SWIFT) unit. The SWIFT unit allows the ejection of unwanted ions at specifically chosen mass ranges during the experiments. The laser light from the argon ion laser (Spectra-Physics Stabilite 2017) enters the FTICR cell via a shutter, a lens system to broaden the beam so as to cover the entire cell through a sapphire window and is reflected at the back of the cell by a slightly concave mirror. The laser power was adjusted by a calibrated laser power controller from 0.05 to 1.1 W at a wavelength of 514.5 nm. Indene and all reference compounds were commercially available and used for the experiments without further purification.

Scheme 3 shows a typical pulse sequence of the ion formation, ejection, isolation and detection used in the pure two-photon dissociation experiments.

Following electron ionisation of indene at a pressure of  $10^{-8}$  Torr, the indene radical cation was isolated by the application of several SWIFT pulses and subsequently irradiated with the laser light of 514.5 nm. A detection pulse was triggered at the end of each sequence. For details about the duration of the various pulses see Scheme 3. After Fourier transformation the heights of the peaks due to the indene



Scheme 3. Pulse sequence applied for the study of the two-photon dissociation process of  $M^+$ , presented in Scheme 1. The duration of the pulses was: quench 5 ms; electron beam ionization 500 ms; ion ejection pulse 1 and 2 to isolate  $M^{+*}$  16 and 8 ms, respectively; laser on 500 ms; detection 5 ms. 20 pulse sequences were accumulated to obtain  $[M^+(t)]$  at a laser intensity  $I$ .



Scheme 4. Pulse sequence applied for the study of the proton transfer process from excited  $M^{+*}$ , presented in Scheme 2. The laser pulse (depicted in dotted lines) was applied alternately on and off to obtain a difference spectrum. The duration of the pulses was: quench 5 ms; electron beam ionisation 495 ms; ion ejection pulse 1 to remove all ions with the exception of  $M^{+*}$  515 ms; ejection pulse 2 to isolate  $M^{+*}$  8 ms; a waiting period to carry off excess energy of (cool) the ions 497 ms; laser on 1520 ms; ejection pulse 3 to further isolate  $M^{+*}$  after cooling 8 ms; detection 4 ms. 1000 pulse sequences were accumulated to obtain the difference spectrum.

Table 1

Bracketing of the proton transfer from the indene radical cation to a reference base with the laser light on and off

Reference base	Proton affinity <sup>a</sup> (kJ/mol)	Laser light on	Laser light off	Pressure <sup>b</sup> (Torr × 10 <sup>-7</sup> )
Dimethyl sulfoxide	884.4		+	2.0
Pyrrole	875.4		+	2.0
Thioanisole	872.6		+	2.0
4-Fluoroaniline	871.5		+	2.0
Ethyl vinyl ether	870.1		<sup>d</sup>	2.0
3-Methylphenyl methyl ketone	868.2		+	2.0
3,4-Dihydro-2H-pyran	865.8		+	2.0
Acetophenone	861.1	+	+	2.0
		+	–	1.0
Indene	848.8		<sup>e</sup>	
Di-n-butyl ether	845.7		±	2.0
Cyclohexanone	841.0	+	±	1.1
Indenyl radical	840 ± 1 <sup>c</sup>		<sup>e</sup>	
3-Pentanone	836.6	+	–	2.8
		+	–	2.1
		+	–	1.4
		+	–	0.9
2-Butanone	827.3	+	–	1.0
Cyclopentanone	823.7	+	–	2.5
		+	–	1.0
Acetone	812.0	+	–	1.0
Oxetane	801.3	+	–	1.4
1,4-Dioxane	797.3	+	–	1.0
Dimethyl ether	792.0	–	–	0.9
Toluene	784.0	–	–	1.4

<sup>a</sup> Values have been taken from [17].<sup>b</sup> Ratio of pressures of indene and reference base about 1:100.<sup>c</sup> Obtained in the present work.<sup>d</sup> Charge transfer observed from the indene radical cation to ethyl vinyl ether.<sup>e</sup> Indene and the indenyl radical have been included for completeness.

radical cation with and without irradiation were taken as a measure of their ion abundances.

Scheme 4 gives a typical pulse sequence for the proton transfer bracketing experiments from the indene radical cation with and without irradiation. For details about the duration of the various pulses see Scheme 4.

During the electron beam pulse to generate the indene radical cations, unwanted ions were ejected by application of repeated SWIFT pulses. This was necessary to reduce the number of unwanted ions as much as possible, because the reference compound is present in about a 100-fold excess. Then a waiting period to carry off the excess energy of the indene radical cations, obtained during electron ionisation, by nonreactive collisions was applied. This waiting pe-

riod was followed by a SWIFT ejection pulse to remove the ion/molecule reaction products formed and to isolate the “cooled” indene radical cations with  $m/z = 116$ . Finally these ions were allowed to react for 1500–2000 ms with the laser light on or off followed by a pulse to detect the reactant and product ions.

Difference spectra were obtained by subtracting the Fourier transformed signals of two successive experimental cycles, one with the laser light on and one with the laser light off.

#### 4. Results and discussion

First, experiments were performed to prove that the indene radical cation dissociates following absorption

of two photons. For that purpose the argon ion laser light with the wavelength of 514.5 nm has been used, which is near to the absorption peak in the liquid-phase thermalized UV/VIS spectrum [43] of the indene radical cation.

As noted in Sec. 2, for a pure two-photon dissociation  $-I/\ln\{M(t, I)/M(t, 0)\}$  should be linear with  $1/I$ . Therefore the amount of indene radical cations dissociated at different laser light intensities has been measured and plotted as  $-I/\ln\{M(t, I)/M(t, 0)\}$  versus  $1/I$  in Fig. 1.

Fig. 1 shows that the indene radical cation indeed dissociates following absorption of two photons. In this dissociation the indene radical cation loses a hydrogen atom to give the indenyl cation, a process observed earlier also for protonated naphthalene [29].

The next step was to introduce 3-pentanone into the cell to serve as a proton acceptor from the visible laser light-excited indene radical cation. This proton transfer, which is endothermic and therefore does not occur if the radical cation of indene is in the ground state (PA of 3-pentanone = 836.8 kJ/mol; PA of indenyl radical = 840 kJ/mol), is observed indeed for the excited radical cation of indene.

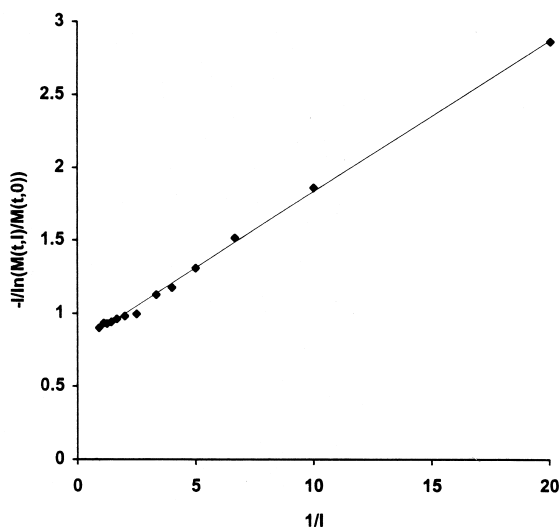


Fig. 1. Fraction of two-photon dissociating indene radical cations as a function of light intensity varied from 0 to 1.1 W at 514.5 nm and plotted according to Eq. (1) (see the text). The pressure of indene was  $1 \times 10^{-8}$  Torr.

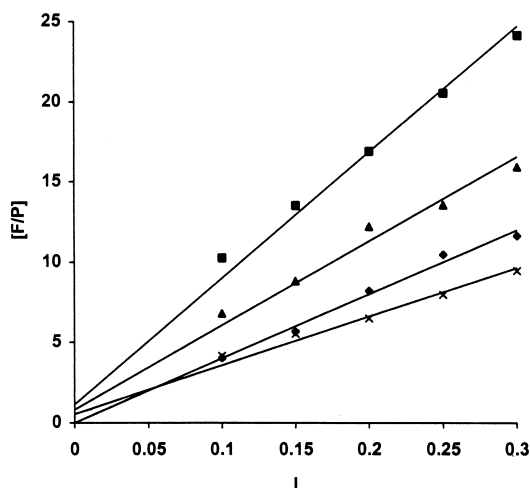


Fig. 2. Ratio of abundances of photofragment ions of the indene radical cation and its bimolecular product ions ( $[F]/[P]$ ) as a function of light intensity at 514.5 nm measured at different pressures and plotted according to Eq. (2) (see the text). The partial pressure of indene is  $1.5 \times 10^{-9}$  Torr and that of 3-pentanone  $9.1 \times 10^{-8}$  (square),  $1.4 \times 10^{-7}$  (triangle),  $2.1 \times 10^{-7}$  (diamond), and  $2.8 \times 10^{-7}$  Torr (cross).

According to Eq. (2), the ratio of abundances of photofragment ions  $F$  of the indene radical cations (because of the two-photon dissociation process) and product ions  $P$  (because of proton transfer to 3-pentanone) should depend linearly on the laser light inten-

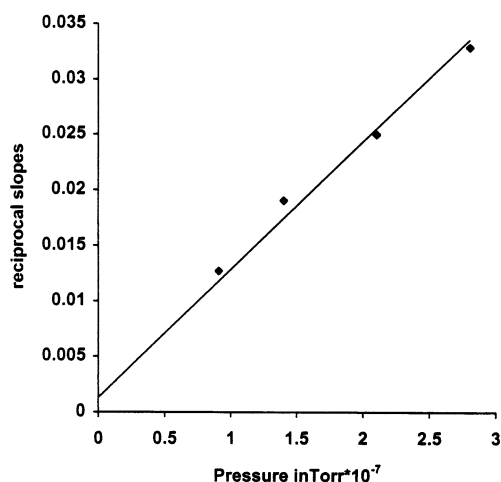


Fig. 3. Reciprocal slopes of the lines in Fig. 2 as a function of pressure (see the text).

sity  $I$ . This has been confirmed by measurements at different pressures of 3-pentanone as shown in Fig. 2.

A plot of the reciprocal slopes of the straight lines in Fig. 2 versus pressure yields the linear relationship between the ratio of abundances of product and photofragment ions and pressure as shown in Fig. 3 and in agreement with Eq. (2).

In the bracketing experiments at a total pressure of  $1 \times 10^{-7}$  Torr (ratio of pressures of indene and reference base about 1:100) a waiting period of 500 ms was inserted in the pulse sequence following the ejection pulse 2 (see Scheme 4). This waiting period is sufficiently long to carry of the excess energy of the indene radical cations, obtained during electron ionization, by non-reactive collisions.

The results of the bracketing experiments obtained with the laser light on and off have been listed in Table 1.

The data in Table 1 show that the threshold for a thermoneutral proton transfer from the indene radical cation with the laser light off takes place to a base having a proton affinity of  $843 \pm 2$  kJ/mol. This value becomes  $795 \pm 3$  kJ/mol with the laser light on, indicating that an endothermic proton transfer of 48 kJ/mol (0.50 eV) can be effected from the indene radical cation when excited by laser light of 514.5 nm, that is 2.41 eV.

## 5. Conclusions

Although the bracketing method has its limitations, the results show that it can be applied to study the change of proton transfer capability of visible laser light-excited ions with respect to their ground state. It remains the question, however, why at most 0.5 eV of the excitation energy of 2.41 eV could be used in the present experiments. We assume that this result indicates that the proton transfer rate constant  $k_3$  in Scheme 2 is significantly smaller than the relaxation rate constant  $k_1$ . This will be the subject of further more detailed experiments on the overall reaction kinetics.

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