

# A Study of Light-Induced Proton Transfer from Gas Phase (Radical) Cations to Reference Bases. Bracketing of Proton Transfer from Excited Ions and Associated Reaction Kinetics

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By use of Fourier transform ion cyclotron resonance, it is shown that protonated naphthalene when excited with laser light of 488 nm is more reactive in proton transfer to reference bases than in its ground state. The excitation leads to reaction with bases for which proton transfer in the ground state is endothermic up to a detected maximum of 60 kJ/mol. For indene radical cations excited at 514.5 nm, it is shown that the rate constant for proton transfer to 3-pentanone is either about 10 or about 100 times lower than the rate constant for relaxation by collisions with 3-pentanone. From the energy deposited in the ions, 0.5–0.6 eV is available for proton transfer to a base which seems reasonable when taking into account a complete randomization of the initially deposited energy. (*J Am Soc Mass Spectrom* 2001, 12, 359–366) © 2001 American Society for Mass Spectrometry

Ground state reactions between ions and molecules in the gas phase have been studied extensively by use of various experimental methods, in particular flowing afterglow (FA) [1–3] and Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry [4, 5]. These studies have provided a wealth of information and a detailed knowledge on ion/molecule reaction mechanisms and kinetics [6–13], ion structures [14, 15], and thermodynamic properties [16]. Much less is known, however, about the change of such properties when the ions are excited. For example, the gas-phase reactivity of a number of small excited ions, such as  $\text{NO}^+$ ,  $\text{O}_2^+$ ,  $\text{HCl}^+$ , and  $\text{HCO}^+$  has been investigated using the ion monitoring technique [17–19]. The monitoring of such difference in reactivity may shed some further light on at present not fully understood mechanisms of matrix assisted laser desorption/ionization (MALDI) [20–27] where pulsed laser light and a chromophore as matrix are used to evaporate and protonate analyte molecules. This protonation of the analyte molecules has been proposed to occur in the gas phase by reaction of the electronically excited matrix molecules

with ground state analyte molecules [23]. The ejection of species into the gas phase and possible ionization processes in MALDI mass spectrometry have been described [24]. Recent studies propose multicenter excitation of matrix molecules and charge transfer from neutral excited matrix molecules to other neutral molecules, whereby the generated charged matrix species subsequently protonate the analyte [26–28].

In previous articles from this laboratory, the reactions of laser-light excited gas-phase ions were investigated where a proton is transferred from excited indene radical cations or excited protonated naphthalene to reference bases [29, 30]. In the study on the indene radical cations [30] it was observed that the laser-light excited gas-phase ions transfer a proton to reference bases with much lower proton affinities than the ground state proton affinity of the donor, which in the ground state is an endoergic reaction. It appeared that this endoergicity should not be larger than about 50 kJ/mol (=0.5 eV) notwithstanding the 2.41 eV (=514.5 nm) energy deposition into the indene radical cations. In [30] it was suggested that relaxation of the excited (radical) cations after internal conversion to a highly vibrationally excited electronic ground state is much faster than the intermolecular proton transfer and that this could explain the relatively small amount of the

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total energy deposition available for proton transfer. In the first part of the present paper the application of the bracketing method will be described to measure the threshold of proton transfer from laser-light excited protonated naphthalene to ground state reference bases which have a lower proton affinity than ground state naphthalene. In the second part a model is proposed which has been used to determine experimentally the ratio of the photon absorption cross sections,  $\sigma_1/\sigma_2$  in schemes 4 and 6, and the ratio of the rate constants of relaxation of and proton transfer from excited indene radical cations.

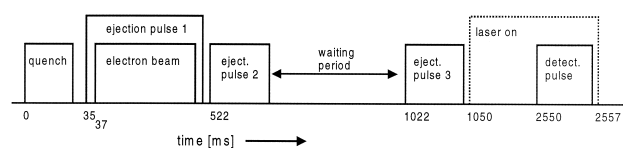
## Experimental

The experiments were performed with a laboratory-built Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with three inlet systems, a 1.4 tesla 12-in. Varian magnet used at 1.25 tesla, and a SWIFT (stored waveform inverse Fourier transform [31]) 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 FT-ICR cell perpendicular to the magnetic field direction via a shutter, a lens system to broaden the beam so as to cover most of the space of the cubic cell (2.5 cm) through a sapphire window and is reflected by a slightly concave mirror positioned behind the cell. The laser power was adjusted by a calibrated laser power controller at a wavelength of 488 nm in the experiments with protonated naphthalene and at 514.5 nm in the experiments with the indene radical cation. Except for indene- $d_3$ , synthesized according to [32], 1-methyl-3,4-dihydronaphthalene [33] and the fluorobenzenes used for bracketing [34], all other compounds were commercially available and used without further purification.

### *Bracketing Experiments of the Proton Transfer from Protonated Naphthalene*

Protonated naphthalene was generated in the cell by electron ionization of 1-methyl-3,4-dihydronaphthalene at a pressure of  $1 \times 10^{-9}$  torr, its structure having been confirmed earlier [29] by the identical collision-induced dissociation spectra of authentic protonated naphthalene and the major fragment ion  $m/z = 129$  from 1-methyl-3,4-dihydronaphthalene. To prevent reaction of the formed protonated naphthalene with its precursor, the pressure of the reference bases used was  $1 \times 10^{-7}$  to  $2 \times 10^{-7}$  torr. Scheme 1 gives a typical pulse sequence for protonated naphthalene with and without irradiation of laser light.

During the electron beam pulse to generate protonated naphthalene, unwanted ions were ejected by application of repeated SWIFT pulses. This was necessary to reduce the number of unwanted ions from the reference compound which was present in about 100-



**Scheme 1.** Pulse sequence applied for the bracketing of proton transfer from excited protonated naphthalene to reference bases. 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 ionization 463 ms; ion ejection pulse 1 to remove all ions with the exception of protonated naphthalene 485 ms; ejection pulse 2 to further isolate protonated naphthalene 16 ms; waiting period to carry off excess energy of (cool) the ions 484 ms; ejection pulse 3 to further isolate protonated naphthalene after cooling 8 ms; laser on 1507 ms; 700 pulse sequences were accumulated to obtain the difference spectrum.

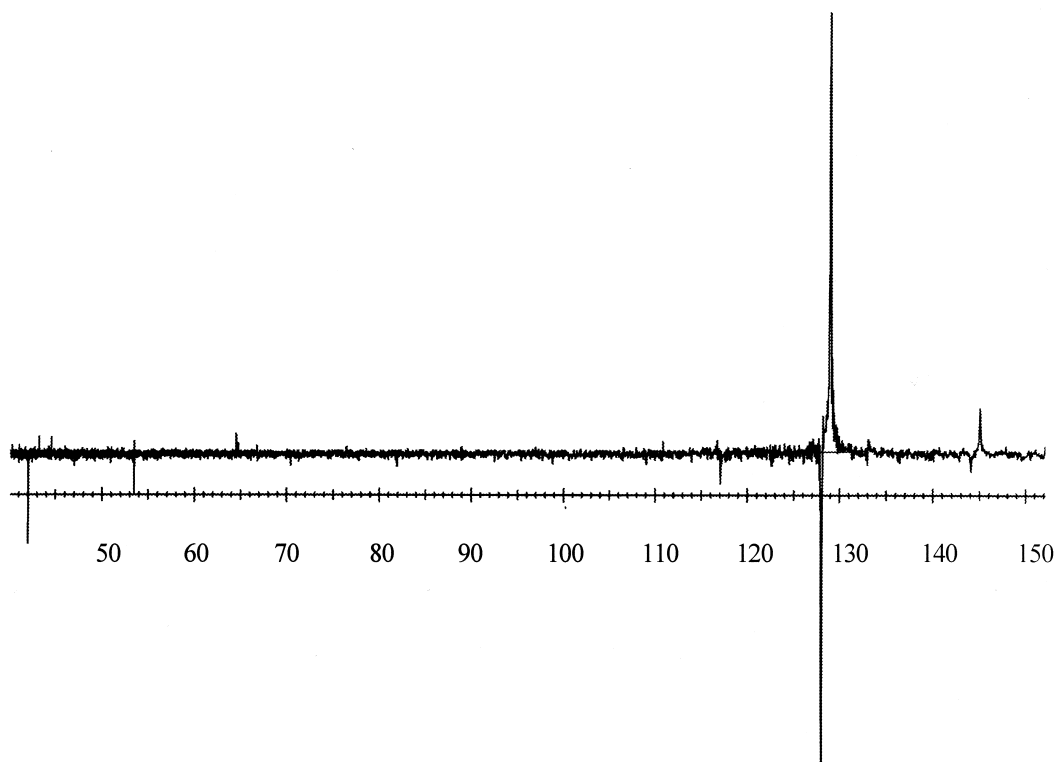
fold excess. Then a waiting period was applied to carry off the excess energy of the protonated naphthalene by nonreactive collisions. The length of the waiting period was chosen such that after this period no reactions of protonated naphthalene were observed (see Figure 1 of [29]). This waiting period was followed by a SWIFT ejection pulse to remove the ion/molecule reaction products formed and to isolate the “cooled” protonated naphthalene with  $m/z = 129$ . Finally these ions were allowed to react for 2000–2500 ms with the laser light on or off. This was followed by a pulse to detect the reactant and product ions. Difference spectra were obtained by subtracting the Fourier transformed signals from two successive experimental cycles, one with the laser light on and one with the laser light off. An example is shown in Figure 1.

### *Experiments Performed on the Indene Radical Cation*

Concerning the indene radical cation, various experiments were performed to determine the rate constants  $k_1$ ,  $k_2$  and ratio's  $\sigma_1/\sigma_2$  and  $k_4/k_3$  in Schemes 4 and 6 which will be discussed in the following section. For a reasonable approximation of  $k_1$ , indene and indene- $d_3$  were introduced into the cell both at a partial pressure of  $2.5 \times 10^{-8}$  torr to measure the rate constant for charge transfer between the molecular ion of indene- $d_3$  and its unlabeled neutral. After isolating the indene- $d_3$  radical cation by application of several SWIFT pulses, the abundances of the formed indene radical cation and reacted indene- $d_3$  were measured at several reaction times.

For determining the ratio of  $\sigma_1$  and  $\sigma_2$  in the pure two-photon dissociation experiments, the typical pulse sequence of the ion formation, ejection, and detection was applied as shown in Scheme 2.

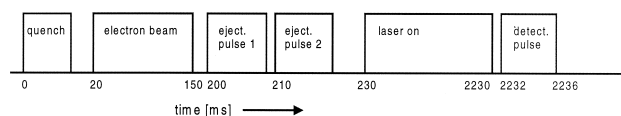
Following electron ionization of indene at pressures from  $3 \times 10^{-8}$  up to  $5 \times 10^{-7}$  torr, the indene radical cation was isolated by application of several SWIFT pulses and subsequently irradiated with laser light of 514.5 nm. A detection pulse was triggered at the end of



**Figure 1.** A difference spectrum of protonated naphthalene irradiated with laser light of 488 nm at 0.1 W and without laser light in the presence of acetonitrile. Acetonitrile (MW is 41) is protonated only when the laser light is on. The precursor ion of protonated naphthalene, that is ionized 1-methyl-3,4-dihydronaphthalene (MW is 144), is capable of capturing a proton as well and dissociates with the laser light on in a similar way as protonated naphthalene, that is by hydrogen atom loss. Therefore, the pressure of the precursor molecule was at least 100 times lower ( $1 \times 10^{-9}$  torr) than the pressure of acetonitrile ( $1.9 \times 10^{-7}$  torr).

each sequence. For details about the duration of the various pulses, see Scheme 2. After Fourier transformation the heights of the peaks due to the indene radical cation with and without irradiation at several laser intensities and pressures of the neutral indene gas were taken as a measure of the ion abundances.

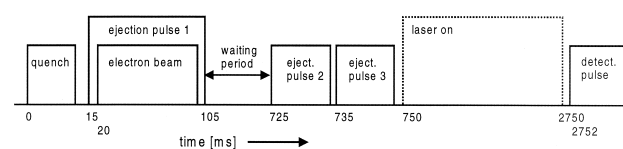
To determine the bimolecular rate constant for proton transfer from the laser-light excited indene radical cation,  $k_3$ , indene was introduced into the cell at a pressure of  $2 \times 10^{-9}$  torr together with the reference base 3-pentanone at pressures from  $1 \times 10^{-7}$  up to  $6 \times 10^{-7}$  torr. Scheme 3 gives a typical pulse sequence for



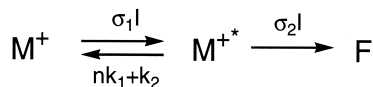
**Scheme 2.** Pulse sequence applied for the determination of the cross sections  $\sigma_1$  and  $\sigma_2$  in the two-photon dissociation process of the indene radical cation, presented in Scheme 4. The duration of the pulses was: quench 5 ms; electron beam ionization 130 ms; ion ejection pulses 1 and 2 to isolate the indene radical cation 8 and 16 ms, respectively; laser on 2000 ms; detection 5 ms. 2000 pulse sequences were accumulated to obtain spectra with and without laser light.

the proton transfer experiments from the indene radical cation with and without irradiation.

Isolation of the indene radical cations by application of repeated SWIFT pulses was followed by a relaxation period of 620 ms to carry off the excess energy of electron ionization excited indene radical cations by nonreactive collisions (six to seven collisions took place). This relaxation waiting period was followed by a SWIFT ejection pulse to remove the ion/molecule



**Scheme 3.** Pulse sequence applied for the determination of  $k_4$  and  $k_3$  presented in Scheme 6. The laser pulse (depicted in dotted lines) was applied alternately on and off to obtain separated spectra. The duration of the pulses was: quench 5 ms; electron beam ionization 80 ms; ion ejection pulse 1 to remove all ions with the exception of the indene radical cations 90 ms; a waiting period to carry off the excess energy of (cool) the ions 620 ms; ejection pulse 2 to isolate the indene radical cations 8 ms; ejection pulse 3 to further isolate the indene radical cations after cooling 8 ms; laser on 2000 ms; detection 4 ms. 3000 pulse sequences were accumulated to obtain the separated spectra.



**Scheme 4.** Reaction scheme for a pure two-photon dissociation process of  $M^+$  (see the text).

reaction products formed and to isolate the “cooled” indene radical cations. Finally, these ions were allowed to react for 2500 ms with the laser light on or off followed by a pulse to detect the reactant and product ions. Separate spectra with the laser light on and with the laser light off were obtained from the Fourier transformed signals of the two successive experimental cycles.

## Background of the Kinetics of the Photochemical Experiments

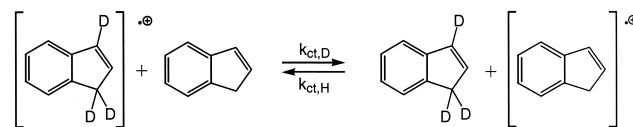
For the discussion in the next section of the results obtained, the background of the kinetics of two-photon dissociation will be given. This will be followed by the expanded kinetic model for intermolecular proton transfer from gas phase ions, such as the indene radical cation.

### Two-Photon Dissociation

Two-photon photodissociation of gas phase ions has been studied since the mid seventies [35–39]. To be certain that the proton transfer occurs from excited ions, it must be shown that they obey the rules of two-photon dissociation. That is, evidence should be provided for the existence of an excited state in between the ground state and the dissociation limit of the ions. Of course, also important is the lifetime of such an excited state after internal conversion to a vibrationally excited ground state, which can be as long as 500 ms for aromatic radical cations (for more details see [29, 39, 40]). Scheme 4 presents the case for a two-photon dissociation of the ion  $M^+$  where the symbols  $\sigma_1$  and  $\sigma_2$  are the cross sections for the first and second photon absorption,  $I$  the laser 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.

To determine the ratio of the photon absorption cross sections,  $\sigma_1/\sigma_2$ , of the indene radical cation, the value of  $k_1$  is needed. Assuming that relaxation of the excited indene radical cation in the two photon dissociation occurs purely via charge exchange with neutral indene, the collisional relaxation rate constant  $k_1$  will be about equal to the rate constant for charge transfer from the ground state indene- $d_3$  radical cation to neutral indene. This system has been chosen to be able to observe experimentally the charge transfer as shown by the reaction equation in Scheme 5.

The exact solution of the differential equation for the kinetic model in Scheme 4 yields



**Scheme 5.** The reaction equation for the charge transfer from the indene- $d_3$  radical cation to neutral indene and vice versa.

$$1 - F(t) = 1/(r_1 - r_2) \cdot (r_1 e^{-r_2 t} - r_2 e^{-r_1 t}) \quad (1)$$

where  $1 - F(t)$  is the fraction of the remaining indene radical cations after an irradiation time  $t$  and

$$r_{1,2} = 1/2 \{ (I\sigma_1 + I\sigma_2 + k_2 + nk_1) \pm \sqrt{[(I\sigma_1 + I\sigma_2 + k_2 + nk_1)^2 - 4I^2\sigma_1\sigma_2]} \} \quad (2)$$

As discussed in an earlier paper [38] the following approximation is valid:

$$r_1 = (I\sigma_1 + I\sigma_2 + k_2 + nk_1)$$

$$r_2 = I^2\sigma_1\sigma_2 / (I\sigma_1 + I\sigma_2 + k_2 + nk_1)$$

where  $r_2 \ll r_1$  and for times  $t \gg (I\sigma_1 + I\sigma_2 + k_2 + nk_1)^{-1}$  the second term in eq 1 becomes vanishingly small. This leads to a single exponential behavior for  $1 - F(t)$  from which it follows that [38]

$$-I/\ln\{1 - F(t)\} = (nk_1 + k_2)/I\sigma_1\sigma_2 + (\sigma_1 + \sigma_2)/\sigma_1\sigma_2 t \quad (3a)$$

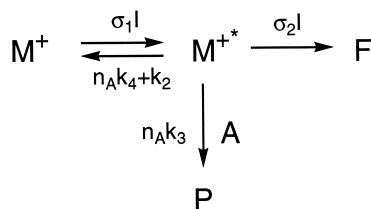
or

$$-I^2/\ln\{1 - F(t)\} = k_2/\sigma_1\sigma_2 t + I(\sigma_1 + \sigma_2)/\sigma_1\sigma_2 t + nk_1/\sigma_1\sigma_2 t \quad (3b)$$

By substituting the measured  $k_1$  in eq 3b, and by measuring the amount of fragment  $F(t)$  when varying the pressure and laser light intensity it is possible to calculate the ratio  $\sigma_1/\sigma_2$  and the radiative relaxation rate  $k_2$  using multiple regression. However, the subscripts 1 and 2 of the absorption cross sections are interchangeable in eq 3, so that it is not possible to assign experimentally determined values specifically to  $\sigma_1$  or  $\sigma_2$ . Therefore, two solutions of the ratio of the absorption cross sections are possible, which are  $\sigma_1/\sigma_2$  and  $\sigma_2/\sigma_1$ .

### Proton Transfer

Scheme 6 is an extension of Scheme 4 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  $A$ ,  $k_4$  the collisional relaxation constant for indene radical cations in the



**Scheme 6.** Reaction scheme for a pure two-photon dissociation process of  $M^+$ , in which the singly photon excited  $M^{+*}$  reacts with molecule A to give products P in competition with deactivation and absorption of a second photon to give fragments F (see the text).

presence of substrate molecules A, and  $k_3$  the bimolecular rate constant for reaction of  $M^{+*}$  with A.

From Scheme 6 it follows that the ratio of product P and fragment F ion abundances is given by eq 4:

$$P/F = n_A k_3 / \sigma_2 I \quad (4)$$

The solution of the differential equation for the kinetic model in Scheme 6, assuming—as in the case of two-photon dissociation at pressures in the order of  $10^{-7}$  torr [38]—that the radiative relaxation rate  $k_2$  is much smaller than the collisional relaxation rate  $n k_4$  and can be ignored, leads to eq 5:

$$\begin{aligned}
 -I(1 + I\sigma_2/n_A k_3)/\ln[1 - F(t)] &= (k_4 + k_3)/k_3 \sigma_1 t \\
 &+ (\sigma_1 + \sigma_2)/\sigma_1 k_3 t (I/n_A)
 \end{aligned} \quad (5)$$

Thus, a plot of  $-I(1 + I\sigma_2/n_A k_3)/\ln[1 - F(t)]$  versus  $I/n_A$  at several laser intensities and several pressures of the reference base should result in a straight line with

$$\text{The intercept } \phi = (k_4 + k_3)/k_3 \sigma_1 \quad (6)$$

and

$$\text{The slope } \epsilon = (\sigma_1 + \sigma_2)/\sigma_1 k_3 \quad (7)$$

From  $\phi$  and  $\epsilon$  and the determined ratio of  $\sigma_1/\sigma_2$ , the ratio of  $k_4$  and  $k_3$  can be calculated. It should be noted that, because of the ambiguity in the ratio of  $\sigma_1$  and  $\sigma_2$  (see above), this procedure leads to two possible values for the ratio of  $k_4$  and  $k_3$ .

## Results and Discussion

### Bracketing of the Proton Transfer from Laser-Light Excited Protonated Naphthalene

In our previous paper [29] it has been shown that protonated naphthalene dissociates following absorption of two photons of 488 nm and that following laser-light excitation it can transfer a proton to a suitable base in an endoergic reaction.

The results of bracketing experiments for this proton transfer performed in the present study are summarized in Table 1. They show that the excited protonated naphthalene ions can transfer a proton to a base having a proton affinity of  $744 \pm 2$  kJ/mol.

This means that, within the detection limit for these rather slow reactions, the proton transfer reaction can be as endoergic as 60 kJ/mol (0.6 eV) which is a relatively small amount of the energy (2.54 eV) initially deposited in the protonated naphthalene. This is surprisingly similar to the behavior of indene radical cations where 48 kJ/mol (0.5 eV) of the deposited energy (2.41 eV) appeared to be available for an endoergic proton transfer reaction. From UV-VIS spectra of protonated naphthalene in glasses it is known that in addition to phosphorescence also fluorescence occurs

**Table 1.** Bracketing of the proton transfer from laser-light excited protonated naphthalene to a reference base

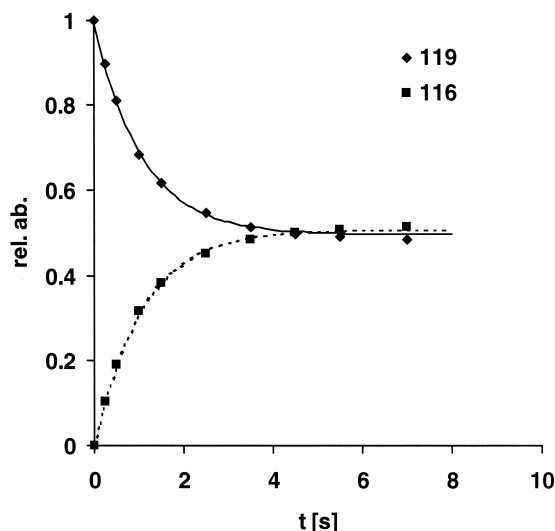
Reference base	Proton affinity (kJ/mol) [16]	Reaction	Pressure (torr $10^{-7}$ )
Naphthalene <sup>a</sup>	802.9		
Acetonitrile	779.2	+	2.3
Benzyl alcohol <sup>b</sup>	778.3	+	1.3
Ethylene oxide	774.2	+	2.0
Cyclopentene <sup>c</sup>	766.3	–	2.9
Nitromethane <sup>d</sup>	745.6	–	1.0
Cyclopropane	750.3	+	1.0
Chloro-acetonitrile	745.7	+	1.7
1,3,5-Trifluorobenzene	741.9	–	2.0
1,2,4-Trifluorobenzene	729.5	–	2.3
Iodoethane <sup>c</sup>	724.8	–	2.0
1,2,3-Trifluorobenzene	724.3	–	2.3
1,4-Difluorobenzene	718.7	–	2.0
Formaldehyde	712.9	–	1.9
Ethylene	680.5	–	2.0
Fluoromethane	598.9	–	2.0

<sup>a</sup>Naphthalene has been included for completeness.

<sup>b</sup>Complete H<sub>2</sub>O loss observed following proton transfer.

<sup>c</sup>Charge transfer observed.

<sup>d</sup>Proton transfer too slow for observation of product ions.

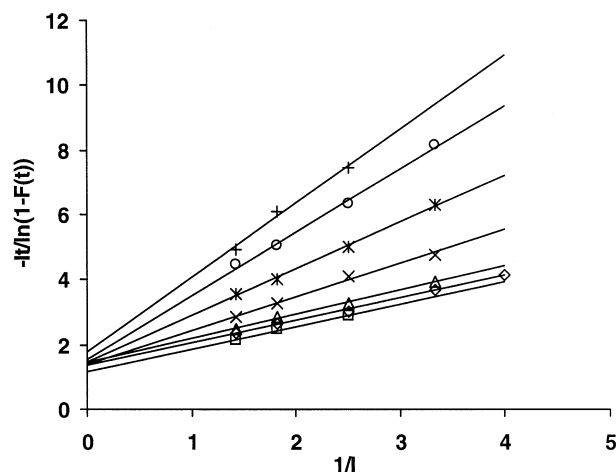


**Figure 2.** The relative abundances during the formation of an equilibrium of the via charge exchange formed indene radical cation ( $m = 116$ , filled square) and the reacting indene- $d_3$  radical cation ( $m = 119$ , filled diamond) measured as function of the reaction time. The pressure used for both neutrals was  $2.5 \times 10^{-8}$  torr.

[41–45]. The time for relaxation of the excited singlet state by fluorescence will be much smaller than the time between collisions in the ICR cell. Ab initio calculations on the energy of the triplet state of protonated acetonitrile as a possible product from reaction of protonated naphthalene in the triplet state, for which the lifetime is unknown, with acetonitrile have shown that this pathway is energetically unaccessible without a change of spin during the reaction. It is therefore anticipated that a significant part of the laser-light excited protonated naphthalene species undergoes internal conversion to a highly vibrationally excited ground state, which as in the case of radical cations [39, 40] will have a lifetime sufficient for a subsequent bimolecular reaction.

#### Determination of the Ratio of the Relaxation Rate of and the Rate of Proton Transfer from the Excited Indene Radical Cation

*Charge transfer from the indene- $d_3$  radical cation to neutral indene.* As discussed above, the ratio of the relaxation rate of and the rate of proton transfer from the excited indene radical cation  $k_4/k_3$  can be derived from the ratio of the cross sections for the first and second photon absorption,  $\sigma_1/\sigma_2$ , in the two-photon dissociation process. For the last ratio the rate constant  $k_1$  is required. This rate constant  $k_1$  has been obtained from the measurement of the rate constant for charge transfer from the ground state indene- $d_3$  radical cation to neutral indene, assuming that the relaxation of the excited indene radical cation occurs via this charge exchange. Figure 2 shows the decay of the molecular ion of indene- $d_3$  and the rise of the molecular ion of indene as a function of time. From an exponential fit of the curves



**Figure 3.**  $-It/\ln[1 - F(t)]$  vs.  $1/I$  for the indene radical cation at different pressures (see eq 3a). Pressures were:  $50 \times 10^{-8}$  (plus),  $43 \times 10^{-8}$  (open circle),  $30 \times 10^{-8}$  (star),  $20 \times 10^{-8}$  (multiplication),  $13 \times 10^{-8}$  (open triangle),  $3 \times 10^{-8}$  (open diamond),  $7.5 \times 10^{-8}$  (open square) torr.

in Figure 2 the rate constant for charge transfer has been derived to be  $7 \times 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . It should be noted that this is not an absolute value. It is, e.g., not corrected for the difference between the pressure in the ICR cell and its value read from the ionization gauge.

*Two-photon dissociation of indene radical cations at 514.5 nm.* As in previous papers [38], Figure 3 shows  $-It/\ln[1 - F(t)]$  versus  $1/I$  for different pressures (see eq 3a). In this earlier work the values of  $\sigma_1/\sigma_2$  and of  $k_2$  were determined from the intercept by plotting the slopes of the curves versus pressure. In the present work we used multiple regression instead (see eq 3b). The resulting value of  $\sigma_1/\sigma_2$  was 9 (or 1/9), whereas  $k_2$  was  $2 \text{ s}^{-1}$ .

*Proton transfer from the indene radical cation to 3-pentanone.* Subsequently the ratio of the rate constants for relaxation of and proton transfer from the excited indene radical cation,  $k_4/k_3$ , in the presence of a gas-phase neutral reference base has been determined.

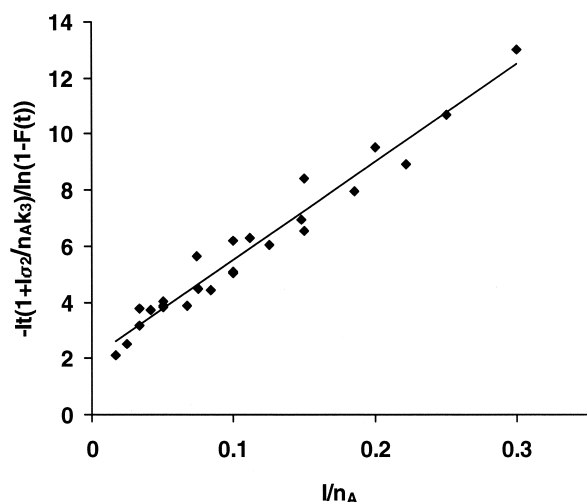
To this end the laser light intensity and the pressure of the neutral reference base 3-pentanone in the presence of indene radical cations have been varied.

The results are plotted as  $-It(1 + I\sigma_2/n_A k_3)/\ln[1 - F(t)]$  versus  $I/n_A$  (eq 5) in Figure 4.

From the intercept and the slope of the line in Figure 4 the ratio  $k_4/k_3$  has been calculated using eqs 6 and 7 given above. The results have been summarized in Table 2.

#### Discussion

Although the value of  $k_4/k_3$  may be either about 100 or about 10 (Table 2), it is clear that for the single photon excited indene radical cation the rate of its proton transfer to a base is considerably slower than its rate of



**Figure 4.**  $-\ln(1 + I\sigma_2/n_A k_3)/\ln[1 - F(t)]$  vs.  $I/n_A$  for indene radical cations in the presence of neutral 3-pentanone at different pressures and light intensities (see eq 5).

relaxation by nonreactive collisions. Here it should be noted that Scheme 6 is of course a simplification and that during relaxation the overall rate of proton transfer will decrease. One may therefore assume that the major part of the reaction products will be formed when the average internal energy is still relatively high. Taking a CH stretching frequency of  $3000\text{ cm}^{-1}$ , the observed 0.5–0.6 eV energy available for proton transfer corresponds with 1.5 vibrational quanta in the relevant CH bond. Assuming energy randomization, this does not seem unreasonable for the possibility of reaction. Because prior to energy randomization internal conversion to a highly vibrationally ground state has to occur, it is important to measure the quantum yields for fluorescent and phosphorescent relaxation of the single photon excited indene radical cation to estimate the amount of internal conversion.

## Conclusions

In this study it has been shown possible to determine the threshold for proton transfer from laser-light excited protonated naphthalene to a base in the gas phase by use of the bracketing method as applied in our previous study to the laser-light excited indene radical cation [30]. For protonated naphthalene excited by light of 488 nm (2.54 eV) it has been found in this way that the proton transfer to a base can be as endoergic as 60

**Table 2.** Ratio  $k_4/k_3$  determined from the intercept and slope of the line in Figure 3 and use of the determined value for  $\sigma_1/\sigma_2^a$

$\sigma_1/\sigma_2$	$k_4/k_3$
9	9
1/9	80

<sup>a</sup>Because of the symmetry of the formula for the two-photon dissociation process, two values for the ratio  $\sigma_1/\sigma_2$  are possible.

kJ/mol. This value is very similar to that for the radical cation of indene excited by light of 514.5 nm (2.41 eV) where the proton transfer to a base can be as endoergic as 48 kJ/mol. The observed 0.5–0.6 eV energy available for proton transfer to a base seems reasonable when taking into account a complete randomization of the initially deposited energy in the ions.

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