

Laser induced reactions in a 22-pole ion trap

Stephan Schlemmer^{1,2} and Oskar Asvany¹

¹ Raymond and Beverly Sackler Laboratory for Astrophysics, Leiden Observatory, PO Box 9513, 2300 RA Leiden, The Netherlands

² I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany

E-mail: schlemmer@ph1.uni-koeln.de

Abstract. The method of laser induced reaction (LIR) is used to obtain an IR spectrum of bare CH_5^+ in the range of 250 to 3200 cm^{-1} . The experimental spectrum compares rather favorable to theoretical predictions based on molecular dynamics simulations except for the very low frequency range below 500 cm^{-1} . An equation relating the experimental LIR signal to the absorption coefficient and the rate of reaction of the excited species as well as a simple model for the reaction rate coefficient of the laser excited molecules is derived. A variety of LIR schemes are exemplified and their value for IR spectroscopy of molecular ions is discussed.

1. Introduction

Dissociative recombination (DR) is one of the most important processes in the interstellar medium since it is the final step in a series of ion molecule reactions which lead to the rich variety of gas phase molecules in this astrophysical environment [1]. The present debate on the size of the rate coefficients for DR for many systems is closely related to the influence of vibrational and rotational excitation [2]. In order to unravel this influence the ro-vibrational or rotational population of an ensemble of ions has to be determined, e.g. by means of spectroscopy, see also the contribution by Kreckel *et al.* [3]. However, spectroscopy of molecular ions is a rather difficult task. By nature they are transient species, which are hard to form in sufficiently high densities to do absorption spectroscopy. In addition, due to the formation process they are often electronically or vibrationally excited. Recent developments in this field make use of VUV ionization of initially cold parent molecules. REMPI techniques have been used for about twenty years to prepare ions in well defined ionic states [4]. This method has the disadvantage that only species with favorable resonant intermediate states can be accessed. This difficulty is circumvented when using synchrotron radiation ionizing the cold molecules in a one photon process [5,6]. With the advent of high power VUV lasers such experiments can be of table top size [7] with even higher resolution compared to synchrotron facilities. All these techniques are restricted to primary ions or to molecular ions which have a favorable neutral precursor.

With the availability of intense tunable IR radiation the photodissociation of covalently bound molecular ions became possible. The benefit of this technique lies in the preparation of mass selected parent ions and the very efficient detection of the photoproducts which overcomes the limitation of producing ions in small quantities. Prominent examples include the vibrational spectra of polycyclic aromatic hydrocarbon (PAH) cations [8] and the spectrum of the H_5O_2^+ molecule [9]. Interpretation of these infrared multiphoton dissociation (IRMPD) spectra is difficult. In contrast, spectra of weakly bound systems, such as solvated ions like $\text{CH}_5^+(\text{H}_2)_n$ [10, 11] or others can be obtained after the absorption of only one photon [12]. One disadvantage of this method is that the spectra are always shifted with respect

to the bare ion. However, a strong advantage of the latter methods lies in the fact that experiments start with mass selected, favorably cold ions without restrictions to primary ions. Molecular beams combined with ionization as well as guiding and trapping techniques are used to prepare the ions. The benefit of the trapping technique lies in the confinement of the ion cloud and in the exceptional detection efficiency of mass selected products. The use of higher order multipole ion traps allows for the preparation of cold parent ions.

Laser induced reactions (LIR) combines the advantages of the trapping technique with the idea of using a chemical reaction to probe the internal state of the parent ion. Chemical probing simply separates reactive from non-reactive species. A very comprehensive example of chemical probing without the use of a laser is the distinction between the metastable HOC^+ ion from its ground-state HCO^+ counterpart. While the metastable molecule undergoes efficient proton transfer with CH_4 , this process is endothermic for the ground state species. Thus the amount of metastable species is inferred in a trap experiment by the detection of CH_5^+ ions [13]. In LIR, laser excited species are detected via chemical probing due to the different reactivities of ground state and excited species.

Here the LIR spectrum for CH_5^+ is presented and the correlation between the LIR signal and the traditional absorption coefficient is derived. After the description of the setup in the experimental section, the measured spectrum is compared to a calculated one in the result section. An equation for the LIR signal and a simple model for the reaction rate coefficient of the excited species is derived. In the discussion section several possible LIR schemes are discussed and their benefits for future ion spectroscopy are explained.

2. Experimental section

The experimental procedure is described using the setup shown in figure 1. Central part of this apparatus is a 22-pole ion trap which has been described in detail in [14]. The CH_5^+ parent ions were produced by ionization of pure methane gas and the subsequent reaction $\text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CH}_3$ in an external storage ion source. Ionizing electrons with low kinetic energies (< 18 eV) were utilized to avoid internal excitation of the species. Trapping the ions in this source allowed to keep the pressure of the methane gas below 10^{-5} mbar and to cool the CH_5^+ cations to the source temperature of 350 K by non-reactive collisions. After mass selection in the first mass filter, an ensemble of several thousand CH_5^+ ions was stored for 4 s in the cold CO_2 gas environment of the 22-pole ion trap and exposed to the tunable IR light of the free electron laser FELIX [15]. The trap temperature was kept at $T = 110$ K in order to minimize freeze-out of CO_2 . Due to this freeze-out the effective target gas density could not be determined. Instead, it has been adjusted by monitoring the product signal (without laser interaction) in order to maximize the CO_2 density without allowing for products without laser interaction. Even though the rate for this process is much lower, at rather high target densities the rate at which products can be formed even without laser interaction could be substantial. After the storage period, the number of the mass selected reaction products were counted and the laser was tuned to the next frequency. For improving the S/N ratio, the scan was repeated two times.

The FELIX laser was operated at its maximum repetition rate of 10 Hz with pulses having a typical length of $7 \mu\text{s}$, a 1 GHz substructure and an energy content varying from 10 to 30 mJ (at user station), depending on the wavelength region. Laser power measurements have been carried out at the point where the beam entered the trapping machine. The unblocked passage of the IR beam through the machine has been checked by the transmission of a He-Ne laser beam coaxially to the IR beam and by monitoring the outcoupled IR beam using a pyroelectric detector. Synchronization of the laser pulses of FELIX and the ion pulses of the 22-pole trapping machine was not necessary due to the long ion trapping time of 4 s and the high laser repetition rate.

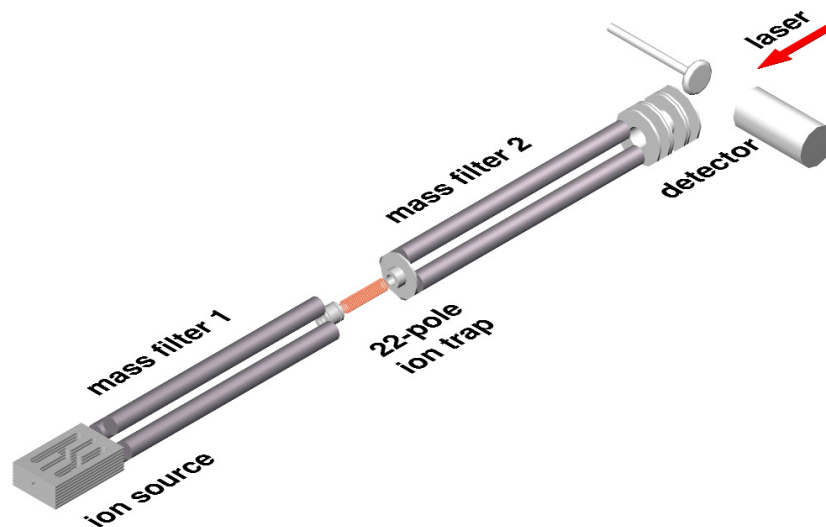
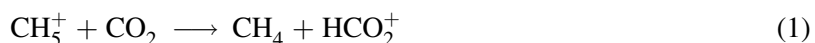


Figure 1. Schematic setup of a trapping apparatus as used for laser induced reactions (LIR). The ions are generated and collected in the *storage ion source*, mass selected in the quadrupole *mass filter 1* and then stored in the *22-pole ion trap*. On entrance the ions are cooled down to the ambient cryogenic temperature by a short intense helium pulse. During the storage period of several seconds, the ions are subject to reactant gas molecules and tunable *laser* light (coming from the right through the axially transparent setup). The result of this interaction is detected by extracting the stored ion cloud into *mass filter 2* and counting the number of product ions in the *detector*. By repeating this process while scanning the IR laser, an IR action spectrum of the stored parent ions is recorded.

3. Results, analysis and discussion

For LIR of CH_5^+ use has been made of the similarity of the proton affinity for methane and CO_2 . The reaction



is endothermic by only 3 kJ/mol. As it turned out IR excitation of the parent ion is promoting the proton transfer. Detection of HCO_2^+ could be used to record an action spectrum of CH_5^+ . The result is shown in figure 2(a). The spectrum contains two main bands, one at the position of the C-H stretch region (3000 cm^{-1} , [16]) and one in the H-C-H bending region (1200 cm^{-1}). In addition the stretching region has a structured low frequency part which has been associated with a vibration of those hydrogen atoms in CH_5^+ which entertain a three center two electron (3c-2e) binding [17]. This interpretation stems from the comparison to the theoretical spectrum which is shown in figure 2(b). For the underlying interpretation of the spectral features see [17]. Comparison of experiment and theory are quite favorable for the main experimental features. However, for a more quantitative comparison attention has to be paid to the LIR intensities.

LIR intensities

The collision with the neutral reactant gas is an integral part of the detection in a LIR spectrum. This has to be taken into account when interpreting a LIR action spectrum and comparing it with theoretical absorption spectra. A model for the kinetics of the LIR process is depicted in figure 3(a) where the situation for an endothermic process (I) or for a thermoneutral bimolecular reaction with a barrier (II) is shown. The kinetics for LIR of the endothermic proton transfer is described by photon absorption (rate K_1) which leads to the population of the excited state. From this state the parent ion can either react to products (rate K_2) or back to the ground state (rate K_3). In a trap experiment products usually can not

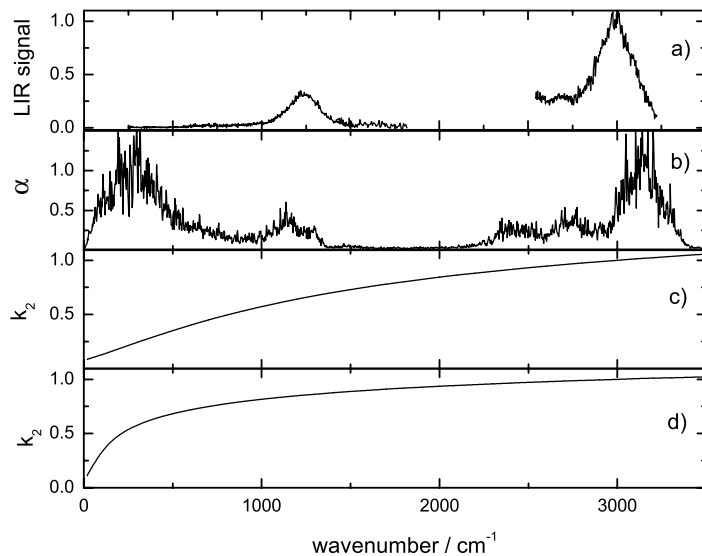


Figure 2. IR spectra of bare CH_5^+ : (a) experimental LIR spectrum, (b) theoretical absorption spectrum, $\alpha(\nu)$, as calculated by Marx and Kumar [17], (c) model description for k_2 assuming a redistribution of the absorbed photon energy, $h\nu$ among all degrees of freedom of the $\text{CH}_5^+ + \text{CO}_2$ collision system, (d) same as (c) but redistribution of the excitation energy only within the CH_5^+ molecule.

undergo the back-reaction (rate K_{-2}) since no neutral reactants for this reaction are available. In this simple model the total rate at which products are formed will be given by

$$K = K_1 \cdot \frac{K_2}{K_2 + K_3}. \quad (2)$$

The excitation rate, K_1 , is given by the product of the Einstein B coefficient for the particular transition times the population of the ground state, abbreviated g , and times the energy density of the laser field, ρ [18]. Here it is assumed that only one ro-vibrational state is excited. If more than one state is excited the sum of the products $B \cdot g$ has to be taken into account. The consequences of this to a low resolution spectrum will be discussed below. The reaction rate K_2 is given by the product of the rate coefficient k_2 times the number density of the reactant molecule, $[\text{CO}_2]$. The relaxation of the excited parent ion is given by the Einstein A coefficient for fluorescence (in fact the sum of the Einstein coefficients of the ro-vibrational transitions) and by the rate of quenching, k_3 times $[\text{CO}_2]$. It has been found by numerical simulations of the LIR experiment of the stretching vibration of C_2H_2^+ that the sum of the collisional quenching rate coefficient, k_3 and the reaction rate coefficient, k_2 add up to the collisional rate coefficient which can be approximated by the Langevin limiting rate, $k_L \sim k_{\text{coll}} = k_2 + k_3$. Making these assumptions also for the case of CH_5^+ , equation (2) can be rewritten as

$$K = B \cdot \rho \cdot g \cdot \frac{k_2 \cdot [\text{CO}_2]}{A + k_{\text{coll}} \cdot [\text{CO}_2]}. \quad (3)$$

The denominator in this expression is composed of one term involving a collision with CO_2 and one without. Therefore a low pressure and a high pressure limit can be distinguished. The more relevant case, where enough target gas is supplied to obtain a maximum LIR signal is given in the high pressure limit ($A \ll k_{\text{coll}} \cdot [\text{CO}_2]$):

$$K = \frac{k_2}{k_{\text{coll}}} \cdot B \cdot \rho \cdot g \quad (4)$$

More detailed density dependencies have to be recorded in future experiments to justify this assumption and also to rule out contributions to the LIR signal from any CH_5CO_2^+ clusters formed in the trap experiment. In general only a small fraction of the stored parent ions are excited by the laser. If no competing reaction reduces the number of parent ions a simple expression for the number of product

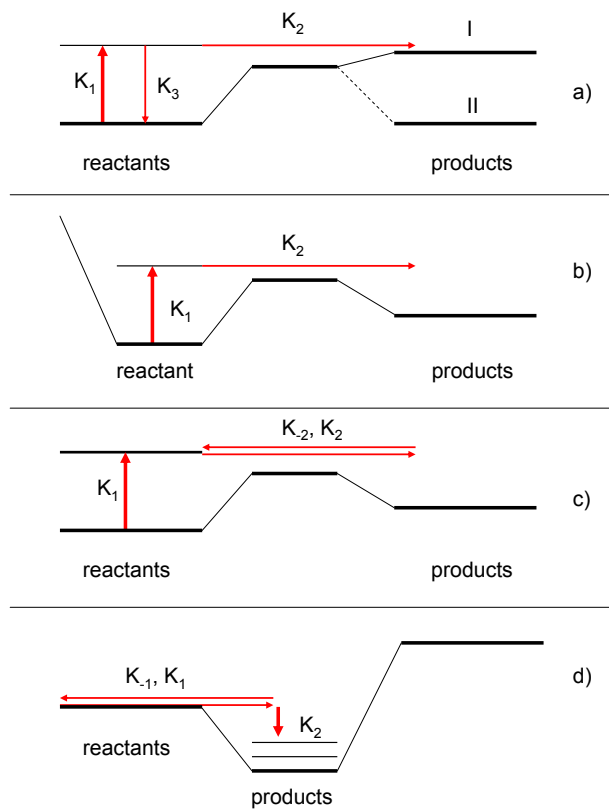


Figure 3. Schematic description of model reaction systems suitable for LIR spectroscopy. (a) bimolecular reaction initiated by laser excitation of a ro-vibrational state. Details of the rates K_i are given in the text. (b) unimolecular reaction: Vibrational predissociation spectroscopy. (c) shift of the equilibrium of a bimolecular reaction due to laser excitation. (d) stimulated association of a molecule.

ions can be derived for a given number of initially stored primary ions and a fixed storage time, Δt :

$$[\text{HCO}_2^+] = [\text{CH}_5^+] \frac{k_2}{k_{\text{coll}}} \cdot B \cdot \rho \cdot g \cdot \Delta t \quad (5)$$

For comparison of experimental and theoretical spectra the LIR signal is divided by the spectral energy density ρ of the laser. This LIR signal is indeed shown in figure 2(a).

The number of states pumped at the same time depends on the resolution of the laser used. The spectral resolution of FELIX is bandwidth limited to about 0.5%, $\Delta\nu \approx 5 \cdot 10^{-3} \nu$. For an even distribution of rotational lines in the spectrum it can be assumed that the number of states pumped at once, g , is also proportional to the bandwidth and thus to the frequency of the laser, $g \sim \Delta\nu \sim \nu$. In this circumstance the LIR signal is in fact proportional to the product of the rate coefficient k_2 times the absorption coefficient α .

$$[\text{HCO}_2^+] \sim \alpha(\nu) \cdot k_2 \quad (6)$$

On the basis of this simple analysis a quantitative comparison between the LIR action spectrum and the theoretically predicted spectrum becomes possible. In the theoretical approach the full vibrational spectrum (absorption coefficient $\alpha(\nu)$) of bare CH_5^+ has been computed at finite temperatures from the Fourier transform of the classical time-autocorrelation function of the total dipole moment. According to equation (6) the ratio of the experimental and the theoretical spectrum should give an idea about the mode specific behavior of the reaction under consideration. Comparing the C-H stretch region to the H-C-H bending region, see figure 2(a), the relative intensities for the experiment and theory are about 3 : 1 in both cases. Therefore one would conclude that the rate coefficients, k_2 , are comparable too for these two vibrations.

A large difference is detected when comparing the intensities at much lower wavenumbers. A clear LIR signal is detected down below 500 cm^{-1} . However, it is decreasing strongly already below 1000 cm^{-1} . In contrast, the theoretical work predicts substantial absorption below 500 cm^{-1} . As a result one is tempted to conclude that the excitation of very low frequency vibrations does not promote the proton transfer. This would not at all be surprising since the reaction is endothermic and therefore the addition of a small amount of energy in form of a vibrational excitation of CH_5^+ might not be sufficient to overcome the endothermicity efficiently.

Such a behavior of the wavelength dependence of the rate coefficient, k_2 , might be described by a rather simple model in which the mode selective excitation may be distributed into all degrees of freedom. This effective increase of the collision temperature leads to an enhancement of k_2 . For a floppy molecule like CH_5^+ with large anharmonicities and large amplitude motions such a redistribution of the excitation energy is quite possible. After all, such a redistribution might also come about in the course of the collision which leads to the formation of products. It is straightforward to calculate the effective temperature increase due to the absorption of a photon with energy $h\nu$ by equating the energy content of the system prior and past the absorption process

$$\langle E(T) \rangle = \langle E(T_0) \rangle + h\nu \quad (7)$$

As the reaction is thermally activated the Arrhenius expression might be used to describe the temperature dependence of the rate coefficient, k_2 .

$$k_2(\nu) \sim \exp\left(\frac{-E_a}{kT(\nu)}\right) \quad (8)$$

This simple behavior is plotted as a function of the excitation frequency in figure 2(c) and (d) for two cases. In both cases the activation energy is $E_a = 3\text{ kJ/mol}$ [19]. The calculations have been normalized to the corresponding value at 3000 cm^{-1} . In both cases there is a clear increase in the reaction rate going from very low frequencies up to the C-H stretching region. The shape of both curves is slightly different. For the calculation in figure 2(c) it is assumed that the photon energy is distributed among all degrees of freedom (translation, rotation, and *active* vibrational states) of both, CH_5^+ and CO_2 . The vibrational frequencies for this have been taken from the harmonic analysis of the CH_5^+ [20] and the well known frequencies of CO_2 . This description resembles the assumption that the energy is distributed during the collision prior to the exchange of the proton. At present it is quite unclear whether this is the case. Therefore as another possibility the redistribution only among the vibrational degrees of freedom within the CH_5^+ subunit has been calculated assuming that the increased CH_5^+ temperature is governing the temperature dependence of k_2 . The result is shown in figure 2(d). At first glance the two situations do not differ a lot. However, on the one hand figure 2(c) shows a shallower increase at low frequencies as compared to figure 2(d). On the other hand this trend is reversed for higher frequencies. As a consequence there is only a difference of 15% when comparing the C-H stretching region to the H-C-H bending region for the case (d) while case (c) shows a drop of about 35%. In view of the comparison of the experimental and theoretical results of figure 2(a) and (b), case (d) seems more favorable. However, both model calculations are unable to explain the discrepancy between theory and experiment in the low frequency regime.

The approximations made for the present comparison between theory and experiment as well as for the modeling of the rate coefficient k_2 need refinement. However, the present treatment represents the first detailed attempt to link LIR action spectra to theoretical absorption spectra. More detailed experiments exploring the density dependence of the LIR signal of CH_5^+ are necessary to justify the assumptions made in the present analysis. In addition, more quantitative calculations of the influence of the limited resolution of the laser excitation on the LIR signal are necessary. An alternative approach is the use of high resolution lasers so that most of the rotational and potentially low frequency vibrational substructure will be resolved. In such a case the LIR signal will be given by the product of the Einstein B coefficient and k_2 . Due to the simple relation between B and α a detailed comparison between experiment and theory is possible and favorable due to fewer assumptions.

4. Future perspectives of LIR

Up to date several reaction systems have been studied with the LIR method for bimolecular reactions which is depicted in figure 3(a). The slightly endothermic charge transfer (CT) process between N_2^+ and Ar has been initiated by electronic $A \leftarrow X$ excitation of the N_2^+ parent ion. After rapid fluorescence a large fraction of the laser excited N_2^+ is found in vibrational excited states. In collisions with Ar CT is energetically allowed and proceeds. Rotationally resolved spectra of N_2^+ have been recorded and the rate coefficients for the associated processes have been determined [21]. Another study concerns the vibrational excitation of the $C_2H_2^+$ ion. In a first set of experiments the C-H stretching region has been explored. Employing a difference frequency mixing laser system rotationally and fine-structure resolved spectra have been recorded. Using a numerical simulation of the reaction system under consideration detailed rate coefficients and the fluorescence lifetime of the ν_3 mode of $C_2H_2^+$ have been determined [18]. More recently the antisymmetric cis-bending vibration of $C_2H_2^+$ has been detected with LIR. The vibrational frequency of this vibration and the size of the Renner-Teller splitting have been determined experimentally for the first time [22]. A detailed analysis of this work which reveals for example that the fluorescence lifetime of the ν_5 mode is on the order of 100 ms is underway [23].

All these reactions fall in the class of endothermic reactions depicted in figure 3(a). The constraints imposed by this reaction scheme seem to restrict the number of possible candidates substantially. However, as an example, proton transfer as in the present case is a reaction for which it is not so hard to find a neutral species with a slightly smaller PA. This leads to a rather large class of ions which can become the subject of LIR. Another class concerns the hydrogen transfer reaction as has been used for the $C_2H_2^+$ system. Other systems like the slow reaction of C_3H^+ with H_2 are interesting candidates.

Another set of reaction systems is depicted in figure 3(b). This scheme shows the unimolecular decay of a vibrationally excited parent ion which has been widely used in many laboratories to obtain vibrational predissociation spectra of weakly bound complexes as mentioned above. In view of the present study on CH_5^+ the work on the solvated CH_5^+ is especially interesting. Successive solvation of the parent ion by H_2 molecules leads to a freeze-out of scrambling in the CH_5^+ core. This transition becomes apparent in the IR spectrum of C-H stretching region as the broad vibrational band separates into distinct features. Due to the availability of intense IR laser fields, e.g. FELIX, it became possible to extend the scheme (b) to covalently bound molecules by multiple absorption of photons which can heat up the molecule to the dissociation limit.

LIR of bimolecular processes, like in the present case, has the big advantage over the vibrational predissociation spectroscopy that no matrix shifts hamper the interpretation of the spectra. In addition only one photon is needed to promote the reaction. Therefore the spectra can be linked to theoretical work. Moreover, LIR spectra contain the interesting information about the mode specific reactivity, i.e. the influence of specific internal motions to promote a reaction.

LIR can be extended further by at least two more schemes which are depicted in figure 3(c) and (d). In many reaction systems which are almost thermoneutral as shown in figure 3(c) reactants and products are separated by a small barrier which can be overcome to some degree even at low temperatures. One example is the isotopic exchange of a hydrogen atom by a deuterium atom as in the case of the prototype reaction $H_3^+ + HD \rightarrow H_2D^+ + H_2$. Without the influence of a laser field an equilibrium situation between the forward and backward reaction (rates K_2 and K_{-2}) is established. The excitation of one of the species shifts the equilibrium substantially. Thus the excitation of the parent molecule is detected by an increase of products like in case (a).

In all cases discussed so far a barrier of some kind on the reaction pathway was essential for LIR to work. In figure 3(d) the stimulated association of a molecule is depicted. When the ion collides with the neutral partner a new molecule or complex can be formed when excess energy is carried away by the emission of a photon. This exothermic reaction can be enhanced by stimulating the emission of a photon. For this method to work the rate of stimulated emission needs to be faster than the one for spontaneous emission. With the use of intense laser light this LIR scheme shall become feasible. One of the most interesting aspects of this approach lies in the fact that vibrational stabilization can be distinguished

from electronic transitions simply by the frequency range of the transition. In this way the physics and chemistry of molecules at the dissociation threshold can be explored experimentally. In conclusion a wide field of applications is foreseen for LIR studies.

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