

## Laser Induced Reactions in a 22-Pole Ion Trap

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Trapping of molecular ions in high order multipole traps is a well established versatile tool for investigating ion-molecule reactions. Unimolecular decomposition of complexes close to the dissociation limit<sup>1</sup>, bimolecular reaction<sup>2</sup> as well as termolecular association<sup>3</sup> have been studied for many reaction systems. The high sensitivity of the method has been demonstrated for various reactions at low temperatures and low densities where radiative association prevails.<sup>1,4</sup> In most associative reactions the rate coefficient is proportional to the lifetime of the collision complex which is strongly dependent on the total energy above dissociation. Using laser methods, e.g. REMPI, reactant ions can be prepared in particular quantum states in order to find out which kind of energy, i.e. which degree of freedom, drives a reaction. For the association of  $\text{CO}^+ + 2 \text{CO} \rightleftharpoons (\text{CO})_2^+ + \text{CO}$ ,  $\text{CO}^+$  reactants have been produced selectively with respect to their rotational state<sup>5</sup>, and it turned out that rotational and translational energy equally shorten the lifetime of the collision complex.

For endothermic reactions or reactions which are hindered by a barrier we developed the method of laser induced reaction (LIR) in order to drive a reaction which is slow at the temperatures of a trap experiment<sup>6</sup>. Here cold trapped molecular ions are excited to a particular quantum state and the reaction is monitored by the very sensitive detection of the products (chemical probing). As a first example we demonstrated the method for the charge transfer (CT) reaction  $\text{N}_2^+ + \text{Ar} + h\nu \rightarrow \text{Ar}^+ + \text{N}_2$  where laser excitation of  $\text{N}_2^+$  (A-X) is followed by “rapid” fluorescence into (mostly) vibrationally excited  $\text{N}_2^+$ . The vibrational energy is sufficient to surmount the endothermicity of this CT reaction and it is well known that this excitation readily leads to reaction in almost every collision. Scanning the laser frequency of the ~786 nm laser diode LIR provides a method of action spectroscopy. A fraction of the R<sub>11</sub> branch of the  $\text{N}_2^+$  spectrum is shown in Fig. 1.

The most interesting features of this spectroscopy are that (1) detection via chemical probing leads to spectra which are basically background free. (2) Correspondingly the S/N level of a spectrum is given by the total number of product ions. Note that Fig. 1 shows the result for only a few thousand parent ions. (3) The ions are cold and therefore the level pumped by the laser has a significant population thereby increasing the sensitivity of the method. (4) The trapped parent ions are mass selected. Therefore the spectra are not spoiled by contributions from other ions which is a major draw back in conventional spectroscopy of molecular ions in plasma tubes. These advantages of action spectroscopy also hold for the method of vibrational predissociation spectroscopy for the investigation of the structure and dynamics of weakly bound (van der Waals) complexes which is well established in several laboratories, see e.g. Ref. 8. Note however, that the recent development is an extension of the method of laser induced reaction from unimolecular towards bimolecular processes. The sensitivity of LIR depends on several parameters due to the competition between reaction and relaxation of the excited species.

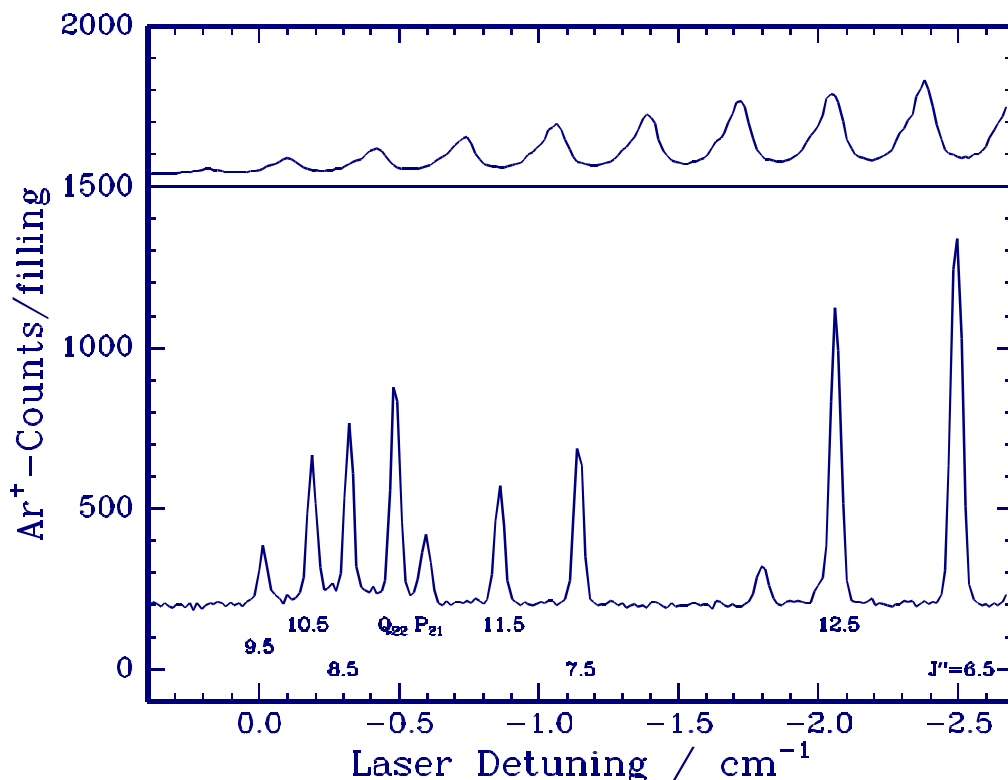


Figure 1: Rotationally resolved action spectrum of  $N_2^+$  in the region of the band head of the  $R_{11}$ -branch of the  $(A^2\Pi_u(v=2) \leftarrow X^2\Sigma_g(v=0))$  transition. The temperature stabilized diode laser is tuned by scanning the injection current of the diode. *Upper trace:* Fringes of a 9.8 GHz etalon are used for frequency calibration. *Lower trace:*  $Ar^+$  ions from laser induced charge transfer serve as a monitor for detection of the spectrum. Note that the spectrum is essentially background free.

More recently we applied LIR to the reaction  $C_2H_2^+ + H_2 \rightarrow C_2H_3^+ + H$ . This reaction is endothermic by about 50 meV<sup>7</sup> and has a rate coefficient well below  $10^{-12}$  cm<sup>3</sup>/s at the temperatures of our experiment (10 - 150 K). The only other reaction channel, radiative association ( $\rightarrow C_2H_4^+ + h\nu$ ), is a slow process for this system at densities below  $10^{11}$  cm<sup>-3</sup>. Therefore at low temperatures  $C_2H_2^+$  parent ions can be stored for long times. Such a sample has been exposed to IR light from a pulsed laser system at about 3140 cm<sup>-1</sup> in order to excite the asymmetrical C-H stretching mode ( $\nu_3$ ) of the acetylene ion. This frequency has been produced by difference frequency generation of a Nd:YAG pumped dye laser with the fundamental of the seeded Nd:YAG. Scanning the laser frequency,  $C_2H_3^+$  products were collected after a storage time of two seconds for twenty trap fillings. The result of such a scan is shown in Fig. 2. It shows the two P-branches of the  $\nu_3$  fundamental for the two spin orbit levels of  $C_2H_2^+$ . The positions of each individual rotational level are depicted by the two scales at the top. The line positions were taken from the high resolution data of Oka's group<sup>9</sup>. Obviously, they are in very good agreement with the present result. The S/N ratio is slightly reduced as compared to the  $N_2^+$  results which is mainly due to initially hot acetylene ions which lead to an increased background level.

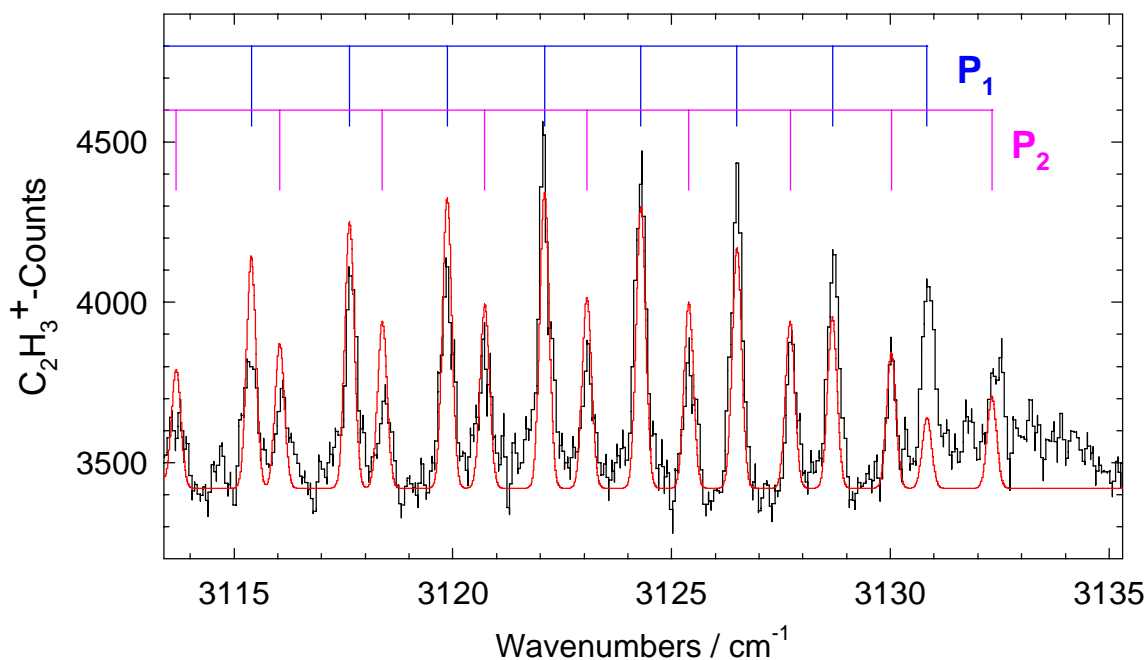


Figure 2: P-branch of the LIR action spectrum ( $\text{C}_2\text{H}_2^+ + \text{H}_2 + h\nu_{\text{IR}} \rightarrow \text{C}_2\text{H}_3^+ + \text{H}$ ) of acetylene (exp. conditions  $T = 90 \text{ K}$ ,  $[\text{H}_2] = 2.7 \cdot 10^{11} \text{ cm}^{-3}$ , storage time = 2 s, 20 trap fillings per point). The two scales depict the spectral positions for the rotational states of the two spin orbit levels of  $\text{C}_2\text{H}_2^+$ . The gray solid line is a simulation of the spectrum which is explained in the text. Differences in intensity of the calculated and measured spectrum indicate that rotation of  $\text{C}_2\text{H}_2^+$  hinders reaction.

Nevertheless this spectrum presents the first result of a more general scheme for high sensitivity, high resolution IR spectroscopy. Its necessities are (i) a bimolecular reaction which is slightly hindered in one direction, (ii) competitive reaction channels must not be much faster and (iii) the reactivity must be enhanced by the laser excitation. At first sight this restricts the number of possible candidates substantially. However, there are whole classes of reactions which fulfil these requirements, e.g., isotope exchange reactions which due to the difference in zero point energy are always hindered in one direction.

In addition to the spectroscopic information the results from our LIR trap experiments contain information about the kinetics and dynamics of the involved reaction steps. For example the number of product ions in the action spectra do not only depend on the absorption intensity of the parent ion but also on the relaxation rate of the excited state and the reaction probability of the corresponding quantum state excited. In order to show this difference the experimental spectrum of  $\text{C}_2\text{H}_2^+$  in Fig. 2 is compared to a simulation, which is based on (i) the thermal population of the ground state levels, (ii) the probability for absorption, and (iii) radiative relaxation of the excited ion. The calculated spectrum underestimates the contribution of the smaller rotational levels (right in Fig. 2) and overestimates the contribution of the larger

rotational levels (left) for both fine structure contributions. Although this analysis does not account for the complete kinetics describing the stored ion cloud, we conclude that the rate coefficient for vibrationally excited  $C_2H_2^+$  depends on the rotational state. It is surprising, that rotational energy hinders the weakly endothermic reaction.

Besides the main steps (excitation, relaxation, reaction) which are directly related to the LIR process several other processes influence the finite ensemble of ions (hole burning, radiative association, rotational and fine structure relaxation). The role of all these processes has been studied by determining the temporal evolution of the trap content under different conditions (laser intensity, pulsed and continuous mode, target gas density, temperature). For both reaction systems, various rate coefficients have been measured. For  $N_2^+$  the most surprising result concerns a slow rotational relaxation in the ground state. Fine structure and hyperfine structure relaxation are also very slow, as expected. For  $C_2H_2^+$  a preliminary analysis of very recent measurements with a cw lead salt diode laser reveals that more than ten collisions are necessary for the excited species to react. This indicates that the vibrational energy of almost 400 meV is not available in every collision to overcome the much smaller endothermicity of the reaction or that the C-H stretching motion is not driving the reaction. This work is still in progress. In future studies we want to apply this new method to other interesting reactions, e.g.,  $C_3H^+ + H_2$ ,  $CH_5^+ + X$ , etc.

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