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Enhancing of the signal-to-noise ratio in MATI spectra

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Abstract

The aromatic hydrocarbon derivative *p*-xylene has been investigated using MATI spectroscopy. The apparatus used in this experiment was a standard reflectron time-of-flight mass spectrometer (ReTOF). A study of the dependence of the MATI signal on the laser intensity has been performed showing that the MATI signal strength and thus the signal-to-noise ratio of the MATI spectrum can be greatly enhanced. The spectral resolution is not affected by this signal enhancement.

Keywords: MATI spectra; Signal-to-noise ratio; *p*-Xylene; Multiphoton absorption; Multiphoton ionization

1. Introduction

Zero kinetic energy (ZEKE) and mass analyzed threshold ionization (MATI) spectroscopy have become widespread techniques to study molecular ions and opened new ways in the investigation of highly activated atomic and molecular states. Ionization energies determined by ZEKE spectroscopy, which leads to the best resolutions in this field, show an error of only 0.2 cm^{-1} [1–3]. MATI spectroscopy, though based on the same physical principles as ZEKE spectroscopy, can be performed with a simpler set-up than ZEKE and offers the possibility of mass analysis, so that even mixtures can be investigated [4,5]. The resolution and signal strengths are normally reduced [4] compared to similar ZEKE experiments because ions are detected instead of electrons. While the MATI resolution can be enhanced to reach the near-ZEKE resolution using specially shaped electrical pulses [6,7], the reduced signal strength and the signal-to-noise ratio remain a problem typical for MATI experiments. This problem becomes worse when going via less intensive intermediate states.

Addressing this problem of less intense signals, we recorded MATI spectra of *p*-xylene with a standard reflectron time-of-flight mass spectrometer (ReTOF) generally used in our experiments [8]. To be able to perform MATI experiments minor alterations have been applied to the instrument described in Section 2. No pulse forming devices, such as a function generator, have been added. We increased the MATI signal strength by increasing the intensity of the pump laser system and were thus able to record spectra via less intensive intermediate states. This provides a solution to the problem outlined above. No effect on the peak positions and only a small effect on the resolution were observed. This will be demonstrated by comparing the obtained ionization energies and peak positions

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with recently reported values. The dependence of the MATI signal on the laser intensity will be shown. It should be noted that the effect induced by increasing the pump laser intensity is observed only for alkyl aromatic compounds so far. Other molecules have not yet been investigated with this experimental set-up.

2. Experimental

A normal MATI experiment requires the following steps: excitation of the molecules in a field free region with a laser, applying of a positive spoiling field to spatially separate any prompt ions from the still neutral MATI molecules which is usually turned on some 100 ns after the excitation (field strength about −1 V/cm), then applying a negative extraction field which ionizes the MATI states and accelerates all the ions towards the detector and a device to suppress the prompt ion signals [9].

The apparatus used in this experiment is a standard ReTOF. Its ion source is a two-stage Whiley–McLaren type. As stated in the literature, MATI spectroscopy is possible using a standard reflectron mass spectrometer [10] which can be used in any experiment with laser excitation and ionization. In our instrument, the ion source had been slightly changed concerning the diameter and the distance of the three electrode plates. In the normal set-up the distances between the electrodes were 1.6 and 1.4 cm and the diameter of the plates 9 cm. With this set-up the extraction pulse could not be delayed sufficiently. A delay of 5 μs is normally enough to achieve a spatial separation of the prompt ions and the MATI neutrals, which is large enough to suppress the prompt ion signal with the reflector. But with the old set-up the ion signal vanished completely after a delay of only 2 μs. To reduce disturbances by stray fields and to get the electric field between the plates more homogenous, the distances were set to 2.8 and 1.2 cm and the diameter of the plates to 15 cm. Thus, the shielding against stray fields was improved. Additionally, the field disturbance caused by the holes in the plates at the spot of ionization respectively along the flight path of the molecules was thus reduced. With this configuration it is possible to delay the extraction pulse considerably longer (8 μs and more) without losing the ion signal. The voltage for the spoiling field is applied to the second plate whereas the voltage for the extraction pulse is applied to the first electrode. The third plate remains grounded. The ion source is thus operated in a single-stage mode.

The sample to be investigated is seeded in Argon carrier gas and enters the ReTOF through a pulsed valve (General Valve) with a 0.15 mm orifice. A skimmer with an opening of 0.65 mm is located 5 cm downstream to produce a supersonic beam. The ion source where the excitation of the molecules takes place via a two-color-two-photon resonant process follows behind the skimmer. No other plates, e.g., *X*–*Y*-deflection electrodes or an electrical Einzel lens, are present to reduce any possibility of stray fields. Leaving the ion source the ions enter an 80 cm field free drift tube ending in a two-stage reflectron which increases the mass resolution and at the same time suppresses the prompt ion signals. This reflectron returns the ion beam back to the detector, which consists of a stack of two multichannel plates (Hamamatsu F4704).

The excitation of the molecules is achieved using two Nd:YAG pumped dye lasers. The first system used to excite the molecules to the S_1 state is a Lambda Physics FL3001 dye laser pumped by a Lumonics HY1200 Nd:YAG laser. This is called the pump laser system in this paper. The second laser system used to ionize the excited molecules is an LAS 205 dye laser pumped by a GCR 150 Nd:YAG laser. Each output beam of the dye laser is frequency doubled by a BBO-I crystal. The laser intensity of the FL3001 is adjusted to the required strength by detuning the optimal SHG angle of the BBO crystal. For wavelength calibration, we use a Hamamatsu 2783 neon hollow cathode lamp which allows an accuracy of better than 2 cm^{-1} in this experiment.

Switching the high voltage pulse is done by a Behlke HS 56-01 fast thyristor switch. We use the driving circuit described in the operation manual which allows a switching time of about 10 ns. The detector's signal is fed into a LeCroy 534M digital oscilloscope.

In all measurements the spoiling field's strength is −1 V/cm. It is switched on 200 ns after the laser excitation. Five microseconds later, the extraction field is switched on with a field strength of 830 V/cm. The voltages of the two stages of the reflectron are optimized to completely suppress the direct ion signals and to maximize the mass resolution. In a linear MATI set-up [11,12], the mass resolving power is in general between 100 and 150. In experiments using a reflectron [10,13], it is about 1000 so that molecules with higher molecular weights can be investigated. The digitized data are read out from the oscilloscope by a computer program with boxcar functionality.

This program is also used to tune the wavelengths of the dye laser systems. The signals were averaged over 100 shots with the laser operating at a repetition rate of 10 Hz.

For the study of the dependence of the MATI signal on the pump laser intensity, the probe laser wavelength was set to the maximum position of the corresponding MATI signal. The obtained signals (one-color, two-color, and MATI) were averaged over 300 laser shots and the area under the peaks taken as the peak intensity value for the pump laser intensity used. The power of the pump laser was measured with a pyroelectric detector Molectron J9LP-80. The sensitivity of this device is 575 mV/mJ.

3. Results and discussion

p-Xylene was chosen in this experiment for the reason that it was already investigated by Schlag and coworkers [14] using a similar set-up. Thus, the results concerning the ionization energy could be compared. Obtaining MATI spectra for *p*-xylene is less problematic than for other substances because the MATI signal is quite intense when going via the vibrationless S_1 state. When going via higher lying vibrations of the S_1

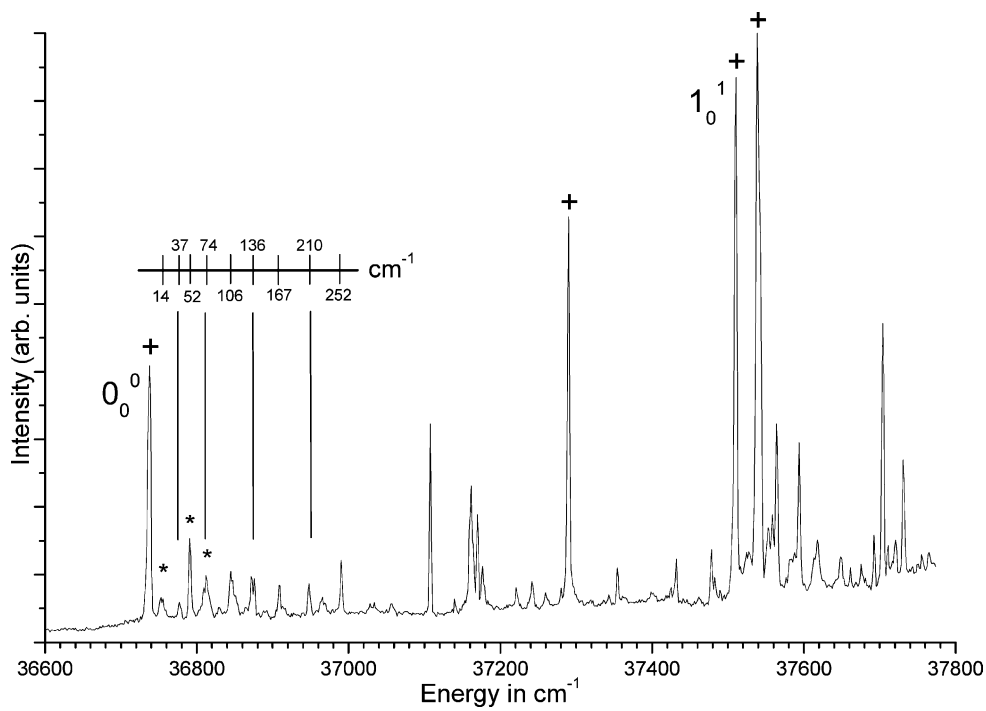

Fig. 1. 1C2P spectrum of *p*-xylene. The indicated frequencies show torsions of the methyl groups. Torsions that are also present in toluene are marked with an asterisk (∗). A plus sign (+) marks the vibrations used as intermediate states.

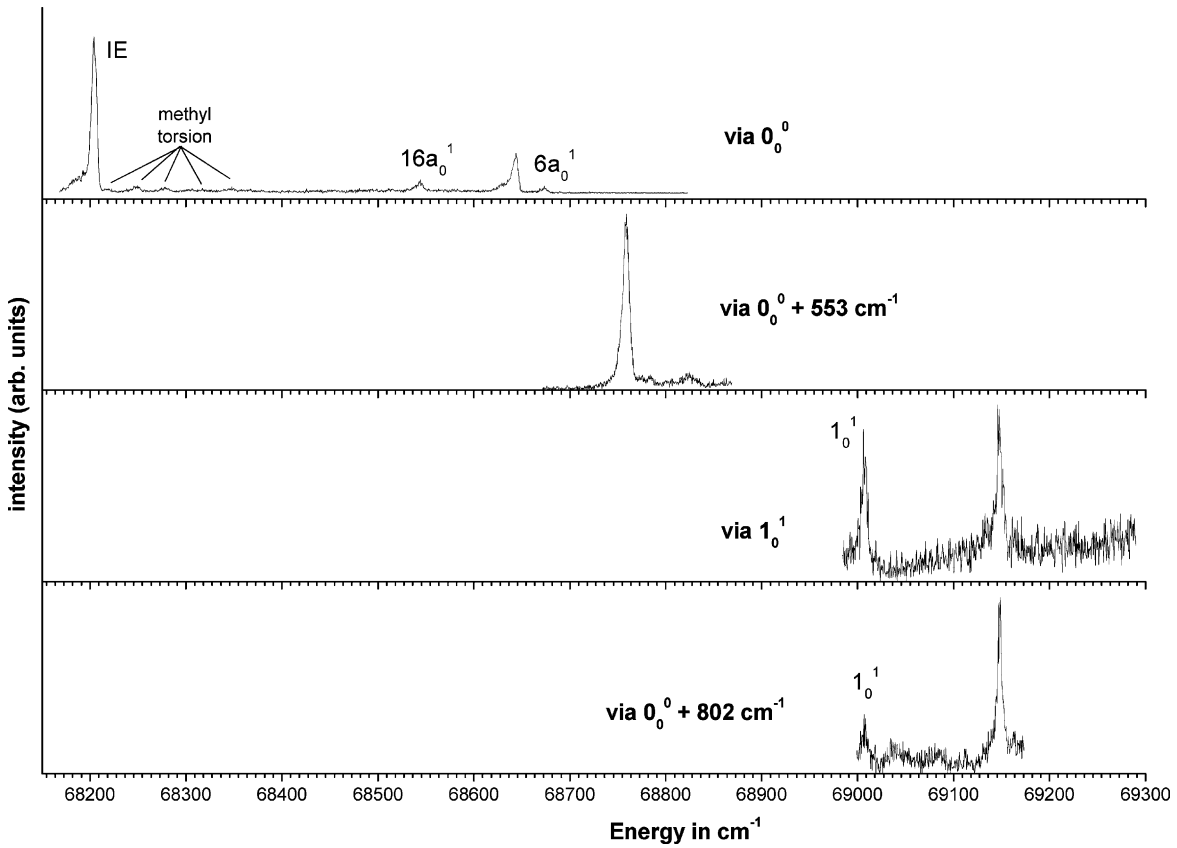

Fig. 2. MATI spectra of *p*-xylene via different intermediate states. The FWHM of the ionization threshold peak is 7 cm^{-1}.

state it, on the other hand, is rather difficult to obtain MATI spectra with a reasonably good signal-to-noise ratio. So these states provide a good basis for testing the increase of signal strength by increasing the pump laser intensity.

We have recorded MATI spectra via the 0–0 transition of the S_1 state and via the vibrations at 553, 774, and 802 cm^{-1} (37,291, 37,512, and 37,540 cm^{-1}). The assignment of the vibrations of *p*-xylene in the S_1 state has not been done so far. Our peaks are in very good agreement with the spectrum obtained by Ebata et al. [15] regarding the intensive peaks at 553, 775, and 802 cm^{-1} (see Fig. 1). The origin is found at 36,738 cm^{-1} in our measurements whereas a value of 36,728 cm^{-1} in Ebata et al.'s spectrum and of 36,733 cm^{-1} in the measurements of Breen et al. [16] is reported. The peak at 775 cm^{-1} was assigned to the 1_0^1 transition while the others have not been assigned. DFT calculations for *p*-xylene are currently performed by our group to fill this gap and allow for a more complete assignment of the peaks.

In the MATI spectra (Fig. 2) via the vibrationless S_1 state there are three dominant peaks. The first one is assigned to the ionization energy. This value is with 68,204 cm^{-1} and a FWHM of 7 cm^{-1} in quite good agreement with the value determined by Schlag and coworkers with ZEKE spectroscopy [14]. Their value is 68,186 $\pm$ 2 cm^{-1}. The difference of about 15 cm^{-1} is partly caused by the different energy Schlag and coworkers took for the vibrationless S_1 state. They followed the work of Ebata and used a value of 36,728 cm^{-1} which is already 10 cm^{-1} lower than

Table 1
MATI peaks of *p*-xylene

Intermediate state[a]	This work	Held et al. [14][b]	Assignment
36738	0		IP
	18	14	Methyl torsion
	44	45	Methyl torsion
	76	76	Methyl torsion
	113	112	Methyl torsion
	144	144	Methyl torsion
	341		16a[c]
	440		
	470		6a[c]
37291	555		
37512	803		1[c]
	944		
37540	803		1[c]
	944		

[a] Energy in cm^{-1}.
[b] Energy in cm^{-1} relative to origin.
[c] This work.

ours. This discrepancy is too large to be explained by calibration errors which should be less than $2\,cm^{-1}$ by using a hollow cathode lamp. Except for this value, the spectra are in excellent agreement. All the internal rotor states are clearly visible as seen in Table 1. These rotor states have similar energies as the ones in a toluene spectrum. This underlines the fact that they are caused by torsions of a methyl group, as described in the paper of Schlag and coworkers. The other peaks of the MATI spectrum also appear in their ZEKE spectrum, but have not been assigned yet. The peak at $341\,cm^{-1}$ ($68{,}545\,cm^{-1}$) is consistent with a similar signal at $334\,cm^{-1}$ in ethylbenzene [17] and a peak at $344\,cm^{-1}$ recently published by Lin et al. [18] in *p*-methyl aniline. Therefore, we assign this signal to the out-of-plane bending vibration 16a. The peak at $470\,cm^{-1}$ is in good accordance with a corresponding signal at $457\,cm^{-1}$ in *p*-methyl aniline and $463\,cm^{-1}$ in toluene. Because of this consistency, we assign this peak to the in-plane-bending vibration 6a. For the intense peak at $440\,cm^{-1}$ ($68{,}644\,cm^{-1}$) an assignment is currently not possible.

The MATI spectra via the vibration at $553\,cm^{-1}$, the 1_0^1 vibration of the S_1 state, and via the vibration at $802\,cm^{-1}$ have been measured with the increased intensity of the pump laser system and are also shown in Fig. 2. For the vibration at $553\,cm^{-1}$, one single peak appears in the MATI spectrum. In the case of the other two intermediate states the two peaks in each spectrum are clearly visible though the signal-to-noise ratio is much worse. At normal laser intensity it was possible to record a 2C2P REMPI spectrum via these intermediate states, but no MATI spectrum could be obtained. This is due to the high vibrational excitation. A general accepted rule is that the higher the vibrational excitation energy the less intensive the MATI signal. This is one reason why the vibrations chosen as an intermediate state for the two photon excitation normally appear close to the origin. Only in rare cases they can be found a few $100\,cm^{-1}$ shifted to higher energy. In our case, we chose vibrations which appear more than $750\,cm^{-1}$ higher than the origin. Although it should have been impossible to record MATI spectra via these levels, the increased intensity of the pump laser system allowed the measurements presented. We did not scan to lower energies than the ones displayed here because no two photon signal was obtained at excess energies lower than about 540 and $750\,cm^{-1}$, respectively.

The MATI peak at $555\,cm^{-1}$ represents the same vibration as the intermediate state employed to record this peak. Its assignment is therefore not possible either. Scanning to higher energies no other peaks could be observed. The assignment of the two MATI signals obtained via the 1_0^1 vibration is quite difficult. While the peak at $944\,cm^{-1}$ still remains unassigned, we designate the peak at $803\,cm^{-1}$ to be the ring-breathing vibration 1. We assume that the same value as the vibration at $802\,cm^{-1}$ in the first electronic state is only coincidental and that this peak is shifted from 775 cm^{-1} to this value. The main reason for this assumption is the fact that this peak is very intensive when activating the molecules via the vibration 1 and less intensive when going via the vibration at $802\,cm^{-1}$. The vibration used as an intermediate state is in many cases the first very intensive peak in the MATI spectrum. Therefore, this is a strong hint that the observed MATI peak at $803\,cm^{-1}$ is the vibration 1 and not the unassigned peak at $802\,cm^{-1}$ in the S_1 state.

The spectra were recorded using the increased intensity of the pump laser. As described in ref. [19], the ZEKE signal strength is higher when the ion density is increased, for example, by using a third laser beam. Increasing the intensity of the pump laser leads also to a higher ion density. Due to the higher population of the S_1 state the signal is increased, but there is also another effect. If the spoiling field is present during the laser excitation (the so-called in-field excitation method), a great amplification of the ZEKE signal is observed. In contradiction to this, in delayed-field experiments, where the spoiling field is switched on some time after the laser excitation, this effect does not dramatically affect the ZEKE signal's intensity. In both cases no effect on the peak's shape is observed.

Under the conditions employed here (delayed-field excitation), a different behavior is observed. We show for the first time that the MATI signal strength is increased strongly by increasing the pump laser intensity. There are only small effects on the signal shape. The intensity of the pump laser system was carefully increased, so that at a spoiling field strength of -1 V/cm the direct ion signal could be completely suppressed by setting the reflectron voltages to proper values. In some cases the one-color-two-photon signal was by far stronger than the two-color-two-photon signal. Therefore, the latter could no longer be observed, but the MATI spectra could still be recorded with a good signal-to-noise ratio because only the MATI ions still reached the detector and produced a signal.

For demonstration purposes, Fig. 3 shows the normal MATI signal of the vibrationless $S_1 \leftarrow S_0$ transition of *p*-xylene in comparison to the signal obtained under the same conditions but with an increased intensity of the pump laser system. In this case the signal height could be increased by a factor of 6. The signal-to-noise ratio is also improved. To show the influence on the peak position and the peak width, the right-hand side of the figure shows the two peaks in a normalized form. There is almost no difference visible

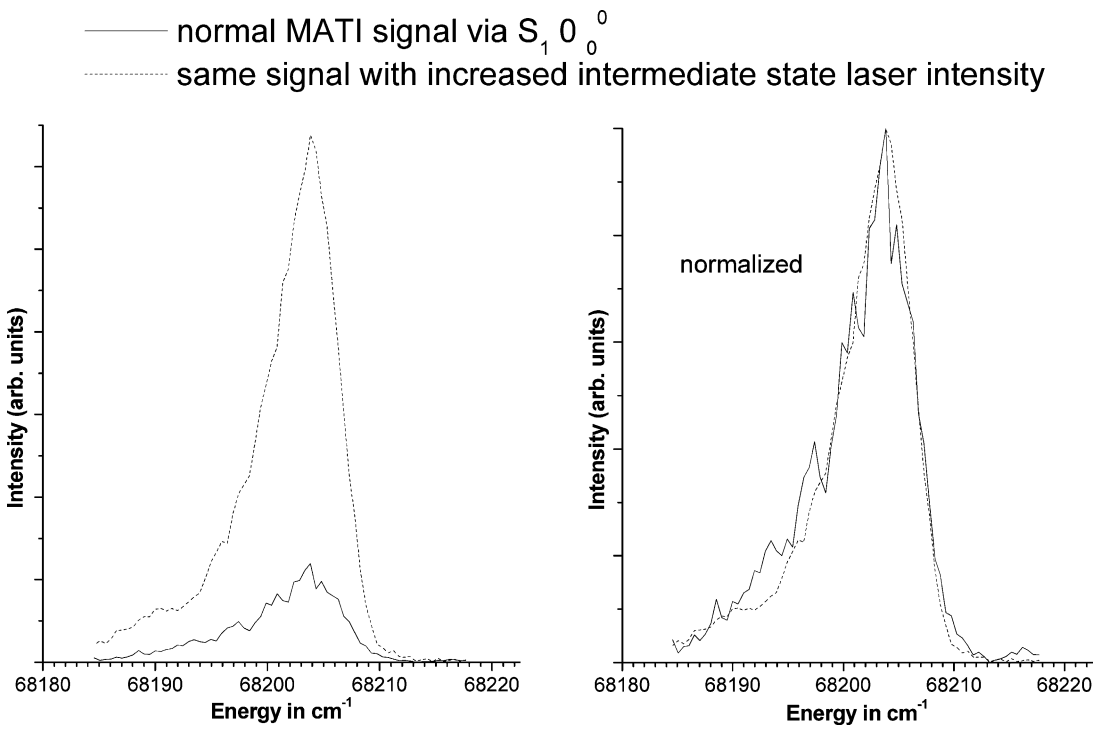

Fig. 3. A stronger pump laser intensity leads to an enhancement of the MATI signal (left) while the spectral resolution is not changed (right), shown here for *p*-xylene. The FWHM is 7 cm^{-1} for both laser intensities.

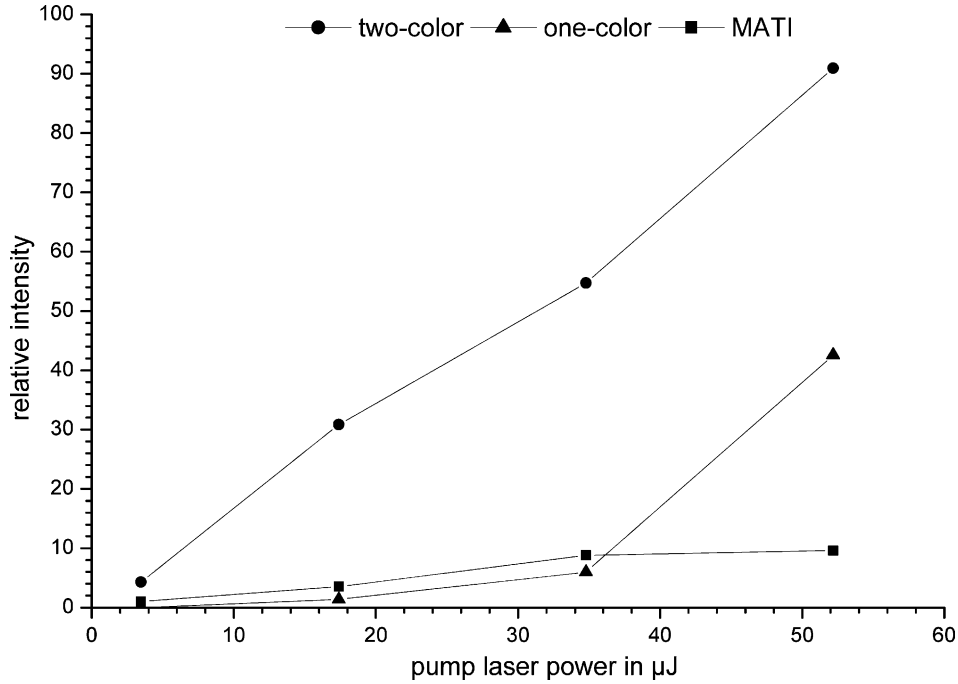

Fig. 4. Signal strengths for various pump laser intensities when using the S_1 0–0 transition as an intermediate state. The signal intensity is given in relation to the MATI signal at a pump laser intensity, where no one-color signal is produced (leftmost point). At the rightmost point the two-color signal is no longer suppressed by the reflectron and starts to affect the MATI spectrum.

which means that neither the FWHM nor the peak position has changed. In this relation it is important to repeat that the spoiling field strength was the same in both cases. The signal intensity was limited by the restriction to keep the strength of the spoiling field at −1 V/cm to completely suppress the signal produced by direct ions. As a conclusion, it can be said that MATI spectra can be obtained with the same resolution and better signal-to-noise ratio by increasing the intensity of the pump laser system. Thus, even peaks which could not be detected before due to their low intensity can now be investigated.

To show the dependence of the MATI signal on the pump laser intensity, the same experiment was repeated for various intensities. Fig. 4 shows the strength of the MATI signal, the two-color signal and the one-color signal. The latter two were recorded under the same conditions as the MATI signal but without the spoiling field. We could not go to higher pump laser intensities because the two-color signal could not be suppressed completely for higher values and would contribute to the MATI signal. The MATI signal and the two-color signal is in the case of *p*-xylene with the vibrationless S_1 state as an intermediate state already under normal conditions quite intense. Thus, only small variations of the pump laser intensity already lead to strong influences on the MATI signal.

As can be seen in Fig. 4, the one-color signal and the two-color signal are much stronger than the MATI signal. Their increase when going to higher pump laser intensities is also stronger. The leftmost value represents the normal conditions. The pump laser intensity is that much reduced that there is no one-color signal produced by the pump laser. The two-color signal is still present and the MATI signal is weaker than this signal. The reason is that it is only a fraction of the molecules forming the two-color signal that produce the MATI signal. When the pump laser intensity is

increased, the one-color signal appears. The two-color signal increases as well as the MATI signal. Because the spoiling field retards the movement of all ions no matter what kind of process they were formed by, the one-color signal and the two-color signal are still suppressed by the reflectron. So when recording the MATI spectrum with the increased pump laser intensity, there is no difference visible except the increased strength of the recorded signal. This increased strength in turn leads to a better signal-to-noise ratio. Both facts are already shown in Fig. 3. With further increasing of the pump laser intensity the one-color signal becomes stronger and at a certain point stronger than the MATI signal. This signal and the two-color signal also increase in intensity. At the rightmost point the two-color signal starts to appear in the MATI spectrum. It is no longer completely suppressed by the reflectron so that this laser power marks the maximum value that is applicable to enhance the MATI signal. From Fig. 4, it can be derived that a signal gain of factor 8 can be achieved without losing spectral resolution. The *y*-axis shows the intensity in relation to the MATI signal strength under normal conditions (no one-color signal visible).

In the case of the 0–0 transition of the S_1 state as an intermediate state the enhancement of the MATI signal is limited because the signals are already quite strong under normal conditions. In this case there is normally no need to increase the MATI signal because the signal-to-noise ratio of MATI spectra is in general sufficient to clearly locate the peak positions and determine the spectral resolution. If the signal obtained has a relatively weak intensity, this enhancement might still be of great help. When other states, e.g., higher vibrations of the S_1 state, are chosen as an intermediate state, the situation might change completely. As already stated above, the MATI signal becomes less intensive using intermediates states of higher energy. Under certain circumstances it might even be impossible to record MATI spectra because the two-color signal is already quite weak. This is the case when the S_1 vibrations at 775 cm^{-1} (1_0^1 vibration) and 802 cm^{-1} are employed. To be able to record MATI spectra, a way of increasing the MATI signal's intensity is then absolutely necessary. Therefore, we chose another intermediate state to show the increase of the MATI signal strength when going to higher pump laser intensities. This was the still unassigned vibration at 553 cm^{-1} (37,291 cm^{-1}). With this state it is possible to show this influence. It is not possible, for example, with the 1_0^1 vibration because there the highest intensity where the direct ions can still be suppressed with the reflectron has to be used to produce a MATI signal. If the pump laser intensity is set to a value where only a two-color signal is produced, the MATI signal at 68,759 cm^{-1} is very weak. It does not appear as a constant signal but more like intensive noise at a certain flight time. But even with this weak signal it is possible to record a MATI spectrum as shown in Fig. 6. When the intensity of the pump laser is increased the signal at first becomes stable and then more and more intense. Fig. 5 shows the strength of the one-color signal, the two-color signal, and the MATI signal. The *y*-axis is again scaled so that it shows the intensity in relation to the MATI signal recorded at a pump laser intensity that does not produce a one-color signal. Two things are obvious: First, the maximum laser intensity applicable before the two-color signal becomes visible in the MATI spectrum is higher. The reduced signal strengths are responsible for this. The second and more important fact is that the achievable enhancement of the MATI signal is of a factor of 50 with the intermediate state employed here. Compared with the factor 8 for the intense S_1 0–0 transition as an intermediate state, this is a further enhancement which leads in this case of relatively weak signals to the possibility of recording MATI spectra with comparable signal-to-noise ratio as in the case of strong signals.

Fig. 3 shows that the enhancement of the signal strength does not lead to a loss of spectral resolution. The FWHM is 7 cm^{-1} which is the normal value we achieve in all the measurements with our set-up. To show the spectral resolution of the MATI peaks with the increased pump laser intensity, Fig. 6 displays the normalized MATI peaks via the S_1 vibration at 553 cm^{-1} for various laser intensities. The peak recorded at 3.5 μJ (solid curve) is the reference peak. It shows a FWHM of about 6.3 cm^{-1} which is slightly

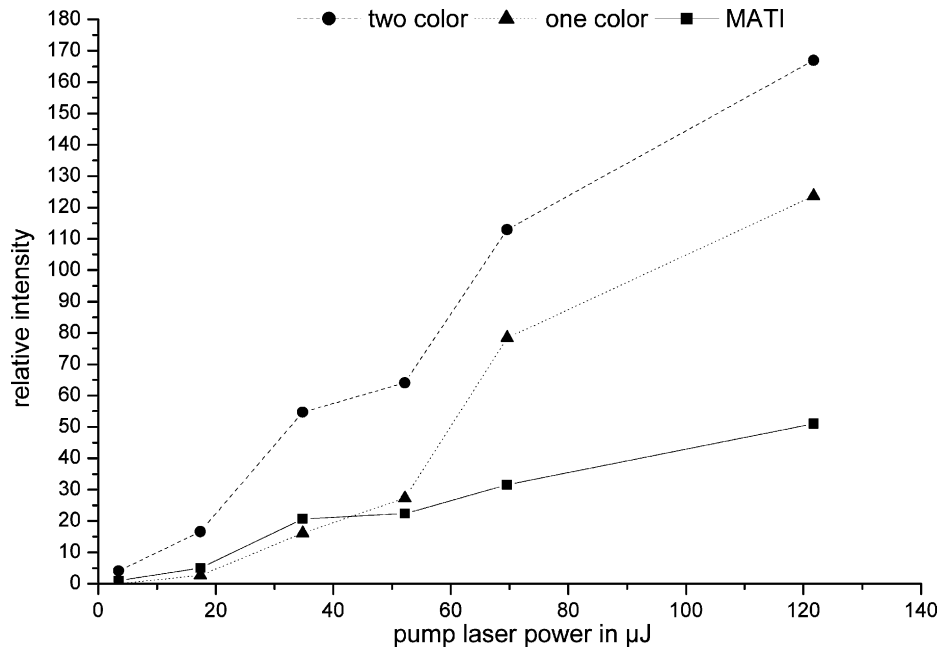

Fig. 5. Same as Fig. 4, but with the S_1 vibration at 553 cm^{-1} used as an intermediate state. A much higher signal enhancement is achieved in this case.

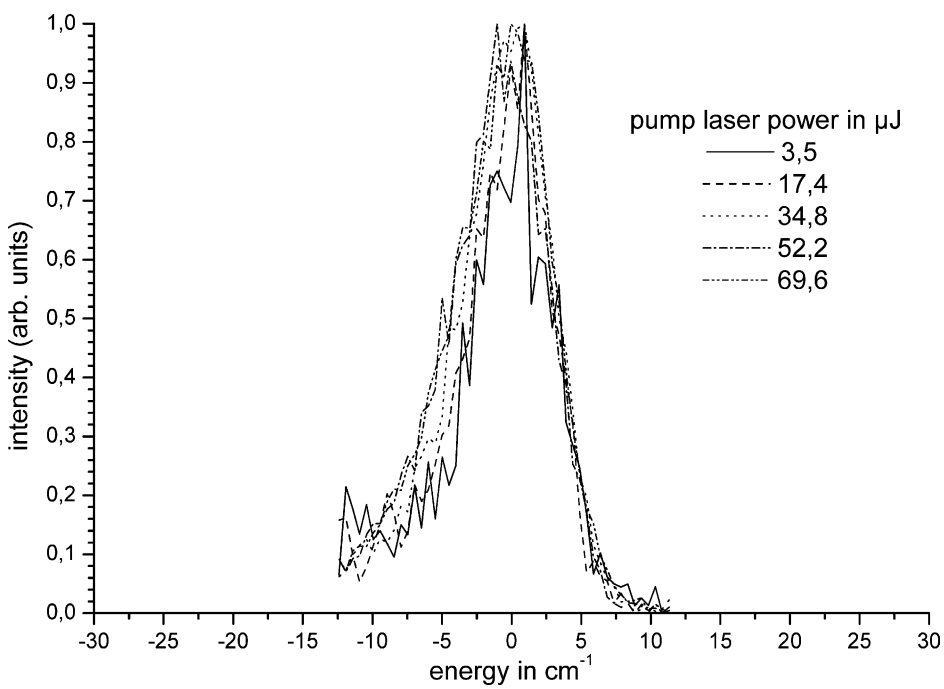

Fig. 6. Normalized peak shapes for various pump laser intensities employing the S_1 vibration at 553 cm^{-1} as intermediate state. A minor loss of resolution is observed due to a more intense red edge of the peaks with higher pump laser intensity.

below our normal resolution. The largest FWHM in this figure is with 7.7 cm^{-1} slightly above our normal resolution. While the blue edge of the peak is nearly the same for all the displayed peaks, the red edge leads to the increased FWHM. The peak center remains constant. Compared with the peak shape of the reference peak an improvement of the signal-to-noise ratio is observed. The conclusion is that the increase of the pump laser intensity leads to an increased signal strength and better signal-to-noise ratio of the MATI signal with negligible influence on the resolution.

The function of neighboring ions has been discussed in many papers [19–22]. In some cases no signal change was observed when the ion density is increased [21,23], while others show a clear dependency on the ion density. A possible explanation for this might be a saturation effect. The ZEKE/MATI signal cannot exceed the number of optically absorbing Rydberg states [19]. Above the saturation limit there is no further enhancement of the signal by additional ions. Below this limit the ZEKE/MATI signal shows a strong dependence on ion density. Martin and Hepburn [20] show for Argon that at high ion densities the ZEKE/MATI signal does not increase with increasing ion density but it shifts to lower energy. There are only slight changes in the peak widths. At lower ion density they also report a ZEKE/MATI signal increase with increasing ion density. In this case a strong change in the peak widths is observed. Neither we nor Schlag and coworkers observed this loss of resolution caused by higher ion densities. Additionally, we observe a large signal enhancement due to higher intensity using delayed-field excitation.

4. Conclusion

In this paper, we have shown the MATI spectra of *p*-xylene for various intermediate states. The ionization energy for this molecule determined in this work is 68,204 ± 5 cm^{-1}. This is in quite good agreement with previously reported values. Additionally, we have recorded MATI spectra via intermediate states which have not been used as intermediate states before. Thus, we were able to report some new vibrations of *p*-xylene in highly excited Rydberg states for the first time. This was made possible by increasing the intensity of the pump laser system resulting in an increased MATI signal, so that even vibrations at higher excess energies (800 cm^{-1}) could be used as an intermediate state. In a further study on the dependence of the MATI signal strength on the pump laser intensity, we have shown that is possible to increase the MATI signal strength up to a factor of 50. It is also reported for the first time that it is possible to greatly enhance the MATI signal strength without losing spectral resolution due to changing of the peak width or shifting of the peak center. The factor by which the signal can be increased in turn is dependent on the corresponding two-color signal strength obtained under normal conditions for MATI/two-color REMPI experiments (pump laser intensity reduced so that no one-color signal is observed). When employing the intermediate states of *p*-xylene at high excess energy, it is even impossible to record MATI spectra without this signal enhancement.

Regarding the signal intensity and the signal-to-noise ratio, MATI is in general inferior to ZEKE spectroscopy. As shown in this contribution, a disadvantage of MATI spectroscopy compared with ZEKE spectroscopy can thus be reduced in its influence. Our experimental set-up now allows the acquisition of MATI spectra for substances under those conditions in which only weak or even no MATI signals have been obtained so far.

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